Examination of the Amphiphilic Properties of Dumb-bell-Shaped Polyoxometalate-Organic Hybrid Materials

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Examination of the Amphiphilic Properties of Dumb-bell-Shaped Polyoxometalate-Organic Hybrid Materials

by

Mauricio F. Misdrahi

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Abstract

Polyoxometalate (POM) molecular clusters exhibit a great diversity of sizes, nuclearities, and shapes providing singular properties for forming hybrid materials and supramolecules. These hybrids are formed by linking one, two and three Wells-Dawson type clusters, \([\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]^{9-}\), with different linear (TRIS)-linker ligands between the TRIS moieties. Laser light scattering (LLS) reveals the presence of self-assembled vesicular structures in water/acetone mixed solvents, while the vesicle size increases with increasing acetone content, suggesting a charge regulated process. The hybrids show amphiphilic behaviors like surfactants, but also demonstrate different properties such as the unusual large entropy contribution to the vesicle formation and the involvement of amphiphilic tetrabutylammonium (TBA) counter-ions, due to their unique large polar head groups, complex organic linkers and their special molecular architectures. Bending energy theory and elastic constants are used to successfully explain the vesicle formation and stability in solution. The vesicle size increases in proportion with the elastic modulus \(k_c\) and reveals an important role of the organic ligands on the process during vesicle formation. Interfacial behavior is shown for all the five heterotungstate dumb-bell shape hybrids with the water sub-phase and form thin films or monolayers similar to some ionic surfactants. In addition, calorimetric studies reveal an important L/S interface adsorption. The occupied molecular area shows a different molecular binding orientation. The space between both polar heads dictates a packing and horizontal molecular adsorption interface. Numerous astonishing and fascinating phenomena have been observed in these novel hybrid systems.
Chapter 1: Introduction to POM Containing Hybrid Materials

1.1 Overview of studies

Combining well organized inorganic structures with organic molecules is a novel strategy to develop new complex and functionalized macromolecules. For this reason, it is of great interest to develop such organic–inorganic hybrid materials and explore their physicochemical properties and potential applications. The analysis and characterization of hybrid materials may increase awareness of their unique and interesting properties as new paths in technology and provide state-of-the-art tools in the manipulation of new molecular structures.

1.2 Organic-inorganic hybrids materials

The desire to combine the properties of inorganic and organic compounds in a novel and unique molecules has been topic of research since many centuries ago. This challenge can be found in casein paints used in ancient times. Iron oxide pigments dispersed in organic binders such as olive oil, eggs, etc. were employed to elaborate paints.\textsuperscript{1,2} However, this hybrid concept was not mentioned until the development of polymers and new materials. Currently, the study of inorganic–organic hybrid materials has drawn extensive attentions in different fields in recent years.\textsuperscript{3-10} Various POM-containing hybrid materials have been synthesized\textsuperscript{11-14} in the past decades via different approaches; some of them include diverse inorganic structures and functional organic groups.\textsuperscript{15-22} We can classify the hybrid organic-inorganic materials in two large different families depending of the nature of the bonds between the organic and inorganic part.
The first family corresponds to hybrid materials where weak or secondary bonds are presented between the organic and inorganic interface such as hydrogen bonds, electrostatic interactions and Van der Waals forces. The second family corresponds to hybrid materials where covalent or primary bonds are attached to the organic part with the inorganic molecule.23

1.3 First Class of organic-inorganic hybrids

One of the simplest types of organic-inorganic hybrid materials is to embed organic dyes in an inorganic network. An inorganic network can be formed by metal alkoxides solutions or a sol acting as molecular precursors (M(OR)ₙ where M =Si, Sn, Ti, Zr, Al Mo, V, W, Ce, etc; R is an alkyl or aryl group) in solvents through the sol-gel process or chemical solution deposition to fabricate hybrid materials through hydrolysis and condensation reactions.24 For example, different dyes such as rhodamines, pyranines, porphoryns, phtalocyanines, etc. have been incorporated in inorganic networks such as silicas, aluminosilicates or transition metal oxides. Another important type of hybrid materials is the embedding of inorganic particles in polymers. For example, inorganic filler such metal carbonates, metal silicates, etc. improve mechanical properties of polymers and increase the viscosity of the final system as is required. To avoid agglomeration of the inorganic particles and have a homogeneous system, a selection of one or a blend of different solvents must be added. The selection of the solvent is important to adjust the rheological properties of the system. These techniques have been used to prepare hybrid components in ceramic industry. All these systems have proved to work and constitute the initial stages of the hybrid materials. With the advance of the
technology the polyoxometalates have occupied an important niche area in different fields of science. POMs represent some of the largest inorganic molecules known so far which possess very rich physical and chemical properties and they are particularly important building blocks for forming hybrid materials. Therefore, they are unique candidates for potential applications for electronic and catalytic materials. A large portion of common POMs are hydrophilic. The incorporation of organic components introduces novel properties for the inorganic functional clusters, and increases the compatibility of the POMs in organic media. These organic-inorganic hybrids will combine not only the advantages of one individual inorganic and organic components, also the close interaction and synergistic effect between them and the surrounding systems.

1.4 Classification and segmentation of polyoxometalates

The polyoxometalate chemistry is diverse and rich in properties such as molecular composition, surface charge, size, shape, nuclearity, solubility, etc. and also proposes innovative solutions in different fields. To have a better understanding and assist in the selection process for a specific objective the POMs may be classified or split in groups. A simple and effective manner is to divide the POMs in two large subclasses, namely, isopolyoxometalates and heteropolyoxometalates.

1.4.1 Isopolyoxometalates or homopolyoxometalates

Isopolyoxometalates are polyanions containing transition metals and are composed of various metal-oxide frameworks with general formula \( \{M_{m}O_{y}\}^{n-} \) (M=transition metal,
Oxygen). The diversity of the metal central atom (M) vary from 2 up to more than 150. Some examples include V, Nb, Ta, Mo, W, etc. A typical example of this class of POMs is perfectly represented by one hexamolybdate Lindquist anion \( \{\text{Mo}_6\text{O}_{19}\}^{2-} \). It is the most well known isopolyoxometalate and shows symmetrical structure as a result of a fusion of six octahedrons sharing a common vertex. In addition, this Lindquist type has been used as a template to build more sophisticated and complex POMs. For example, a family made of five isopolyanion members have been synthesized from five octahedron polytungstate capped on both sides by two phosphate tetrahedrons. Due to the fact that isopolyanions just present one metal, they are often much more unstable than their heteropolyanion counterparts.

1.4.2 Heteropolyoxometalates

Heteropolyoxometalates are metal-oxide clusters with general formula \([X_{x}M_{m}O_{y}]^{n-}\) (X=heteroatom, M=transition metal, O=oxygen). This family can be classified in three main subclasses: (i) Keggin; (ii) Wells-Dawson; (iii) Anderson. Berzelius experimentally prepared the first polyanion \([\text{PMo}_{12}\text{O}_{40}]^{3-}\). After 100 years, Keggin, determined the structure of a similar compound \([\text{PW}_{12}\text{O}_{40}]^{3-}\) by x-ray diffraction. Keggin’s heteroelement shows a 4-coordinated or tetrahedral structure. The framework is constituted by addenda atoms. Similar to Keggin structure, Wells-Dawson POMs presents heteroelement tetrahedral coordination. However, this particular type of POM presents two coordinate heteroelements instead of one and a double tetrahedral template is shaped. Anderson POM shows a crown configuration of six octahedrons sharing
vertices containing 6 coordinated atoms. Figure 1.1 shows some common representations of heteropolyoxametales by polyhedra structures.

![Polyhedra structures](image)

**Figure 1.1.** Polyhedra representation of typical POMs. X is the heteroelement and M is typically Mo, V or W. The general structure formulas are: Keggin structure $\text{XM}_{12}\text{O}_{40}^n$; Lindqvist structure, $\text{M}_6\text{O}_{19}^n$; Wells-Dawson structure, $\text{X}_2\text{M}_{18}\text{O}_{62}^{n-}$ and Anderson structure, $\text{XM}_6\text{O}_{24}^n$.

1.5 Second class of organic-inorganic hybrids

The second hybrid materials class conforms organic molecules that are attached to the inorganic molecule by covalent or primary bonds. Lacunary species are capable to react with organic molecules to fabricate hybrid materials. To generate lacunary species is commonly done after the formal remotion of one metal from the original POM. The diversity of electrophilic groups available combined with the various topologies observed in lacunary heteropolyoxometalates explains the recent development of such organic-inorganic hybrids. On the other hand in nonlacunary heteropolyoxometalates the negative charge is delocalized over the entire structure. Therefore make these oxygen atoms more nucleophilic or reactive toward electrophilic groups such as organophosphonates, organoarsenates, organotin, etc.
1.5.1 Monodentate alkoxides

Alkoxides complexes leads to fast ligand exchange through hydrogen bond associations. The versatility of the coordination modes of alkoxo ligands is very useful to synthetized promising supramolecules. For example, numerous compounds base on \( \{ \text{Mo}_2\text{O}_4 \}^{2+} \) dinuclear unit fragment in which the two molybdenum centers are coupled by a single metal-metal bond have been developed. A rich family of recurrent structural pattern \( \{ \text{Mo}_2\text{O}_4 \}^{2+} \) shows assemblies of two, three, four or six units through bridging oxygen donor ligands. Pyridine, halide, alkoxide, and alcohol ligands occupy the peripheral positions of the molybdenum oxide cores.\(^{35}\)

1.5.2 Tris-alkoxides

The overall functionality of tris alkoxides provides examples of coordinate species to functionalized Anderson-type polyoxometalates. For example, the unsymmetrical hybrid Mn-Anderson polyoxometalate cluster \([\text{TBA}]_3[\text{MnMo}_6\text{O}_{18}(\text{C}_4\text{H}_6\text{O}_3\text{NO}_2)(\text{C}_4\text{H}_6\text{O}_3\text{NH}_2)]\), has been synthesized and crystallized by Cronin et al.\(^{36}\) The strategy to build such compound is via a simple and convenient coupling reaction with aldehydes. Alkoxides, tris(hydroxymethyl) aminomethane (\(\text{C}_4\text{H}_6\text{O}_3\text{H}_3\text{NH}_2\)) and tris(hydroxymethyl) nitromethane (\(\text{C}_4\text{H}_6\text{O}_3\text{H}_3\text{NO}_2\)) were utilized as the sources for the capping of both sides of the Mn-Anderson cluster. Studies of X-ray crystallography and electrospray ionization mass spectrometry (ESI-MS) characterized the hybrid compound. In addition, the free reactive pendants amino and amido groups (NO\(_2\) and NH\(_2\)) can be used as a potential routes to build new compounds.\(^{37}\)(Fig. 1.2) Similar approach has been used to synthesize a complete Anderson-type
heteropolyoxomolybdates family containing tridentate ligands. The general formula

\[ \text{[MMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CR}\}_2]^{3-} \] (M=Mn\text{III}, Fe\text{III}) and \[ \text{[H}_2\text{MMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CR}\}_2]^{2-} \] (M = Ni\text{II}, Zn\text{II}), (R = CH$_3$, NO$_2$, CH$_2$OH), were successfully prepared and characterized by Infrared spectra, NMR and X-ray diffraction.\(^{38}\)

![Figure 1.2. Polyhedra representation of X-ray crystal structure of compound [TBA]$_3$[MnMo$_6$O$_{18}$(C$_6$H$_5$O$_3$NO$_2$)(C$_6$H$_5$O$_3$NH$_2$)](Left). Polyhedral representation of (TBA)$_3$[MnMo$_6$O$_{18}$(C$_4$H$_6$O$_3$NH$_2$)](Right)](image)

**1.5.3 Organosilyl derivates**

The first organosilyl family was developed by Knoth\(^{39}\) in 1979. Four different [\(\alpha\)-SiW$_{11}$O$_{39}\{O(SiR)_2\}]^{4+} \) (R=C$_2$H$_5$, C$_6$H$_5$, NC(CH$_2$)$_3$, C$_3$H$_5$). hybrids were obtained. Organosilyl derivatives have been obtained from reactions between lacunary heteropolyoxometalates containing nucleophilic properties from the oxygen atoms and the electrophilic properties of RSi$^{3+}$ group. Depending on the pH stability of the lacunary heteropolyoxometalate two main approaches have been used for the synthesis of these hybrids. With an organotrichlorosilane, the lacunary heteropolyoxometalate is phase transferred in a suitable organic dissolving agent and is then reacted with an organotrichlorosilane. In the second approach, organotrialkoxosilane is reacted with lacunary heteropolyoxometalate in a mixed solvent in the presence of hydrochloric acid to control the hydrolysis and condensation of the organosilane groups.
1.5.4 Organotin derivates

Among all different hybrid compounds organotin, derivates show high stability of Sn-C bond toward hydrolysis and, the different coordination numbers of Sn between 5 to 7 provide a unique features. Organotin derivatives are essentially synthesized in water by reaction of organotrichlorotin reagents with lacunary polyoxometalates. Heteropolytungstates containing an organotin moiety plus Co or Zn as central atom, M₆H[XW₁₁O₃₉SnPh]ₙH₂O (M=Me₄N or Bu₄N; X = Zn or Co) were prepared by Liu et al. and characterized by IR, UV/VIS and NMR spectroscopy and electrochemistry. The results show that these two anions possess Keggin-like structures and have studied the antitumoral activity of different organotin fragments to Hela and SSMC-7721 tumor cells. Also, Pope et al. synthesized two tungstoantimonates base on dimers of the trivacant polyoxometalates [R-XW₉O₃₃]⁻ (X=As³⁺, Sb³⁺). Three phenyltin are linked to both tungstoantimonates forming a rigid central ring structure.

The group of Kortz has reacted monophenyltin {SnPh}³⁺ and the dimethyltin {Sn(CH₃)₂}²⁺, with different preformed polyoxometalates structures to form a variety of oligomeric molecular systems to three-dimensional assemblies. The tetrameric hybrid organic-inorganic tungstoarsenate is composed of four (α-AsW₉O₃₃) fragments that are grafted to three dimethyltin groups and three (As)³⁺ atoms. Figure 1.3 shows the tetrameric hybrid.
Figure 1.3. Tetrameric, hybrid organic–inorganic tungstoarsenate (III) \([\{\text{Sn}(\text{CH}_3)_2(\text{H}_2\text{O})\}_2\{\text{Sn}(\text{CH}_3)_2\}\text{As}_3(\alpha\text{-AsW}_9\text{O}_{33})\}_4]^{-21}\). (48)

Another important contributor is Hasenkopf et al.\textsuperscript{49-53} who prepared hybrid organic/inorganic Wells-Dawson polyoxotungstate through addition of functionalized tricholorostannanide to lacunary \(\alpha_2\) and \(\alpha_1\)-[P\(_2\)W\(_{17}\)O\(_{61}\)]\textsuperscript{10-}. Basically, functional groups were grafted and later reacted to form complex structures onto heteropolyoxotungstates in acetonitrile solutions. The results show an efficient method to fabricate a new hybrid family with more than 20 functionalized Wells-Dawson members.

Also, hybrid organic/inorganic Wells-Dawson polyoxotungstates tin-centered adducts of general formula [PW\(_{11}\)O\(_{39}\){SnCl}]\textsuperscript{4} have been prepared by Neumann et al.\textsuperscript{54}. A new and simple method for the preparation of organic inorganic hybrids has been developed. With primary, secondary, and tertiary amines or a tertiary phosphine in THF, NMR techniques made possible the identification of these hybrid compounds as adducts formed upon the interaction of the amine with the Sn-Cl center of the polyoxometalate.
1.6. Organoimido compounds from Group V

Most of organoimido compounds belong to Lindquist type polyoxomolybdate. Zubieta et al.\textsuperscript{55} reports the first hybrid organonitrogen in 1988. The Reaction of [MoCl\textsubscript{4}(NNMePh)] with [Mo\textsubscript{2}O\textsubscript{7}] and tetrabutyl ammonium (TBA) as countercation yields an organomido coordination complex [Mo\textsubscript{6}O\textsubscript{18}(NNMePh)]. Four different subclasses have been identified for organoimidates compounds. (i) monofunctionalized [MoW\textsubscript{5}O\textsubscript{18}(NAr)]\textsuperscript{2-} anions; (ii) monofunctionalized [Mo\textsubscript{6}O\textsubscript{18}(NR)]\textsuperscript{2-} and [Mo\textsubscript{6}O\textsubscript{18}(NAr)]\textsuperscript{2-} anions; (iii) difunctionalized cis and trans [Mo\textsubscript{6}O\textsubscript{17}(NAr)\textsubscript{2}]\textsuperscript{2-} anions; (iv) hexamolybdate dimmers [O\textsubscript{18}Mo\textsubscript{6}N(R)NMo\textsubscript{6}O\textsubscript{18}]\textsuperscript{4+}. Where R=alkyl group and multifunctionalized organoimididos [Mo\textsubscript{6}O\textsubscript{19-x}(NAR)x]\textsuperscript{2-} anions x>2. The first class of hybrid includes two different transition metals (Mo and W). The synthesis under mild conditions and in high yields of [MoW\textsubscript{5}O\textsubscript{19}]\textsuperscript{2-} heteropolyoxometalate and aromatic amines produces two similar compounds, [Mo\textsubscript{6}O\textsubscript{18-}(NAr)] and [Mo\textsubscript{6}O\textsubscript{18}(NArI)]. The notable functionalization of this hybrid is an organic \(\pi\)-electrons from the aryl-imido organic group that may extend their conjugation to the inorganic framework, resulting in possible synergistic effects. Both, arylimido mixed-metal hexametalates structures are confirmed by elemental analysis, spectroscopic measurements, and X-ray single-crystal structure determination.\textsuperscript{56} The second class is much more rich in organoimido derivates and include a great variety of alkyl and aryl groups. Maatta et al.\textsuperscript{57} introduced a variety of isocyanate RNCO (R \textsubscript{n}=\textsuperscript{n-}butyl, cyclohexyl and 2,6 diisopropylphenyl groups in to hexamolybdate cluster [Bu\textsubscript{4}N]\textsubscript{2}[Mo\textsubscript{6}O\textsubscript{19}] in pyridine solution. All these complexes were characterized by (\textsuperscript{1}H, \textsuperscript{14}N, \textsuperscript{17}O, and \textsuperscript{95}Mo) NMR and electronic spectroscopy, and single-crystal X-ray diffraction studies. An important contribution in the organoimido field was given by Peng
et al. \textsuperscript{58} who described an proficient process based on the use of dicyclohexylcarbodiimide (DCC) in acetonitrile. Wei \textit{et al.} \textsuperscript{59} studied an efficient and convenient reaction of DCC as a dehydration agent that effectively facilitate the reaction of $\text{[Mo}_6\text{O}_{19}]^{2-}$ with aromatic amines (see Fig. 1.4).

![Hexamolybdates with functional amines represented by ball-stick model.](image)

The third class presents $\textit{cis}$ and $\textit{trans}$ configurations for difunctionalized $\text{[Mo}_6\text{O}_{17}(\text{NAr})_2]^{2-}$ anions. One example of $\textit{cis}$ configuration is the hexamolybdate $(\text{Bu}_4\text{N})_2\text{[Mo}_6\text{O}_{17}(\text{NAr})_2]^{2-}$ (Ar = o-CH$_3$C$_6$H$_4$). Two $p$-toylimido pendant groups are linked to hexamolybdate at $\textit{cis}$ position.\textsuperscript{60} On the other hand, a disubstituted imido $\textit{trans}$ configuration $\text{[Bu}_4\text{N}]_2\text{[Mo}_6\text{O}_{17}(\text{NAr})_2]$ (1, Ar = 2,4-Me$_2$C$_6$H$_3$) was synthesized and characterized by IR spectroscopy, elemental anal., UV-visible absorption spectroscopy, and single-crystal x-ray diffraction.\textsuperscript{61}

The last class presents different hexamolybdate dimmers and multifunctionalized organoimidos. Hexamolybdate dimmers was produces by the reaction of $n$-propyamine with polymolybdates and $N,N'$-dicyclohexylcarbodiimide (DCC) in dry acetonitrile.
produces \([\text{Mo}_6\text{O}_{18}\text{NC}(\text{C}_2\text{H}_3)]=\text{C}(\text{C}_2\text{H}_3)\text{NM}_6\text{O}_{18}]\). Specially, this dimmer possesses a C=C double bonds which is valuable and essential in many areas of chemistry and polymers. The hybrid was characterized by \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy and definitely confirmed by X-ray single-crystal diffraction.\(^62\) On the other hand, one a multi-substituted organoimido POM is synthesized with the molecular formula \(\text{MO}_6\text{O}_{16}(2,6-\text{Me}_2-\text{NC}_6\text{H}_3)_2(\mu_2-2,6-\text{Me}_2-\text{NC}_6\text{H}_3))^{2-}\). Bridging oxygen groups were replaced by organoimido compounds in DCC. X-ray single diffraction studies shows stable crystals that can be recrystallized in acetonitrile or acetone. IR spectra confirms the decrement of the number of oxo ligands by imido ligands.\(^63\)

1.7 Organophosphonate derivates

Organophosphonate derivates can be classified in three groups. The first group corresponds to polyoxomolybdate hybrids. The first heteropolyanion of this derivates was reported by Stallik\(^64\) in 1976. Crystals and molecular structures of pentamolybdomethylphosphonate compound, \((\text{NH}_4)_4[(\text{CH}_3\text{P})_2\text{Mo}_5\text{O}_{21}]\cdot5\text{H}_2\text{O}\) were successfully synthesized and characterized by X-Ray crystallography. The core presents a pentamolybdate structure linked by two monophosphonate ligands. Over time, various molybdenum coordination compounds have been developed. Hexanuclear arquitectures\(^65\) were synthesized such as \([\{(\text{C}_6\text{H}_5\text{P})\text{Mo}_6\text{O}_{21}(\text{H}_2\text{O})_3\}_2\}^4\). Also, dodecanuclear heteromolydates with four phosphante groups \([(\text{RPO}_3)_4\text{MoO}_{34}]^4\) (\(\text{R}=\text{CH}_3\) or \(\text{C}_2\text{H}_5\)) were prepared and isolated. They were characterized by elemental analysis, X-ray analysis, FT-IR, Raman, UV–VIS and cyclic voltammetry.\(^66\) The second important group corresponds to organophosphonoyl polyoxotungstates of Formula
[C₆H₅P(O)]₂Xⁿ⁺W₁₁O₃₉(1²⁻ⁿ⁻) (Xⁿ⁺ = P⁵⁺, Si⁴⁺) that constitute the first molecule in its class and was prepared, purified and characterized by elemental analysis IR, ¹H, ³¹P, and ¹⁸³W NMR by Hill, et al.⁶⁷ It’s chemical structure corresponds to a Keggin derived lacunary complex. The synthesis was prepared by reaction of the lacunary complexes, α-Xⁿ⁺W₁₁O₃₉(1²⁻ⁿ⁻), with phenylphosphonoyl dichloride in acetonitrile solution. Since then, many other chemical structures with different metal transition elements have been elaborated. Functionalization of [α-[RP(O)]₂SiW₁₁O₃₉⁴⁻] hybrid anions consist of an α-[SiWₙ₁₁O₃₉] framework on which is grafted two equivalent organophosphoryl groups through P–O–W bridges.⁶⁸ Going one further step, organothiophosphoryl polyoxotungstates α-[RP(S)]₂PW₉O₃₄⁵⁻ (R = C₆H₅, C₆H₁₁) in the presence of Bu₄NBr acting as phase-transfer reagent were obtained in acetonitrile.⁶⁸ The hybrid anion consists of α-[PW₉O₃₄] framework on which two functional groups are grafted through P-O-W bridges. The third group consists of polyoxovanadate hybrids. One of the first polyoxovanadates was developed by Müller⁶⁹ in 1995. The treatment of vanadium pentoxide with tert-butylamine and triethylamine in the present of phenylphosphoric acid produces a singular hybrid composes of two open truncated cones and a close nanodimensional cavity. Another example of this kind of group members was developed by Yamase.⁷⁰ A Spherical potassium-capped vanadium methylphosphonate, [H₆KV₁₂O₂₇(VO₄)(PO₃CH₃)₃]⁵⁻ and [H₃KV₁₂O₂₇(AsO₄)₄]⁶⁻-isostructural ε-Keggin fragment anion were prepared. Nine V⁴⁺O₆ octahedra and three VO₄ tetrahedra geometrical groups were obtained.
1.8 Heteropolyoxometalate oligomers

An oligomeric hybrid compounds have developed by the reaction of bis(electrophilic) species with a divacant heteropolyanions. [γ-SiW₁₀O₃₆]₈ and two types of bis(phosphonates) i.e. para-xylylenebis(phosphonate) that provides electrophilic groups that were reacted producing one bifunctionalized hybrid.⁷¹

The first Wells-Dawson based dumb-bell clusters [(n-C₄H₉)₄N]₁₀H₂[(P₂W₁₅V₃O₆₂C₄H₆CH₂)₂O] was synthesized in good yield starting from TBA₅H₄[P₂V₃W₁₅O₆₂] with pentaerythritol in dry acetonitrile in reflux conditions.⁷² These hybrid clusters carry ten negative charges and their inorganic heads are linked by an alkoxy group. The ten negative charges are shared by the two Wells-Dawson heteropolyanions cluster heads and are counter-balanced by tetrabutylammonium cations (TBA).

Different Chemical Reviews related to polyoxometalates and hybrids organic-inorganic have been published in the past two decades.⁷³ Gouzerh and Proust⁶ have published a complete review for organometallic derivates and POMs. This review covers POM’s where some {MOⁿ⁺}ⁿ⁺ have been replaced by distinct species. The review has been structured according to the classification of incorporated ligands as main-group element-centered ligands. For example, polyoxometalates incorporating halides,⁷⁴,⁷⁵ peroxo-complexes of molybdenum, tungsten and vanadium,⁷⁶ thiopolyoxometalates,⁷⁷ oxocarbon ligands,⁷⁸, etc. Cronin et al.⁶² has published a didactic manuscript about isopolyanions and heteropolyanions that includes plausible synthesis routes to nanomaterials in different fields.⁶² Dolbecq et al.⁷⁹ has published the most contemporary review in hybrid organic-inorganic polyoxometalates including multiple-functionalized
organic groups that are covalently linked via \( p, d \) and \( f \)-block elements to a great variety of well-organized heteropolyoxometalates unit structures. Also, the manuscript includes reactivity applications for covalently functionalized POMs such as post-functionalization of hybrids, grafting of hybrid POM on planar surfaces and hybrid polymers.
Chapter 2: Methods and Experimental Techniques

2.1 The principle of a laser light scattering

Scattering technique is an indispensable tool for colloid science and nanotechnology (1-1000 nm). The basic of scattering experiment is to send a monochromatic light directly to a sample (Fig. 2.1). The intensity of the scattered radiation is measured by a detector as a function of a scattering angle (θ). However the essential variable is the vector \( q \) whose magnitude depends on the incident wavelength and scattering angle. LLS provides useful and reliable information about different physical properties such as particle size, shape, molecular weight by mass, and internal structure.

![Diagram showing laser light scattering](image)

**Figure 2.1.** Schematic diagram showing one detector measures laser light scattering form a particle. The light scattering intensity depends on scattering angle.\(^42\)
2.2 Static light scattering (SLS)

SLS was employed to measure the radius of gyration \(R_g\) of the samples in solution and \(R_g\) can be defined as follows:

\[
R_g = \sqrt{\frac{1}{V} \int r^2 dv}
\]

(2.1)

Where \(r \approx R_h\) (hydrodynamic radius) and \(V\) is the volume of the particle. Resolving eq. 2.1 for different shapes we obtain the following \(R_g\) values:

\[
\begin{align*}
R_g &= R_h \\
R_g &= \sqrt{\frac{3}{5}} R_h = 0.77 R_h \\
R_g &= \frac{1}{\sqrt{12}}
\end{align*}
\]

\[\text{Figure 2.2. Radius of gyration } (R_g) \text{ for different geometrical shapes.}^{48}\]

The spectrometer was equipped with two lasers operating at 532 nm and 633 nm, respectively. The sample chamber was thermostated and could be controlled to within (0.1 °C). The basis of the SLS data analysis is the Rayleigh-Gans-Debye equation,\(^{81}\) which is used to determine the radius of gyration \(R_g\) of large assemblies in our current case. The scattering vector \(q\) is defined as:

\[
q = (4\pi\lambda/\lambda)\sin(\theta/2)
\]

(2.2)
where $n$ is the refractive index of the solution, $\lambda$ is the wavelength of the incident laser beam ($\lambda=532$ nm), and $\theta$ is the angle of scattering measurement.

### 2.3 Dynamic light scattering (DLS)

DLS which is also known as photon correlation spectroscopy uses the scattered light to measure the diffusion coefficient of the particles. The intensity-intensity time correlation function for DLS measurements, was measured by means of a BI-9000 AT multi-channel digital correlator. The normalized electric field time correlation function was then analyzed by the CONTIN method, which yields information on the distribution of the characteristic linewidth ($\Gamma$). The particle’s apparent diffusion coefficient $D$ was obtained from $\Gamma=Dq^2$ and then its average hydrodynamic radius ($R_h$) depends of size and shape and was calculated according the Stokes-Einstein equation:

$$R_h = k_BT/6\pi\eta_0D$$  \hspace{1cm} (2.3)

where $k_B$ is the Boltzmann constant, $\eta_0$ is the viscosity of the solvent, and $T$ is the temperature of the solution. The apparent $D$ values measured at different scattering angles are extrapolated to zero scattering angle in order to obtain $R_{h,0}$.

### 2.4 Transmission electron microscopy (TEM)

The samples were prepared by pipetting 5 $\mu$L of each solution (1 mg/mL) onto a carbon-coated TEM grid. The TEM studies were performed by JEOL 2000FX microscope operating up to 200 kV.

### 2.5 Zeta potential analysis ($\zeta$)

Zeta Potential is a well-known and reliable technique that has been used in chemistry to measure colloidal particles stability. Zeta potential is a quantitative measurement
between the charge that develops at the particle interface and the liquid medium and one important feature to measure the $\zeta$ is often experimentally accessible.

The net charge around the particle associates the counterion around the Stern layer region. The counterion distribution increases close to the surface charge and starts to decrease and shape a diffuse layer. Therefore a double layer is formed in the region of the particle liquid interface. The double layer prolongs in liquid and it is quantitative represent by the Debye length ($1/\kappa$) which is in fact the double layer thickness. Increasing the Debye length the double layer increases and the particles are most stable. Thus, the double layer is responsible to provide electrostatic repulsion between ionic colloidal particles and stabilize the system. Figure 2.3 shows the representation for double layer including the Stern layer and the zeta potential value on close relation with $1/\kappa$.

![Figure 2.3. Stern layer, double layer and zeta potential representation in a charge spherical particle.](image)
The origin of the charge can be attributed to different surface mechanisms. One of them is to immerse particles in pure or mixture of liquids promoting an ionization of surface groups. Another method is to promote surface charges by adding ionic amphiphilic molecules or surfactants. The specific adsorption and specific characteristic of ionic heads can provide different charge density onto the surface particles. Furthermore, altering or modifying the liquid environment for instance changing the pH, can lead a protonation or deprotonation process onto the surface particles and also influence the ionic surfactant charges. Exist more methods to charge particles. For example, dissolution of ionic solids (salts) in liquids. Also, soluble salts provide ions and, isomorphous substitution where one similar size atom replaced another in crystal lattice, for example in clays.\(^8\) Figure 2.4 shows the mechanisms to charge surface particles.

(a) Ionisation of surface groups  

\[
\begin{align*}
\text{pH}< 7 & \quad \text{Al-O-H} \\
\text{pH}> 7 & \quad \text{Al-O}^{-}
\end{align*}
\]

(b) Ion Adsorption  

\[
\text{Clay} \quad \text{Al}^{3+} \quad \text{Si}^{4+}
\]

(c) Dissolution of ionic solids

(d) Isomorphous Substitution

---

**Figure 2.4.** Four different mechanisms to charge colloidal particles in liquids.
2.6 Langmuir-Blodgett (LB) monolayers

Langmuir-Blodgett monolayers have been studied for many years with specific attention to barrier properties, nonlinear optics, pyroelectricity, etc.\textsuperscript{84-86} LB has been proved to be a reliable technique to study amphiphilic molecules at interface.\textsuperscript{87} Its different attractive characteristics such as an intrinsic monolayer orientation, structure order, well defined segregate phases and precise control of the monolayer thickness are all of them invaluable. The first point of the LB deposition process is the creation of a well defined monolayer at the air-water interface. Transfer and deposit the monolayer to a specific solid support requires a compression to maintain a constant surface pressure. Mainly, the deposition process depends on the hydrophilicity and hydrophobicity of the solid support. The monolayer fabrication process and different monolayer phases are showed in Fig. 2.5.

![Figure 2.5](image)

\textbf{Figure 2.5.} Process to fabricate hybrid surfactant monolayer at liquid-air interface using Langmuir-Blodgett technique. The hybrid surfactant is dissolved in chloroform acetonitrile 90-10 \% vol. solution. (a) The solution is spread over the water phase meanwhile the chloroform evaporates allowing the hybrid surfactants migrate to the interface. (b) Movable barriers manipulate the area per molecule forming a continuous and compress film. (c) The film is transfer to a solid substrate where the monolayer finally collapsed. Surface pressure and molecular area graph showing different monolayer phases at isothermal conditions.
Chapter 3: Examination of the amphiphilic properties of dumb-bell shaped \( \{P_2V_3W_{15}\}_2\)-bis(tris)-amino ligands hybrid surfactants

3.1 Introduction

Polyoxometalates (POMs) represent a large group of giant metal-oxide inorganic clusters with rich physical and chemical properties and potential applications as electronic and catalytic materials.\(^8\) The incorporation of organic components can sometimes modify the electronic properties of the POMs.\(^8,79\) At the same time, hydrophobic organic components are added to the usually hydrophilic POM clusters and result in possible amphiphilic properties, which can increase the compatibility of the POMs in organic media. The resulting hybrid materials will combine not only the advantages of individual inorganic and organic components, but also exhibit close interaction and synergistic effect between them.\(^28,37,89\) Various POM-containing hybrid materials have been synthesized in the past few years via different approaches,\(^90-93\) some of which include diverse inorganic structures and functional organic groups.\(^94,95\)

POM based inorganic-organic hybrid materials might demonstrate amphiphilic features in selective solvents, as confirmed by some preliminary studies from different groups. Recently, Liu\(^96\) showed that Anderson-based hybrids \([\text{TBA}]_3[\text{MnMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CNHCO-(CH}_2\text{)}_n\text{CH}_3\}_2]\) (where TBA\(^+\) = tetrabutylammonium cation and \(n=6,16\)) slowly self-assembled into bilayer vesicular structures in mixed solvents of acetonitrile (MeCN) and water. Furthermore, the same types of hybrids can form reverse vesicles in MeCN/toluene mixed solvents.\(^97\) The
vesicles were detected by and studied by laser light scattering and confirmed by TEM techniques. Fig. 3.1 shows the proposed self-assembly model.

**Figure 3.1.** First vesicular formation by Mn-Anderson-C16 hybrid surfactant in MeCN/water mixed solvent.

Hexagonally packed cylinders have been detected by Landsmann *et al.* A lacunary polyoxometalate species $[\text{PW}_{11}\text{O}_{39}]^{7-}$ works as an inorganic multinuclear head with two alkylsiloxy attached groups. The results is a synthesis for a complete family of anionic hybrid surfactants $[\text{PW}_{11}\text{O}_{39}(\text{SiC}_n)_2](\text{NR}_4)_3$ (R=Me, Et, Bu). The solubility in water and apolar solvents is very limited. On the other hand, the hydrophilic countercation exchange to fabricate $[\text{PW}_{11}\text{O}_{39}(\text{SiC}_n)_2](\text{Na})_3$ ($n=8$, 12, 16) increases the solubility in water significantly in the similar manner to ionic surfactants. DLS provides evidence that micelles scale with the length of the alky chain. Also, depending on length tail and counterions hydrophilicity different liquid crystals in lyotropic phases are formed with water.

Recently, a novel hexavanadate head cluster capped with two C18 alkyl chains, $[\text{V}_6\text{O}^{13-} \{(\text{OCH}_2)_3\text{CCH}_2\text{OOC(CH}_2)_16\text{CH}_3\}_2]^{2-}$, (Fig. 3.2) shows unique blue luminescence
properties by replacing the counterions TBA for protons. This proton interchange increases the solubility in water and shows an efficient surface tension reduction ca. 43 dynes/cm at 1.0 mg/mL at liquid/vapor interface. Furthermore, the hybrid surfactants show a self-assembly process to form bilayer vesicles in aqueous and water/acetone mixture solutions.\textsuperscript{99}

![Figure 3.2. Hexavanadate hybrid surfactant. Two C\textsubscript{18} alkyl chains have been grafted onto opposite sides.](image)

### 3.2 Dumb-bell shaped hybrid surfactants

Five members of novel polyoxometalate (POM) based inorganic – organic hybrids are explored in polar solvents for their surfactant behavior. These dumb-bell shaped hybrids with the general formula \( \{P_2V_3W_{15}\}^2\text{bis(TRIS)} \)-ligands are formed by linking two Wells-Dawson type clusters, \([P_2V_3W_{15}O_{62}]^{9-}\), with different linear bis(TRIS) linker ligands \(L^1 - L^5\) containing oxalamide (\(L^1\)), malonamide (\(L^2\)), succinamide (\(L^3\)), 2,2'-bipyridine (\(L^4\)), and alkyl ether (\(L^5\)) functionalities between the two TRIS moieties (Scheme 1.1).
Scheme 1.1. Diagrams of the bis(TRIS) ligands $L^1$ – $L^5$ used in this study to synthesize the hybrids 1 – 5 respectively.

The new materials were well characterized by elemental analyses, IR and NMR spectroscopy and by ESI-MS spectrometry.\textsuperscript{100,101} One of these ‘dumb-bell’ hybrids (1) was characterized by single crystal X-ray crystallography as well. The X-ray crystallography and ESI-MS analyses have confirmed the formation of dumb-bell shaped hybrids 1-5. Initial studies into their thermal stability showed that these compounds were stable up to approximately 225°C.\textsuperscript{100,101}
Table 3.1. Five dumb-bell shaped inorganic-organic hybrid molecules. The inorganic parts are Wells-Dawson type clusters, connected by five different bis(TRIS) ligands: $\text{L}^1$–$\text{L}^5$. The second column shows approximate lengths of each hybrid. (●) Tungsten; (○) Vanadium; (●) Phosphorous; (●) Oxygen; (●) Carbon; (●) Nitrogen. Hydrogen does not appear just for clarity purposes.

<table>
<thead>
<tr>
<th>Molecular Formulae of Hybrids</th>
<th>Polar head to polar head length, nm</th>
<th>Hybrid Material Molecular Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{TBA}_{10}\text{H}_2[(\text{P}<em>2\text{V}<em>3\text{W}</em>{15}\text{O}</em>{59}(\text{OCH}_2)_3\text{CNHCO})_2]$</td>
<td>4.03</td>
<td><img src="image1.png" alt="Structure 1" /></td>
</tr>
<tr>
<td>$\text{TBA}_{10}\text{H}_2[(\text{P}<em>2\text{V}<em>3\text{W}</em>{15}\text{O}</em>{59}(\text{OCH}_2)_3\text{CNHCO})_2\text{CH}_2]$</td>
<td>4.12</td>
<td><img src="image2.png" alt="Structure 2" /></td>
</tr>
<tr>
<td>$\text{TBA}_{10}\text{H}_2[(\text{P}<em>2\text{V}<em>3\text{W}</em>{15}\text{O}</em>{59}(\text{OCH}_2)_3\text{CNHCOC}_2\text{H}_3\text{N})_2]$</td>
<td>4.25</td>
<td><img src="image3.png" alt="Structure 3" /></td>
</tr>
<tr>
<td>$\text{TBA}_{10}\text{H}_2[(\text{P}<em>2\text{V}<em>3\text{W}</em>{15}\text{O}</em>{59}(\text{OCH}_2)_3\text{CNHCOC}_2\text{H}_3\text{N})_2]$</td>
<td>4.72</td>
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<tr>
<td>$\text{TBA}_{10}\text{H}_2[(\text{P}<em>2\text{V}<em>3\text{W}</em>{15}\text{O}</em>{59}(\text{OCH}_2)_3\text{CCH}_2)_2\text{O}]$</td>
<td>3.35</td>
<td><img src="image5.png" alt="Structure 5" /></td>
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</table>

3.3 Experimental Section

3.3.1 Sample preparation. Crystals or powders of each hybrid material were carefully weighed and dissolved in filter (0.2 μm) acetone. Subsequently, filter (0.2 μm) deionized water was added drop wise with gentle stirring until the desired concentration is reached. The same gentle agitation applied overnight and the solutions were stored at room temperature for 2 hours to attain equilibrium before any studies.

3.3.2 Static and dynamic light scattering (SLS and DLS). SLS and DLS were employed to characterize the morphology and particle size of the hybrid materials. SLS
experiments were performed at scattering angles 15° – 45°, at 2° intervals. For DLS measurements, the sample solutions were filtered by using 0.2 microns membranes into dust-free light scattering cells. The apparent $D$ values measured at 90, 60, 45 and 30 scattering angles are extrapolated to zero scattering angle in order to obtain $R_{h,0}$.

3.3.3 Transmission electron microscopy (TEM). The samples were prepared by pipetting 5 $\mu$L of each solution (1 mg/mL) onto a carbon-coated TEM grid. The TEM studies were performed by JEOL 2000FX microscope operating up to 200 kV.

3.3.4. Zeta potential analysis ($\zeta$). All the $\zeta$ potential analysis measurements were performed using a Brookhaven Instrument Inc. Zeta PALS Analyzer. The sample chamber was maintained at 23 ± 0.1 °C. The instrument is equipped with a red laser operating at 660 nm wavelength and accuracy ±2% for filtrated samples.

3.4 Self-assembly of the Wells-Dawson type cluster based dumb-bell hybrids 1 – 5 in selective solvents

All the five types of Wells-Dawson based dumb-bell hybrids are insoluble in water but quite soluble in acetone and water/acetone mixtures. The solubility varies depending on the type of the organic linkers in the middle of the dumb-bells. The solutions were monitored by using LLS technique for any possible formation of large assemblies. All the hybrid solutions reach equilibrium within 24 hours and there was not further change (i.e., no more additional self-assembly) in solution for up to 90 days, as confirmed by LLS studies.

Formations of supramolecules structures by the five hybrids are observed in mix acetone/water (20 -70 %vol. acetone) solutions using light scattering techniques. SLS
studies reveal relatively strong scattered intensities from such solutions (> 2,000 kcps at 90° scattering angle; for comparison, pure benzene has an intensity of 100 kcps) and DLS studies reveal a narrow particle size distribution with an average $R_h$ value in the range of 142 to 162 nm depending on the type of hybrid (Figure 3.3). For a specific type of hybrid molecule, the large assemblies show a simple relation of $R_g/R_{h,0} \approx 1$, indicating that the assemblies are likely hollow vesicles, as we demonstrated before.\textsuperscript{102}

![CONTIN analysis for the DLS studies on various 1.0 mg/mL hybrid surfactants in 50/50 vol% acetone/water mixed solvent.](image)

**Figure 3.3.** CONTIN analysis for the DLS studies on various 1.0 mg/mL hybrid surfactants in 50/50 vol% acetone/water mixed solvent.

The TEM studies further confirm the formation of hollow vesicular structures in hybrid solutions (Figure 3.4). It is conclusive that the various dumb-bell-shaped hybrid surfactants self-assemble into vesicles in water/acetone mixed solutions. It is reasonable to believe that the dumb-bell hybrids would use their two polar POM clusters to face the
hydrophilic solvent while their organic linkers would form a hydrophobic domain in the middle. The semi hollow structure for hybrids 1 containing oxalamide functionality in the linker and for hybrid 3 containing succinamide functionality, is attributed to a greater number of hybrid molecules in the vesicle promoting a more compact distribution and smaller vesicle size. Unsurprisingly, both hybrids present the lowest $R_g$ and $R_{h,0}$ values allowing a better packing association and decreasing the hybrid-hybrid average distance.

![Figure 3.4. TEM shows the presence of hollow sphere vesicles corroborating the light scattering results. All the solutions were analyzed in acetone/water at 50% vol. and 1.0 mg/mL. The hybrid surfactants with a) oxalamide, b) malonamide; c) succinamide; d) 2-2' bipyridine, e) pentaerythritol functionalities on the linkers have their $R_{h,0}$ values 142, 162, 155, 159 and 174 nm respectively.](image-url)
3. 5 The state of Counter-cations (TBA) on the vesicle formation

It is always an interesting question that how the hybrid materials form closely packed hydrophobic layers in their vesicles. These hybrids are different from conventional surfactants in that they have large polar head groups. Consequently, the bulky head groups will make the close packing of hydrophobic domains (here the alkyl chains) very difficult due to the spatial obstruction. We speculate that the large TBA cations will get involved in forming the hydrophobic domains by contributing their long chains.\textsuperscript{103-105} Furthermore, these cations might further effectively screen the repulsive interactions between adjacent POM clusters on vesicle surface, as suggested schematically in Figure 3.5.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{vesicle_diagram.png}
\caption{Cartoon of the vesicle formation occurring in the presence of hybrid surfactants and TBA counter-cation in water/acetone mixtures.}
\end{figure}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
Protein & Concentration (M) \\
\hline
\textit{a} & 1x10^{-4} \\
\hline
\textit{b} & 1x10^{-3} \\
\hline
\end{tabular}
\caption{Concentration of Proteins in Solution}
\end{table}

\textsuperscript{\textsuperscript{1}}\textsuperscript{H} NMR DOSY experiment was performed to determine the diffusion coefficients of protons in solution to confirm the binding between TBA and hybrid surfactants.\textsuperscript{106} 1x10^{-4} M of \textit{n}-tetrabutyl ammonium iodide (TBAI) (as a reference) and hybrid 5 in 50/50 vol\% acetone-\textit{d}_6/D\textsubscript{2}O solution were prepared in order to compare the diffusion...
coefficients of their protons. As shown in Figure 3.6, the four groups of protons from the $n$-butyl chains of TBAI show diffusion coefficients of $4.08$, $4.47$, $4.00$ and $3.74 \times 10^{-10}$ m$^2$/s, respectively. On the other hand, the same proton groups from TBA in hybrid 5 have values of $2.93$, $3.03$, $2.70$, $3.00 \times 10^{-10}$ m$^2$/s, respectively, suggesting that the TBA ions move much slower in the presence of hybrid vesicles. It is clear that TBA counter-cations are closely associated to the large vesicles due to electrostatic interactions.

![Figure 3.6](image.png)

**Figure 3.6.** $^1$H DOSY was elaborated to infer the TBA binding onto the polar heads. Four different diffusion coefficients are clearly identified and corresponding to the peaks 1 to 4 respectively.

This experiment cannot directly confirm the involvement of the alkyl chains on TBAs into the hydrophobic region since in such a case the protons will almost immobile and do not generate any signals from NMR DOSY studies.
3.6 Determination of the critical association concentrations (CAC) of the vesicle formation

The CAC is defined as the concentration to associate amphiphilic molecules in solution. Different techniques to measure this relevant point are found in previous studies such as surface tension, turbidity, static light scattering (SLS), etc. Precisely, SLS technique is used because it provides accurate values in many different colloidal and polymeric systems.\textsuperscript{107} The scattered intensity ($I$) keeps a direct square proportion to the vesicle size ($I \propto R_h^2$). These vesicles are detected as an inflexion point as a result to increase the scattered intensity adding small increments of hybrid surfactant in solution. Figure 3.7-A shows a typical measurement for a hybrid surfactant at different temperatures by using SLS. Figure 3.7-B corroborates this trend where the CACs for the first three members of the family, 1, 2 and 3 are shown at 25°C. The trend indicates a hydrophobic contribution that decreases the CACs values due to more methylene groups.

The rest family members also follow a similar trend or behavior and the values became lower at greater temperatures.
Figure 3.7. (A) Critical aggregation concentration (CAC) result of hybrid 1 in 50% vol. acetone/water solution at 25, 35 and 45°C. (B) CAC for the first three members of the hybrid family in 50% vol. acetone/water solution at 25°C (♦) 1, CAC = 1.34x10^-4 mmol/L; (■) 2, CAC = 0.89x10^-4 mmol/L; (▲) 3, CAC = 0.45x10^-4 mmol/L.
3.7 Methylene group effect

Figure 3.8-A shows the CAC trend for hybrids 1, 2 and 3 in a strong dependency of methylene groups at three different temperatures (25, 35 and 45°C). The trend shows that increasing -CH$_2$- groups the CAC decreases. A similar comparison can be observed on CMC values for nonionic surfactants (i.e. oxyethylene n-alkyl alcohols, β-glucoside) and ionic surfactants (i.e. alkyl sodium sulfates). The CMC decreases as a function of alkyl length of the surfactants, as a consequence to increase the free energy.$^{108-111}$ However, anionic surfactants present CMC values in the range of $10^{-1}$ to $10^{-3}$ M and nonionic surfactants present two order of magnitude less than anionic.$^{112}$ In contrast, these novel hybrid surfactants present CACs values around $10^{-7}$ to $10^{-9}$ M which are significantly smaller than conventional amphiphilic molecules. Similar results have been obtained by Liu$^{113}$ on {Mo$_{72}$Fe$_{30}$} polyoxometalates to form blackberries (BB). The CAC value is ca. 1.26x$10^{-7}$ M at 50°C. To form {Mo$_{72}$Fe$_{30}$} BBs the major attraction forces are physical interactions and not chemical bonds. Probably, the same physical interactions such long-range like-charge attraction via TBA countercations and also hydrophobic associations are responsible to initiate the vesicular formation process for our system. Figure 3.8-B shows the effect of the temperature for hybrids 1, 2 and 3 in function of the CAC, increasing the temperature the CAC decreases. This behavior is similar to oxyethylene alkyl-chains (C$_n$E$_m$) nonionic surfactants$^{114}$ and opposite for anionic surfactants such as sodium alkyl sulfonates where, increasing the temperature the CMC is increased.$^{115}$ To explain the nonionic surfactant behavior we assume that the countercations (TBA) effectively neutralize most of the anionic charges and therefore the repulsions between
polar heads are decreased allowing a vesicle formation. Therefore, increasing the counteraction (TBA) association causes a decrement in the CAC.\(^{116}\)

![Figure 3.8-A](image-url)  
**Figure 3.8-A.** Effect of the methylene group (-CH\(_2\)-) values for hybrids 1, 2 and 3.
The CAC value for the last two members, hybrids 4 and 5 are \(2.7 \times 10^{-5}\) and \(2.3 \times 10^{-6}\) mmoles/L respectively at 25°C. This result shows in certain way the effect of the organic linkers in the vesicular process. A plausible explanation to this behavior is that the polar heads are not completely neutralized or completely bound by TBA countercations and mutual charge repulsion is presented.

### 3.8 Thermodynamic parameters for the hybrid surfactants self-assembly

The thermodynamic parameters of vesicle formation can be obtained from the temperature dependence of the CAC values which can provide useful information about the driving force behind vesicles formation from the hybrid surfactants. The standard enthalpy (\(\Delta H^\circ_m\)) value can be determined using the Gibbs-Helmholtz equation.\(^\text{81}\)
\[
\Delta H_m^o = -T^2 \left( \frac{\partial (\Delta G_m^o / T)}{\partial T} \right)_p
\]  

The change in entropy (\(\Delta S_m^o\)) can be calculated by Gibbs relation using the following equations:

\[\Delta G_m^o = RT \ln X_{CAC} \]  

(3.2)

\[\Delta G_m^o = \Delta H_m^o - T \Delta S_m^o \]  

(3.3)

Figure 3.9 shows the results for all hybrid family and all of them present a change in free energy (\(\Delta G_m^o\)) which is negative indicating that the formation of vesicles is spontaneous process. The values of standard enthalpy changes (\(\Delta H_m^o\)) for association are all positive (see eq.3.1), implying that the vesicle formation process is endothermic. The negative values of \(\Delta G_m^o\) are attributed to large positive \(T \Delta S_m^o\) values. These features are quite typical for the self-assembly of amphiphiles in polar solvents because the self-assembly process is accompanied by breaking some ordered solvent structures around hydrophobic domains.
Figure 3.9. Gibbs free energy change for the hybrids (1 – 5) at different temperatures.

To compare these unique hybrid surfactants with conventional ionic surfactants, previous studies showed that sodium dodecyl sulfate (SDS) and dodecyl pyridinium bromide (DPB),\textsuperscript{118} revealed that the vesicle formation is also an entropy-driven process. Furthermore, ionic Gemini surfactants with different spacer length report $T\Delta S^\circ_m$ values between 14.6 to 29.2 KJ/mol at 25°C.\textsuperscript{119} Our $T\Delta S^\circ_m$ results are 6 times greater at the same temperature (see Table 3.2)
We speculate that this significant differences may be attributed to the hydrophobic and bulky TBA counter-cations (each hybrid molecule has 10 TBA counter-ions). The TBA ions possess long hydrophobic tails which might be involved in the vesicle formation process by destroyed well organized water molecules around their tails and increasing the entropy of the system. In addition, a close entropy analysis reveals that the space length or distance may modify such property. A progressive entropy increment is presented as the length or distance between the polar heads is increased (see Fig.3.10). A greater space between the polar heads may provide more freedom for the hybrid molecules to rotate. This greater degree of molecular freedom increases the entropy of the system.

### Table 3.2. Thermodynamic parameters for dumb-bell hybrids 1-5.

<table>
<thead>
<tr>
<th>Hybrid</th>
<th>Temp., °C±0.2</th>
<th>ΔG°m, KJ/mol</th>
<th>ΔH°m, KJ/mol</th>
<th>TΔS°m, KJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>-48.1</td>
<td>44.5</td>
<td>92.6</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>-51.7</td>
<td>47.6</td>
<td>99.3</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>-54.5</td>
<td>50.7</td>
<td>105.2</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>-51.6</td>
<td>43</td>
<td>94.6</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>-53.5</td>
<td>45.9</td>
<td>99.4</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>-58.1</td>
<td>48.9</td>
<td>107.1</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>-50.8</td>
<td>47.2</td>
<td>98.0</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>-54.5</td>
<td>50.4</td>
<td>104.9</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>-57.6</td>
<td>53.7</td>
<td>111.3</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>-45.7</td>
<td>57.9</td>
<td>103.6</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>-48.7</td>
<td>61.8</td>
<td>110.5</td>
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</tr>
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<td>42.1</td>
<td>94.0</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>-55.1</td>
<td>44.9</td>
<td>100.0</td>
</tr>
</tbody>
</table>
Figure 3.10. Hybrid surfactants length between polar heads increases the entropy.

3.9 Surface charge regulates the self-assembly of hybrid surfactants

It is known that for the formation of shell-like assemblies, the size of the assemblies has a clear trend with the solvent content (in dielectric constant) if the self-assembly process is charge-regulated. This is confirmed in the different “blackberry”-type structures formed by various fully hydrophilic, highly soluble macroions in polar solvents,\(^ {120} \) which are driven by the counter-ion-mediated attraction and hydrogen bonding. Separately, the bilayer vesicle formation in different solvents for the Mn-Anderson-C\(_{16}\) hybrid surfactant and for one of the dumb-bell hybrid \(^ {5} \)\(^ {15} \) were also charge regulated. To go one step further, here we compare the average assembly sizes of the five
types of dumb-bell hybrids under the same experimental conditions (e.g., solvent content and temperature). Figure 3.11 shows that a linear relationship between the vesicle’s average \( R_{h,0} \) value and the inverse dielectric constant \( (1/\varepsilon_r) \) is observed for each of the five systems, further confirming that the five dumb-bell hybrids follow very similar self-assembly mechanisms. The slopes of the linear regressions shown in Figure 3.11 reveal the magnitude of the attractive forces among the monomers on vesicle surface, accordingly to the relation obtained by Kegel, et al.\textsuperscript{121} first in blackberries formed by \{Mo\textsubscript{132}\} polyoxometalate clusters:

\[
R \approx -48\lambda_b\mu/\zeta^2 \quad (3.4)
\]

\[
\lambda_b = e^2/4\pi\varepsilon_0\varepsilon_r k_B T \approx 56/\varepsilon_r \quad (3.5)
\]

where \( \mu \) is the cohesive bond energy and can be described as the energy that can divide an assembly into isolated monomers. \( \zeta \) is the Zeta potential, \( \lambda_b \) is the Bjerrum length, \( \varepsilon_0 \) is the vacuum permittivity, \( \varepsilon_r \) is the relative dielectric constant of the solvent, \( e \) is the electron charge, \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature.

The cohesive bond energy must be capable to maintain the monomers assembled and stable at equilibrium conditions. Hence, the cohesive bond energy has a direct relation with the stability of vesicular structures. To study the stability of the vesicles formed by five types of hybrid surfactants in acetone/water we have calculated the cohesive bond energy \( (\mu) \), and consequently the chemical potential \( (\Delta\mu^e) \) for the vesicle formation. The chemical potential is calculated assuming a hexagonal arrangement; the effective number of bonds of one hybrid cluster is therefore three \( (\Delta\mu^e=3\mu) \). The \( \mu \) values are shown in Table 3.3
Table 3.3. Zeta potential for vesicles ($\zeta$), Cohesive bond energy ($u$) and chemical potential ($\Delta\mu^0$) for all five dumb-bell hybrids 1 – 5.

<table>
<thead>
<tr>
<th>Dumb-bell hybrid</th>
<th>$\zeta$, $k_BT$</th>
<th>$u$, $k_BT$</th>
<th>$\Delta\mu^0$, $k_BT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1.10</td>
<td>-1.84</td>
<td>-5.52</td>
</tr>
<tr>
<td>2</td>
<td>-1.39</td>
<td>-2.60</td>
<td>-7.81</td>
</tr>
<tr>
<td>3</td>
<td>-1.63</td>
<td>-3.92</td>
<td>-11.77</td>
</tr>
<tr>
<td>4</td>
<td>-1.52</td>
<td>-11.73</td>
<td>-35.18</td>
</tr>
<tr>
<td>5</td>
<td>-2.45</td>
<td>-7.52</td>
<td>-22.56</td>
</tr>
</tbody>
</table>

Hybrid that shows a greater slope indicates a larger $u$ value, i.e., stronger attraction among unimers. We speculate that the interpretation of all above values can be explained by the rigidity and hydrophobicity of the organic parts. The first three hybrids, with similar organic linkers, exhibit rigid properties in the following order: 1>2>3; less carbon atoms in the linker suggest more rigidity of the hybrids. This may explain the difference in the cohesive energy values. Apparently, the volume, length and rigidity of the organic linker control the curvature of the vesicles and prescribe the structure. In addition, hybrid 3 is the most hydrophobic among these three and has the highest $u$ value. A possible reason is an associative interaction between the succinamide groups. Succinamide monomers tend to associate into clusters in water/acetone mixed solvents, suggesting that succinamide might contribute additional attractive force to the vesicle formation.

The hybrids 4 and 5 possess much more negative $\Delta\mu^0$ values than the first three hybrids 1 - 3. This could be due to their very different organic ligands from 1 - 3. Hybrid 4 has
very rigid aromatic rings, and consequently shows the strongest attraction among all the five hybrids.

According to the solubility parameters hybrid 5 has the most hydrophobic organic ligand. Consequently, it has the smallest slope among the five hybrids as shown in Figure 3.11. A possible reason is that in 5, the hydrophobic domain is so dominant that it minimizes the effect of electrostatic interactions. Furthermore, hybrid 5 starts to form vesicles in solvents with relatively low acetone contents, which also suggests the contribution from hydrophobic interaction. For comparison, the thermodynamically stable blackberries have $u$ values around -5 to -7 $k_B T$. 

![Graph showing the linear dependence between $R_{h,0}$ and $1/r$. The slopes are as follows: (♦) 1, 4124 nm; (■) 2, 3649 nm; (▲) 3, 3975 nm; (×) 4, 10922 nm and (٭) 5, 3380 nm.]

**Figure 3.11.** Hybrid surfactants show a linear dependence between $R_{h,0}$ and $1/r$. The slopes are as follows: (♦) 1, 4124 nm; (■) 2, 3649 nm; (▲) 3, 3975 nm; (×) 4, 10922 nm and (٭) 5, 3380 nm.
3.10 Vesicle stability as a result of cohesive bond energy

The CAC values can be further used to determine the thermodynamic properties during the vesicle formation. For hybrid 5, the CAC is $2.3 \times 10^9$ mol/L at 298K in acetone/water mixed solvent containing 50 vol% acetone. By assuming that vesicles consist of predominantly a hexagonally array, it is possible to obtain the cohesive bond energy ($u$) by the following equation:\textsuperscript{122}

$$X_{CAC} \approx e^{\frac{n_b u}{k_B T}}$$

(3.6)

where $n_b$ is the average number of bonds per molecule (here is three). The obtained value is ca. $-7.0k_BT$. This result is very encouraging because of its proximity with our previous result of ca. $-7.5 k_BT$ (see Table 2) obtained from a different approach. Then, the chemical potential ($\mu^0$) is calculated using the following equation:\textsuperscript{126}

$$X_{CAC} \approx e^{\frac{\mu^0}{k_B T}}$$

(3.7)

where ($\mu^0$) is the difference in chemical potential between a hybrid surfactant in a vesicle and in solution and is ca. $-22.56k_BT$.

Among all the hybrid surfactants, hybrid 4 exhibits the highest cohesive bond energy ($u$). Hybrid 4 has bulky aromatic rings and the largest distance between two polar head groups (ca. 1.60 nm). We consider that this space is enough to allow these $\pi-\pi$ associations. In comparison, hybrid 5 presents the most hydrophobic organic linker among these hybrids. However, the distance between two polar head groups probably is not enough to allow intermolecular associations through the middle part, due to the electronic repulsions between the adjacent POM groups on vesicle surface. In such a case, we speculate that the TBA counter-cations get involved into the vesicle formation.
by contributing their alkyl chains into the hydrophobic layers of the vesicles. On the other hand, bis(TRIS)-ligands $\text{L}^1$, $\text{L}^2$ and $\text{L}^3$ have similar organic middle parts and their cohesive bond energies are proportional to the number of carbon atoms in their linkers.

### 3.11 Formation of the vesicles using Rayleigh-Gans-Debye analysis in water/acetone mixtures.

Another important issue to be considered is the scattered intensities at different solvent polarities. SLS studies disclose that the scattered intensities are recognized at least for two different possibilities. The first one is an increase in the vesicle’s concentration and the second one is attributable to an increase in the vesicle’s size or $R_{h,0}$. To determine which one is the most dominant the Rayleigh-Gans-Debye equation is employed:

$$I \approx C \cdot M_w = C \cdot R_{h,0}^2$$

(3.8)

where $I$ is the scattered intensity, $C$ is the concentration and $M_w$ is the molecular weight in g/mol.

SLS analysis for hybrid 1 and, hybrid 4 reveals an increment of the scattered intensity between 5 to 6 times for both. This is observed when both hybrid surfactants change the solvent polarity from 20 to 50% acetone/water solution. Hybrid surfactant 1 is the most hydrophilic member of the family and shows the less pronounced slope. On the other hand hybrid surfactant Hybrid 4 is the second most hydrophobic and presents the most pronounced slope (Figure 3.11). A close analysis at different acetone/water compositions reveals that hybrid 1 hydrodynamic radius at zero angle increases from 41.3 to 63.3 nm; the size difference is ca. 22 nm. By contrast, in Hybrid 4 the $R_{h,0}$ increases
from 36.1 to 93.3 nm; the size difference is ca. 57 nm. According to these results and Rayleigh-Gans-Debye equation (3.8); we can conclude that the increment in the scattered intensity for Hybrid 1 is related to the formation of more vesicles when more acetone is supplemented. On the other hand, in the case for Hybrid 4, the increment is coming from a development in the vesicle size \(R_{h,0}\) at different solvent polarities. A similar analysis is used for Hybrids 2 and 3 at different acetone/water contents. Both hybrid surfactants present analogous scattered intensities and \(R_{h,0}\) values and the primary difference between both is just one carbon located in the middle organic part. No notable differences are found between them. However, Hybrid 5 is the most hydrophobic member of the family and presents a similar elevation slope than hybrid 1, 2 and 3 but the vesicle size is greater. We speculate that this difference is the result of having a greater solvophobic region than the others; therefore more interactions or associations are formed with the TBA\(^+\) counterions allowing to reach such vesicle sizes.

3.12 Bending and edge interchange energies and elastic constants influence

The self-assembly of amphiphilic molecules into vesicles is recognized as a bending process. The bending energy and the elastic modulus of vesicle formation for charged lipids, phospholipids and nonionic, ionic and catanionic surfactants in aqueous solutions have been well studied.\(^{127-129}\) The so-called elastic constants including the spontaneous curvature \(LC_{sp}\), the elastic modulus \(k_c\) and the Gaussian bending constant \(k'\) can be applied to describe the properties of surfactant films and to predict the vesicle size.\(^{130}\) For example, the bending elastic modulus \(k_c\) for phospholipid systems lie in the range of 1-20 \(k_BT\) \(^{131,132}\) and the bending modulus for SDS is ca. 7.06 \(k_BT\) (at \(T=298K\)).\(^{133}\) These
values can serve as a good reference for our current study to clarify the similarities and differences between the conventional surfactants and the hybrids. Our current systems are much more complicated because there are the special polar head groups, mixed solvents and large, amphiphilic counter-ions, the dumb-bell shaped molecular architectures, and various structures of the organic linkers. For example, adding more -CH$_2$- group into the middle linker increases the linker’s flexibility and hydrophobicity while adding aromatic rings increases the linker’s rigidity. Based on a theoretical model proposed by Liposwsky$^{134}$ the bending and edge energies for the vesicle formation of these hybrid surfactants are calculated for spherical cap geometry by the following equations:$^{135}$

$$E_{\text{bend}} = 2\pi k_c (L C - L C_{sp})^2$$  \hspace{1cm} (3.9) \\

$$E_{\text{edge}} = 2\pi L \lambda \sqrt{1 - (L C/2)^2}$$  \hspace{1cm} (3.10)

with $C$ being the curvature of the vesicle($1/R_{h,0}$), ($L=2R_{h,0}$) being the length of the membrane, $k_c$ being the elastic modulus, and ($\lambda$) being the edge energy per unit length (with a value of $1 \times 10^{-20}$ J/nm).$^{54}$ The spontaneous curvature ($L C_{sp}$) is observed in cationic, anionic surfactant mixing solutions that present non ideal behavior promoting inside or outside different compositions in the membrane.$^{136}$ Due to the fact that our monolayer or membrane, that later evolves to vesicles, is not the result of ionic surfactants blend the spontaneous curvature ($L C_{sp}$) is negligible. In addition, one important property of these novel hybrid surfactants is their symmetrical dumb-bell anionic polar heads that forms a symmetrical sphere shape avoiding any possible influence.

The complete vesicle formation is achieved at $L C=2$. Consequently, Eq. (3.9) is simplified to:$^{137}$
In Eq. (3.11) the number two on denominator implies that the hybrid surfactants just form vesicles with one monolayer instead of two which is the case for conventional surfactants.

A common vesicle formation process is described in Figure 3.12, starting from the membrane formation. As the membrane grows in size, the edge energy increases due to the increased exposure of the solvophobic edge to the solvent until it reaches a critical value, followed by a bending process where the membrane possesses intrinsic elastic properties due to molecular structure or associations. If the edge energy exceeds the bending energy, the film starts to bend. When the curvature of the membrane reach a certain critical value \((LC_{\text{critical}})\) of ca. 1.8, the membrane will close spontaneously to form a complete spherical vesicle. Figure 3.13 shows the competition between bending energy and edge energy for hybrid 5 to form one vesicle.

![Figure 3.12. Process of vesicle formation: (a) membrane formation; (b) bending process; (c) edge energy overcomes bending energy; (d) vesicle formation.](image_url)
Figure 3.13. Bending and edge energies of hybrid 5. The edge energy and bending energy presents a competition process. As the LC increases the edge energy decreases until \( LC_{\text{crit}} \) value is reached and the vesicle will form spontaneously.

\( \pi-A \) isotherms (Figure 5.1) and Eq. 3.12 are used to calculate the elastic constants and bending energies of various dumb-bell shaped hybrids. The two-dimensional surface compression modulus (\( C_{S}^{-1} \)) is referred as the equilibrium in plane elasticity modulus.\(^{139,140} \) Also, the \( C_{S}^{-1} \) was defined by Davis\(^{141} \) to make possible comparisons with elastic modulus of area compressibility data\(^{62,63} \) and it is calculated from the following relation:

\[
C_{S}^{-1} = A \frac{\partial \pi}{\partial A}_T \tag{3.12}
\]

where \( A \) is the area of the monolayer at \( \pi=0 \) and \( (\partial \pi/\partial A)_T \) is the slope at liquid condensed phase.
For comparison, SDS anionic surfactant has a bending energy value ca. 90 $k_B T$ and form small radius micelles ca. 1.8 nm.\textsuperscript{142} On the other hand, vesicles from cationic-anionic (catanionic) surfactants such SOS/CTAB presents a bending energy ca. 610 $k_B T$ and correspondingly average vesicle $R_h$ value around 20 nm.\textsuperscript{135} The current hybrid surfactants have vesicles with bending energies similar to those in the vesicles from catanionic systems, but they are significantly larger. We speculate that this difference in vesicle size is due to the special molecular morphologies of the hybrids and the amphiphilic counter-cations. The dumb-bell shape enable the hybrids to form bilayer structures by using only one layer of the molecules, which increases the rigidity of the membrane and consequently increases the bending energy compared to conventional surfactants. This feature favors the formation of larger vesicles. In addition, the TBA counter-ions might participate in the vesicle formation by contributing their alkyl chains to the hydrophobic domains, which again increases the rigidity and length of the membrane by decreasing the electrostatic repulsions. With dominant bending energy, the precursor membrane could be larger. Consequently, the elastic modulus would also increase, resulting in larger vesicle size. This is exactly what we have observed in various hybrid vesicle systems, as shown in Figure 3.14 the increment of elastic modulus increases the average size (in $R_{h,0}$) of the vesicles. In addition, Figure 3.15 shows the hybrid lengths and its influence to elastic modulus. The trend follows a liner behavior for the alkyl-amide groups. However, hybrid 4, which possess aromatic rings do not follow the same behavior. In fact, the rigid aromatic groups increase the elastic modulus.
Figure 3.14. Vesicle size (in $R_{h,0}$, this is $R_{h,0}$ value extrapolated to zero scattering angle) increases with increasing elastic modulus of the hybrid surfactants. (♦) Hybrid 1, (■) Hybrid 2, (▲) Hybrid 3, (×) hybrid 4 and (٭) Hybrid 5. (b). A stretch relation is observed between the polar-polar head length and the elastic modulus for the hybrid family except for hybrid 4. (■).

Figure 3.15. Vesicle size (in $R_{h,0}$, this is $R_{h,0}$ value extrapolated to zero scattering angle) increases with increasing elastic modulus of the hybrid surfactants.
3.13 Effect of electrostatic interactions on the vesicle’s elastic properties in acetone/water mixed solvents.

The effect of charge on bending constants of surface membranes indicates that the elastic constants behave differently with different surface charge density or surfactant concentration.\textsuperscript{143-145} The elastic modulus $k_{ele}^c$ increases until the surface charge is completely saturated. On the other hand, the Gauss modulus $k_{ele}^{c'}$ decreases (become more negative) with increasing surface charge. In our current case, each dumb-bell hybrid molecule contains ten negative charges and ten TBA counter-ions. Winterhalter and Helfrich\textsuperscript{146} proposed to calculate the electric contribution to the bending modulus using the following equations:

$$k_{ele}^c = \frac{\sigma^2(1+\delta^2)}{\varepsilon_w \chi} \frac{3}{4\chi^2}$$ \hfill (3.13)

$$k_{ele}^{c'} = -\frac{\sigma^2(1+\delta^2)}{\varepsilon_w} \left( \frac{1}{2\chi^2} + \frac{d}{2\chi} \right)$$ \hfill (3.14)

where $k_{ele}^c$ is the bending modulus and $k_{ele}^{c'}$ is the modulus of Gaussian curvature, the superscript “ele” refers to the electrostatic contributions without taking in consideration of other forces such as Van-deer Waals forces, etc. The surface charge density $\sigma$ is in C/m\textsuperscript{2}; $2\delta$ is the surface charge difference between the inner and the outer monolayer and is negligible here due to the symmetrical feature of the hybrids, $d$ is the thickness of the membrane and it assumes here to be the total head to head distance of the hybrid surfactants, $\varepsilon_w$ is the dielectric constant of the water and $\chi$ is the Debye screening length.

The surface charge was calculated using the Hückel equation:

$$\mu_0 = q/(6\pi \eta r)$$ \hfill (3.15)
where $\mu_0$, $q$, $\eta$, and $r$ are the absolute mobility of particles, the effective charge on particles, the solvent viscosity and the particle radius, respectively.\textsuperscript{21}

The five hybrids have the same number and type of polar head groups and charges; therefore we would expect similar electrostatic contributions to the bending modulus ($k_c^{\text{ele}}$) to their vesicles. However, the real situation is more complicated. The $k_c^{\text{ele}}$ and surface charge for all five hybrids; are clearly different, as shown in Figure 3.16. A linear relationship between the surface charge density and $k_c^{\text{ele}}$ is observed and the electrostatic contributions to $k_c$ are around 15 to 25 %. That means that these unique polar head groups and counter-cations (TBA) condensation have a significant contribution to the bending energy of vesicle formation.

**Figure 3.16.** Influence of the surface charge per vesicle ($\sigma$), and its effect to form vesicular structures at 25°C.
A summary on the electrostatic and elastic properties of the vesicles formed by five types of hybrids are summarized in Table 3.3. The Invagination length sets the length scale at which we expect to find the first membrane development stage but showing promise or potential to form the vesicle. Our analysis shows that the invagination lengths ($\xi=\frac{k_c}{\lambda}$) for hybrid 1, hybrid 2, and hybrid 3 have similar values around 12±3 nm, in a good agreement and correlation with the estimated value for phospholipid membranes (6.9 - 10 nm). In contrast, the invagination lengths for hybrid 4 and hybrid 5 are almost doubled. It could be attributed to the rigidity of the organic linkers. More rigid linkers such aromatic rings lead to more rigid membranes; and therefore greater invagination lengths.

Another important issue is the Gaussian modulus shown in Table 3.4; the Gaussian modulus increases as the surface charge decreases. However, in our case there are some discrepancies specifically for the hybrid 4 and hybrid 5 vesicles. The Gaussian modulus behavior depends on the vesicle thickness (see eq.18) and for our system the thickness was considered the head to head distance of each hybrid molecule.

Finally, the stability or instability of the vesicles is dictated by the term $2k_c^{ele}+k_c^{ele}$. When $2k_c^{ele}+k_c^{ele}>0$ the vesicles are stable and when $2k_c^{ele}+k_c^{ele}<0$ the vesicles are instable. In our case all the vesicle formations have $2k_c^{ele}+k_c^{ele}$ values>0; thus the hybrid vesicles are stable in solution.
Table 3.4 Electrostatic and elastic properties for the five hybrid surfactants are shown. The test conditions were in water/acetone at 50% Vol. content and 25°C

<table>
<thead>
<tr>
<th></th>
<th>Hybrid 1</th>
<th>Hybrid 2</th>
<th>Hybrid 3</th>
<th>Hybrid 4</th>
<th>Hybrid 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration in mg/mL</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$\xi$ = in nm</td>
<td>12.7</td>
<td>10.2</td>
<td>13.2</td>
<td>16.8</td>
<td>22.3</td>
</tr>
<tr>
<td>$\sigma$, A·s/m²x10⁻⁴</td>
<td>1.79</td>
<td>1.45</td>
<td>1.04</td>
<td>0.92</td>
<td>1.21</td>
</tr>
<tr>
<td>$k_c$, k_BT</td>
<td>30.9</td>
<td>24.7</td>
<td>17.8</td>
<td>40.8</td>
<td>54.1</td>
</tr>
<tr>
<td>$k_c^{ele}$, k_BT</td>
<td>10.9</td>
<td>6.1</td>
<td>4.4</td>
<td>7.7</td>
<td>16.4</td>
</tr>
<tr>
<td>$k_c^{ele}$, k_BT</td>
<td>-7.5</td>
<td>-4.2</td>
<td>-3.0</td>
<td>-5.4</td>
<td>-11.3</td>
</tr>
<tr>
<td>$\lambda$ in J/nm x 10⁻²⁰</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>$E_{bend} = 4\pi k_c$, k_BT</td>
<td>389</td>
<td>310</td>
<td>224</td>
<td>512</td>
<td>680</td>
</tr>
<tr>
<td>$E_{edge}$, k_BT</td>
<td>1089</td>
<td>1233</td>
<td>1183</td>
<td>1206</td>
<td>1331</td>
</tr>
<tr>
<td>$E_{ves}^{ele} = 2\pi(2k_c^{ele} + k_c^{ele})$, k_BT</td>
<td>89.3</td>
<td>49.9</td>
<td>36.2</td>
<td>63.3</td>
<td>136</td>
</tr>
</tbody>
</table>

In summary, the POM-organic hybrids indeed demonstrate certain typical amphiphilic behavior in polar solvents. Their large, rigid polar head groups and the unique molecular architecture render their self-assembly new features such as the very high entropy gain and the involvement of the amphiphilic counter-ions for the self-assembly, and the different organic linkers make the self-assembly behavior highly adjustable. With similar molecular architectures, these hybrid surfactants demonstrate similar and predictable self-assembly behaviors, which will certainly enrich the family of amphiphilic surfactants, and at the same time expand the applications of the POM materials to organic media.
Chapter 4: Spontaneous vesicle formation of different hybrid surfactants families: Organoamine Monomeric and Trimeric Wells-Dawson heterotungstates & bola bis(organoimido)-bridged hexamolybdate

4.1 Introduction

In the previous chapter we have showed that the dumb-bell shaped hybrids containing two Wells-Dawson type clusters linked together by organoamines groups forms vesicle structure in acetone/water mixed solvents.\textsuperscript{100} Therefore these innovative molecules can be treated as surfactants due to their intrinsic amphiphilic properties to form well-defined hollow structure and spherical morphology. In these first two sections of this chapter the objective is to study the influence of one and three polar Wells-Dawson heterotungstate heads under similar solution conditions and their contribution to form vesicle. The last sections analyze three different types of hybrid bola bis(organoimido)-bridge hexamolybdates in tolune/MeCN solutions.

4.2 Experimental Section

4.2.1 Sample preparation. Homogeneous and clear solutions for benzene tris-\{P\textsubscript{2}V\textsubscript{3}W\textsubscript{15}\}; triazine tris-\{P\textsubscript{2}V\textsubscript{3}W\textsubscript{15}\}; hexanamide-\{P\textsubscript{2}V\textsubscript{3}W\textsubscript{15}\} and hexadecanamide-\{P\textsubscript{2}V\textsubscript{3}W\textsubscript{15}\} were prepared in acetone/water (20-50\%vol.acetone) blends. For such purpose, fine powder crystals of each hybrid were carefully weighed and dissolved in acetone. Subsequently, deionized water was added drop wise with gentle stirring until the desired concentration is reached. In a second set of experiments, Wells-Dawson dumbbell hybrids 1-3 and crystals of bis(organoimido)-hexamolybdates compounds 1-3 were
dissolved in toluene/MeCN mixed solvents containing 5, 10, 15 and 20 Vol. % of toluene, respectively, to make 0.1 mg/mL. After filtered by 0.45 micron pore size membrane filters, the clear the solutions were stored at room temperature for 2 hours to attain equilibrium before any studies.

4.2.2 Static and Dynamic Light Scattering (SLS and DLS). SLS and DLS were employed to characterize the morphology of the hybrid materials. SLS experiments were performed at scattering angles 30° – 90°, at 5° intervals. For DLS measurements, the sample solutions were filtered by using 0.2 microns membranes into dust-free light scattering cells. The apparent $D$ values measured at 90, 60, 45 and 30 scattering angles are extrapolated to zero scattering angle in order to obtain $R_{\text{h,0}}$.

4.2.3 Transmission electron microscopy (TEM). The samples were prepared by pipetting 5 μL of each solution (1 mg/mL) onto a carbon-coated TEM grid. The TEM studies were performed by JEOL 2000FX microscope operating up to 200 kV.

4.3 Wells-Dawson heterotungstes $\text{P}_2\text{W}_{15}\text{V}_3$-tris-hexanamide ($\text{C}_6$) and $\text{P}_2\text{W}_{15}\text{V}_3$-tris-hexadecanamide ($\text{C}_{16}$)

Wells-Dawson clusters were synthesized with the general formula $[\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]^{9-}$. Two different ligands hexanamide ($\text{L}^6$) and hexadecanamide ($\text{L}^7$) were covalently capped into the oxavanadato TRIS moieties. (Scheme 4.1)

Scheme 4.1. Organic amino-linkers $\text{L}^6$ and $\text{L}^7$. 

58
The new materials were well characterized by elemental analyses, IR and NMR spectroscopy and by ESI-MS spectrometry. Figure 4.1 shows the Wells-Dawson hybrid surfactants representation and some physical properties.

**Figure 4.1.** Wells-Dawson hybrid surfactants with different alkyl chains. (above) Hybrid 6; Mw is 5105 g/mol. (below) Hybrid 7; Mw is 5245 g/mol.

### 4.4 Self-assembly of $P_2W_{15}V_3\text{-tris-C}_6$ and $P_2W_{15}V_3\text{-tris-C}_{16}$ in water/acetone mixtures

Both hybrids are quite soluble in acetone solutions but insoluble in water. DLS technique was employed to detect any possible aggregate formation in acetone/water solutions (0.1 mg/mL). The scattered intensity was 2500 to 3000 Kcps. According to the eq. (3.8) the scattered intensity is related to a concentration or size fluctuation. CONTIN analysis method shows large vesicles in solution that contribute to large scattered intensity. The results show an average $R_{h,0}$ for hybrids 6 and 7 are 205 and 221 nm and SLS studies shows $R_g$ values ca. 215 and 210 nm. The ratio $R_g/R_{h,0}\approx 1$ and a spherical hollow structure is anticipated. Figure 4.2 shows the intensity-intensity time correlation function at 30 degrees angle and the $R_h$ values corresponds in the maximum peak.
4.3 shows TEM images at equilibrium conditions and provide clear evidence of hollow structures in acetone/water solutions.

Figure 4.2. Hybrids 6 and 7 at 30° angle detector. The systems were evaluated in 50% vol. acetone/water solution at 7 days.

Figure 4.3. TEM images for hybrids 6 (A) and 7 (B) in 50% vol. acetone / water solution.
4.5 Tuning the vesicle size by manipulating the solvent polarity

Figure 4.4 shows the vesicle self-assembly size regulation between hybrids 6 and 7 at different solvent polarity conditions. Increasing the acetone content hybrid 6 is more insoluble and promotes a larger self-assembly vesicle sizes. Apparently, this self-assembly is formed by two layers or one bilayer similar to phospholipids. Also, similar results were found in the Mn-Anderson hybrid surfactants. The small organic linkers (C₆) from the hybrid 6 presents a more rigid tail and less free energy than the hybrid 7 which possesses more (-CH₂-) groups in the middle organic group and increases the flexibility. Hybrid 6 forms larger bilayer membranes promoting the formation of larger vesicles. Also, is probably that the flexible packing from hybrid 7 allows to form smaller vesicles.

![Figure 4.4](image.png)

**Figure 4.4.** Self-assembly for hybrids 6 and 7 at 0.1 mg/mL at different solvent dielectric constant conditions.
4.6 Self-assembly for trimeric heterotungstates in water/acetone solutions

An original and innovative Wells-Dawson trimeric heterotungstate couple is fabricated from covalent connection of three \([P_2V_3W_{15}O_{62}]^{9-}\) POMs via linear tris(tris(hydroxymethyl)aminomethane) ligands in acetonitrile solvent (see Fig. 4.5). Laser light scattering (LLS) technique was used to detect any possible formation of large assemblies in solution. The scattered intensity \((I)\) gives relevant information of supramolecule status on concentration and size \((I \propto C \text{ and } I \propto R_h^2)\). In our particular case, the average \(I\) shows values > 4,000 kcps at 90° scattering angle; (for comparison, pure benzene has an intensity of 100 kcps). Therefore, our studies reveal the formation of supramolecules due to the amphiphilic nature of these hybrids. In addition, static light scattering (SLS) provides \(R_h/R_g\) ratio close to 1, which it indicates a hollow structure.

![Figure 4.5](image.png)

**Figure 4.5.** Schematic representation of hybrid surfactants benzene tris-\([P_2V_3W_{15}]\) (left) and triazine tris-\([P_2V_3W_{15}]\) (right) (●) Tungsten; (●) Vanadium; (●) Phosphorous; (●) Oxygen; (●) Carbon; (●) Nitrogen. Hydrogen does not appear just for clarity purposes.

To confirm our LLS studies TEM images show two vesicles in acetone/water at 50% vol. (Fig. 4.6) These elements clearly indicate that our supramolecule is in fact a
vesicle. Figure 4.6 shows the propose self-assembly model to form vesicles in acetone/water solutions.

![Figure 4.6. Vesicle formation in acetone/water mixed solutions. TEM images for hybrids benzene tris-\{P_2V_3W_{15}\} (left) and triazine tris-\{P_2V_3W_{15}\} (right). X-ray scanning confirms the hybrids into the vesicles.](image)

Also, in the previous chapter we were able to establish the prominent role of the countercations (TBA) to form the vesicles. The TBA molecules effectively screen the negative charges between adjacent POM clusters on vesicle surface and form closely packed hydrophobic layers in their vesicles.\(^{149}\) It assumes the same counter-cation role in our current trimer family. The effect probably would be more stronger due to the fact one more polar heads are involved and also more TBA molecules in this vesicular formation process. Dynamic light scattering and CONTIN method\(^82\) provide, the hydrodynamic radius (\(R_h\)) of the supramolecules at different acetone/water solutions. The average vesicle size can be tuned by the solvents’ polarity (i.e., dielectric constant) with larger vesicles formed in less hydrophilic solvent.\(^{121}\) A similar comparison between the \(R_{h,0}\) at different acetone content (i.e. dielectric
constant) against our first five dumb-bell shape hybrid surfactants is showed in Figure 4.7. This trend clearly shows the polar head contribution to form larger vesicles under the same conditions. However, the organic linker also modifies the vesicle size. The benzene ring is more hydrophobic that the triazine ring. The hydrophobicity of the organic compound triggers the formation of larger vesicles. On the other hand, the triazine which is more hydrophilic and forms smaller vesicles. These results are also in accordance with our previous five dumb-bell hybrid study and clearly confirm the same previous trend, decreasing the solvent polarity the shell size increasing.\textsuperscript{149} This suggests that the vesicle shells present a strong relation with the surface charge where a greater value exerts a larger repulsion among the shells and therefore the vesicles remain smaller.

**Figure 4.7.** An additional POM cluster head increases the vesicle size. The average $R_h$ value in acetone / water % vol. 50 for hybrid 1 and 2 is 144 to 128 nm respectively. In contrast, the five previous hybrids show values between ca. 65 to 95 nm.
4.7 Bis (organoimido)-Bridged Hexamolybdates

Organoimido substituted POMs is an interesting class of hybrid POMs attributable to their potential applications in catalysis, photo-electric cells and medicines.\textsuperscript{150} Recently, Wei et al.\textsuperscript{151} studied the alkylimido hexamolybdates, $[\text{Mo}_6\text{O}_{18}\text{NCH}_2\text{R}]^2-$ hybrid. A carbon-carbon double bond (C=C) near to nitrogen atom forms at elevated temperature via the so-called DDHC reactions (doubly dehydrogenative coupling). Currently, many new derivatives have been synthesized with Peng's DCC practice using amines as starting raw materials. This time a new set of alkylimido hexamolybdates has been synthesized introducing a series of flexible ligands, including functional bis-arylamines bearing o-alkoxy chain substituents, to construct the building of interconnected polyoxometalate hybrids.\textsuperscript{152} The synthesis was done by refluxing reactions of $[\text{n-NBu}_4]\text{[α-Mo}_8\text{O}_{26}] (\text{n-NBu}_4 = \text{TBA})$, bis-arylamines (1,2-bis(o-aminophenoxy)ethane, $\text{C}_2$; 1,4-bis(o-aminophenoxy) butane, $\text{C}_4$; or 1, 6-bis(o-aminophenoxy) hexane, $\text{C}_6$) hydrochlorides, and DCC at the mole ratio of 2:1:2 in dry acetonitrile proceed smoothly and afford the molecule-bola bis(organoimido)-bridged hexamolybdates: $[\text{n-NBu}_4]\text{[Mo}_6\text{O}_{18}(2,2'-\text{NC}_6\text{H}_4\text{OC}_n\text{H}_{2n}\text{OC}_6\text{H}_4\text{N})\text{Mo}_6\text{O}_{18}] (n = 2$ (Hexamolybdate 1), 4 (Hexamolybdate 2), 6 (Hexamolybdate 3)), in 20-60% yield.\textsuperscript{152}
Figure 4.8. Stick and ball representation of bis(organoimido)-hexamolybdates dumb-bell hybrid crystals. The organic middle linker has been modified increasing by two carbons. Hexamolybdate 1 (left); Hexamolybdate 2 (middle); Hexamolybdate 3 (right). The counteraction is TBA and each hybrid contains 4 negative charges.

Surfactants and biolipids are known to assemble into vesicular and other structures due to their amphiphilic nature in solution. The POM-organic hybrids also contain both hydrophilic and hydrophobic domains. As the result, their self-assembled structures have been identified in different hybrid systems with various molecular architectures.72,96 Two typical examples of vesicle formation are: Mn-Anderson POM with two long alkyl chains and, two V₃-capped Wells–Dawson-type clusters linked by organic ligands (dumb-bells). The current new hybrids can also be treated as “dumb-bell” shaped hybrids but with bulky organic ligands, and are ideal systems to explore the role of middle organic linkers to the self-assembly behaviour into vesicles.

Clear solutions of bis(organoimido)-hexamolybdate compounds 1-3 in toluene/MeCN mixed solvents containing 5, 10, 15 and 20 Vol. % of toluene, respectively were monitored by static light scattering (SLS) and dynamic light scattering (DLS) techniques. The fast, significant increase of the scattered intensity from SLS
studies indicates the formation of supramolecular structures in the above solutions. The CONTIN\textsuperscript{82} analysis of the DLS studies (Fig.4.9) confirm the formation of large structures in solution and provides their average hydrodynamic radius ($R_{h,0}$) values. The relation of $R_{h,0} \approx R_g$ for the large assemblies is observed for all the large structures in those solutions, suggesting that the assemblies are hollow spherical vesicular structures.\textsuperscript{153}

![Graph](image_url)

**Figure 4.9.** CONTIN analysis of DLS study on bis (organoimido)-hexamolydates compounds 1-3 MeCN/Toluene in 90/10 Vol. % solution at 90°.

These vesicles structures are further confirmed by TEM studies on these large assemblies, as shown in Figure 4.10, where a remarkable contrast between the central areas of the assemblies and the periphery area can be observed for all the assemblies.
Figure 4.10. TEM images showing a hollow vesicle structure of the self-assembly of bis (organoimido)-hexamolybdates 2 in 10% vol. toluene/MeCN solution.

For the three bis (organoimido)-hexamolybdates with different organic linkers, their vesicle sizes are quite similar in a given solvent. The hybrid with longer alkyl chain length forms slightly smaller vesicles. Meanwhile, The vesicle size increases with increasing toluene content in the mixed solvent. Figure 4.11 shows that the hydrodynamic radius $R_{h,0}$ of the vesicles increases with the toluene content. The effect of the solvent content can be further clarified when the x-axis in Figure 4.11 is changed to $1/\varepsilon_r$, with $\varepsilon_r$ being the solvent dielectric constant. This is the typical feature for a charge-regulated self-assembly process. 121,154
Figure 4.11. Hydrodynamic radius at zero ($R_{h,0}$) as a function of the inverse dielectric constant of MeCN/toluene.

A comparison between the vesicles of the current three hybrids with bulky organic ligands and that of the previously studied dumb-bell hybrids 1, 2 and 3 would be interesting. In both cases vesicle structures are formed and the vesicle size increases with decreasing solvent polarity. The dumb-bell hybrids have a little less surface charge density than our three bis(organoimido)-hexamolybdates hybrids (ca. 10% difference), but the difference in their slopes shown in Figure 4.12 is significant. When the solvent becomes more non-polar, the vesicle size of dumbbell hybrids 1, 2 and 3 grows much faster, suggesting a much stronger attraction for these types of hybrids. This can be explained by their different organic ligands and consequently the corresponding molecular packing for the vesicle formation. The shape of dumbbell hybrids 1-3 are close
to a cylinder which can be easily closely packed via hydrophobic interaction between the organic linkers and with the help of TBA counter-ions. On the other hand, the current bis (organoimido)-hexamolybdates are more or less spherical in the overall shape with much more dominant organic components. Geometrically it is more difficult to form closed packing. At last, the solvent composition (MeCN and toluene) might also have an impact. Apparently the aromatic rings from bis(organoimido)-hexamolybdates are more compatible with toluene than the oxalamide group, which might decrease the solvent-phobicity of the organic linkers of bis(organoimido)-hexamolybdates 1-3 and therefore decrease the strength of the solvent-phobic interaction among the organic ligands.

![Graph](image.png)

**Figure 4.12.** Three different organic-inorganic hexamolybdates 1, 2, 3 are compared with three hybrids 1, 2 and 3dumb-bell shape in 0.1 mg/mL MeCN/Toluene solution.
Overall, the current vesicles are assembled mainly by solvent-phobic interactions and are completely different in nature from the vesicle-like, blackberry type structures which are formed by various hydrophilic POMs and other types of macroions in polar solvents via counter-ion-mediated attraction and hydrogen bonding.\textsuperscript{105,154-156}

Although previous studies considered that the counter-cations (TBAs) plays an important role on the vesicle formation,\textsuperscript{72,157} our studies clearly find that the nonpolar solvent toluene is vital to the formation of vesicles for bis(organoimido)-hexamolybdates 1-3. The result shows that just the TBA\textsuperscript{+} without the toluene does not promote any vesicle formation in the solution of bis (organoimido)-hexamolybdate 2, while the size of the assemblies increased with the increasing concentration of additional TBA\textsuperscript{+} ions in the mix solution of MeCN/ Toluene (Figure 4.13).

\textbf{Figure 4.13.} Adding small amounts of TBA in MeCN solution to the hexamolybdate 1.
In summary, the functional bis-arylamines with flexible o-alkoxy chains are effective ligands for the preparation of length adjustable inorganic-organic-inorganic POM-based hybrids. They have been employed successfully to prepare organoimido derivatives of hexamolybdate cage through one-step reaction in the present of DCC. The molecular structures of hexamolybdates 1-3 have been confirmed by single-crystal X-ray diffraction studies, and shown that the derivatives of POMs are nano-scale molecule-bolas.\textsuperscript{152} ESI and UV-Vis spectra indicate that hexamolybdates 1-3 retain integrity of the two hexamolybdate cages linked by bis-arylamine ligand structure and be stable at least at the concentration ranges 0-250 µM in dry acetonitrile. i.e. these bis-arylamine ligands connect two hexamolybdate effectively whenever in solid or in solution. It can be speculated that they could be used as more impactful nexuses and the cages as nodes to form zero dimension nano-molecules, one dimension chains, or multidimensional framework. Remarkably, these hybrids are capable of undergoing a supramolecular self-assembly process in MeCN/toluene mixtures, which leads to the formation of vesicles; the unprecedented formation of such structures from hybrids with different lengths. These POMs-based derivatives could pave the way for many future materials applications and the further studies are in progress.

4.8 Effect of the organic linkers on the vesicle size

The primary difference among all the hybrid surfactants is their organic linkers. The solubility parameter (δ) has been widely used in many different fields, especially in mixture of solvents or polymers, for estimating the degree of hydrophobicity for the organic components.\textsuperscript{158,159} For high molecular weight polymers the Small method\textsuperscript{160} is
broadly applied. It is based on the addition of the attraction constants for all the organic
groups. Each organic group has different energy of vaporization and molar volumes and
both terms determine the δ value. This well accepted approach enables us to study the
effect of hydrophobicity of the middle organic linker on the vesicle formation. As shown
in Figure 4.14, the vesicle sizes formed by different hybrids decreases with increasing the
polarity of the organic middle part. It is quite remarkable how the lower polarity leads the
vesicle size to grow. Figure 4.14 shows the vesicle size by different hybrids where the $R_h$
decreases with increasing the polarity of the organic middle part. This can be understood
in terms of free energy. In a spontaneous vesicle formation process the initial step is to
form a membrane or disk. The length of this membrane depends of its free energy. The
greater the free energy or solvophobicity that is exposed to the solvent, the greater the
membrane is due to more molecules are associated. As the length is increasing the
membrane becomes more rigid until eventually the disk is going to bend to minimize the
free energy. At a certain critical length a spontaneous vesicle is formed.\textsuperscript{134}
Figure 4.14. Organic linker polarities modify $R_{h,0}$ values at 50% vol. acetone/water content. Solubility parameters for all the Wells-Dawson hybrids. It is quite remarkable how the lower polarity leads the vesicle size to grow. The polarity of the organic linkers was calculated using the Small’s method.
Chapter 5: Surface behavior of Wells-Dawson dumbbell shape hybrid surfactants at water/vapor and liquid/solid interface

5.1 Introduction

In this chapter the behavior interface (L/V) and (L/S) are studied by Langmuir-Blodgett and calorimetric techniques respectively. The behavior at water/vapor (L/V) interface brings relevant physicochemical information to study the nature of the molecules such as hydrophobicity and miscibility in the liquid sub-phase (water). The early studies on traditional amphiphiles clearly show the importance of the number and length of the hydrophobic chains on the L/V behavior.\textsuperscript{161} The segregation between the solvophobic region and water at interface provides strictly lyophilic and lyophobic domains instead of having just one with average properties, and consequently the possibility of studying the organization of the molecules.\textsuperscript{162} Therefore, Langmuir-Blodgett technique is the reliable method for such studies.\textsuperscript{163} Taking advantage of the amphiphilic properties of the hybrid surfactants is possible to form monolayers at L/V interface. The first hybrid surfactants monolayer formed by this technique is attributed by Chambers.\textsuperscript{164} A bis(alkyl) substituted, asymmetric polyoxometalate $\left\{\left[\text{CH}_3(\text{CH}_2)_3\text{N}\right]_4\left[\text{CH}_3(\text{CH}_2)_{11}\text{Si}\right]_2\text{OSiW}_{11}\text{O}_{39}\right\}$, was formed and oriented in a monolayer and multilayer thin films using Langmuir–Blodgett techniques.

The adsorption of amphiphilic molecules on liquid/solid (L/S) interface depends on many different variables such as: modifying the solvent polarity, pH, solid surface composition, surface area, etc. All of them will tune the synergism or antagonism of the system.\textsuperscript{165}
5.2 Experimental Section

5.2.1 Langmuir-Blodgett (L-B) Isotherm studies. Solutions for different hybrid surfactants were prepared in 90/10 vol% chloroform/acetonitrile at 20 °C. Deionized water (18.2 MΩ·cm, pH≈6, after treated by Milli-Q water purification system) was used at sub-phase. All monolayer measurements were made using a Nima 612D film balance (Nima Technologies, Coventry England), equipped with a LB dipper. All isotherms were determined at 25 °C. The typical Langmuir-Blodgett procedure compromise a 20 minutes wait period after spreading the solutions over the water sub-phase before any compression is applied.

5.2.2 Isothermal titration calorimetric (ITC) studies. A 0.1 mmoles/L hybrid surfactant solution in acetonitrile was placed in the 1.5 mL calorimetric cell. 6.3 mmoles/L of TiO2 dispersion in acetonitrile were used for hybrids 1, 2 and 4 titration. A 10.4 mmoles/L TiO2 dispersion in acetonitrile for hybrids 3 and 5. The hybrid solutions were loaded into a 250 μL calorimetry syringe. The TiO2 dispersion was placed in the 1.5 mL calorimetric cell. The temperature of the cell was kept constant at 25 °C.A 25 injection matrix was used for the 10 μL injections between each one every 20 s. A 180 s delay was used in between injections. The cell was mixed at 500 rpm. The heat of dilution was previously determined between the TiO2 particles and acetonitrile and rest from the results.
5.3 Monolayer formation of Wells-Dawson heterotungstates hybrids at water/vapor L/V) interface behavior

Previous studies with polyoxyethylene nonionic surfactants L/V interface show a vertical orientation of the ethylene oxide chains and the surface films become more expanded with increasing length of the ethylene oxide chains. Modifications in the hydrophobic structure group at constant ethylene oxide mole ratio present a small effect on the molecular areas in contrast to variations in the length of the ethylene oxide chains. On the other hand, anionic surfactant studies of sodium alkylbenzene sulfonates having side chains from C_{10} to C_{18} showed an area per molecule reduction as the molecular weight increases when electrostatic repulsion between anionic polar heads is similar for each member. However, the van der Waals forces between the hydrophobic-carbon tails increases with the length of the chain. That means that the longer the alkyl-benzene chains are the surfactant is more easily compressed.

In our study Figure 5.1-A, B show the five π-A isotherms recorded from the five hybrid solutions.
Figure 5.1. Surface pressure π-A isotherms on a water sub-phase. (A): (a) hybrid 1; (b) hybrid 2; (c) hybrid 3. (B): (d) hybrid 4; (e) hybrid 5. The LC area/molecule are 160, 230, 174, 146 and, 300 Å², respectively. All the isotherms collapse around 100 Å² which is the cross sectional area for all these hybrid surfactants.
The measured molecular area, shape and phase transitions are quite different, which indicates the contribution from the organic linkers to the L/V phase behavior. Hybrid 1 and hybrid 2 isotherms (Figure 5.1-A,B) exhibit just one phase instead of two. Due to the nature of these novel hybrid surfactants is difficult to determine the phase state. However, Harkins\textsuperscript{168} has proposed a classification according the compressibility modulus, $C_\text{s}^{-1}$ (eq.13) that can characterize the monolayer state. Hybrid 1 and Hybrid 2 are almost in agreement with the range of $1 \times 10^{-2}$ to $5 \times 10^{-3}$ that corresponds to LC phase. In addition, an analogy shows that hybrid 3 (Fig. 5.1B-(c)) presents a LE surface pressure phase around 15 mN/m. In contrast, hybrid 1 and hybrid 2 show a much larger surface pressure segment that is different from 15 mN/m and therefore a liquid condensed phase LC is confirmed. Hybrid 3 presents two well-defined phases, a LE phase and a liquid condensed LC phase coupled with a pronounced plateau allowing the coexistence of both phases and a collapse pressure at 100 Å\textsuperscript{2}. Increasing the hydrophobicity the hybrid is more spreadable in the sub-phase water. Apparently, our results are in contradiction because our first three members do not show a conventional surfactant behavior where increasing the hydrophilicity, the surfactants molecules are more expanded on the water sub-phase. However, cationic Gemini surfactants made up by two amphiphilic moieties connected by a spacer group (s), 18-s-18; offer a similar behavior than our hybrids. The isotherms moves to the right with the increase of the carbon number of the spacer group, (s), indicating a more expanded area.\textsuperscript{169} Similar behavior appears in our system and clearly shows the effect of the space length for our organic linkers. Increasing the organic linker distance the isotherm is more expanded. Besides hydrophobic associations, other forces such as electrostatic interactions and hydrogen bondings might also affect the
surface pressure according to literature.\textsuperscript{170} However, in our current case, the fact that the hybrids have very limited solubility in water suggests very weak hydrogen bonding formation between the linkers, and the contribution from electrostatic interaction should be the same for all of them due to the same polar heads. Therefore, the geometrical constrains force to lay the organic linkers under the water and restrict a fold position on the monolayer at L/V interface.

As shown in Figure 5.1B, both $\pi$-$A$ isotherms for hybrid 4 and hybrid 5 present LE and LC phases connected with a plateau. The LE areas per molecule for hybrid 4 and hybrid 5 are extrapolated to zero pressure to obtain ca. 205 and 348 A\textsuperscript{2} per molecule, respectively. A detailed analysis shows that the isotherms present different LE phases. Hybrid 5 shows a pronounced LE phase region shifted to the right. This untypical behavior is a symptom of strong expansion over the water phase where hybrid 5 is spread. Another possibility is the formation of multi-layers at interface. Therefore, the most expanded isotherm is presented by hybrid 5 which has the shortest organic linker distance ca. 0.2 nm. This can be explained as perpendicular orientation on the sub-phase water and the short organic groups probably do not lie under the water. In this case, just the anionic polar heads are in contact with the sub-phase water exerting a better hydrophilic affinity than the rest member of the family. In contrast, hybrid 4 possesses rigid $\pi$-$\pi$ bonds that may create significant attractive interactions. A different type of cationic gemini surfactants, (18-$p$-xylyl-18), shows that the $\pi$–$\pi$ interactions from aromatic functional groups can promote the formation of networks or self-associations.\textsuperscript{171,172} These hydrophobic interactions help to maintain the surfactant molecules associated. In addition, the associate hybrids are
more restricted to expand and therefore a more compressed isotherm is formed. Figure 5.2 shows the proposed model to represent the monolayer or membrane formation process for our hybrid surfactant system at L/V conditions at 25°C.

![Figure 5.2](image)

**Figure 5.2.** Monolayer formation for the dumb-bell shaped hybrid surfactants at water/vapor interface (a) LE/Gas phase; (b) LE phase and (c) LC phase. TBA counter-cations are not shown. However, we speculate that TBA ions might play a role by locating between the polar head groups to decrease the electrostatic repulsion.

The organic linkers also control the behavior of hybrids at water/air interface. From the $\pi$-$A$ isotherms, the packing of hybrids into monolayer at interface becomes more ordered when the linker becomes more hydrophobic. Liquid expanded and liquid condensed phases are clearly located and connected through a plateau, suggesting that the hybrids behave similar to some cationic gemini surfactants which possess similar molecular architectures. However, in overall the hybrids demonstrate weaker capability of forming monolayers at interface.

### 5.4 Adsorption of Wells-Dawson hybrid surfactants at the solid/liquid interface (L/S)

Different adsorption studies related to polyelectrolytes, surfactants and polymers have been explored with different solids substrates in the past. The results clearly depend
on both sides, physicochemical solid properties and the liquid medium. For example, electrokinetic studies show adsorption of SDS on titanium dioxide (TiO$_2$) in aqueous and water solvents mixtures. The organic ion associates onto pigment surface meanwhile the Na$^+$ counterion remains in solution.$^{173}$ Most of the adsorption studies have been done in aqueous solutions, water/solvent mixtures and not many in one solvent component. In this context, an adsorption study at L/S interface of these novel hybrid surfactants onto TiO$_2$ particles in a middle polarity solvent (MeCN) is explored by ITC technique. On the other hand, TiO$_2$ pigment particles have been selected due to its hydrophilic surface properties, wide research literature, low toxicity risk and its use in surface chemistry and catalysis as a solid support.$^{174}$

About the techniques, one important number of adsorption studies have been measured indirectly by the depletion method. The depletion method consist on prepare several particle dispersions and centrifuge to separate the continuous and disperse phases and determine the free surfactants or polymer in the supernatant. This determination can be effectuated by different techniques such as refractive index, chromatography, UV/VIS, etc. Isothermal titration calorimetry (ITC) provides direct adsorption measurements and the affinity of the hybrid-TiO$_2$ system.

5.5 Langmuir adsorption isotherms at liquid/solid interface in MeCN dispersions.

Langmuir isotherm can be used to model simple an easy isotherms.$^{40}$ The assumptions are equivalent energy surface sites and monolayer formation. The total cumulate molar heat evolved for n injection (Q) is calculated from eq.

$$Q_{tot}(T,P)=\Sigma q_i/\Sigma c_i \Delta V$$  \hspace{1cm} (5.1)
where \( c_i \) and \( \Delta V \) are the molar concentration and the volume of hybrid added to the cell during the injection \( i \), respectively. The Langmuir isotherm expression to use in calorimetry is as follows: \(^{175}\)

\[
\frac{1}{Q_{\text{tot}}} = \frac{1}{\Delta H_{\text{ads}}^{\text{sat}}} K_{\text{ads}}^\text{sat} \frac{1}{[S]} + \frac{1}{\Delta H_{\text{ads}}^{\text{sat}}} \tag{5.2}
\]

where \([S]\) is the molar concentration of adsorbed hybrid surfactant. To calculate the surface saturation in (mg/mL) the following expression is used: \(^{176}\) (see Fig. 5.3)

\[
\Gamma_{\text{max}} = (C_0 - C) V_{\text{cell}} / m_{\text{sp}} \tag{5.3}
\]

where \( C_0 \) and \( C \) are the concentration before the adsorption and the concentration at equilibrium, respectively. \( V \) is the solution volume (mL), \( m \) is the particle amount (g) and \( a_{\text{sp}} \) is the particle specific surface area (m\(^2\)/g). The adsorbed surface area per molecule (\( A \)) is calculated by:

---

**Figure 5.3.** Different Langmuir isotherms for all the five hybrids.
\[ A(\text{nm}^2/\text{molecule}) = \frac{M_w}{0.0602\Gamma_{\text{max}}} \] (5.4)

Figure 5.4 shows all the isotherms for the five hybrids. Hybrids 2, 3 and 4 present a larger heat of adsorption. That means a larger affinity between them and the TiO\textsubscript{2} particles. A detail analysis reveals that hybrids 3 and 4 present a co-operative regime until a plateau is reached. The presence of amino groups impart cationic physicochemical properties that improves considerably the association or binding of many substrates, materials, solids, etc. On the other hand, Hybrid 2 presents a slightly non-co-operative regime follows by a co-operative until the equilibrium is reached. Hybrids 1 and 5 present less affinity to the surface where the heath of adsorption is much more less and the co-operative slope is less pronounce.

**Figure 5.4.** Binding isotherm shows the head of adsorption in relation with the hybrid surfactant/TiO\textsubscript{2} molar relation.
Figure 5.5. Isothermal titration calorimetry (ITC) graph for hybrid 1.

Table 5.1 shows all \( \Delta H_{\text{ads}}^{\text{satn}} \) values are negative that indicates an enthalpy driving force process. Hybrids 2, 3 and 4 present the larger \( K_{\text{ads}} \) values. A low \( K \)-value shows a weak adsorption meanwhile, larger \( K \)-values indicates a strong or more affinity adsorption.

Table 5.1. Some thermodynamic properties of hybrid surfactants onto TiO\(_2\) particles in acetonitrile solutions at 25\(^\circ\)C.

<table>
<thead>
<tr>
<th>Hybrid</th>
<th>( \Delta H_{\text{ads}}^{\text{satn}} ) (Kcal/mole)</th>
<th>( K_{\text{ads}} \times 10^3 ) (L/mol)</th>
<th>( \Gamma_{\text{max}} ) (mg/m(^2))</th>
<th>Occupied Area/molecule (nm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hybrid 1</td>
<td>-25.9</td>
<td>9.99</td>
<td>14.3</td>
<td>1.22</td>
</tr>
<tr>
<td>Hybrid 2</td>
<td>-64.1</td>
<td>10.58</td>
<td>4.54</td>
<td>4.04</td>
</tr>
<tr>
<td>Hybrid 3</td>
<td>-64.0</td>
<td>13.53</td>
<td>4.15</td>
<td>4.24</td>
</tr>
<tr>
<td>Hybrid 4</td>
<td>-49.2</td>
<td>11.78</td>
<td>3.87</td>
<td>4.59</td>
</tr>
<tr>
<td>Hybrid 5</td>
<td>-25.8</td>
<td>7.36</td>
<td>14.4</td>
<td>1.21</td>
</tr>
</tbody>
</table>
Unsurprisingly, these hybrids present the larger occupied area that strongly suggests that these hybrids are lay down onto the TiO$_2$ surface. Therefore, two polar heads are strongly adsorbed to the polar pigment surface increasing the affinity and the $K$-values. However, this situation is unlike due to the repulsive electrostatic charges between the TiO$_2$ particle and the polar heads. Experiments show the zeta potential for TiO$_2$ in MeCN is around -70 mV at 1 mg/mL. One possible explanation is the space between the polar heads allows the organic middle part to be adsorbed. Thus, the amine organic linker is strongly attached to the TiO$_2$ particle allowing the hybrid surfactant to be laid down.

The huge dumb-bell polar heads increase the occupied area per molecule onto TiO$_2$. To compare the results adsorption isotherms of aliphatic alcohols (methanol, ethanol and 1-propanol) on TiO$_2$ show that increasing the carbon chain the adsorption increases. The molecular cross sectional areas of the adsorbed alcohols, MeOH, EtOH and 1-PrOH from the monolayers analysis are 0.273, 0.305 and 0.351 nm$^2$ respectively.
Chapter 6: Hybrid Blackberry from Keplerate \{\text{Mo}_{72}\text{Fe}_{30}\} Polyoxometalate and Nonionic Triblock Copolymer EO\textsubscript{99}PO\textsubscript{69}EO\textsubscript{99} in Aqueous Solutions

6.1 Overview of studies

Triblock copolymer EO\textsubscript{99}PO\textsubscript{69}EO\textsubscript{99} (F127) associates to Keplerate \{\text{Mo}_{72}\text{Fe}_{30}\} macroanions to form novel hybrid blackberries (BB) in aqueous solutions. The formation of such hybrid supramolecules was monitored by laser light scattering (LLS) and corroborate by TEM, SEM and Raman vibrational technique. The full process involves different complex phases and mono and bimodal distributions. The first phase shows F127 as free unimers and micelles below or above the CMC respectively, and \{\text{Mo}_{72}\text{Fe}_{30}\} clusters deprotonation to form macroanions in aqueous solutions. The second phase involves a molecular rearrangement and induces a broad distribution with just one peak. The third phase shows a rich micellar complex with relative high scattered intensities after 30 days. Finally a hybrid sphere blackberry is formed where the PPO group is bended and attached to \{\text{Mo}_{72}\text{Fe}_{30}\} blackberry leading the PEO groups oriented to the aqueous phase.

6.2 Introduction

Polyoxometalates (POM) are a unique molecular class with singular properties, and represent some of the largest inorganic molecules, and make them good candidates for potential applications such as electronic and catalytic materials.\textsuperscript{88} On the other hand, amphiphilic block copolymers have been studied in the past decades due to particular properties such as: micelle formation, good biocompatibility, self assembly temperature
dependence, and potential applications in medicine, advance technology and photonic crystals.\textsuperscript{8,149}

The \{Mo\textsubscript{72}Fe\textsubscript{30}\} cluster Keplerate molecule demonstrates an anionic behavior and self-assembly process in water, as showed by preliminary studies by different groups.\textsuperscript{102,179} Liu et al.\textsuperscript{104,180} showed that \{Mo\textsubscript{72}Fe\textsubscript{30}\} macroanions acts in dilute aqueous solutions as a weak inorganic acid that can potentially deprotonated its 30 Fe\textsuperscript{III} water layers depending on the pH. At certain \{Mo\textsubscript{72}Fe\textsubscript{30}\} cluster concentration it forms unique and well distributed single-layer spherical hollow vesicle in water which is called blackberries (BB). The driving force is primarily governed by a delicate balance that involves electrostatic attractive forces coming from the presence of countercations (H\textsuperscript{+}).\textsuperscript{181} Therefore, adjusting the pH of the cluster solution leads to formation of different BB’s sizes. Furthermore, Different studies have showed cationic surfactant and POM electrostatic interaction to form new hybrid molecules.\textsuperscript{11} Previous studies between the water soluble \{Mo\textsubscript{72}Fe\textsubscript{30}\} macroanions and metal salt countercations have studied by LLS, ASAXS and ITC techniques. This selective association among all cations is base on the type of valance conditions and hydrated size ions.\textsuperscript{182} Oleinikova et al. studying water molecules interactions at the surface of \{Mo\textsubscript{154}\} noticed that the self-assembly process is not stable without tetrahedral water layers or cation condensation located between the macroion inducing electrostatic attraction.\textsuperscript{183,184} On the other hand, water soluble poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) block copolymer, EO\textsubscript{99}PO\textsubscript{69}EO\textsubscript{99} (abbrev. F127) presents a nonionic electrostatic character, self-assembly to form micelles and not pH dependence in aqueous solutions. Interactions between F127 and ionic surfactants in water have been studied by LLS and isothermal titration
The results show association hydrophobic regimes and synergistic behavior when ionic surfactants are associated with F127 forming copolymer complexes. In addition, the association between long cationic surfactants CTAB and CTAT can interact with highly charge \( \{ \text{Mo}_{72} \text{V}_{30} \} \) clusters regulating the BB size. Furthermore, preparation of \( [\alpha-\text{PW}_{12}\text{O}_{40}]^{3-} \) Keggin POM and styrene-vinyl cationic block copolymer poly(styrene-b-4-vinyl-N-methpyridinium iodide) composites and their self-assembly into micelles and vesicles have been reported by Bu et al. These are direct proofs that anionic BBs can be treated as a host with clear associations with mono or divalent ions and ionic surfactants. However, all these host-guest complexes are primarily based on electrostatic interactions and nonionic hosts have been left behind. As far as we know, the association between a nonionic block copolymer and \( \{ \text{Mo}_{72} \text{Fe}_{30} \} \) anionic cluster has not been studied at all. Different approached to provide new and unique properties for block-copolymers have been proposed in the past few years via different mechanisms, some of them include diverse inorganic structures and functional organic groups.

In this chapter, we report our systematic studies on \( \{ \text{Mo}_{72} \text{Fe}_{30} \} \) and \( \text{EO}_{99}\text{PO}_{69}\text{EO}_{99} \) block copolymer by exploring their self-assembly and assembly sizes in aqueous solutions.

**6.3. Experimental section**

**6.3.1 Sample preparation.** Amphiphilic block-copolymer Pluronic F127 or Poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) triblock copolymer \( (\text{EO}_{99}\text{PO}_{69}\text{EO}_{99}) \) was obtained from BASF, Inc. \([\text{Mo}^{\text{VI}}_{72}\text{Fe}^{\text{III}}_{30}\text{O}_{252}(\text{CH}_3\text{COO})_{12}\{\text{Mo}_2\text{O}_7(\text{H}_2\text{O})\}_2\{\text{H}_2\text{Mo}_2\text{O}_8(\text{H}_2\text{O})\}(\text{H}_2\text{O})_{91}]^{\text{ca. 150H}_2\text{O}}\)
abbrev. \{Mo_{72}Fe_{30}\} crystals were prepared according to the method and literature.\textsuperscript{193} The fine crystals or powders were carefully weighed and dissolved water with gentle agitation. Pluronic F127 solutions were prepared at 200 RPM in cool water at 2°C for 2 hrs and let them rest for 24 hrs. at 5°C.

6.3.2 Static and dynamic light scattering (SLS and DLS) SLS and DLS were employed to characterize the morphology of the hybrid material. The $\theta$ angle of scattering measurement. SLS experiments were performed at 30°–90°, at 5° intervals. For DLS measurements, the normalized electric field time correlation function was then analyzed by the CONTIN method,\textsuperscript{82} which yields information on the distribution of the characteristic linewidth ($\Gamma$). The sample solutions were filtered by using 0.2 microns membranes into dust-free light scattering cells.

6.3.3 Transmission electron microscopy (TEM) The samples were prepared by pipetting 5 \textmu L of each solution (1 mg/mL) onto a carbon-coated TEM grid. The TEM studies were performed by JEOL 2000FX microscope operating up to 200 kV.

6.3.4 Raman spectroscopy

The Raman spectra of the \{Mo_{72}Fe_{30}\} polyoxometalate and triblock copolymer F127 were obtained by a high resolution Raman spectrometer system (Horiba-Jobin Yvon LabRam HR) equipped with three laser excitations (532, 442, and 325 nm). The visible laser at 532 nm (green) was used to generate the Raman spectrum. The calibration of each laser line was performed with an Hg lamp by adjusting the groove gratings to match the zero position and minimize the error of the linearity across the full Raman spectrum.
range. The polyoxometalate, F127 and mixture samples consist of 1 mg/mL in solution. All of them were placed in cells and dry until a fine and uniform powder was obtained.

6.4 Hybrid blackberry formation between \{\text{Mo}_{72}\text{Fe}_{30}\} macroanion and nonionic triblock copolymer \text{EO}_{99}\text{PO}_{69}\text{EO}_{99}.

Nanocluster \{\text{Mo}_{72}\text{Fe}_{30}\} presents an unusual and thermodynamic stable self-assembly process to form blackberries (BB) in solution.\textsuperscript{194} These BB are predominately formed by a delicate balance between electrostatic forces and counterions condensation.\textsuperscript{104} In contrast, surfactants form micelles in water exposing their hydrophilic heads to the aqueous phase forming a hydrophobic core commonly composed of alkyl chains. In a similar manner \text{EO}_{99}\text{PO}_{69}\text{EO}_{99} associates by hydrophobic interactions where the block copolymer amphiphilicity leads to self-aggregation process at certain critical aggregation concentration (CAC).\textsuperscript{54} Intuitively, block copolymers are high molecular weight surfactant due to the fact that they show an amphiphilic behavior and form aggregates in solutions. Therefore, the association between block copolymers and surfactants can be thought as a spontaneous process where the Van der Waals forces are the driving force. ITC studies provide evidence of different ionic surfactants such sodium dodecyl sulfate (SDS) and tetradecyltrimethylammonium bromide (TTAB)\textsuperscript{195} binding with F127. In addition SDS interacts not just with block copolymers, also with different nonionic polymers such cellulose ethers and poly(ethylene oxide).\textsuperscript{33} All these are examples where the hydrophobic moieties contribute to form macromolecules or complex micellar systems. In our particular study the association is different due to the fact that \{\text{Mo}_{72}\text{Fe}_{30}\}
macroanion does not present any hydrophobic groups and F127 does not present any surface charge.

Different molar ratios of \( \{\text{Mo}_{72}\text{Fe}_{30}/\text{F127}\} \) solutions were prepared and monitored by LLS technique for any possible formation of large assemblies at 30°C. All solutions reach equilibrium within 30 days and there was not further change (i.e., no more additional self-assembly) for more than 100 days, as confirmed by LLS studies. Fig. 6.1 shows the \( R_h \) progress for \( \{\text{Mo}_{72}\text{Fe}_{30}\} \) at 1.6x10\(^{-5}\) M (0.2 mg/mL) and F127 at 1.0x10\(^{-4}\) M (2.0 mg/mL) with molar ratio \( \text{F127}/\{\text{Mo}_{72}\text{Fe}_{30}\}=6.5 \) using DLS technique. The whole association process can be divided in four different phases. The first phase shows a bimodal distribution for \( \{\text{Mo}_{72}\text{Fe}_{30}\} \) and F127 micelles at 5 days. F127 molecules are presented as unimers and \( \{\text{Mo}_{72}\text{Fe}_{30}\} \) as macroanions due to a partial deprotonation of \( \{\text{Mo}_{72}\text{Fe}_{30}\} \) clusters in solution. The second phase presents a broad uniform distribution from a bimodal to at 10 days. Size distribution analysis indicates a narrow shape and apparently all the free F127 unimers have disappeared. At this point is not clear what types of aggregates, micelles or micellar complex systems are formed. However, \( R_h \) value for F127 micelles is ca. 12 nm\(^{185}\) and is very close to our current \( R_h \) measurement ca. 10 nm. Probably the broad distribution is a symptom of some F127 micelles, free unimers, \( \{\text{Mo}_{72}\text{Fe}_{30}\} \) clusters and some F127-\( \{\text{Mo}_{72}\text{Fe}_{30}\} \) interactions. The third phase shows one narrow distribution peak at 30 days. Therefore, we speculate that F127 associates with the \( \{\text{Mo}_{72}\text{Fe}_{30}\} \) BB and a micellar rich complex is formed with a \( R_h \) ca. 45 nm. The fourth phase is from 60 to more than 100 days when a F127/\( \{\text{Mo}_{72}\text{Fe}_{30}\} \) presents a broad and stable distribution indicating a possible rearrangement to form a new hybrid blackberry with a \( R_h \) ca. 85 nm. Also after 100 days the broad distribution remains
constant. For comparative purposes \{\text{Mo}_{72}\text{Fe}_{30}\} at 0.2 mg/mL solution were monitored and 43 shows a narrow peak distribution in aqueous solution. Previous studies has shown that the size of these BB is ca. 20 nm.\textsuperscript{194} In our study the \{\text{Mo}_{72}\text{Fe}_{30}\} shows a value of 29 nm. This discrepancy can be understood in terms of pH and concentration.

![Figure 6.1](image-url)

Figure 6.1. Monitoring CONTIN analysis by DLS technique for \{\text{Mo}_{72}\text{Fe}_{30}\} at 0.2 mg/mL adding 2.0 mg/mL of F127 solution in water. \{\text{Mo}_{72}\text{Fe}_{30}\} blackberries (red) appear just for comparative purposes.

Fig. 6.2 shows the scattered intensity at different F127 concentrations below and above the F127’s CMC. However, the scattered intensity is much more prominent above than below the CMC due to the fact that rich micelle complexes are formed. SLS studies shows broad scattered intensity peaks and soon after that relatively low scattered intensities (> 500 Kcps at 90° scattering angle; for comparison, pure benzene has an intensity ca. 100 Kcps). These discrepancies can be attributed to an initial formation of
F127 micelle, triblock copolymer rich complexes and also interactions of free unimers with \{Mo_{72}Fe_{30}\} macroanions. Large rich micellar complexes increase significantly the scattered intensity due to the fact that $I \propto R_h^2$. After certain time a peel-off mechanism is behind the dissociation for such rich complex.\textsuperscript{196} It seems that \{Mo_{72}Fe_{30}\} prefers or select to self assemble to form BB surrounding of F127 lead to form a new hybrid BB. Finally, the hybrid maintains a constant $R_h$ above 100 days.

**Below CMC Intensity vs Days**
Figure 6.2. Scattered intensity fluctuations of ${\text{Mo}}_{72}{\text{Fe}}_{30}$ and F127 at different concentrations as a function of time in days. The concentration is for F127 in mg/mL.

The morphology for all the large assemblies show a simple relation of $R_g/R_h \approx 1$, indicating that the assemblies are likely hollow or semi-hollow vesicles and not angular dependence were found. This morphology is supported by TEM and SEM images (Fig.6.3).
Figure 6.3. TEM and SEM show the presence of sphere vesicles corroborating the light scattering results. The solution was analyzed in water and the concentration was $\{\text{Mo}_{72}\text{Fe}_{30}\}$ 0.2 and F127 0.5 mg/mL (left and middle) and $\{\text{Mo}_{72}\text{Fe}_{30}\}$ 0.2 and F127 1.0 mg/mL (right) at equilibrium conditions.

6.5 $\{\text{Mo}_{72}\text{Fe}_{30}\}$ and F127 hybrid BB formation characterized by Raman spectra.

To corroborate this hybrid BB and complement our results Raman spectroscopy provides a fingerprint for specific chemical bonds and symmetry for molecular structures. Fine powders of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ crystals, F127 and $\{\text{Mo}_{72}\text{Fe}_{30}\}/\text{F127}$ mixtures were prepared. The Raman spectrum shows a possible association between a nonionic block copolymer and $\{\text{Mo}_{72}\text{Fe}_{30}\}$ macroanions. Polyoxometalate $\{\text{Mo}_{72}\text{Fe}_{30}\}$ possesses its most intense peak in the Raman spectrum at 949 cm$^{-1}$ due to the totally symmetric $\nu-(\text{M}=\text{O})$ in phase breathing type vibration. Our results clearly support the previous characterization where fine powder crystals of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ are located on the vibrational band of 947 cm$^{-1}$ (Fig.6.4 blue line). To identify any interaction or association a solution containing $\{\text{Mo}_{72}\text{Fe}_{30}\}$ and F127 were carefully prepared and dry until a uniform powder (dry solution) is formed. The Raman spectrum shows a clear large shift to 1107 cm$^{-1}$ (Fig.6.4 red line) around 17%. This shift clearly indicates a change in the $\{\text{Mo}_{72}\text{Fe}_{30}\}$ cluster due to F127 association. On the other hand, a physical blend mixing
just powders of \{\text{Mo}_{72}\text{Fe}_{30}\} crystals and F127 powder particles at 50% in weight was prepared. The Raman spectra shows a slight shift to 930 cm\(^{-1}\), less than 2%, suggesting that no chemical association has been progressed which obviously is the current case (Fig.6.4, purple line). This shift probably is influence by the large poly(ethylene oxide) groups coming from F127. Due to these experiments we assume an intimate association between the \{\text{Mo}_{72}\text{Fe}_{30}\} macroanions and the nonionic triblock copolymer forming a new hybrid blackberries.

![Raman spectra](image)

**Figure 6.4.** Raman spectra (\(\lambda=532\) nm) of polyoxometalate \{\text{Mo}_{72}\text{Fe}_{30}\} and EO\(_{99}\)PO\(_{69}\)EO\(_{99}\) block copolymer.

### 6.6 Nonionic tri-block copolymer F127 regulates hybrid BB size

Previous studies has reported the vesicle size can be regulated by changing the pH of the solutions.\(^{104}\) These macroions self-assembly is possible due to attractive forces
coming from the presence of countercation. One particular case would be that water ligands are attached to Fe^{III} and are replaced by a F127 molecules. However, this molecule substitution is highly improbably due to the medium is water decreasing the F127 binding probability. As we already mentioned, F127 associates with different type of molecules i.e. sodium dodecyl sulfate binds to the free F127 unimers forming complex micelles^{186} and cationic surfactant hexadecyltrimethylammonium chloride (CTAC) interacts with F127 in dilute aqueous solution^{200}. To represent this association Fig. 6.5 shows a propose model where the driving force between \{Mo_{72}Fe_{30}\} and F127 can not be electrostatic due to the fact that F127 does not have any charges on the surface. We assume that secondary bonds are the driving forces such as hydrogen bonds between the water layers and the poly(propylene-oxide) (PEO) groups. In such case, the PEO group is almost completely bended and adsorbed to \{Mo_{72}Fe_{30}\} macroanion and the poly(ethylene-oxide) hydrophilic groups are oriented to the water. At the same time, the PEO group regulates the surface negative charges of the \{Mo_{72}Fe_{30}\} BB. Therefore, this charge regulation process modifies also the final hybrid BB size.
Figure 6.5. Cartoon shows the F127 associates with the water layer around the Fe$^{III}$. Increasing the amount of F127 around the cluster the negative charges decrease allowing different BB’s sizes.

6.7 Influence of nonionic F127 to self-assembly \{Mo$_{72}$Fe$_{30}$\} macroanions in aqueous solution

Our attention is to study how F127 modifies the \{Mo$_{72}$Fe$_{30}$\} BBs size. For this purpose different F127 molar solutions in water were prepared and added to the \{Mo$_{72}$Fe$_{30}$\} clusters solution. Figure 6.6 shows the vesicle size in relation with F127. Increasing the F127 molar ratio the BBs also increasing their size. The full size is developed between 5 to 7 moles of F127 per mole of \{Mo$_{72}$Fe$_{30}$\}. Intuitively, we can correlate this number of moles with the number of negative charges around each \{Mo$_{72}$Fe$_{30}$\} (7 charges at pH 3.5 and .0 mg/mL).\textsuperscript{104}
6.8 Monitoring \{\text{Mo}_{72}\text{Fe}_{30}\} blackberries adding block copolymer F127 in aqueous solution

Our previous result shows a clear association of \{\text{Mo}_{72}\text{Fe}_{30}\} clusters and F127. We speculate that this association takes part at the beginning with \{\text{Mo}_{72}\text{Fe}_{30}\} clusters and not at the end where the BBs are already shaped. To corroborate our hypothesis F127 solution is added to already \{\text{Mo}_{72}\text{Fe}_{30}\} BB. For this purpose \{\text{Mo}_{72}\text{Fe}_{30}\} BB solutions were prepared at $1.0 \times 10^{-5}$ M (0.2 mg/mL) and also F127 solutions were arranged at $1.6 \times 10^{-5}$, $3.2 \times 10^{-5}$, $6.4 \times 10^{-5}$ and $9.5 \times 10^{-5}$ M. LLS technique was employed to detect any possible formation of rich micellar complex or hybrid BB. Figure 6.7 shows the $R_h$ distributions values were any changes or associations were detected by DLS technique. These results in certain way probe that F127 is just associated when the \{\text{Mo}_{72}\text{Fe}_{30}\} is as macroanion at the beginning of the process.
Figure 6.7. DLS distribution for \{\text{Mo}_{72}\text{Fe}_{30}\} BB at 0.2 mg/ml and F127 at 0, 0.2, 0.4, 0.8 and 1.2 mg/mL. The \(R_h\) values are 24.3, 23.6, 24.2, 21.6, 23.3 nm respectively. The scattered intensity for all the samples is in the range of 1500 to 2800 Kcps.

6.9 pH Dependence for \{\text{Mo}_{72}\text{Fe}_{30}\} macroanions and hybrid BB \{\text{Mo}_{72}\text{Fe}_{30}\}/F127 below the CMC

Keplerate \{\text{Mo}_{72}\text{Fe}_{30}\} clusters become macroions due to a partial deprotonation process in aqueous solutions. This process includes a coordination of Fe bonded with single water layers. Each complex has the potential to deprotonate 30 sites. However, previous studies has proved that 1.0 mg/mL of \{\text{Mo}_{72}\text{Fe}_{30}\} possesses 7 to 8 charges in pH 3.5 in aqueous solution\textsuperscript{104,180}, that means just a few H\textsuperscript{+} are dissociated from each \{\text{Mo}_{72}\text{Fe}_{30}\} and transform this unique POM in a weak inorganic acid. The degree of deprotonation can be modified by adding HCl and NaOH. Increasing the pH \{\text{Mo}_{72}\text{Fe}_{30}\} macroanions possess more charges due to electrostatic repulsion among each anionic
{Mo$_{72}$Fe$_{30}$} and therefore the BB size decreases. Figure 6.8 compares {Mo$_{72}$Fe$_{30}$} BBs and {Mo$_{72}$Fe$_{30}$}h/F127 hybrid BBs systems at different pH in aqueous solutions. It is remarkable how the addition of F127 below the CMC forms larger hybrid BBs independently of the pH.

![Graph showing the comparison of average $R_h$ for {Mo$_{72}$Fe$_{30}$} blackberries and {Mo$_{72}$Fe$_{30}$}/F127 at different pH in aqueous solutions measure by LLS.](image)

**Figure 6.8.** Comparison of average $R_h$ for {Mo$_{72}$Fe$_{30}$} blackberries and {Mo$_{72}$Fe$_{30}$}/F127 at different pH in aqueous solutions measure by LLS.

In summary, a hybrid blackberry is formed between polyoxometalate {Mo$_{72}$Fe$_{30}$} and block copolymer F127. LLS, TEM, SEM and Raman vibrational technique provide a clear evidence of this unique association. The full process involved different phases and the critical step is at the beginning where {Mo$_{72}$Fe$_{30}$} are macroanions. Due to the fact that F127 nature is nonionic, attraction between both by electrostatic charges is
eliminated. The driving force apparently is composed by as intimate interaction among the water layers around the cluster periphery and the poly(propylene oxide) middle part of the molecule. These interactions can be secondary forces such as hydrogen bonds. Therefore, one significant difference to form hybrid BBs is the driving force. On the other hand, F127 is capable to regulate the final hybrid BB size. Increasing the molar ratio of F127 the surface charge of the \{Mo_{72}Fe_{30}\} macroanion decreases and the hybrid BB increases. Below the F127 CMC the association still remains at different pH in solutions. Our study shows an average $R_h$ size ca. 10 nm above a classic \{Mo_{72}Fe_{30}\} BBs.
Chapter 7: Conclusions

In summary, the POM-organic hybrids indeed demonstrate certain typical amphiphilic behavior in polar solvents. The formation of vesicles by these dumb-bell anions is challenging due to their very bulky polar head. Their large, rigid polar head groups and the unique molecular architecture render their self-assembly new features such as the very high entropy gain and the involvement of the amphiphilic counter-ions for the self-assembly, and the different organic linkers make the self-assembly behavior highly adjustable. With similar molecular architectures, these hybrid surfactants demonstrate similar and predictable self-assembly behaviors, which will certainly enrich the family of amphiphilic surfactants, and at the same time expand the applications of the POM materials to organic media. These unique hybrids show interfacial behavior. The organic linkers control the behavior of hybrids at water/air interface. From the $\pi$-A isotherms, the packing of hybrids into monolayer at interface becomes more ordered when the linker becomes more hydrophobic. Liquid expanded and liquid condensed phases are clearly located and connected through a plateau, suggesting that the hybrids behave similar to some cationic gemini surfactants which possess similar molecular architectures. These findings should provide new pathways on the design of better carriers for polyelectrolytes in general and, for polyoxometalates building blocks structures in particular. The physicochemical implication of combining the advantages of both organic functional groups and inorganic species could be especially fruitful from the technological and biological science viewpoint.
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SUMMARY

Accomplished Chemist with experience and expertise in surface chemistry in the area of additives such as wetting agents, defoamers, dispersants and rheology modifiers with a focus on customer needs and environmental demands. International background supporting Latin America and South Africa in the development, marketing, and technical service in the field of coatings, adhesives and inks in waterborne systems. Author/co-author of 5 published technical articles and presenter at 15 technical conferences at the international level. Fluent speaker of Spanish.

PROFESSIONAL EXPERIENCE

Brenntag LatinAmerica 2010-Present
Marketing manager for Paints, Coatings and Construction

Lehigh University, Bethlehem, PA 2008-2010
Ph.D in Polymers Science and Engineering (Grad. May 2011)
Topic: Inorganic-organic hybrid materials; polyoxometalates and, block copolymers

Air Products and Chemicals, Allentown, PA 2001-2008

Sr. Principal Applications Chemist

• Customer technical assistance to introduce new products in Latin American region achieving 220% increase in volume and 150% in revenue in FY07 over FY06.
• Provide technical service to increase the revenue from US $3.5 Million to US $5.0 Million from 2001 to 2007 in Latin America.
• Technical team member for hyper-dispersants with a revenue contribution of US $2 Million.
• Air Products and Chemicals’ silver award of recognition to provide technical service in wetting agents for metallic, organic and inorganic pigment, 2005.
• Mexican Institute of Paint and Ink Technologists (IMTPYT); Best Conference Award, 2003. “Acrylic-Urethane Polymers in Waterborne Industrial Coatings”.
• Technical lead for a new global product program in architectural coatings; developed several prototypes such as wetting agents, molecular defoamers and multifunctional additives. Directed 1 technician.
• Applied surface chemistry to support investigations of new additives to improve performance in colloidal systems.
• Provided technical service demonstrating the use and advantages of epoxy curing agents (polyamides, amines, etc) and acrylic-urethane systems to existing clients.
• Support new product introductions by formulated coating performance data and prepared reports.
• Solve industry challenges in coating systems by conducting more than 40 city and customer meetings.
technical seminars.
- Develop the region providing training for sales personnel, distributors, and customers.
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**Hercules Aqualon, Mexico City** 1996-2001

*Technical Manager for Latin America*

*Architectural Coatings, Construction Industry and Personal Care*

- Build, manage and administrate a new laboratory in Mexico City to provide technical service for coatings, construction and personal care for Latin American region. Supervised 2 chemists and 4 technicians.
- Technical key contact to interact with research centers from Germany and USA.
- Recommended and evaluated cellulose ethers, associative thickeners and performance attributes in coatings, emulsions and construction with the objective to maintain the industry leadership.
- Increased 10 to 15% in revenue due to providing technical solutions over 100 Technical Service Projects.
- Collected, analyzed, and interpreted data on different products to promote or maintained existing business.
- Generated performance data to support new product introductions for customers.
- Conducted more than 20 product training for sales personnel, distributors, and customers.

**Pinturas Continex, Mexico City** 1992-1996

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- Responsible for the development of new products related to coatings such as decorative plasters, architectural paints, aluminum pigment coatings. Supervised and directed 2 chemists and 6 technicians.
- Managed quality control to accept or reject new or existing raw material including pigments, polymers and additives.
- Managed quality control for coatings and perform associated tests such as pigment flocculation and color acceptance, general properties, mechanical properties, etc.
- Increased cost effectiveness and improved quality by evaluating optional manufacturing methods in existing products.
- Provided Technical support at job-site and resolution of manufacturing issues.
- Development and introduction of new spray and economic latex paints in the market with revenues of US $1.0 Million.
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