Acid-base Interactions In The Adsorption Of Polymers Onto Inorganic Powders.

ACID-BASE INTERACTIONS IN THE ADSORPTION OF POLYMERS ONTO INORGANIC POWDERS

by

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DEDICATION

The author dedicates this thesis to his mother for everything she has done.

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ABSTRACT

PMMA, a basic polymer, is found to adsorb strongly from neutral organic solvents onto the acidic silanol sites of a silica filler, providing fifty times more adsorption per unit area than is observed on the basic surface of a calcium carbonate filler. Acidic solvents tend to solvate and neutralize the basic groups of the polymer and will prevent adsorption if the solvent is more acidic than the surface sites of the acidic filler; the acidity of competing solvents is a measure of the acidity of surface sites. Similarly, basic solvents tend to neutralize the acidic silanol sites of the silica filler and will prevent adsorption if the solvent is more basic than the ester groups of the polymer; the basicity of competing solvents is a measure of the basicity of the polymer. These rules are found to govern both adsorption and desorption. Similar findings resulted with post-chlorinated PVC, an acidic polymer, in adsorption studies with calcium carbonate, a basic filler.

Dipole-dipole interactions between these polar polymers and polar adsorbents appear to be negligibly small compared to the acid-base interactions.

Mechanisms were formulated for the charge transfer in polymer adsorption onto inorganic solids from low and high dielectric constant solvents. It was shown in the

lower dielectric constant solvents that the charge transfer occurs at the surface of the solid, while in the high dielectric constant solvents the charge transfer occurs in the solution.

PART I

ADSORPTION

Introduction

For the last two centuries researchers of chemical affinity have divided the fundamental classes of compounds into acids and bases.[1] Lavoisier, Davy, Berzelius, Liebig, Ostwald, Arrhenius and Brönsted have attempted to identify the essential atom or function which was inherently responsible for "acidity" or "basicity." It was G. N. Lewis who in 1923 proposed a unifying concept which has organized the acid-base field.[2] "A basic substance is one which has a lone pair of electrons which may be used to complete the stable group of another atom. An acid substance is one which can employ a lone pair from another molecule to complete its stable grouping." The term "Lewis acid" has come to mean an electron-acceptor which is not a proton-donor, but the idea of classifying all acids as electron-acceptors and all bases as electron-donors has proved to explain most specific intermolecular interactions, including hydrogen-bonds.

Many of the recent studies of acids and bases have concerned the relative strengths of acids and bases. A major concern is that the relative strength of a series of acids is different when measured with different bases.

Chatt and Ahrland[3] pointed out that acids and bases which bond covalently (Class B") have an appreciably different order of acid strengths than those which

bond electrostatically ("Class A"). Pearson[4,5] has utilized the nomenclature "hard" and "soft" acid or base (HSAB) to include along with other effects the electrostatic (hard) and covalent (soft) contribution to acid-base interactions. In general "hard-hard" and "soft-soft" interactions dominate soft-hard combinations. Mulliken[6] explained these phenomena theoretically; he used a simplified molecular orbital calculation to describe the ionic-covalent characteristics of charge transfer complexes. Drago[7] used a simple correlation equation for enthalpies of adduct formation in acid-base interactions based on Mulliken's[6] ionic-covalent description of charge transfer complexes.

Most acid-base studies have been concerned with acids and bases in solution but in this study we are concerned with acid-base interaction at the interface between solid particles of inorganic materials and polymer molecules adsorbed from organic solvents. Acidic and basic inorganic solids were studied in solutions of acidic or basic polymers dissolved in a series of solvents which were acidic, neutral, or basic. This system sets up a three-way competition between acid-base interactions: polymer-solid, polymer-solvent and solid-solvent. Experimental evidence clearly demonstrates which of the three is dominant in any particular example.

Theory of Intermolecular Interactions in Solutions and at Interfaces

Intermolecular interactions in solutions have been correlated by the solubility parameter, δ, as developed by Hildebrand and Scott.[8] They expressed the solubility parameter by an equation of the form:

$$\Delta H_M \simeq \Delta U_M = V_m \phi_1 \phi_2 (\delta_1^2 + \delta_2^2 - 2\sqrt{\delta_1 \delta_2}) \qquad (1)$$

where ΔU_M = energy of mixing (or enthalpy if ΔV_{mix} is zero)

ϕ_1, ϕ_2 = volume fractions of the components

V_m = average molar volume based on mole fractions

δ = [C.E.D.]$^{\frac{1}{2}}$

= $[\Delta E_{vap.}/V_m]^{\frac{1}{2}}$

C.E.D. = cohesive energy density

and

ΔE_{vap} = energy of vaporization.

Similarly, interactions at interfaces have been correlated by the surface tension, γ, by the equation of Girifalco and Good[9],

$$W_A = 2\Phi(\gamma_1 \gamma_2)^{\frac{1}{2}} \qquad (2)$$

where W_A is the work of adhesion, γ_1 and γ_2 are surface tensions of the components 1 and 2, respectively, and Φ is an interaction parameter for the particular pair of components.

Both of these approaches employ the geometric mean of the intermolecular forces between unlike components; $[(\delta_1\delta_2)^{\frac{1}{2}}]$ or $[(\gamma_1\gamma_2)^{\frac{1}{2}}]$. However for liquids which show hydrogen bonding or acid-base characteristics, the geometric-mean rule would introduce a serious error in calculating intermolecular interactions.[10]

For polymer adsorption from non-aqueous solvents onto inorganic solids, the dipole-dipole forces, dispersion forces and acid-base interactions are believed to constitute the major attractive forces at the interface.[11] For illustration of the magnitudes of these attractive energies, we consider the interaction between benzene (basic) and phenol (acidic). An estimation of each of these attractive energies could be obtained if we assume that the separation distance between the centers of the attracting groups is 0.4 nm. The calculated energies can be reported in terms of multiples of kT at 25°C. The dipole-dipole forces, $U^{\mu\mu}$, between the two phenol molecules can be calculated as follows:[9]

$$U^{\mu\mu} = 2\mu_1^2\mu_2^2/3kT\ r_{12}^6 = -0.40\ kT \qquad (3)$$

and the dispersion forces, U^d, between the two benzene molecules can be calculated as

$$U^d = -(3\alpha_1\alpha_2/4r_{12}^6)\ 2h\nu_1^o\nu_2^o/(\nu_1^o + \nu_2^o) = -7.5\ kT \qquad (4)$$

where $\mu_1 = \mu_2$ = the dipole moment of phenol

r_{12} = the distance between centers of the phenol molecule dipoles

k = Boltzman constant

$\alpha_1 = \alpha_2$ = the molecular polarizability of the benzene molecule

$\nu_1^o = \nu_2^o$ = the fundamental frequency

h = Planck's constant

The acid-base interactions between the phenol and the benzene (according to Drago[7]) are

$$U^{ab} = \frac{\Delta H^{ab}}{N} = -\frac{1}{N}[C_A C_B + E_A E_B] \equiv -3kT \qquad (5)$$

where H^{ab} is the enthalpy of adduct formation between phenol and benzene, C_A, C_B, E_A and E_B are parameters (see Appendix I) obtained by Drago, and N is Avogadro's number. One can see that the dipole-dipole forces between two phenol molecules (-0.4 kT) are about one-tenth as strong as the acid-base interactions between phenol and benzene (-3 kT) and about five per cent of the dispersion forces between two benzene molecules (-7.5 kT). This illustrates the minor role of dipole-dipole forces compared to dispersion and acid base interactions.

I. Intermolecular Interactions in Solutions

A. Solubility Parameter

In recent years, good progress has been made by Hildebrand[12] and others in predicting the energy of mixing of solvents and polymers

from properties of the pure substances -- with methods based on the solubility parameter concept. This theory relates the energy of mixing to the solubility parameter, which in turn is defined in terms of energies of vaporization of the pure components, as can be seen from equation (1). This theory has been developed for mixing of nonpolar substances. However, many of the solvents and polymers in common use are polar, i.e., have dipole moments or capabilities for hydrogen bonding. It is clear that these factors should be included in the theory. One way of doing this is to take into account the various kinds of interactions, perhaps as done originally by Bondi and Simpkin[13] who introduced the idea of treating intermolecular interactions as a sum of the various kinds of interactions. Prausnitz[14] divided the energy of vaporization into a non-polar dispersion part and a polar part, and Hansen[15] divided the polar part into a dipole-dipole contribution and a hydrogen bonding contribution. Chen[16] suggested that the contribution to the energy of mixing in polymer solutions caused by dispersion forces and dipole forces could be put together in one enthalpy correction parameter χ_H (a Flory-Huggins-type correction parameter):

$$\chi_H = \frac{V_M}{RT} [(\delta_1^d - \delta_2^d)^2 + (\delta_1^P - \delta_2^P)^2] \qquad (6)$$

Since hydrogen bonding strongly influences polymer solubility in solvents, χ_H together with the δ^h's could describe the solubility characteristics. Here δ^d, δ^p and δ^h are the contribution of dispersion, polar and hydrogen bonding to the solubility parameter respectively.

Donor-acceptor complexes are formed when an electron donor group can come into contact with an acceptor group. In a pure substance which is of electron-donating type, δ^h may be zero. When, however, this substance is mixed with a substance which is an electron acceptor (also δ^h small), strong hydrogen bonds will result. One example can be seen from the strong donor-acceptor interaction when polycarbonate (a basic polymer) is dissolved in chloroform, despite the fact that no acid-base interactions occur within the chloroform or within the polycarbonate. Similarly, water may form hydrogen-bonds with the π-orbitals of polystyrene and no hydrogen bonds are known to form within polystyrene. Therefore we cannot attribute any interaction energies within liquids or solids because of interaction energies observed between them.

Pimentel and McCleellan[17] classified liquids into four groups:

1. Proton donors, such as substantially halogenated hydrogen carbons, $CHCl_3$.

2. Proton acceptors, such as ketones, aldehydes, ethers and esters.

3. Substances that are simultaneously proton donors and acceptors, such as water, alcohols, acids and primary and secondary amines.

4. Liquids that are neither proton donors nor acceptors and therefore do not participate in H-bonding formation; paraffins belong to this category.

Most of the early work regarding the effect of hydrogen bonding on solubilities was qualitative and at best semiquantitative. Small[18] proposed that the contribution to the heat of mixing due to hydrogen bonding, h, may be expressed as:

$$h_{\text{due to H-bonding}} = \phi_1\phi_2(A_1 - A_2)(D_1 - D_2) \quad (7)$$

where ϕ_1 and ϕ_2 are the component volume fractions, and A and D refer to (positive) proton-accepting and proton-donating capacities, respectively, of the particular liquids. No numerical values were proposed for A and D, but equation (7) can be used qualitatively. For example, if component 2 belongs to class 4 and component 1 to any other class, both A_2 and D_2 are zero but A_1 and/or D_1 are finite, resulting in a positive contribution to the heat of mixing. But when both components are hydrogen bonded, all four, A_1, A_2, D_1 and D_2 are

non-zero, and the net effect cannot be easily predicted.

Hansen and Skuarup[19] used a value of 5 kcal/mole (21kJ/mole) based on I.R. Spectroscopy as the enthalpy for an O-H---O hydrogen bond; they then considered this enthalpy to be additive for each additional O-H---O bond. However, numerical values for the enthalpies of other types of H-bonds were not assigned. Beerbower and Hansen[20] have compiled values for the enthalpy of hydrogen bond or donor-acceptor group, E^h, using the following equation:

$$E^h = (\delta^h)^2 V_m \qquad (8)$$

Nelson, Hemwall and Edwards[21] proposed a net hydrogen bonding index, θ. Since the effect on component solubility depends on whether hydrogen bonds are broken or formed on mixing, a weighing factor k_i was introduced,

$$\theta = \sum_{i=1}^{n} k_i \phi_i \Gamma_i$$

where ϕ_i is the volume fraction of the component and Γ_i is the hydrogen bonding parameter from Gordy's[22] work (taken as 10 per cent of the wave-number shift produced by the solvent). The weighing factor k_i was taken as 1 for donor-acceptor fluids such as alcohols, zero for ether and +1 for all other substances. The sign and magnitude of θ reflects the H-bonding contribution to solubility. Systems having a large positive value

of are better solvents than those with a negative or a small positive value of .

B. Multi-Dimensional Solubility Correlation.

To obtain reliable predictions of polymer solubility behavior, various workers have attempted to correlate experimental data with specific intermolecular forces. These correlations first characterize the different polymers and solvents on the basis of two or three parameters, and then establish two- or three-dimensional regions of solubility for each polymer.

One of the earliest two-dimensional methods was proposed by Small[18], who used the solubility parameter and the iodine-bonding number, (ℓ/mole). These numbers were obtained by visual matching of the color produced by dissolving iodine in different solvents. A general region of solubility would be obtained. Nobody appears to have used these numbers. Crowley, Teague and Lowe[23] used solubility parameters, δ, the dipole moment μ, and Gordy's hydrogen bonding parameter, Γ, to construct a three-dimensional model for the solubility behavior of polymers. Hansen[24] also used a three-dimensional representation of polymer solubility behavior. He divided the solubility parameter δ into δ^d due to dispersion, δ^h due to hydrogen bonding and δ^p due to polar contributions. Then he proposed

$$\delta^2 = (\delta^d)^2 + (\delta^h)^2 + (\delta^p)^2 \qquad (9)$$

and for the heat of mixing, ΔH_M,

$$\Delta H_M = \Delta H_M^d + \Delta H_M^h + \Delta H_M^p \qquad (10)$$

The use of Hansen's expression of solubility parameter (eq. 9) in the Hildebrand expression involving $(\delta_1-\delta_2)$ introduced many meaningless cross products. The dispersion force term ($\Delta H_M^d \simeq \Delta U_M^d$) can be correctly evaluated by use of the geometric mean,[24]

$$\Delta U_M^d = V_M \phi_1 \phi_2 [\delta_1^d + \delta_2^d - 2(\delta_1^d \delta_2^d)^{\frac{1}{2}}] \qquad (11)$$

as well as the dipole-dipole term, ΔU_M^p,

$$\Delta U_M^p = V_M \phi_1 \phi_2 [\delta_1^p + \delta_2^p - 2(\delta_1^p \delta_2^p)^{\frac{1}{2}}] \qquad (12)$$

In order to calculate the contribution of permanent dipoles to the cohesive energy density, Hansen[25] has used the following formula proposed by Böttcher:[26]

$$(\delta^p)^2 = \frac{12108}{V_m^2} \cdot \frac{\varepsilon-1}{2+n_D^2} (n_D^2 + 2)\mu^2 \quad \text{J/dl} \qquad (13)$$

where ε is the dielectric constant, μ is the dipole moment and n_D is the refractive index. Beerbower[27] used an empirical relationship of the following form for δ^p:

$$\delta^p = A'(\mu/V_m^{\frac{1}{2}}). \qquad (14)$$

and Koenhen and Smolders[28] used Beerbower's expression modified by taking V_m to the power 3/4:

$$\delta^P = A''(\mu/V_m^{3/4}) : \qquad (15)$$

Values of A' and A'' are given in $(volt/m)^{1/2}$ and $(volt/m)^{1/4}$ respectively.

More recent solution studies have relied heavily on infra-red spectra and to a lesser degree on calorimetry to establish the enthalpy of specific interactions of polar groups.

Polymers interact with their surroundings mainly by two kinds of attractive forces, London dispersion forces and specific interactions, namely acid-base interactions. In polymer solutions, the London dispersion forces are predicted and correlated by the Hildebrand solubility parameter theory. Deviations from these predictions are mostly the result of acid-base interactions. For example, polycarbonate (a basic polymer) has a high solubility in acidic chloroform. According to the early solution theory which was concerned only with dispersion forces, we cannot predict which polymers can be blended. An incorporation and understanding of the acid-base interactions could overcome this problem. When polymers interact with solids in adhesives, surface coatings, or in polymer composite, the attractive forces at the interface are considered to include the sum of

dispersion force and acid-base interactions[29] (including hydrogen bonding). Polymer reinforcement appears to require acid-base interactions at the interface.[30]

These shortcomings of the solubility parameter theory can be overcome if we utilize Drago's correlation for the prediction of the enthalpy of donor-acceptor complexes to solvents and polymer-solvent mixtures. His approach was parameterization (Appendix I) on the basis of Mulliken's[31] ionic-covalent description of charge transfer complexes. Drago's procedure makes it possible to predict enthalpies of adduct formation, and the enthalpies predicted can be checked with those measured from the O-H frequency shift correlation, eliminating the need for a tedious calorimetric determination of the enthalpy of adduct formation.

The range of enthalpies for Drago's procedure was established and a linear relationship was demonstrated between the calorimetrically determined enthalpy of adduct formation, ΔH, and the change in the frequency of the O-H stretching vibration, $\Delta\nu_{OH}$ of phenol upon complexation[32]. The relationship is linear over the range of enthalpies from 4.8 to 9.0 kcal/mole (20-40 kJ/mole). The correlation applies to a large range of donors including various oxygen and nitrogen donors and all hydrogen bonds.

The existence of the frequency shift-enthalpy correlation was given substantial support by the analysis providing a theoretical basis for the relationship[33] (Appendix I). It was further predicted that hydrogen bonding acids other than phenol should give linear correlations and that the slope of the line for a given acid should be a function of the inherent acidity of the compound. Then it was found that there was a negligible difference in the slope and intercept of the relation when phenol or substituted phenols were used: i.e., all reactions studied of phenolic acids with bases[33] adhere to one equation, namely,

$$-\Delta H \text{ (kcal/mole)} = 0.0103\ \Delta\nu_{OH}(cm^{-1}) + 3.08 \qquad (16)$$

C. Two Parameter Versus Four Parameter Equation for Acid-Base Correlations

Hammett[34] has developed a substituent constant, σ, to predict the effect of ring substituents on the reactivity of the functional groups of many classes of aromatic compounds. A two-parameter relation between σ for a series of para-substituted phenols and the ΔH with some bases was found to be a linear one. The line slope shows an increase with base strength. The value of the slope for other bases cannot be predicted and would have to be obtained by measuring enthalpies of adduct formation for each base with at least two substituted phenols. The

Hammett linear equation is normally not sufficient to correlate the variety of acid-base interactions even when the processes are quite similar. This is exemplified in the lack of a general correlation between hydrogen bonding energies and those for protonation. Drago's four-parameter equation allows for all these acid-base correlations. So it was of significant importance that Drago has introduced his four-parameter equation in order to improve the ability to fit old data and predict new enthalpies.

Drago's approach[7] appears not only more general, but far more quantitative. He has demonstrated the wide scope and reliability of an equation:

$$-\Delta H^{ab} = C_A C_B + E_A E_B \qquad (17)$$

in which each acid is assigned parameters E_A and C_A and each base is assigned parameters E_B and C_B and ΔH^{ab} is the acid-base enthalpy. Although the equation was originally expected to correlate electrostatic (E) and covalent (C) interactions, these parameters are now considered to be more empirical. By using this equation it is possible to predict enthalpies of specific interactions within 0.4 - 1.3 kJ/mole of the experimental values for nearly a thousand pairs of acid-base interactions, including Bronsted acid-base interactions,

Lewis acid-base interactions and all kinds of hydrogen bonding--even the rather obscure hydrogen-bonding of aromatic rings with hydrogen donors such as alcohols, phenols and carboxylic acids. It was known that the hydrogen bond is formed only when acidic hydrogens can exist. Now hydrogen bonding could be completely predicted by the acidity of the hydrogen and the basicity of the hydrogen acceptor. The acid-base enthalpy, ΔH^{ab} was measured in CCl_4 as a neutral solvent, then C_A and E_A for each acid and C_B and E_B for each base were determined. In these correlations, all predicted values of ΔH_{ab} (up to 80 kJ/mole) checked with measured values within 1.3 kJ/mole (usually within 5 per cent or less).

Arnett, Mitchell and Murty[35] have used the Drago's equation to calculate the enthalpies of hydrogen bond formation. They found for 15 compounds they studied, the average deviation between the calculated and measured results is ±0.5 kcal/mole. They concluded that the use of Drago's four-parameter equation can give reasonable estimates of enthalpies of hydrogen bond formation. An illustration of these interactions can be made using the following two acids and two bases[7] shown in Table 1.

Table 1

Comparison between Measured and Drago's Calculated ΔH^{ab}

Acid			Base			$-\Delta H^{ab}$ (kJ/mol)	
	C_A	E_A		C_B	E_B	Calc	Exp.
Phenol	0.90	8.83	Pyridine	13.06	2.39	33.02	33.44
Phenol	0.90	8.83	Ethyl Acetate	3.56	1.99	20.90	20.06
Chloro-form	0.306	6.77	Pyridine	13.06	2.39	20.48	20.48
Chloro-form	0.306	6.77	Ethyl acetate	3.56	1.99	14.63	15.88

The E and C equation should be compared with the equation developed earlier for predicting polar interactions (hydrogen bonding) when these were thought to be dominated by dipole interactions, and that the enthalpy of such interactions (ΔH_p) was proportional to the product of the squares of the dipole moments ($\mu_A^2\mu_A^2$). This assumption will lead to this geometric mean relationship:

$$(\Delta H_p)^{ab} = [(\Delta H_p)_A(\Delta H_p)_B]^{\frac{1}{2}} \qquad (18)$$

where it was assumed that the enthalpy of polar interactions between unlike molecules is predictable from

the enthalpy of polar interactions of like molecules. Phenol is expected to have hydrogen bonding or acid-base interaction between like molecules. Neither ethyl acetate nor pyridine have hydrogen bonding or acid-base interaction between like molecules. Thus equation (18) would yield a value of $\Delta H_p^{ab} = 0$ for all the four pairs of molecules shown in Table 1.

For the solubility parameter δ, $(\Delta E_{vap}/v)^{\frac{1}{2}}$, the intermolecular interaction can be determined accurately by use of the geometric mean $(\delta_1 \delta_2)^{\frac{1}{2}}$ where the dispersion force interactions are rather well predicted. For poly-functional molecules, one can use δ_1^d and δ_2^d very effectively. But hydrogen bonding and acid-base interactions are not predictable by such a geometric mean, and δ^h and δ^{ab} have no consistent meaning.

II. Intermolecular Interactions at Interfaces

As in the theory of solutions, the interactions at an interface involve molecules with different kinds of intermolecular forces. The free energy change per unit area on separating an interface in a reversible, equilibrium fashion (the work of adhesion, W_A) is composed of[36,37]

$$W_A = W_A^d + W_A^h + W_A^{ab} + W_A^p + W_A^i + \ldots \qquad (19)$$

where d is for London dispersion forces, h for hydrogen bonding, ab for acid-base interaction, p for dipole-dipole interaction, and i for induced dipole-dipole interaction. The work of cohesion ($W_c = 2\gamma$) can similarly be separated into components of surface tension.

$$(\gamma^d,\ \gamma^h,\ \gamma^{ab},\ \gamma^p \text{ and } \gamma^i)$$

In both fields (interactions in solutions and at interface) the first approach was to assume that all molecules interact by only a van der Waals or Lennard-Jones potential.

Forces at interfaces had been recognized mainly as London dispersion forces and other forces such as dipole-dipole and dipole-induced dipole. The dispersion force interactions (between two liquids or between a liquid and a solid) can be rather accurately predicted by the geometric mean of their internal forces as derived from the London force theory as given by Fowkes[38,39]

$$W_{12}^d = 2\ (\gamma_1^d \gamma_2^d)^{\frac{1}{2}} \qquad (20)$$

Some investigators tried equating the proportion of dispersion forces for pairs of gas molecules to that in liquids.[40,41] This would assume that the London dispersion forces, the Keesom dipole-dipole forces and

the Debye dipole-induced dipole forces are equally additive in bulk liquids and that the hydrogen bonds are only dipole interactions. However, it was found that the hydrogen bonding liquids interact far more weakly with hydrocarbons than originally predicted.[12,42] This is due to the fact that only the dispersion force part of the intermolecular forces in hydrogen-bonding liquids can interact with hydrocarbons. Later it was established that hydrogen bonding had no relationship to dipole moments.[17,43] While Hansen[44] has divided the polar part into a dipole-dipole and a hydrogen bond contribution, Drago[45] recognized the significance of acid-base interactions and ignored the dipole-dipole and dipole-induced dipole due to their small contribution to the intermolecular forces.

If we consider the hydrogen bonds and acid-base interactions as donor-acceptor interactions at a liquid/solid interface, we must realize that the work of adhesion resulting from either W_A^h or W_A^{ab} often has no relation to the bonding within either material. In other words, neither W_{A12}^h nor W_{A12}^{ab} is a function of the surface free energy γ^h or γ^{ab} respectively, i.e.

$$W_{A12}^h \neq f(\gamma_1^h, \gamma_2^h) \text{ and} \tag{21}$$

$$W_{A12}^h \neq f(\gamma_1^{ab}, \gamma_2^{ab}) \tag{22}$$

Hence, the geometric mean rule cannot be used to correlate the internal force as a result of either the hydrogen bonding or the acid-base interactions. Thus

$$W_A^h \neq 2[\gamma_1^h \gamma_2^h]^{\frac{1}{2}} \quad \text{and} \tag{23}$$

$$W_A^{ab} \neq 2[\gamma_1^a \gamma_2^b]^{\frac{1}{2}} \tag{24}$$

However, if the distance between dipoles is expressed by the geometric mean and r_{12} is the geometric mean of r_{11} and r_{22} of the pure materials, then dipole-dipole interactions could be correctly treated by a geometric mean expression similar to that of the dispersion forces, and we have:

$$W_A^p = 2(\gamma_1^p \gamma_2^p)^{\frac{1}{2}} \tag{25}$$

so we can express W_A^d and W_A^p using the geometric mean though not W_A^h or W_A^{ab}.

It was of special interest to find some relationship between W_A^h and γ_L^h. Dann[46], utilizing the contact angle (θ) technique, has shown that the frequently suggested relation that W_A^h is proportional to $(\gamma^h)^{\frac{1}{2}}$ to be a poor fit. He used liquids with hydrogen bonding capabilities such as glycols, amides and alcohols on proton-accepting polymers with surface groups like esters, ethers or ketones, as well as polymers with both proton-donor or proton-acceptor surface sites like

amides, alcohols or amines. By utilizing the relation[47]

$$\gamma_L^d = (\gamma_L(1+\cos\theta))^2/4\gamma_s^d \qquad (26)$$

and using paraffin wax with a value of 25.5 mJ/m² for γ_s^d, he was able to evaluate $(\gamma_L - \gamma_L^d)$ for all systems mentioned above. His results show that there is a considerable surface tension in excess of the γ_L^d value, namely $(\gamma_L - \gamma_L^d)$. This excess is due mainly to other intermolecular interactions:

$$\gamma_L - \gamma_L^d = \gamma_L^h + \gamma_L^p + \gamma_L^i \qquad (27)$$

The values of γ_L^p and γ_L^i are almost negligibly small compared to γ_L^h. Therefore, $(\gamma_L - \gamma_L^d)$ for these liquids could be considered as a measure of hydrogen bonding and would be useful for

$$W_c^h \simeq 2(\gamma_L - \gamma_L^d) \qquad (28)$$

In order to relate the work of adhesion W_A to the excess surface tension, Dann plotted $(\gamma_L - \gamma_L^d)$ vs. $W_A - W_A^d$ which implied a direction relationship; therefore W_A^h is directly proportional to γ_L^h, not $(\gamma_L^h)^{\frac{1}{2}}$ as previously suggested. His results indicated that polystyrene (slightly basic) showed a strong adhesion (high W_A) with water (acidic proton donor), and polyvinyl chloride (acidic) adhered more strongly to basic formamide

than predicted by just its hydrogen bonding ability.

Now for the equation of W_A, equation (19),

$$W_A = W_A^d + W_A^h + W_A^p + W_A^i + W_A^{ab} + \ldots \qquad (19)$$

we could put this approximation:

$$W_A - W_A^d = W_A^{ab} \qquad (29)$$

The most widely used equations for "polar" interactions, the geometric mean equations, are suitable for dipole-dipole interactions, but are completely unsuitable for acid-base interactions. Because of the mathematical simplicity of the geometric mean equations, most investigators have used these, unknowingly assuming that polar interactions are dipole interactions rather than acid-base interactions. On the other hand, Drago's correlation assumes dipole interaction to be negligible and that polar interactions are predominately acid-base interactions.

Drago's four-parameter equation is taken to adequately describe the phenomenon of polymer adsorption in solution in particular and the interactions at interfaces in general as acid-base interactions. Using Drago's correlation, it is assumed that the dipole-dipole interactions, ΔH_M^p, are negligibly small compared to ΔH_M^{ab}.

The above assumption is supported by the studies done on characterization of polymer surfaces, the interaction of phenol with copolymers of acrylic acid with ethylene or of vinyl acetate with ethylene.[48] It was found there is negligible dipole interaction and the dominant forces are the dispersion force and the acid-base interactions.

It is the purpose of this research to test the importance of acid-base interactions in polymer adsorption and whether or not the contribution of dipole-dipole interaction is significant in these systems.

III. Mechanical Properties

Studies of mechanical properties[30,49] of filled polymer systems indicated that acid-base interactions at interfacescan have an effect on modulus, tensile strength and glass transition temperature.

Basic inorganic oxides in basic polymer polycarbonate have been shown to yield brittle and conductive films with lumps of aggregated filler at a loading of 20 volume per cent. At the same time these oxides gave tough, low conductivity films when dispersed in an acidic polymer, chlorinated polyvinylchloride, Cl-PVC, even at loadings of 60 volume per cent.[50]

It seems that the acid-base interactions between

polymer and filler surface are necessary to get a uniform dispersion of filler, especially with high volume fractions of fillers where acid-base interactions are anticipated to promote both the amount and rate of adsorption. However, the resulting mechanical properties are strongly dependent on the preferential adsorption of the polymer onto the filler and on the choice of the solvent. Basic solvents are generally better solvents for acidic polymers: Cl-PVC dissolves easily into tetrahydrofuran, THF, but the acidic polymer may interact so strongly with the basic solvent that it will not adsorb onto the basic filler.

EXPERIMENTAL MATERIALS AND TECHNIQUES

I. Materials

A summary of polymers, inorganic solids and solvents used in these studies is given in Tables 2, 3 and 4, respectively.

Table 2

Polymers Used in Adsorption Experiments

Poly(methylmethacrylate) (PMMA)	duPont Lucite 4F	$M_n = 5 \times 10^5$
PMMA	synthesized at Lehigh by Dr. Kim (bulk polymerization)	$M_n = 5.5 \times 10^4$
PMMA	synthesized at Lehigh by Dr. Kim	$M_n = 4.6 \times 10^6$
Chlorinated polyvinylchloride (Cl-PVC)	B. F. Goodrich Geon 603X560	

Table 3

Surface Areas of Fillers Used in Adsorption Experiments

$CaCo_3$	Albacor 5970 Pfizer Minerals, Pigments and Metals Division	$6 m^2/g$ (nitrogen adsorption)
SiO_2	Aerosil 380, Degussa Inc. (fumed silica)	$380 m^2/g$
modified SiO_2	$Al_2(SO_4)_3$-treated Aerosil 380	$95 m^2/g$ (nitrogen adsorption)

Table 4

Solvents Used in Adsorption Experiments

Methylene chloride, CH_2Cl_2	Fisher Scientific Co.(A.R.)
p-dioxane, $C_4H_8O_2$	Fisher Scientific Co.(A.R.)
Chloroform, $CHCl_3$	Baker Analyzed Reagent
Carbon tetrachloride, CCl_4	Baker Analyzed Reagent
Benzene, C_6H_6	Baker Analyzed Reagent
Tetrahydrofuran, C_4H_8O	Baker Analyzed Reagent

II. Adsorption Measurements

The adsorption of PMMA and Cl-PVC onto silica and onto $CaCO_3$ was determined with each of the six solvents of Table 3.

Solutions of 0.3 - 1.8g of polymer in 100 ml of solvent were prepared and allowed to approach equilibrium at 22°C, in closed containers. Then enough filler (inorganic solids) to absorb most of the polymer (a weight of SiO_2 about equal to the weight of the polymer, or a weight of $CaCO_3$ about 50 times that of the polymer) was added. The suspension was stirred using a magnetic stirrer for different intervals ranging between 15 minutes and 60 hours. A period of 15 minutes was sufficient to allow all adsorption to occur as determined gravimetrically. The suspension then was centrifuged

with a Servall SS-1 and duplicate samples of 10 ml of the clear supernatant were evaporated to dryness using a rotary evaporator, then dried for 48 hours at 120-130°C at 1-2 mm of Hg pressure in a vacuum oven. The weight of residual polymer was compared with a blank sample of the original solution.

The amount adsorbed is reported in grams per m^2 of filler surface. Adsorption isotherms in each solvent were obtained to establish the polymer concentration so as to ensure maximum adsorption.

III. Desorption Measurements

Powders remaining after adsorption were centrifuged to free them from most of the polymer solution and oven dried at 120°C. The dry powders were then redispersed in a different solvent, stirred for some time, allowed to stay for periods of half an hour or for two weeks. Again the sample was centrifuged and the supernatant liquid was assayed for dissolved polymer.

Intrinsic viscosities of most of the polymer solutions were determined at 20.5°C, using an Ostwald viscometer.

IV. Hammett Indicator Dyes

To the dried solid powder (0.1g), 3-5 ml of dry benzene was added. Then 2-4 droplets of 0.1% solution of indicator dye in benzene was added. The dyes are

listed in Table 5, which shows their colors and pKa's.

Table 5

Dyes Used in Adsorption Experiments

Hammett Indicator Dye	Basic Color	Acidic Color	pKa
Phenylazo naphthyl-amine	Yellow	Red	+4.0
Butter Yellow	Yellow	Red	+3.3
Benzene azodiphenyl amine	Yellow	Purple	+1.5
Dicinnamal acetone	Yellow	Red	-3.0

RESULTS AND DISCUSSION

I. Reasons for Choosing Materials

A. Solvents

To demonstrate the acidity and basicity of polymer and solvents as given by Drago, we chose six solvents all of which are characterized by C and E parameters.[7,32] The neutral solvent (CCl_4) was the same as Drago's. The basic solvents in order of their increasing basicity are benzene, p-dioxane and THF. Acidic solvents used were CH_2Cl_2 and $CHCl_3$. The values of C and E of the weaker acid CH_2Cl_2 were recently evaluated by Drago.[32] The properties of these solvents are listed in Appendix II.

B. Polymers

We chose polymers which were characterized as acidic or basic. The basic polymer was poly(methyl methacrylate) (PMMA); its ester groups are expected to be as basic as acetate groups (C_B=3.55, E_B=1.99). PMMA was found (from saturation solubilities) to be more readily soluble in THF (δ=10.0, 2.1 g/dl) and dioxane (δ=9.9, 2.0 g/dl) than in benzene (δ=9.15, $\sim$1 g/dl). So the value of 9.3 always cited for the solubility parameter[51] of PMMA is considerably low and should be close to ten.

For the acidic polymer, post-chlorinated PVC was chosen because it was expected to be acidic due to

the electron acceptor capability, but not as acidic as chloroform. Cl-PVC is readily soluble in CH_2Cl_2 (δ = 9.7); a value for its solubility parameter somewhat greater than the usually quoted[51] 9.3 should be used.

C. Inorganic Solids (Fillers)

Silica surfaces have been characterized for acidity due to surface silanol groups.[52,53] Fontana and Thomas[54] have demonstrated by I.R. techniques that an interaction between these acidic hydrogens and the basic methacrylate carbonyl groups does exist. They estimated that about 40 per cent of the ester groups were bound to the silica surface by such an acid-base interaction.

The surface basicity of calcium carbonate resides in the CO_3^{--} anion, a moderately strong electron donor or proton acceptor, as evidenced by the fact that carbonic acid is a weak acid. Fowkes[55] has shown that $CaCO_3$ when used as the basic filler yielded strong interactions with the acidic components of asphalt.

It is important to realize that all acidic fillers surfaces have some basic sites and all basic fillers have some acidic sites, even though they may be predominately acidic or basic.

D. Hammett Indicators

These indicators were used to determine the relative acidity of silicas used. The Hammett acidity function, H_o,[56] is defined in terms of the degree of protonation of weak organic bases of charges Z, i.e., in terms of the acidity constants "K_{HIn}" for the acids conjugate to the indicator base "In." So, we have

$$-\log K_{HIn} = -\log a_H + \log \frac{(m\gamma)^Z_{In}}{(m\gamma)^{Z+1}_{HIn}} \tag{30}$$

$$\text{or} \quad pK_{HIn} = H_o - \log \frac{m^Z_{In}}{m^{Z+1}_{HIn}} \tag{31}$$

$$\text{where } H_o = -\log \frac{a_H \gamma^Z_{In}}{(\gamma_{HIn})^{Z+1}} \tag{32}$$

where a_H, γ and m are the activity, the activity coefficient and the molality respectively.

Values of H_o could be evaluated if pK_{HIn} is known by the ratio of the colored forms of a suitable indicator. If α is the degree of dissociation of the acidic form HIn, then by using a spectrophotometric technique we would have

$$\frac{m^Z_{In}}{m^{Z+1}_{HIn}} = \frac{\alpha}{1-\alpha} = \frac{A-A_a}{A_b-A} \tag{33}$$

where A = adsorption

A_a = adsorption of acidic form

A_b = adsorption of basic form.

Hammett indicator dyes used in this study are shown on Table 5.

II. Plan of Adsorption Measurements

In order to demonstrate the acid-base interaction in polymer adsorption, measurements were designed to determine the adsorption of acidic polymers onto basic inorganic solids and basic polymers onto acidic inorganic solids from the same six solvents. We also want to test whether adsorption would occur when either acceptor-acceptor or donor-donor are the predominant interactions. So acidic and basic polymers were tested for adsorption onto acidic and basic inorganic fillers, respectively.

III. Adsorption of Acidic Polymers onto Acidic Fillers

Since the purpose of this part of the research is to test whether acid-base interactions occur only when the polymer is acidic and the filler is basic, it became necessary to test whether acidic polymers show appreciable adsorption onto acidic fillers.

The adsorption of the acidic polymer post-chlorinated poly(vinyl chloride) onto the acidic silica filler

was insignificant from all six solvents (less than 10^{-6} grams per m^2). For if we take the complete monolayer to be $4x10^{-4}$ g/m^2, this would correspond to about 0.3 per cent of a monolayer for all six solvents. This illustrates that it is not the polarity of either polymers or fillers which determine the adsorption of polymers in solution, but rather their acid-base interactions with the fillers.

IV. Adsorption of Basic Polymers onto Basic Fillers

For the same reasons mentioned above, it was necessary to determine whether significant adsorption from solution occurs when both the polymer and filler have electron donating capabilities.

Table 16 (Appendix I) shows the result of adsorbing of basic poly(methyl methacrylate) (PMMA) onto the basic calcium carbonate filler. The adsorption occurs only from the neutral carbon tetrachloride and weakly basic benzene and it corresponds to only 5 to 7 per cent of a complete monolayer and much less from the other solvents. This demonstrates the fact that just the polarity of the polymer would not guarantee adsorption even onto a polar inorganic solid unless the polymer is basic (acidic) and the solid is acidic (basic). An adsorption of $0.2x14^{-4}$ - $0.3x10^{-4}$ g/m^2 of PMMA onto $CaCO_3$ supports the previously cited conjecture that

$CaCO_3$ has both basic (predominantly) and acidic surface sites.

V. Adsorption of Basic Polymers onto Acidic Fillers

It was essential to establish the polymer concentration at which a given amount of filler would yield a maximum adsorption. Such a relation between the polymer concentration and the amount of polymer adsorbed for a given mass of filler constitutes the adsorption isotherm. Fig. 1 shows the adsorption isotherms of PMMA (Mn = $5x10^5$) onto SiO_2 from CCl_4, C_6H_6 and CH_2Cl_2. A large adsorption is observed from CCl_4 with a plateau corresponding to specific adsorption of $13x10^{-4}$ g/m^2 at a concentration of 0.6 g/dl compared to about $5x10^{-4}$ g/m^2 at a concentration of 0.8 g/dl from the weakly acidic methylene chloride, while PMMA adsorption from the weakly basic benzene shows a plateau of about $6x10^{-4}$ g/m^2, corresponding to a concentration of $\sim$1 g/dl.

The PMMA concentrations of 0.45, 0.70 and 0.80 g/dl from CCl_4, CH_2Cl_2 and C_6H_6, respectively, were considered as the preferred concentration for further adsorption studies.

In order to show the effect of molecular weight on polymer adsorption in solution, three PMMA specimens with molecular weights (M_n) ranging from $5.5x10^4$ to

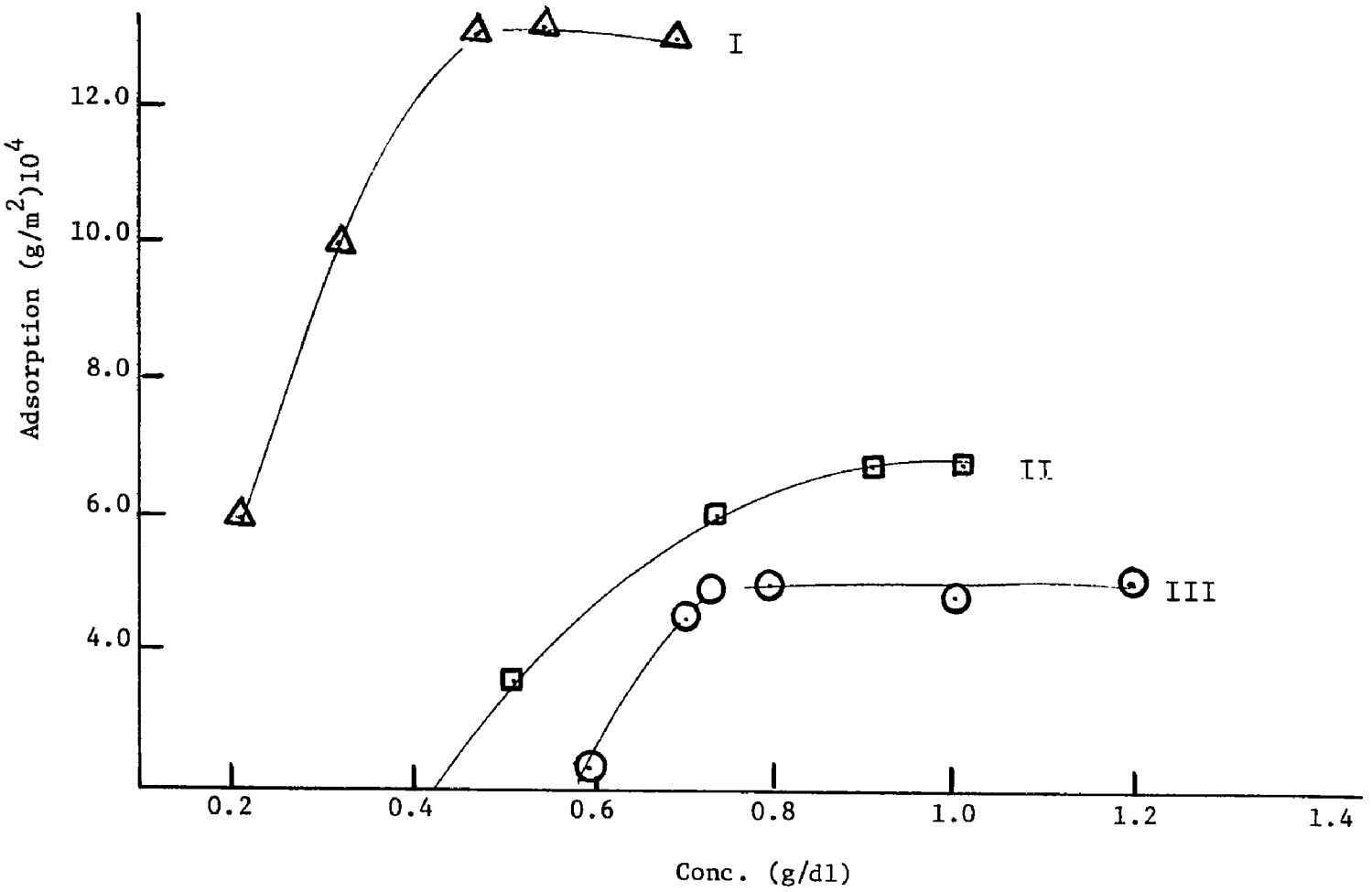

Fig. 1 Adsorption Isotherms of PMMA(5 x 10^5) onto SiO_2(380 m^2/g) from I. CCl_4; II. C_6H_6 and III. CH_2Cl_2.

$4x10^6$ were chosen. Adsorption isotherms of PMMA onto SiO_2 similar to that previously mentioned were determined from CH_2Cl_2. Methylene chloride was chosen as the solvent for testing the effect of molecular weight of PMMA on adsorption isotherms because of the high polymer solubility.

Fig. 2 indicates that PMMA with molecular weight of $4x10^6$ shows an adsorption plateau ($3x10^{-4}$ g/m^2) at a low concentration of 0.4 g/dl while adsorption of PMMA with the lowest molecular weight ($5.5x10^4$) sharply rises and reaches a plateau of $6x10^{-4}$ g/m^2 with concentration of 0.7 g/dl. PMMA ($M_n = 5x10^5$) shows an adsorption plateau at about $5x10^{-4}$ g/m^2 starting at a concentration of 0.8 g/dl. Thus at a PMMA concentration of 0.8 g/dl CH_2Cl_2, it can be seen that the adsorption plateau is the highest with the low molecular weight polymer and the lowest with the high molecular weights. It seems that the longer the molecular chain, the more the degree of entanglement, and the fewer the sites available for adsorption onto the acidic silica. The amount of the basic PMMA (MW = $5x10^5$) adsorbed on the acidic SiO_2 from the six solvents is given in Table 17 (Appendix II). The adsorption was considered as a function of the basicity or the acidity of the solvent as is shown in Fig. 3.

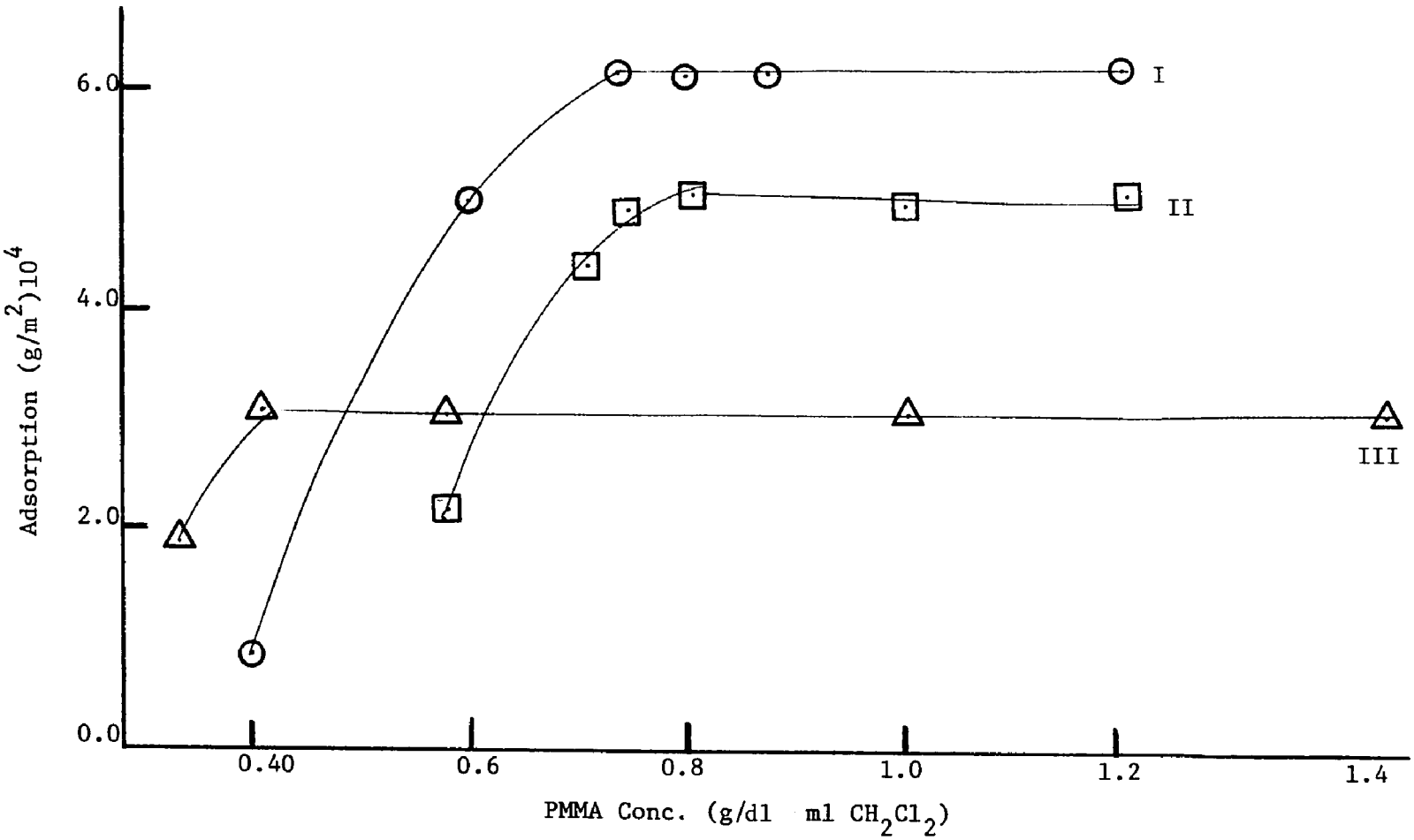

Fig. 2 . Adsorption Isotherms as a function of Molecular Weight
I. 5.5×10^4; II. 5×10^5 and III. 4×10^6

Since Drago has shown that C_B and E_B values depend only on the functional group in the molecule, PMMA is expected to have the same values of C_B and E_B as any other ester. Since we wish to compare solvents with PMMA, the acidity of the acidic solvents $CHCl_3$ and CH_2Cl_2 is measured by their heat of interactions with ethylacetate, an ester which was chosen to compare with the methacrylate groups of the polymer. Thus to assess the acidity of chloroform and methylene chloride as solvents for PMMA, we used Drago's C and E values for the ester ethyl acetate and obtained values of ΔH^{ab} = -14.52 and 6.81 kJ/mole, respectively (Appendix II). Since Drago's data for the basicity of benzene, dioxane and THF allow calculation of ΔH^{ab} for a variety of acids, but not silicic acid, the basicities of the solvents are illustrated by their heats of interaction with t-butanol. By the reasoning described above, we compare the interaction of these basic solvents with silanol groups of the silica surface, where the acidity of the O-H groups in the silica's silanol are considered of the same acidity strength as that of O-H groups in acidic t-butanol. The calculated values of ΔH^{ab} were -13.63, 12.23 and 2.68 kJ/mole for THF, dioxane and benzene, respectively. In Drago's neutral solvent (CCl_4) where heat of acid-base interaction is zero, the

adsorption of the basic PMMA onto the acidic silica is the strongest. As can be seen from Fig. 3 this high adsorption (equivalent to two monolayers) is mainly attributed to acid-base interactions. It was found that the adsorption of PMMA onto SiO_2 is more than forty times that of PMMA onto $CaCO_3$ from the same solvent.

The right hand side of Fig. 3 is a measure of the acidity of the SiOH groups. As the acidity of the solvents increases from CCl_4 to $CHCl_3$, we observed a reduction in adsorption. This trend illustrates that a competition does exist between the acidic solvent and acidic silanol groups of the filler for the basic ester groups of the PMMA. Methylene chloride allows for a full monolayer ($4.8 \times 10^{-4} g/m^2$) of PMMA to be adsorbed onto the silica surfaces while chloroform can allow only for $0.93 \times 10^{-4} g/m^2$ (equivalent to about 0.16 of monolayer).

Chloroform is obviously more acidic than the silanol group; it neutralizes the polymer, allowing little adsorption to occur. Methylene chloride is a much weaker acid and offers little competition to the silanol groups, so it allows the basic polymer to adsorb up to a full monolayer onto the acidic filler. From these competitive experiments we have a rough quantitative estimate of the binding energy of silanol

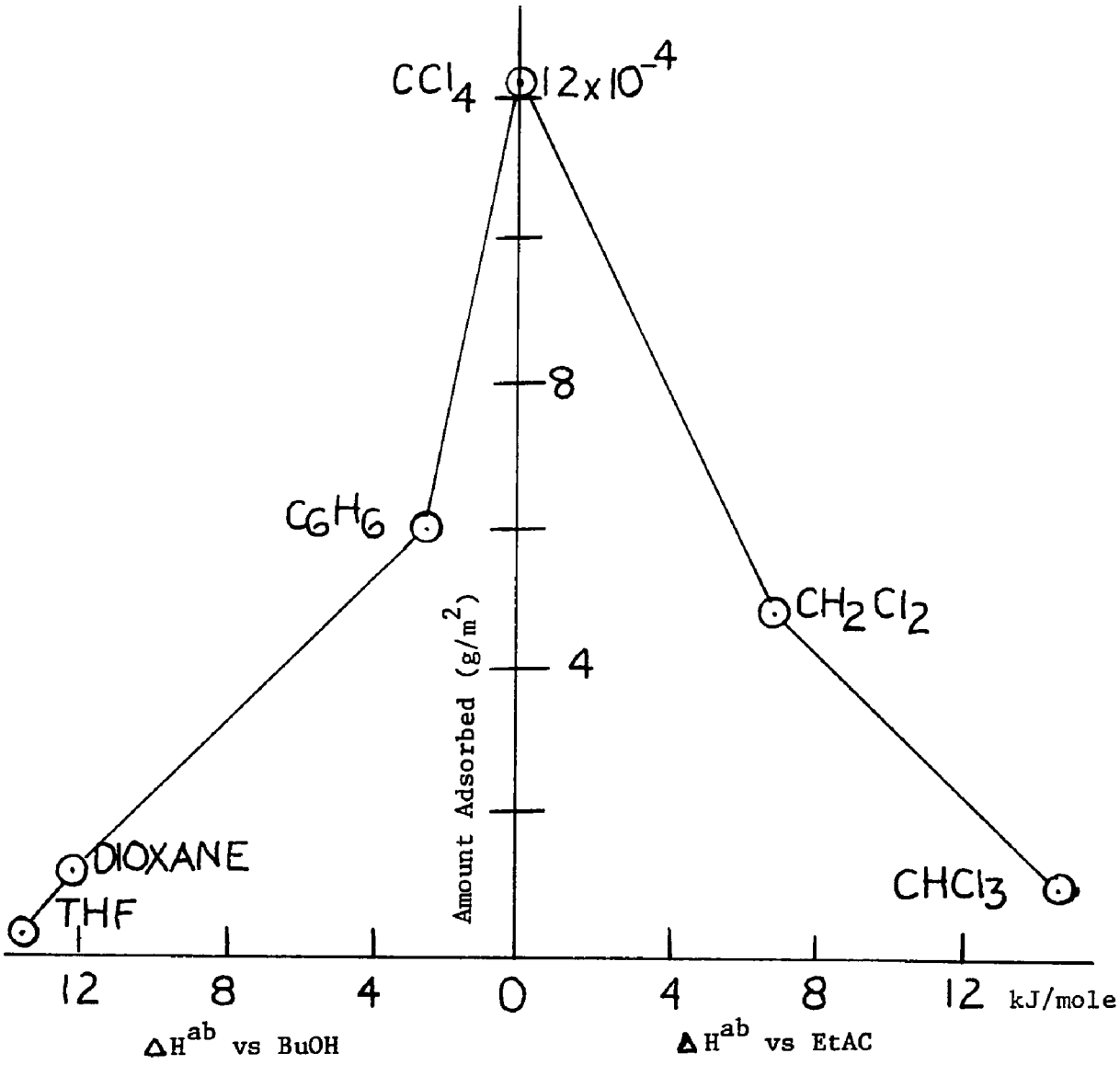

Fig. 3. Adsorption of PMMA ($5\text{-}7\times10^5$) on SiO_2 (380 m^2/g) as a function of the basicity or acidity of the solvent. The basicity is shown as the heat of acid-base interaction with t-butanol (BuOH) and the acidity is shown as the heat of acid-base interaction with ethyl acetate (EtAc).

groups to methacrylate groups. A value of 10kJ/mole would be a fair estimate since the acidity of Si-OH would range between that of methylene chloride and chloroform.

On the left hand side of Fig. 3 we observe the effect of basicity of the solvent on the adsorption of PMMA. As the solvent basicity increases from CCl_4 to THF, we notice a decrease in adsorption. This illustrates competition between the basic solvents and the basic PMMA for the acidic silanol groups of the silica surface. We find that benzene allows $5.95 \times 10^{-4} g/m^2$ (about one monolayer) of PMMA to be adsorbed onto the silica surface while the amount of adsorption from dioxane and THF is $1.3 \times 10^{-4} g/m^2$ (0.2 monolayer) and $0.40 \times 10^{-4} g/m^2$ (0.07 monolayer) respectively. It appears that the basicity of methacrylate groups is much greater than that of benzene but a little less than the basicity of dioxane. So we estimate that the heat of interaction of PMMA with butanol should be closer to the 12.2kJ/mole of dioxane than the 2.7 kJ/mole of benzene. Indeed, Drago's value for the heat of interaction of esters with t-butanol is given as 10.5 kJ/mole.

The question of kinetics versus thermodynamics might arise concerning these measurements of polymer adsorption from organic solvents. If thermodynamics

governs the lack of adsorption from the more acidic or more basic solvents, then these solvents should desorb polymers adsorbed from the more neutral solvents. In order to answer this question the silica with PMMA which has been originally adsorbed from CH_2Cl_2 was dried and stirred in other solvents at 22°C. Solvents chosen to desorb the adsorbed polymer were chloroform, dioxane and THF. The results of the desorption process (which was done in two stages) are shown in Table 6.

Table 6

Desorption of SiO_2 from PMMA by $CHCl_3$, Dioxane and THF

	CH_2Cl_2	Dioxane	THF
After 20 min.	46%	92%	92%
After 2 weeks	96%	98%	97%

These results show that when very little polymer is adsorbed from acidic or basic solvents, this is not because of slow rates of adsorption but because of thermodynamic dictates. This would imply that for separating and identifying polymers a chromatographic technique could be utilized by using a series of solvents of increasing acidity or basicity.

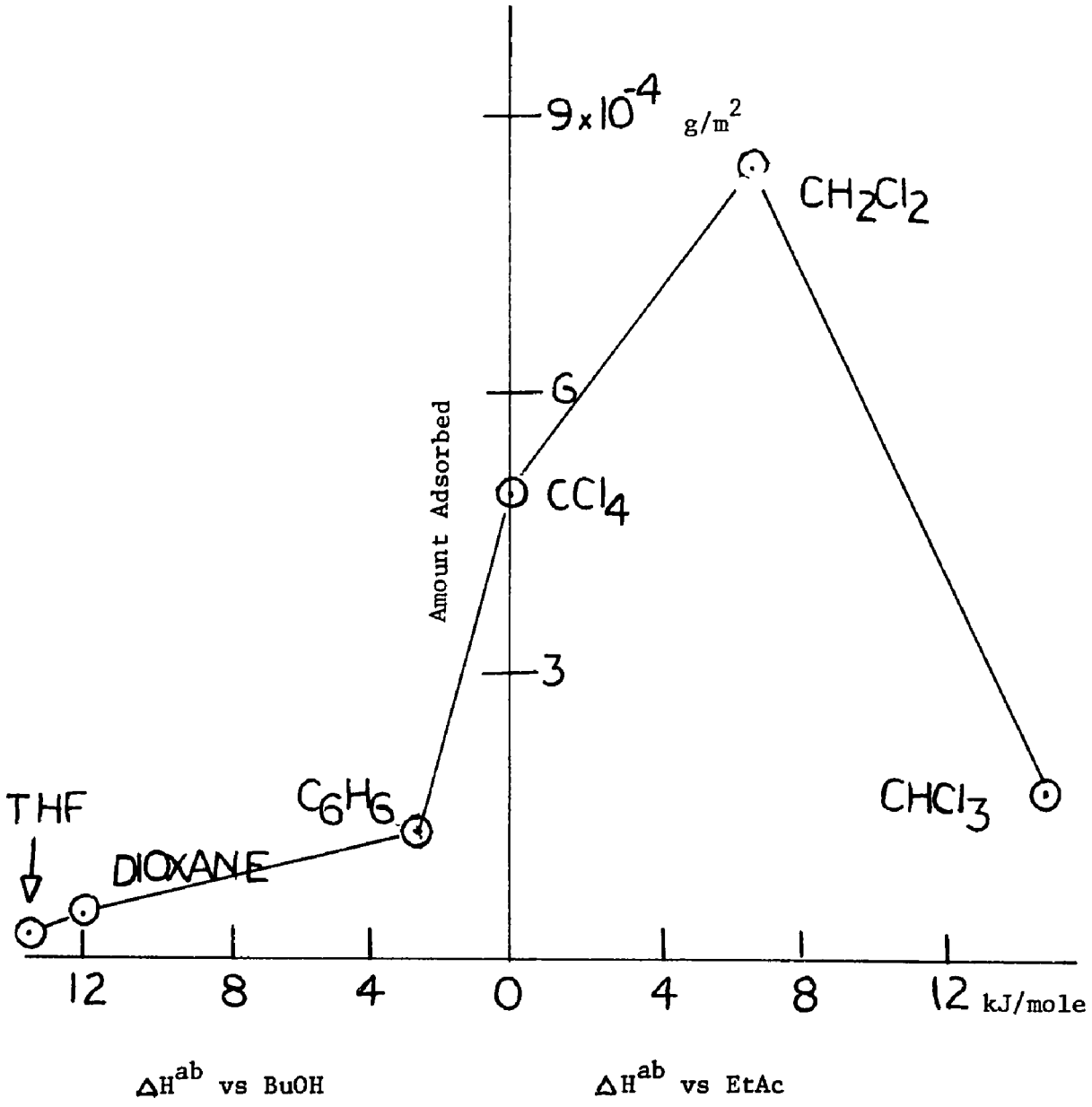

Fig. 4. Adsorption of PMMA ($5\text{-}7\times10^5$) on modified SiO_2 ($Al_2(SO_4)_3$ treated) as a function of the basicity or acidity of the solvent. The basicity is shown as the heat of acid-base interactions with t-butanol (BuOH), and the acidity is shown as the heat of acid-base interactions with ethyl acetate (EtAc).

When a chemically modified silica surface (soaked in aqueous aluminum sulfate overnight, filtered and dried) was used in adsorption of PMMA, an appreciable shift in adsorption toward the acidic solvents results. (Fig. 4) It was expected that aluminum might substitute on a silicon site, thus generating an increase in the surface acidity, a fact which was supported by Hammett acidity indicator changes. The four indicators used were yellow in their basic form. Untreated silica gave a reddish-yellow color with butter yellow indicator, but no change of color on adding benzeneazodiphenyl amine was observed: H_o lies between +3.3 and +1.5. The treated silica gave a purple color with benzene azodiphenyl amine but no change of color when dicinnamal acetone was used. This had led to the conclusion that the aluminum sulfate treatment to the silica had increased the acidity of the untreated silica. H_o now lies between +1.5 and -3.0. Fig. 4 compares the amounts adsorbed on the modified silica as compared with untreated; this shows a decrease in adsorption from methylene chloride and chloroform. The decrease in adsorption from basic solvents could perhaps result if the modified silica had smaller pores and only a fraction of the polymer (30-50 per cent) could adsorb.

VI. Adsorption of Acidic Polymers on Basic Fillers

As has been done for the adsorption of basic polymers onto acidic fillers, adsorption isotherms were necessary to establish the polymer concentration at which a given amount of filler would yield a constant adsorption. Fig. 5 and 6 show such adsorption isotherms of Cl-PVC onto $CaCO_3$ from CH_2Cl_2 and CCl_4 respectively. Fig. 5 indicates that a concentration of about 0.8g of Cl-PVC into 100ml CH_2Cl_2 was sufficient to establish the adsorption plateau at about $4.5\times10^{-4}g/m^2$. Carbontetrachloride (δ=8.6) was a very poor solvent for Cl-PVC. An adsorption plateau was reached at a concentration of 0.75g/1000ml, corresponding to an adsorption of $3.5x10^{-4}g/m^2$.

The amount of the acidic post-chlorinated PVC adsorbed onto the basic calcium carbonate from the same solvents as before is illustrated in Fig. 7. In this figure the acidity of methylene chloride and chloroform is measured by their heat of interaction with ethyl acetate, an ester to be compared with the carbonate group of the filler, and the basicity of the basic solvents is measured by their heat of interaction with chloroform, rather than t-butanol as a model. The reason for choosing chloroform is that we will be comparing the interaction of the chlorinated polyvinyl

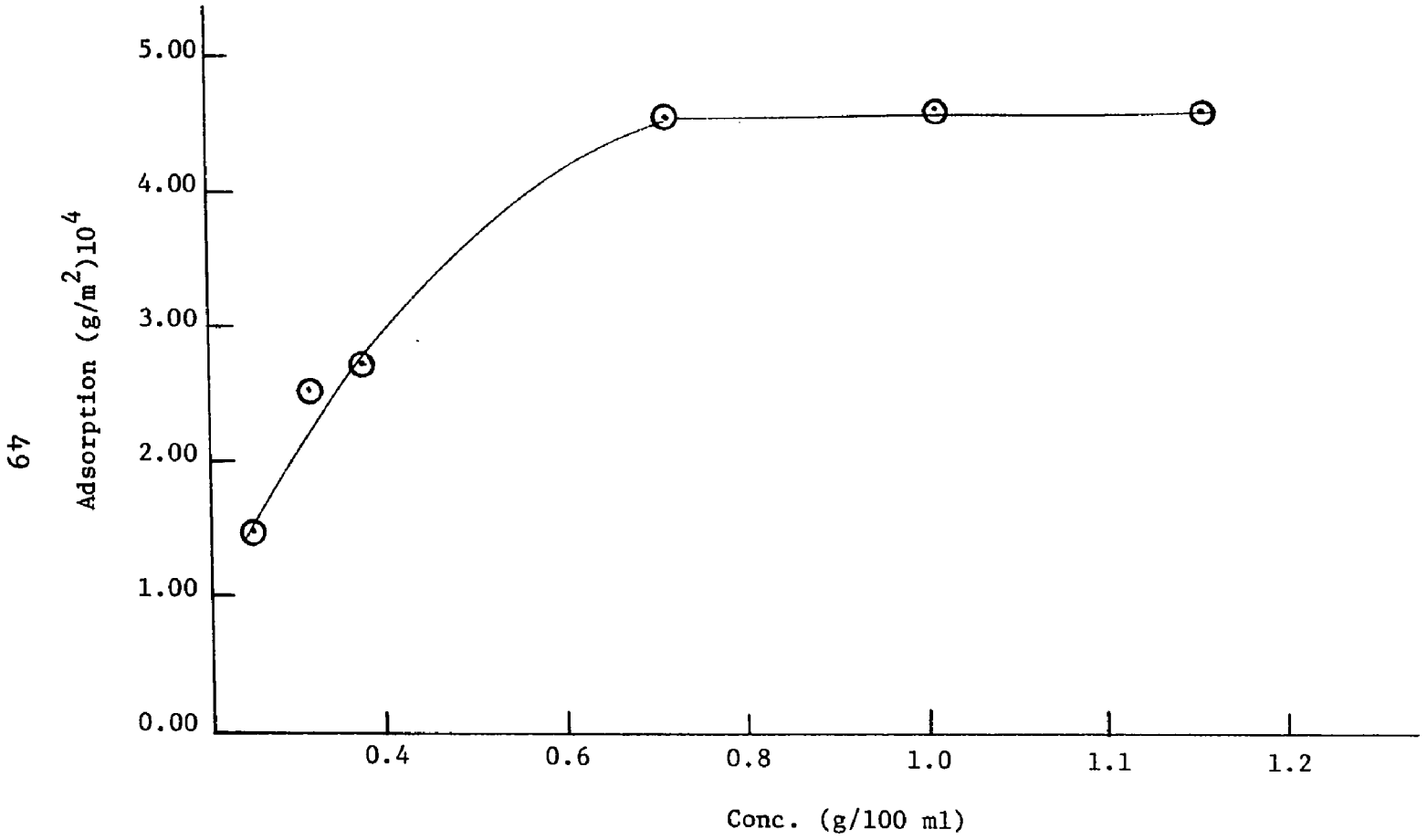

Fig. 5 . Adsorption Isotherm of Cl-PVC onto $CaCO_3$ from CH_2Cl_2

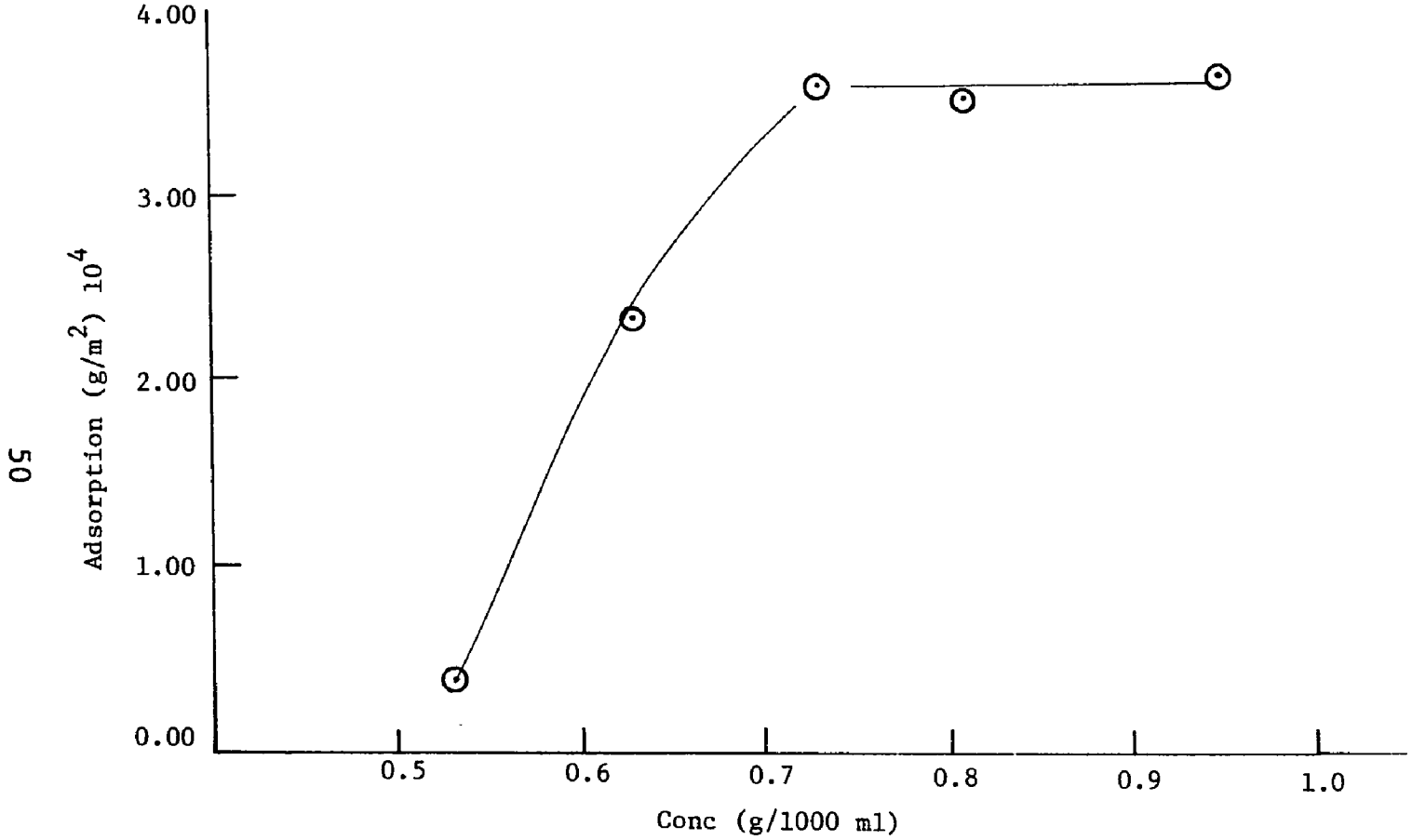

Fig. 6 . Adsorption Isotherm of Cl-PVC onto $CaCo_3$ from CCl_4

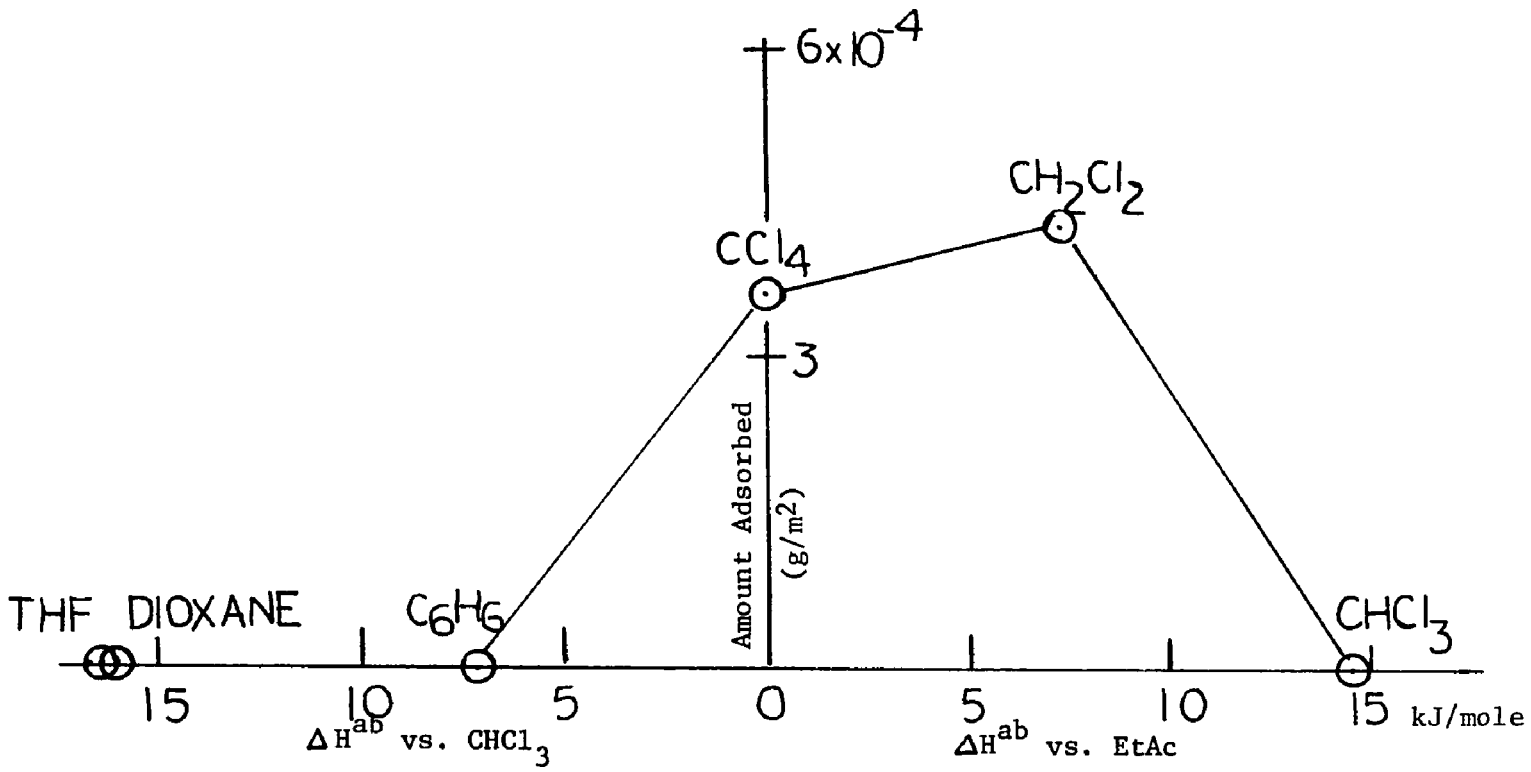

Fig. 7. Adsorption of Cl-PVC on $CaCO_3$ as a function of the basicity or acidity of the solvent. The basicity is shown as the heat of acid-base interactions with chloroform, and the acidity is shown as the heat of acid-base interactions with ethyl acetate (EtAc).

chloride with these solvents, and the (-C-Cl) group in the polymer appears similar to that (-C-Cl) group in the chloroform.

Fig. 7 shows the adsorption of chlorinated polyvinyl chloride as stronger from the neutral solvents CCl_4 and the weakly acidic CH_2Cl_2 where from these two solvents the adsorption of Cl-PVC is 3.6 and 4.3×10^{-4}g per m of calcium carbonate, respectively, which corresponds to about one monolayer of the polymer as compared to less than 0.3 per cent of a monolayer adsorbed on silica from the same solutions. This again demonstrates that the acid-base interactions are the dominant factor in polymer adsorption for this system.

On the left hand side of Fig. 7 the decrease in adsorption with solvent basicity is a measure of the basicity of $CaCO_3$. It is seen that no adsorption occurs from the relatively strongly basic THF and dioxane, and also from the weakly basic benzene This must mean that the basic carbonate groups on the surface of calcium carbonate are weaker bases than benzene in order for the carbonate anions to interact with acids like chloroform. The competition between the basic solvents and $CaCO_3$ for the acidic polymer apparently results in the solvation of the acidic sites on the polymer by basic solvents rather than adsorption of acid polymer sites onto the basic $CaCO_3$ sites.

On the right hand side of Fig. 7 the decrease in adsorption with increasing acidity of the solvent illustrates the competition between acidic solvents and the acidic sites of Cl-PVC for the basic surface of $CaCO_3$. Adsorption occurs from methylene chloride, the weaker acid, but not from the chloroform, the stronger acid. This implies that $CHCl_3$ has neutralized the basic sites on the calcium carbonate so that no acid-base interaction could occur with the polymer. Post-chlorinated PVC polymer is therefore considered to be more acidic than methylene chloride but less acidic than chloroform.

VII. Effect of Acid-Base Interactions on Mechanical Properties

A. Young's Modulus, E

There is reason to believe that acid-base interactions contribute to enhancement of mechanical properties of some filled polymers.[49] The coordinated studies with this research done at Lehigh University by M. Marmo and J. Williams on chlorinated polyvinylchloride filled with calcium carbonate supported this belief. They used the Kerner equation[57] for correlation of the degree of adhesion. The Kerner equation predicts how good adhesion or poor adhesion affects the modulus of filled polymers.

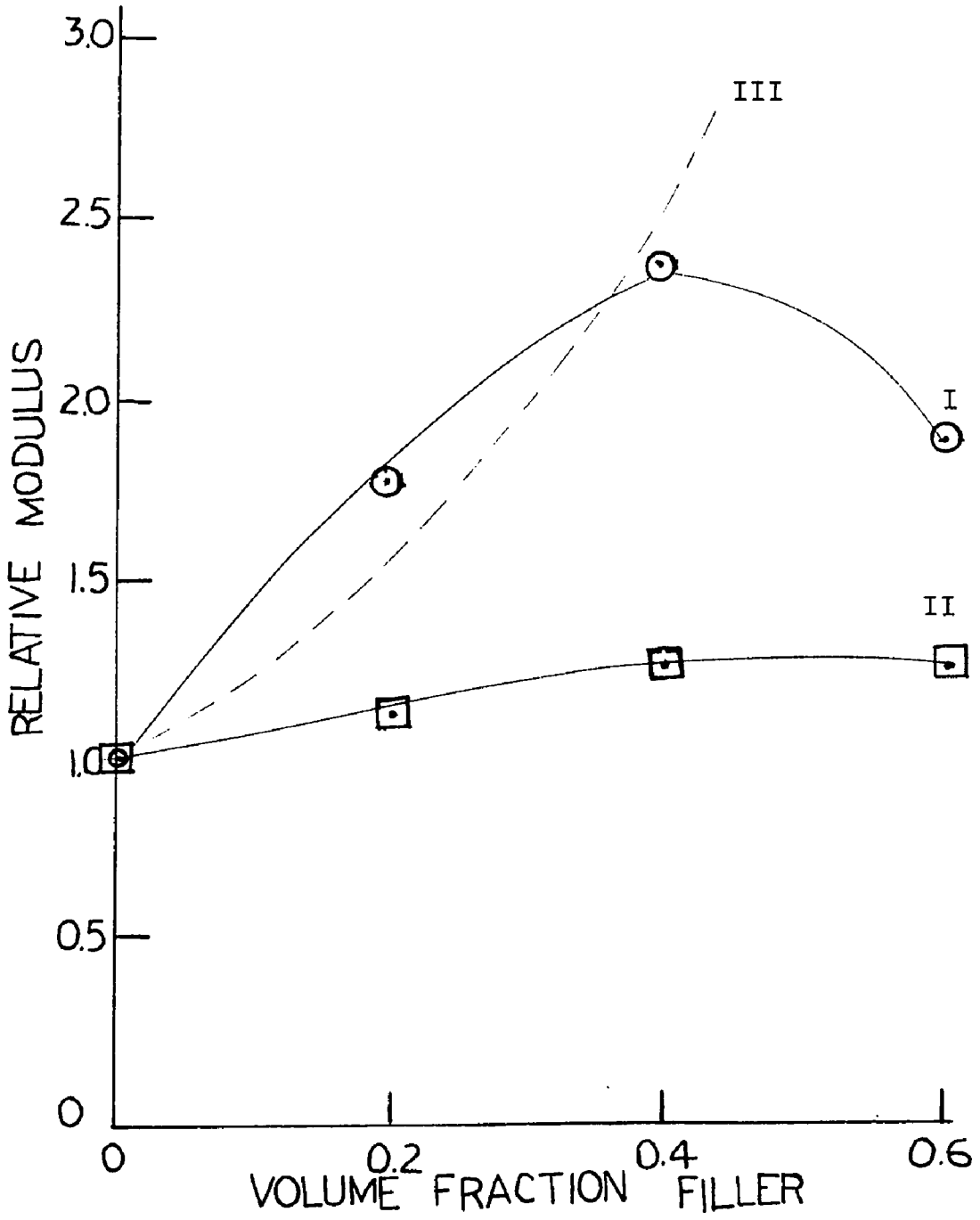

Fig. 8. Relative modulus values for (I) Cl-PVC/$CaCO_3$/CH_2Cl_2, (II) Cl-PVC/$CaCO_3$/THF and (III) Kerner Curve.

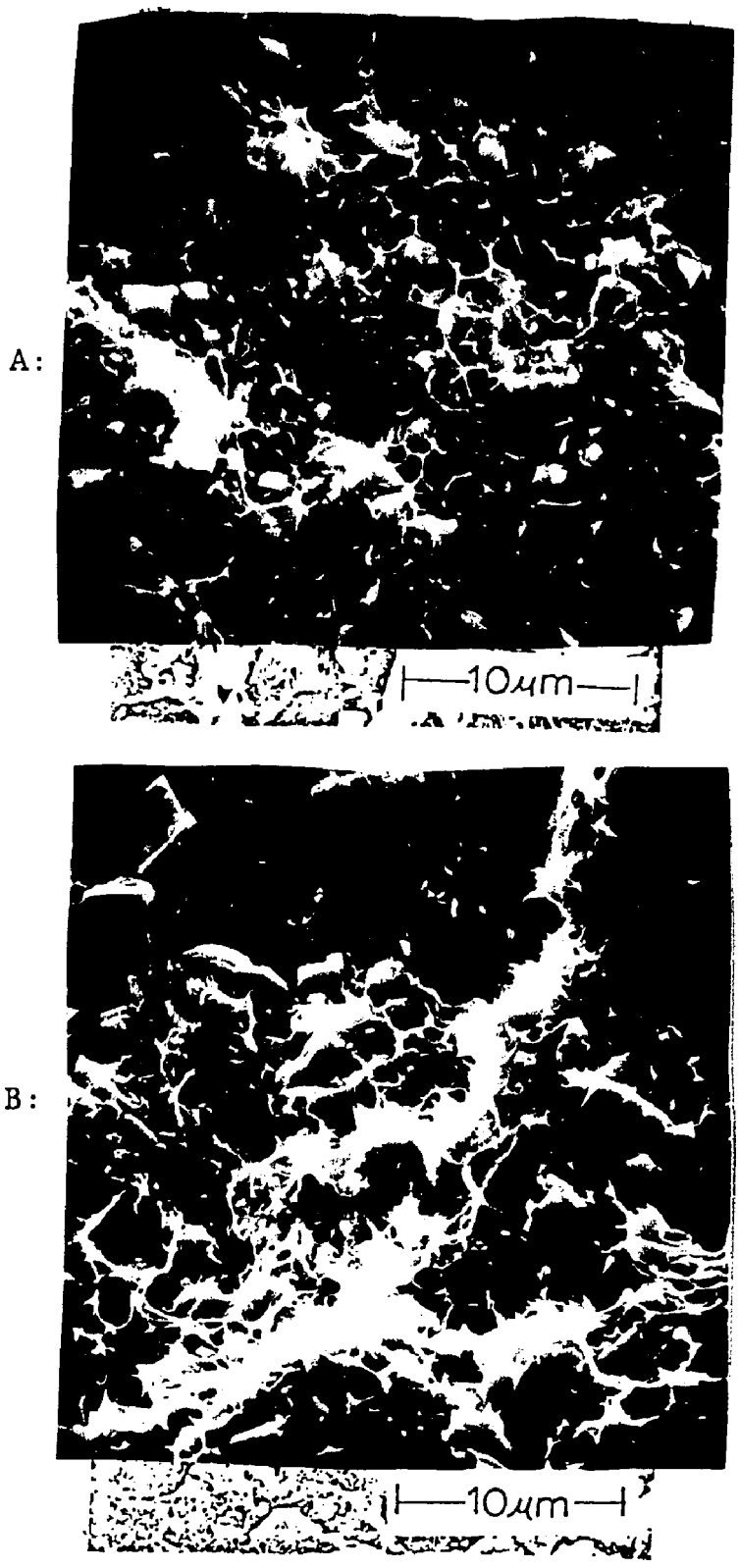

Figure 9: Scanning electron micrographs of fracture surfaces of chlorinated polyvinylchloride filled with calcium carbonate from A: methylene chloride B: tetrahydrofuran.

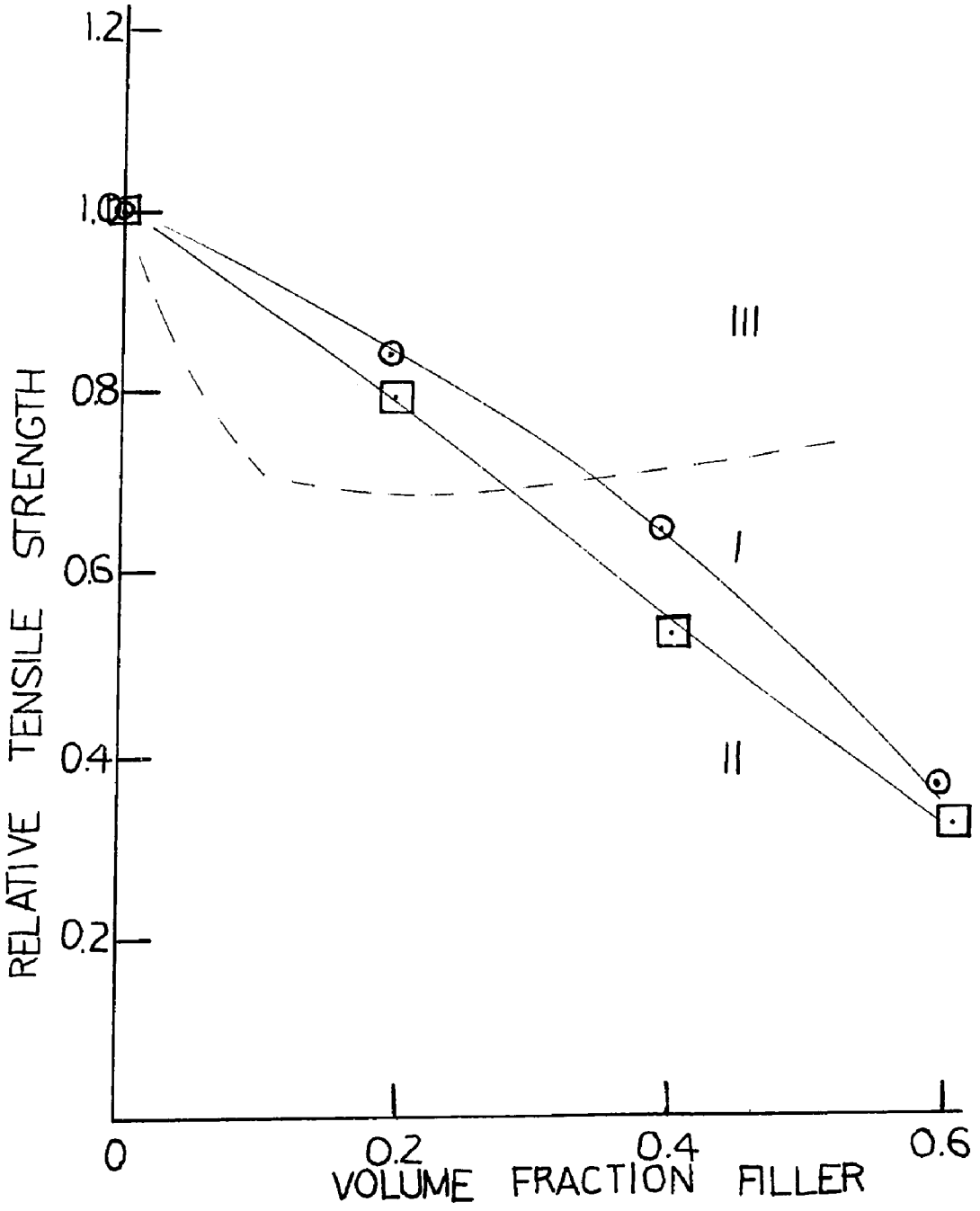

Fig. 10. Relative tensile strength values for (I) Cl-PVC/$CaCO_3$/CH_2Cl_2 , (II) Cl-PVC/$CaCO_3$/THF and (III) Kerner curve (adhesion).

Fig. 8 shows that at low volume fraction, V_f, of chlorinated polyvinylchloride filled with calcium carbonate from methylene chloride, a higher modulus than upper-bound Kerner equation was obtained. For the same system from tetrahydrofuran, lower values were observed than those from methylene chloride. A good adhesion (better coating) of the acidic polymer to the basic particulate filler is clearly evident from the weakly acidic methylene chloride: a case where adsorption was found to be in the order of a monolayer thick. However, from the strongly basic tetrahydrofuran, with lower values of modulus, there was no adsorption observed of chlorinated polyvinyl chloride onto calcium carbonate. An anamolous case was found for PMMA filled with silica from chloroform which indicated good adhesion while little adsorption was observed.

B. Tensile Strength,[30] Ts.

Fig. 10 shows that below volume fraction of 0.2, chlorinated polyvinyl chloride filled with calcium carbonate has a higher tensile strength from methylene chloride than from tetrahydrofuran. This demonstrates once again that for the system where adsorption was observed better mechanical properties are observed.

C. Scanning Electron Microscopy.

A higher level of filler-matrix adhesion of

chlorinated polyvinyl chloride and calcium carbonate from methylene chloride were cited.[49] Fig. 9-A (from Mr. Marmo's research) shows what appears to be wedging of calcium carbonate particles between chlorinated polyvinyl chloride. When tetrahydrofuran was used instead of methylene chloride for the same system, wedging between calcium carbonate particles seems to be predominant, as can be seen in Fig. 9-B. It appears that methylene chloride gives a more uniform dispersion of filler than THF, which showed aggregates and more voids.

D. Glass Temperature,[30] Tg.

Tg for Cl-PVC filled with $CaCO_3$ from CH_2Cl_2 showed a higher value than for the same system when THF was used. It seems that the adsorption process between acidic Cl-PVC and the basic $CaCO_3$ has resulted in decrease in polymer chain flexibility compared to the unfilled polymers, leading to higher Tg's. This could be explained in terms of increasing interfacial bond strength (i.e., good adhesion).

The adsorption of acidic polymers onto basic inorganic fillers could involve a reduction in the degree of freedom (and consequent entropy decrease or "ordering") which could account for a significant and discrete fraction of the total polymer in the matrix, hence restricting the mobility of the polymer segments upon which Tg depends.

E. How Acid-Base Interaction Enhances Mechanical Properties.

The role of acid-base interaction in polymer-filler composites can be established by promotion of adsorption of the structural matrix polymer to the filler surfaces in such a way that a preferential coating with the polymer is predominant. At the same time, particle-particle repulsion is attained by electrostatic charge to the particles. This in effect allows more exposure of the particles' surfaces to polymer adsorption as well as providing a better dispersion of the particles in the liquid polymer.

CONCLUSIONS

Based on the adsorption measurements, the following conclusions can be drawn:

1. The adsorption of polymers onto fillers from organic solvents is dominated by acid-base interactions of the solvent, polymer and filler surface.

2. Acidic or basic solvents tend to compete for the polymer or the filler and if the solvents are acidic or basic enough no adsorption will occur.

3. The fact that such competition between the basic or acidic solvents with polymers or fillers exists provides a means of measuring the acidity or basicity of both polymers and fillers.

4. The interactions of PMMA with the surface silanol groups of silica and Cl-PVC with calcium carbonate indicate that the silanol groups are not quite as acidic as chloroform and the surface of $CaCO_3$ is less basic than benzene.

5. The interactions of the basic solvents THF, dioxane and benzene with SiO_2 in the presence of PMMA lead to the conclusion that PMMA is much more basic than benzene and nearly as basic as dioxane or THF. This is in complete agreement with Drago's measurements of enthal-

pies of interactions.

6. The interactions of the acidic solvents methylene chloride and chloroform with calcium carbonate indicate that the chlorinated PVC is much more acidic than methylene chloride but not as acidic as chloroform.

7. The surface of fillers can be modified to enhance acid-base interactions and increase adsorption.

8. Dispersion forces and electron donor-acceptor (acid-base) interactions constitute the major part of the intermolecular interactions of organic molecules in solutions and at interfaces. Hydrogen bonds are included in acid-base interactions.

9. The neglect of dipole-dipole interactions introduced no error, thus suggesting that dipole-dipole interactions are negligibly small compared to acid-base interactions.

10. The previously termed "polar" interactions are found to be acid-base interactions and not dipole-dipole interactions. This is supported by the fact that donor-donor and acceptor-acceptor interactions are negligibly small compared to donor-acceptor interactions.

11. The effect of the rate of acid-base interactions role in polymer solubilities is important. An acid-base interaction term should be included into the heat of

mixing, H_M, then it could be expressed as follows:

$$\Delta H_M = P\Delta V_M + V_M\phi_1\phi_2(\delta_A^d-\delta_B^d)-\chi_p(C_AC_B+E_AE_B) + \Delta U_{12}^p \quad (34)$$

where χ_p is the mole fraction of acid-base pair per mole of components present, and all other terms are defined as previously given.

12. The goemetric mean equations for "polar" interactions does not apply to acid-base interactions and gives erroneous results.

13. Contact angles measurements as well as competitive adsorption measurements could be utilized to evaluate the acid-base interactions at surfaces and interfaces by using liquids fully characterized (by the method of R. S. Drago) for their acidity or basicity.

14. Using the above two techniques, the acidity or basicity of polymer surfaces and inorganic solids can be determined.

15. The work of adhesion, W_A, expression should include the contribution results from acid-base interactions. This can be expressed as follows:

$$W_A = 2\ \gamma_A^d\gamma_B^d - f(C_AC_B + E_AE_B) \times \frac{\text{moles of acid-base pairs}}{\text{unit area}} + W_A^p \quad (35)$$

and

$$W_A^{ab} = -f(C_A C_B + E_A E_B) \times \frac{\text{moles of acid-base pairs}}{\text{unit area}} \quad (36)$$

$$= -\Delta H^{ab} \times \frac{\text{moles of acid-base pairs}}{\text{unit area}} \quad . \quad (37)$$

where the first term in equation (35) represents the dispersion contribution while the second and third represent the acid-base interactions and the polar interactions respectively. W_A^P is usually small and f is a constant near unity which converts enthalpy per unit area into surface free energy.

16. The understanding of the role of the acid-base interactions in particulate-filled polymers as represented by the trends illustrated by the mechanical properties and SEM could be summarized as follows:

a. Mechanical properties such as modulus and tensile strength could be enhanced by appropriate choice of solvents which relfect high adsorption due to acid-base interactions.

b. Adsorption of polymers onto fillers produce more even dispersion of polymer-coated filler particles and fewer large aggregates of fillers.

PART II

ELECTROPHORESIS

Introduction

Acid-base interactions at the surface of particles involve a certain degree of charge transfer, which may be used as a measure of the strength of acid-base interactions. The process of charge separation at the interface or in solution is carried out by means of electron or proton donor-acceptor processes. We have used electrophoresis to investigate these charge transfers.

Van der Minne[58], Parfitt[59] and Parreira[60] indicated that electrophoresis in organic liquids can give difficulties. The lack of understanding of the chemical nature of the organic ions and their concentration in the vicinity of the particle surface have made the electrostatic stabilization[61,62] not as clear cut as in the case of aqueous media. Fowkes[61,63] and Tamarabuchi[64] have shown that the predominant mechanism for electrostatic charging in dispersions of low dielectric constant (hydrocarbons) is proton-transfer. This proton-transfer between the dispersant and the surface of the dispersed particles occurs with charge transfer at the surface of the particle, where dielectric constant of the organic solvent plays a major role.[65]

The criteria for accurate measurement of electrophoretic mobility of colloidal particles in non-polar

media were first established by van der Minne and Hermanie.[66] Parreira[67] made use of electrophoresis for the study of carbon black in liquids of low dielectric constant and the effect of the chain length of the adsorbate.

Theory of Electrophoresis

Electrokinetic theory involves both the theory of the electric double layer and that of liquid flow, and is quite complicated. Electrokinetic phenomena are related to the nature of the mobile part of the double layer and may, therefore, only be interpreted in terms of the zeta potential or the charge density at the slipping plane. The movement of a charged particle under the influence of uniform potential is known as electrophoresis and the mobility of the particle is known as the electrophoretic mobility, U. In considering the electrokinetic phenomena, it is customary to identify the diffuse part of the double layer with the mobile part of the double layer. The compact part of the double layer is normally assumed to be attached to the particle. The potential between these two kinetic units is the zeta-potential, ζ. It is actually the potential of the "slipping" plane between the layer which is fixed to the particle and the mobile part of the double layer. Although movement of the particles

on application of an electric field may readily be observed in a cell of design appropriate to the system under investigation, it must be clearly established whether such motion is a result of a dielectric polarization effect (where the velocity is proportional to E^2) or due to true electrophoresis (where the velocity is proportional to E); where E is the electric field in volts per meter.

The polarization effect[68] would manifest itself as irregular motion of the particles at about 100 volt per cm (10^4v/m) or more, independent of the direction of the electric field.

I. Cell Geometry

Since the electro-osmotic flow of the medium in the cell is superimposed on the electrophoretic motion, the pure electrophoretic velocity can only be obtained at the stationary levels at which the osmotic flow is zero. The cell being a closed system (constructed of one material and having a uniform cross section) will lead to a laminar parabolic flow pattern between the top and bottom surfaces of the cell. Two such levels exist in any cell (rectangular or cylindrical cross section), and measurements made at both levels should be the same within experimental error. The positions of the stationary levels in a rectangular cell have been

been predicted by Komagata[69] and could be obtained graphically with the help of the van Gils plot.[70] They are found at a distance $h_o = \pm \frac{1}{3}$ from the origin chosen to coincide with the cell center plane. However, this value is valid only for cells the channel width-to-thickness ratio of which approaches infinity. Because most of the rectangular cells do not meet this requirement, the value of h_o is obtained from the corrected expression of Komagata, namely,

$$h_o/b = \pm \frac{1}{3}(1 + \frac{384}{\pi^5 k}) \qquad (38)$$

h_o being the distance from the center of the cell channel, and k the ratio of channel depth, (d) to width (2b). So the depth to width ratio k is very significant in determining the stationary levels.

The following table[69] shows values of k and their corresponding values of h/b.

k	10	15	20	40	100	∞
h/b	0.612	0.602	0.596	0.586	0.580	0.578

From the linear van Gils plot, Fig. 12, the electrophoretic velocity V_e and the electroosmotic velocity V_o can be obtained. The total observed velocity at cell center, $(V_{ob})_c$ is related to V_o and V_e by:

$$V_o = 2[V_e - (V_{ob})_c] \qquad (39)$$

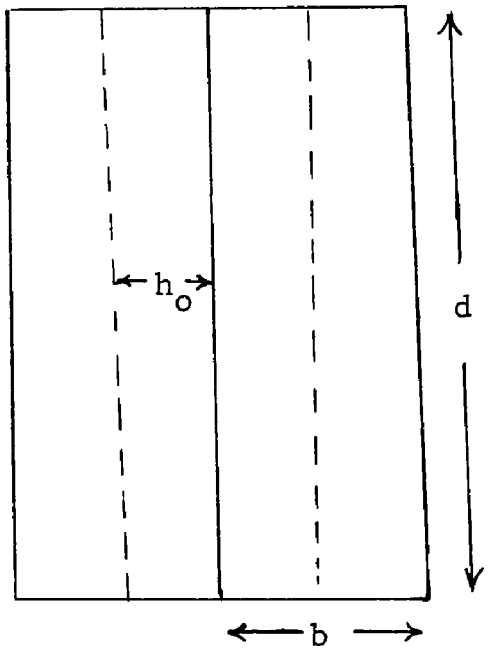

Fig. 11 Rectangular cell, dashed lines represent stationary levels.

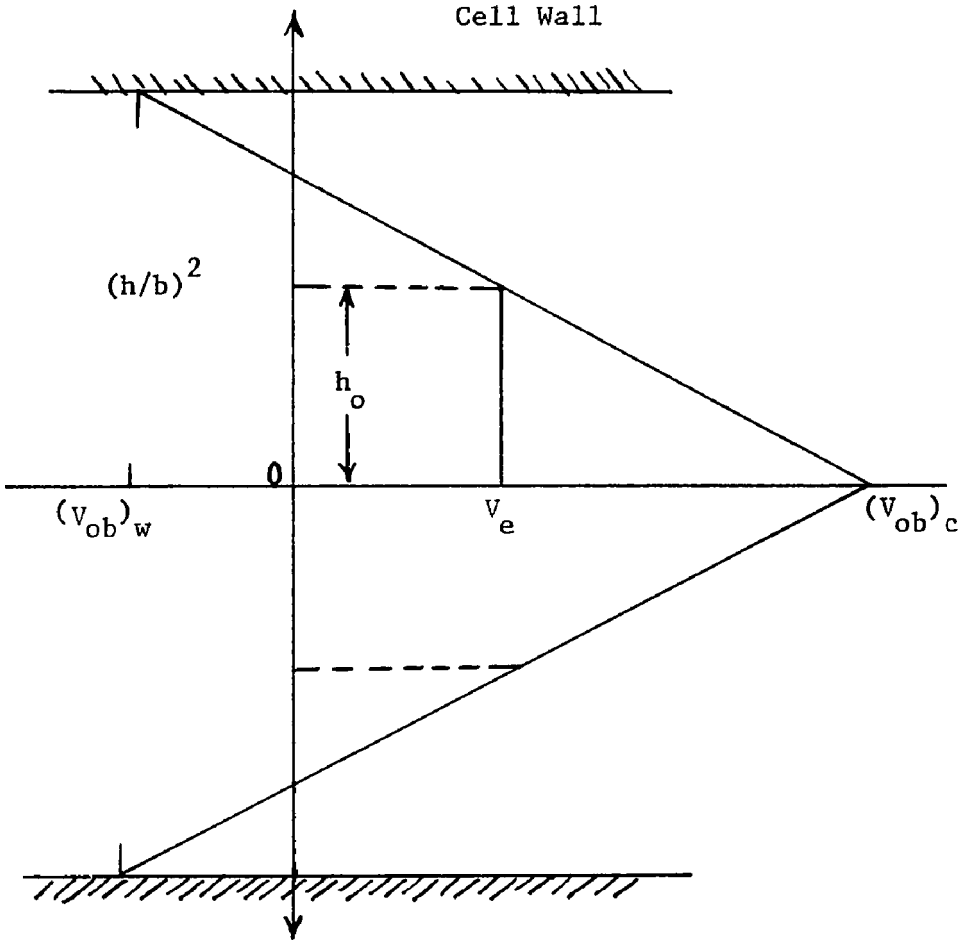

Fig. 12. Linear van Gils Plot, showing the stationary levels (dashed lines) and velocity distributions in an electrophoresis cell.

and the observed velocity at the cell wall $(V_{ob})_w$ could be obtained from:

$$(V_{ob})_w = V_e + V_o \tag{40}$$

II. Zeta-Potential Calculations

For a spherical particle of radius a in aqueous or non-aqueous medium, the ratio of radius curvature to the double layer thickness $1/\kappa$ is of great importance. When κa is large, the double layer is effectively flat and may be treated as such. For spherical particles of radius a in a medium such as $a > 1/\kappa$ or $\kappa a > 1$, the electrophoretic velocity, V_e, is given[71,72] by

$$V_e = \varepsilon_o \varepsilon \zeta / \eta_o \tag{41}$$

while if $a << 1/\kappa$ or $\kappa a << 1$, the electrophoretic velocity would be given by Hückel equation[73] as follows:

$$V_e = 2\varepsilon_o \varepsilon \zeta / 3\eta_o \tag{42}$$

where the permittivity ε and the viscosity η_o (J-sec/m^3) of the medium are assumed to be constant throughout the mobile part of the double layer. ε_o is the permittivity of free space (8.854×10^{-12} coulb/v-m) and ζ is the zeta potential (volt), which would be the resultant potential at the surface of shear due to the charges of the electrokinetic unit and of the mobile part of the

double layer. The quantity V_e/E is defined as the electrophoretic mobility, U (m /v-sec).

$$U = V_e/E \tag{43}$$

Substituting the expression for U into equation (42) gives

$$U = \frac{2}{3} (\varepsilon_o \varepsilon \zeta / \eta_o) \tag{44}$$

Rearranging equation (44) gives the expression for the zeta potential as follows:

$$\zeta = [3\eta_o U/2\varepsilon_o \varepsilon] 10^{-8} \text{ mv} \tag{45}$$

The Hückel equation is mostly applicable to electrophoresis in non-aqueous media of low conductance, since for particles of radius 10^{-8}m suspended in a 1-1 aqueous electrolyte solution would require an electrolyte concentration as low as 10^{-5}M to give $\kappa a = 0.1$. For values of $\kappa a > 100$, a correction, $f(\kappa a, \zeta)$, to the electrophoretic mobility and the zeta potential was given by Henry.[74] Then we have:

$$V_e = [2\varepsilon_o \varepsilon \zeta / 3\eta_o] \cdot f(\kappa a, \zeta) \tag{46}$$

and

$$\zeta = [3\eta_o U/2\varepsilon_o \varepsilon] 10^{-8} \cdot f(\kappa a, \zeta) \tag{47}$$

where $f(\kappa a, \zeta) = 1.0$ for $\kappa a \ll 1$

and 1.5 for $\kappa a > 100$

Parfitt[75,76] used equation (42) ($V_e = 2\varepsilon_o \varepsilon \zeta / 3\eta_o$) for electrophoretic velocity measurements in non-aqueous media.

III. Dielectric Constant and Viscosity

A constant value for the dielectric constant ε and the viscosity η_o of the medium was assumed in the Hückel equation. If the electric field strength close to the shear plane is high enough to cause appreciable dipole orientation, a decrease in ε and an increase in η_o could be generated. Lyklema and Overbeek[77] estimated a negligible effect on ε, but stated a significant change on η_o would occur. Stigter[78] and Hunter[79] suggested that in most practical cases an insignificant change in η_o viscosity would result due to the electric field strength.

For spherical colloidally dispersed particles subjected to a uniform electrophoretic motion, there are two retarding forces caused by the "ionic" atmosphere. The electrophoretic retardation develops from the viscous force of the counter-flowing ions of the diffuse layer as they move in the opposite direction to the particle. The relaxation effect (loss of double layer symmetry) develops as the particle moves through its own double layer. The double layer is continuously being broken down behind the particles and built up in front

of it. Consequently, the center of the ionic atmosphere lies behind the center of the particle. This causes an electric retarding force to be exerted in a direction opposite to the motion of the particle. There is a stationary state which is present shortly after the application of the d.c. field. It is within this stationary state that the relaxation effect occurs.

It is the purpose of this part of the research to demonstrate the effect of the acid-base interactions on the charge transfer phenomenon. The influence of this electron (proton) donor-acceptor role will be investigated and the effect of polymer adsorption related to the enhancement of the charge transfer will be pointed out.

Experimental Details

I. Materials

The polymers, inorganic solids and solvents used in this part of the study are listed in Tables 7 and 8. Many of these are the same as used in the first section of this thesis.

Table 7

Polymers Used in Zeta Potential Experiments

Chlorinated Poly(vinyl Chloride)(Cl-PVC)	B. F. Goodrich	Geon 603x560
Poly(methylmethacrylate) (PMMA)	duPont Lucite 4F	(Mn 5 $x10^5$) Homopolymer
Polycarbonate (PC)	General Electric	Lexan 145

Table 8

Surface Areas of Solids Used in Zeta Potential Experiments

$CaCo_3$	Pfizer, Minerals, Pigments and Metal Div.	6 m^2/g (n_2 adsorption measurements)
CaO	Fisher Scientific Co.	4 m^2/g
Acid-Washed Kaolin	American Standard	120 m^2/g
Bentonite	Fisher Sci. Co.	$\sim$100 m^2/g

Table 9

Solvents Used in Zeta Potential Experiments

Methylene Chloride, CH_2Cl_2	Fisher Analytical Reagent
Tetrahydrofuran, THF	Fisher Analytical Reagent
Methyl ethyl ketone	Fisher Analytical Reagent
Acetic Anhydride	Fisher Analytical Reagent
Acetic Acid	Fisher Analytical Reagent
Nitrobenzene	Fisher Analytical Reagent

II. Experimental Methods

A. Electrophoretic Mobilities

Inorganic solids were added (~0.1 g) to 100ml of the polymer solution. The suspension then was dispersed using Sonifier (20 sec). The clear supernatant was used (after allowing for partial settlement) for electrophoretic mobility measurement.

A Rank Brothers Micro-electrophoresis apparatus was used for these measurements. A cell was made from quartz with the specific dimensions shown on Figs. 13 and 14. Electrophoretic velocities were measured for each system at 3 or 4 depths into the cell on each side of the center and the results were plotted as van Gils

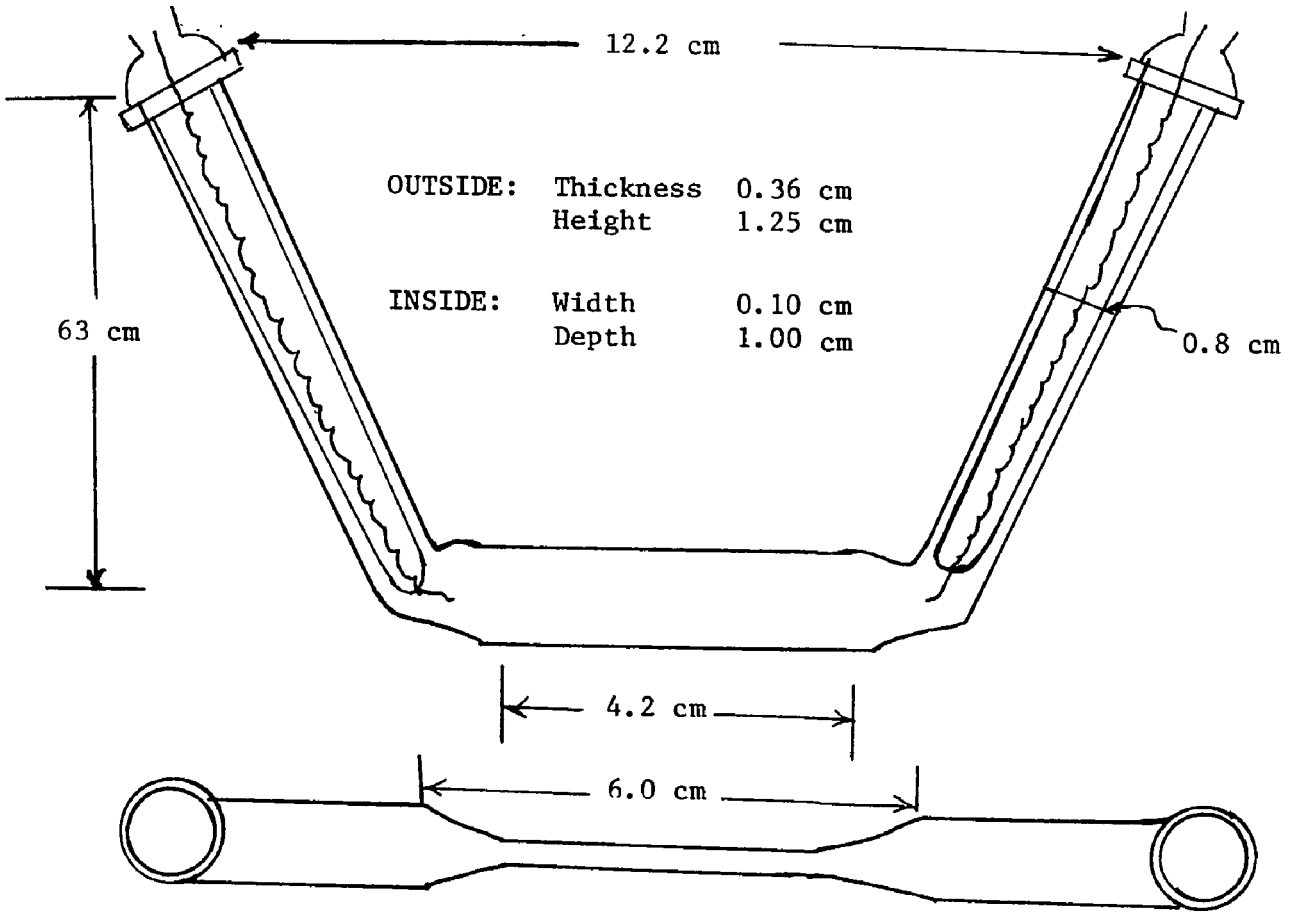

Fig. 13. All quartz rectangular Electrophoretic Cell.

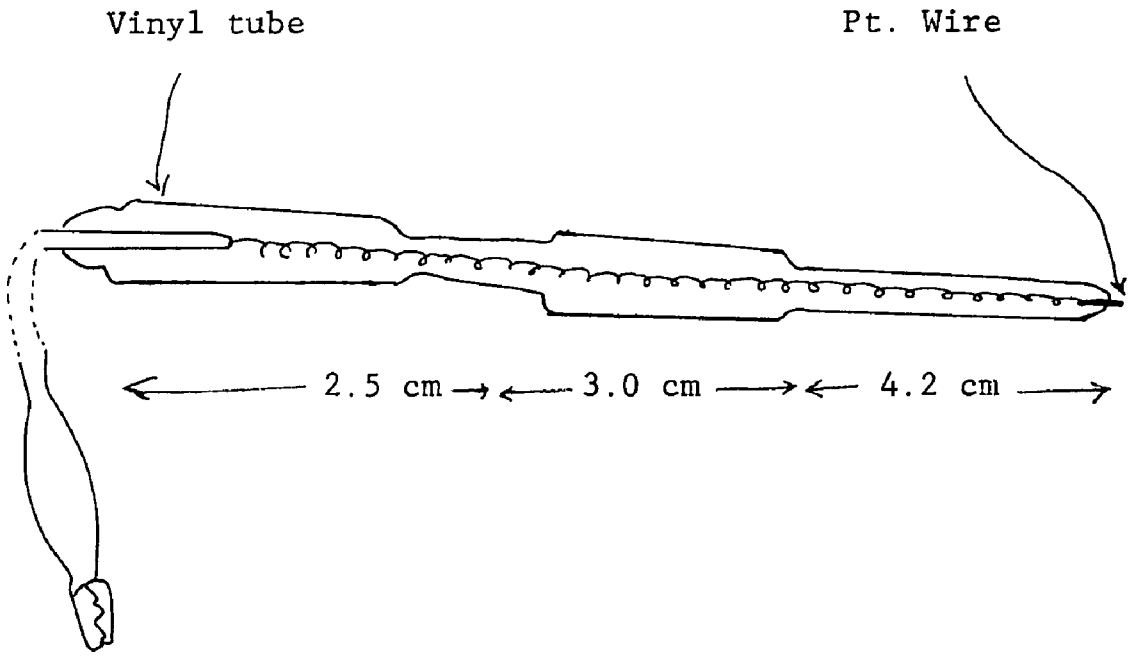

Fig. 14. Cross section of the arm in electrophoresis cell.

diagrams in order to determine V_e and V_o. Viscosities of polymer solutions were determined by use of the Brookfield rotating cylinder viscometer.

B. Adsorption Measurements

Adsorption of PMMA, PC and Cl-PVC onto $CaCO_3$, CaO, acid-washed kaolin and bentonite was determined with one or more of the solvents mentioned in Table 9. The same technique for adsorption in solution was followed as given on p. 27.

Results and Discussion

When acid-base interactions occur between filler particles and polymers dissolved in organic solvents of low dielectric constant, sufficient proton-transfer or electron-transfer can occur to provide appreciable zeta-potentials. The zeta-potential is expected to increase due to charge transfer with stronger acid-base interaction between the filler and polymer. The acidity or basicity of the solvent can obviously influence the degree of interaction between polymer and filler as has been already demonstrated in the previous section. The dielectric constant of the solvent also is expected to strongly influence zeta-potential, for in organic solvents of higher dielectric constant, acid-base interaction between the polymer and solvent can lead to electrostatic charging of dissolved polymer

molecules which can then adsorb on filler particles and provide appreciable zeta-potentials. This latter mechanism is familiar in aqueous media but it also is to be expected in organic solvents of higher dielectric constant when sufficient acid-base interaction occurs to cause ionization.

I. Solid-Polymer Interactions Leading to Dissociation at Solid Interfaces

A. Basic Polymers in Solvents of Low Dielectric Constant

Since charge separation tends to occur in regions of higher dielectric constant, then we anticipate that for low dielectric constant solvents such as hydrocarbons the charge separation will occur at the surface of the particles. A general mechanism proposed for charge transfer in low dielectric constant solvents is shown in Fig. 15.

The basic polymers (dispersants) become positively charged and upon adsorption they confer negative charges to the particles. This mechanism is illustrated for the basic polycarbonate polymer as it adsorbs onto the acid-washed kaolin from methylene chloride (see Table 10). Fig. 17 shows that the kaolin is so acidic that charge transfer occurs between it and the basic polymer rather than between the weakly acidic solvent and the polymer. As the polymer concentration increases, more charge transfer occurs between the polymer and the kaolin particles as evidenced by a higher negative zeta-potential as can be seen from Table 11.

The adsorption of polycarbonate onto bentonite

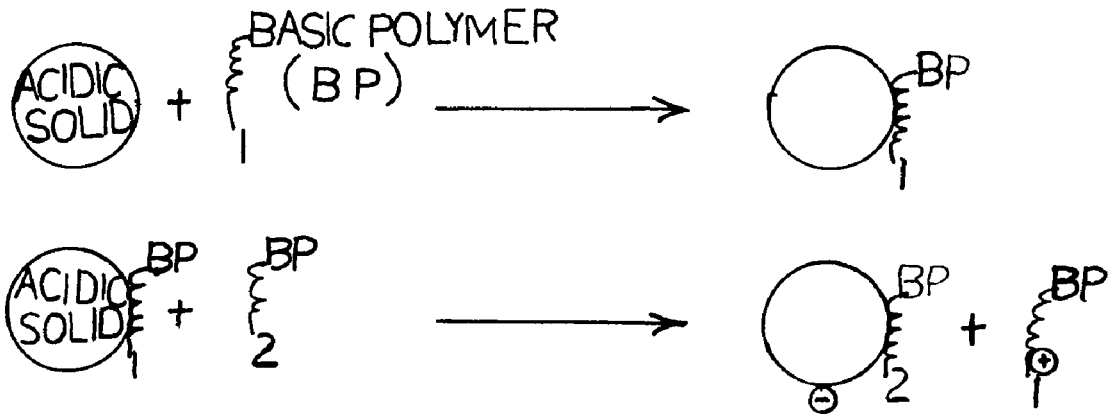

Fig. 15. Mechanism of (basic polymer/acidic solid) charge transfer in low dielectric constant solvents.

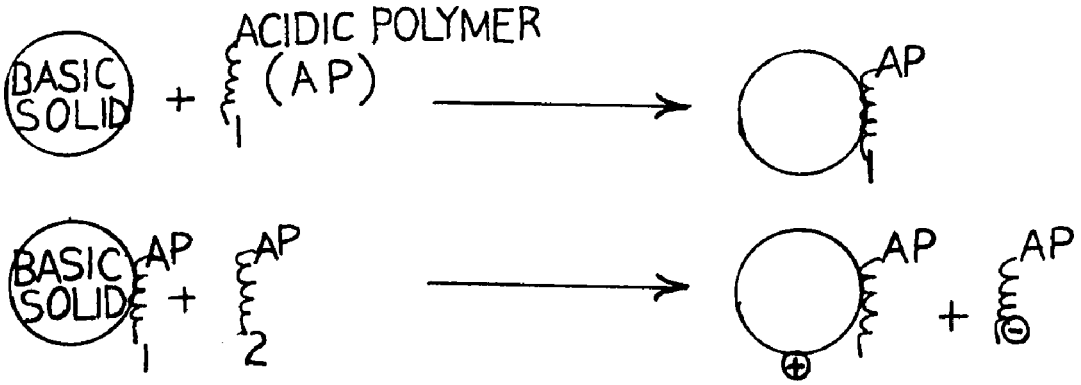

Fig. 16. Mechanism of (acidic polymer/basic solid) charge transfer in low dielectric constant solvents.

Table 10

Adsorption of Basic Polymers onto either Acidic or Basic Solids from Acidic Solvents

BASIC POLYMER	SOLID	SOLVENT	DIELECTRIC CONSTANT	ADSORPTION 10^{-4}(g/m)
PMMA	Acid Washed Kaolin	85% Acetic Anhydride 15% Acetic Acid	20	0.6
PC	Acid Washed Kaolin	CH_2Cl_2	9.08	0.3
PC	Acid Washed Kaolin	Nitrobenzene	35	1.3
PMMA	$CaCO_3$	Acetic Anhydride	20	0.00
PC	$CaCO_3$	Nitrobenzene	35	0.00
PC	$CaCO_3$	CH_2Cl_2	9.08	0.00

Table 11

Effect of change of PC conc. in Acidic and Basic Solvents on Zeta Potential with Acidic and Basic Particles

PARTICLE	SOLVENT	DIELECTRIC CONSTANT,	Zeta Potential at xg PC/dl x≡0.000	0.01	0.10	Solvent 1.00
CaO	THF	7.88	69	+65.8	+48.5	+43
Bentonite	THF	7.88	-10	-12	-79	
CaO	CH_2Cl_2	9.08	-20	-23.2	-6.2	+7.9
$CaCO_3$	CH_2Cl_2	9.08	+116	+113	+99	+39
Acid Washed Kaolin	CH_2Cl_2	9.08	+107	+46	+39	-35
Bentonite	CH_2Cl_2	9.08	-71	-74	-127	
$CaCO_3$	Nitrobenzene	35	-14	-22	-33	-34
Acid Washed Kaolin	Nitrobenzene	35	-59.1	-73.7	-79.8	-64.8

from CH_2Cl_2 (Fig. 18) illustrates that the zeta-potential is more negative with bentonite (probably smaller particles) than with acid washed kaolin from the same solvent.

In further studies with polycarbonate solutions, the effect of the acidity or basicity of the solvent on the zeta-potential was measured (see Fig. 19). The basic tetrahydrofuran competes with the basic polymer (PC) for the acidic sites of bentonite. This competition is evidenced by the more positive zeta-potential from THF compared to that from CH_2Cl_2.

The basic polycarbonate showed no adsorption on the basic calcium carbonate from CH_2Cl_2 (Table 10). It appears that the calcium carbonate gave up electrons to the acidic solvent, but on adding polycarbonate to the solvent, it appears that the basic polymer has tended to neutralize the acidity of the solvent and a decrease in zeta-potential (less positive) is observed on increasing the polymer concentration as can be seen from Fig. 17.

B. Acidic Polymers in Solvents of Low Dielectric Constant

A general mechanism illustrates the charge transfer in low dielectric solutions of acidic polymers as shown in Fig. 16. We see that the charge transfer

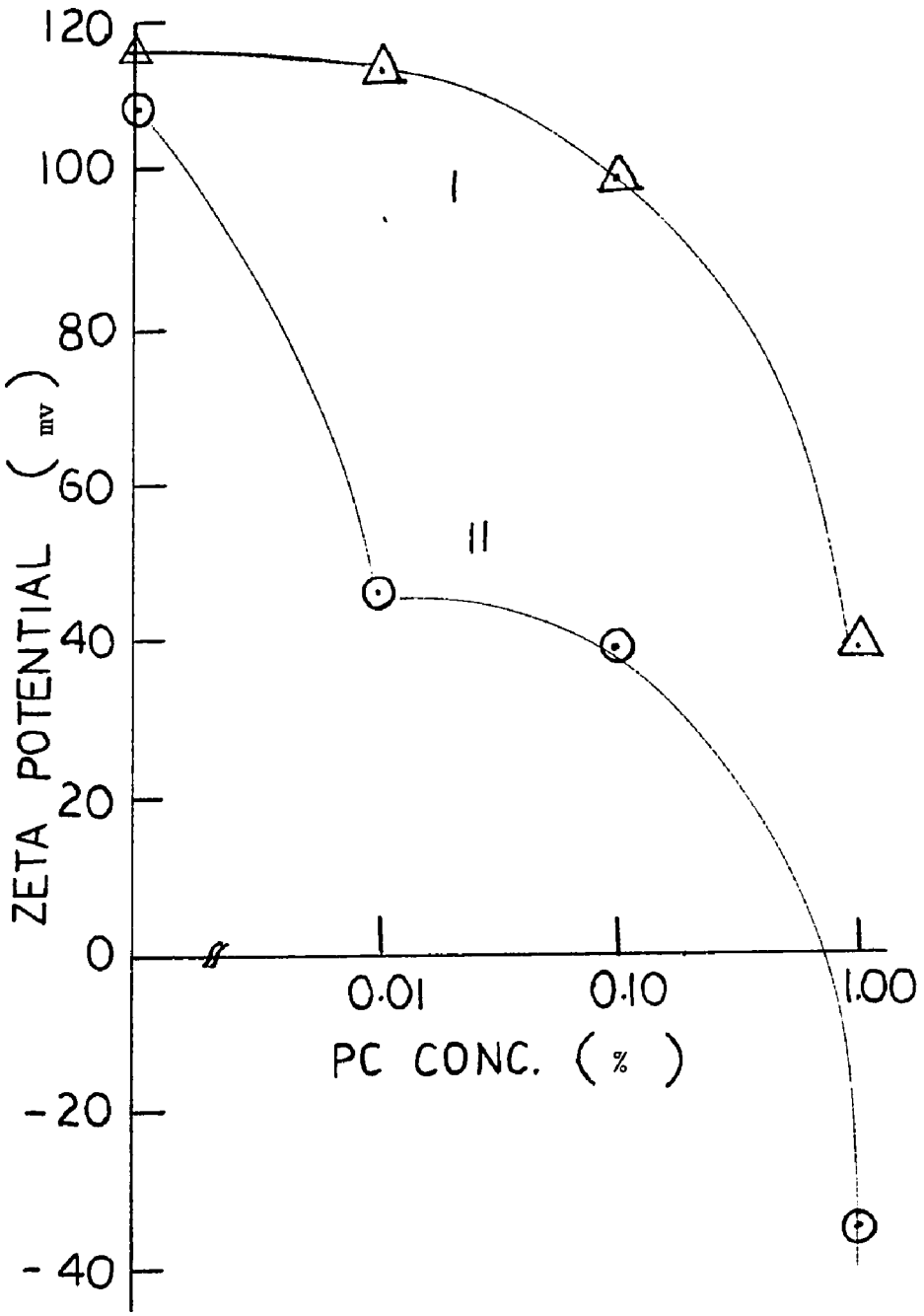

Fig. 17. Zeta potential as a function of polycarbonate concentration in methylene chloride with (I) calcium carbonate and (II) acid washed kaolin.

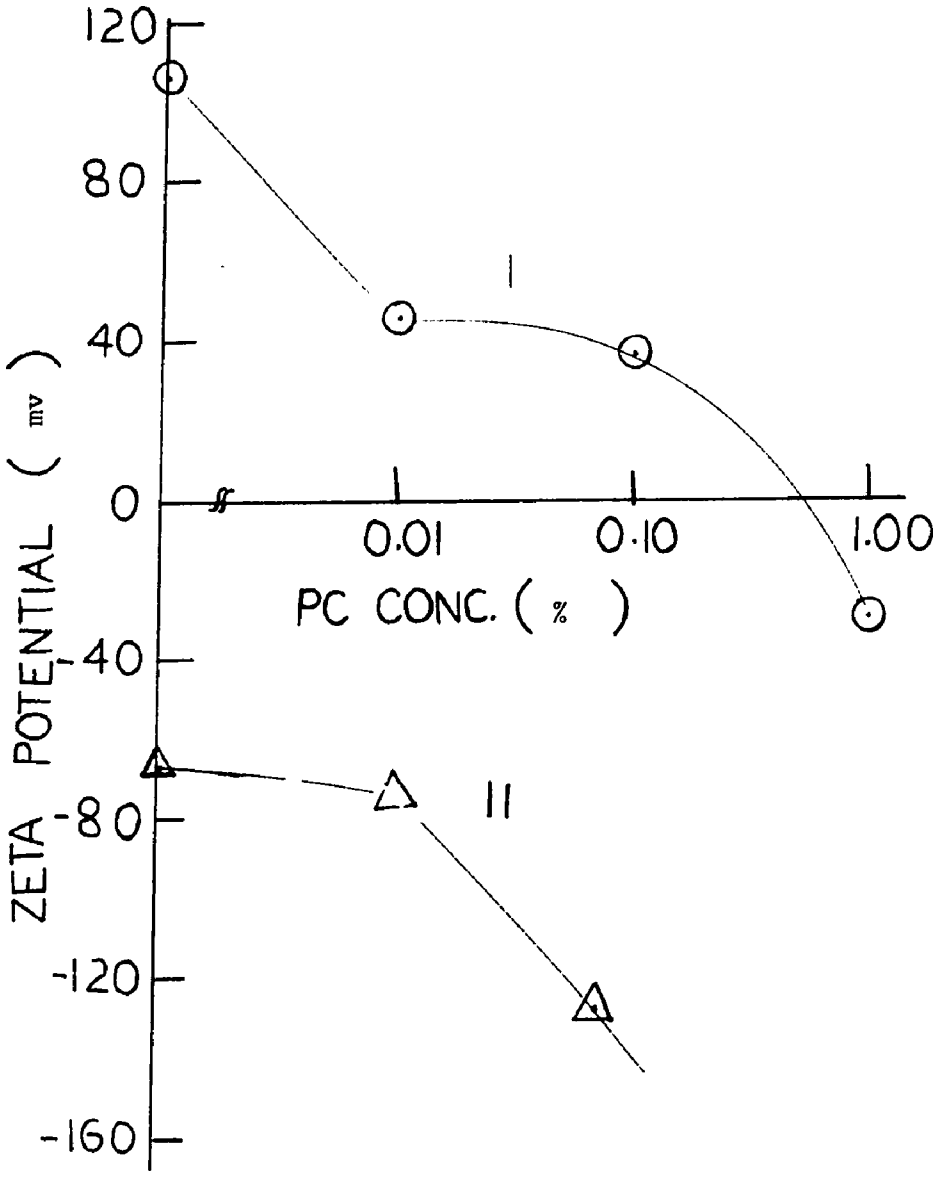

Fig. 18. Zeta potential as a function of concentration of polycarbonate (PC) in methylene chloride with (I) acid washed kaolin and (II) bentonite.

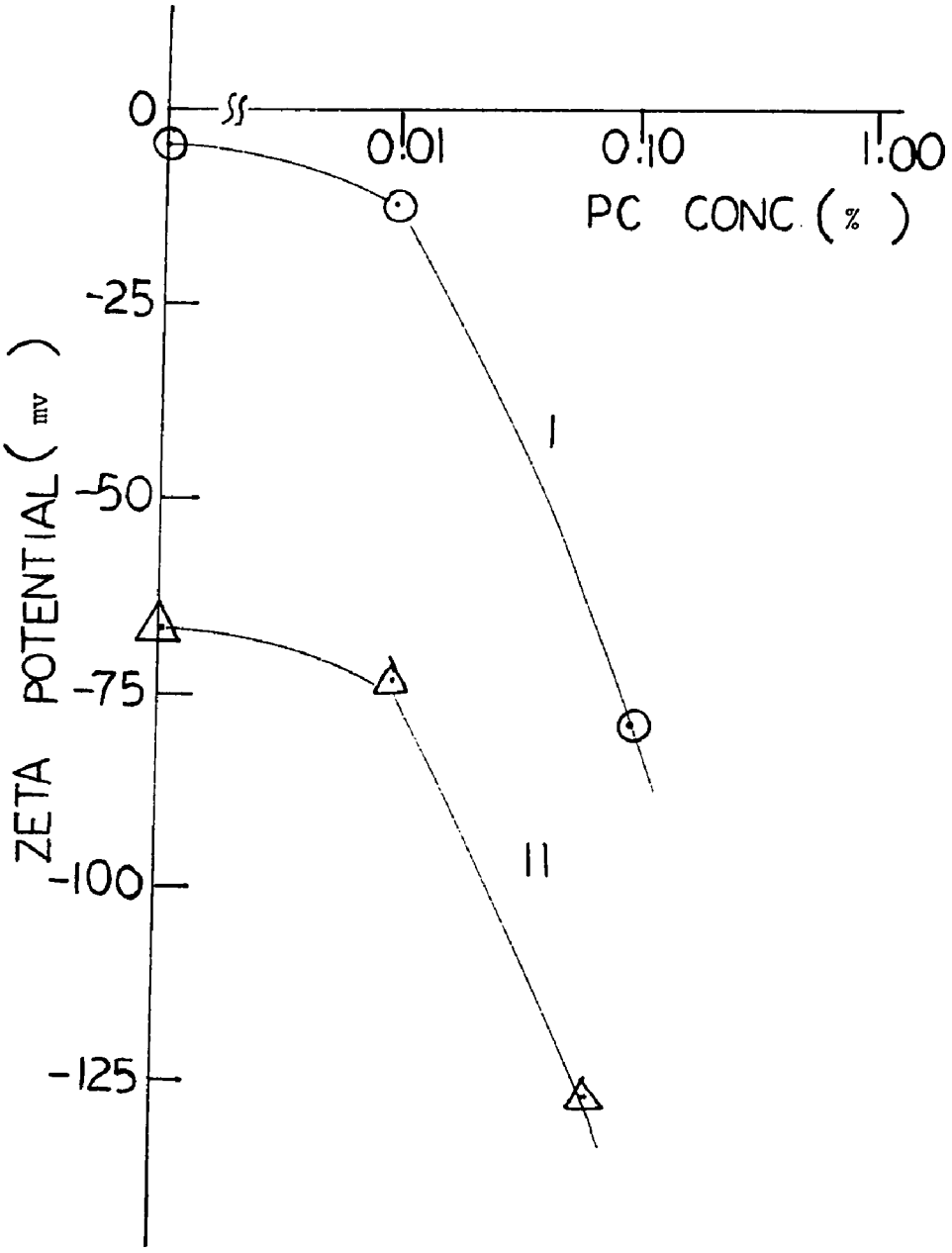

Fig. 19. Zeta potential as a function of concentration of polycarbonate in (I) THF with bentonite and (II) CH_2Cl_2 with bentonite.

occurs at the surface of the solid, i.e., at the high dielectric constant region. When $CaCO_3$ is added to chlorinated polyvinyl chloride in dioxane solution, a positive zeta-potential is developed with increasing acidic polymer concentration (Fig. 20). This is to be expected for low dielectric constant liquids. The Cl-PVC must have picked up electrons from the basic (electron donor) $CaCO_3$. This will leave positively charged particles that will account for the positive increase in zeta-potential.

A similar behavior with slightly higher positive zeta-potential is observed when the more basic calcium oxide is used instead of calcium carbonate. (Fig. 20)

Cl-PVC shows no adsorption onto $CaCO_3$ (Table 12) from THF. A less negative zeta-potential is observed on increasing the polymer concentration (Table 13). It seems that THF donates electrons to the filler $CaCO_3$ to give a negative zeta-potential, but on increasing the Cl-PVC concentration the basicity of the THF is decreased and it donates fewer electrons to the $CaCO_3$, giving less negative zeta-potentials.

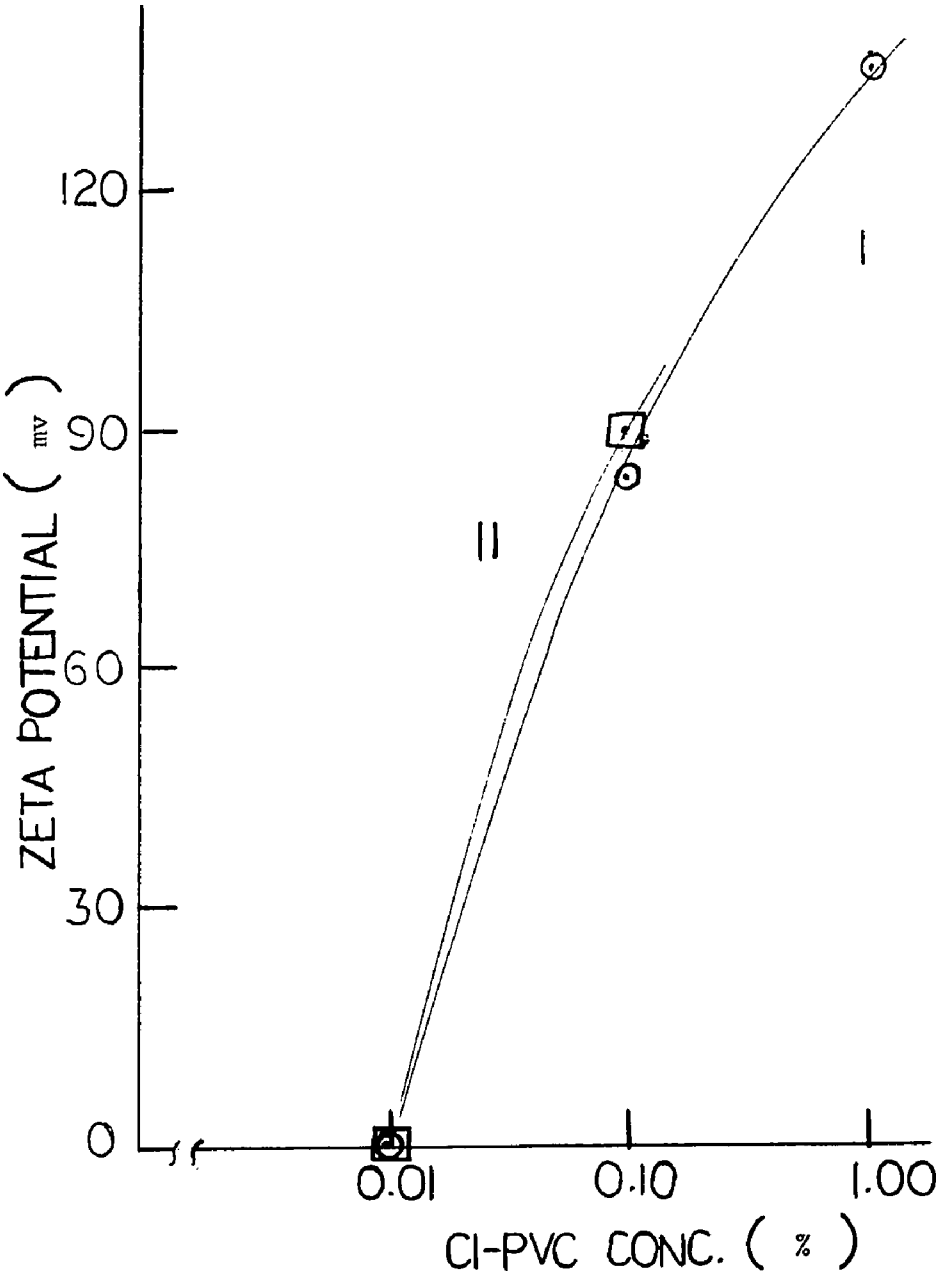

Fig. 20. Zeta potential as a function of Cl-PVC concentration from dioxane onto (I) $CaCO_3$ and (II) CaO.

Table 12

Adsorption of Acidic Polymer onto either Acidic or Basic Solids from Basic Solvents

Acidic Polymer	Solid	Solvent	Dielectric Constant	Adsorption $x10^{-4}$ (g/m)
Cl-PVC	CaO	Dioxane	2.2	0.2
Cl-PVC	CaO	THF	7.88	0.1
Cl-PVC	$CaCO_3$	MEK	18.45	0.0
Cl-PVC	$CaCO_3$	Dioxane	2.2	0.0
Cl-PVC	$CaCO_3$	THF	7.88	0.0
Cl-PVC	Bentonite	THF	7.88	0.0
Cl-PVC	Acid Washed Kaolin	MEK	18.45	0.0

Table 13

Effect of change of Cl-PVC conc. in Acidic and Basic Solvents on Zeta Potential with Acidic and Basic Particles

PARTICLE	SOLVENT	DIELECTRIC CONSTANT	Zeta Potential at xg Cl-PVC/100ml Solvent x=0.00	0.01	0.10	1.00
CaO	Dioxane	2.2		0	+90	
$CaCO_3$	Dioxane	2.2		0	+84	+137
$CaCO_3$	THF	7.88	-42	-45.9	-45	-35.5
CaO	THF	7.88	+67	+65	+52	+4
Bentonite	THF	7.88	-61	-64.8	-18.7	+6.8
$CaCO_3$	CH_2Cl_2	9.08	+46	+42	-23	-33
CaO	CH_2Cl_2	9.08	+69	+69.8	+51.7	+4.3
Bentonite	CH_2Cl_2	9.08	-21	-25.7	-35.7	-14.8
$CaCO_3$	MEK	18.45	-4.5	-28.5	-20.1	-13.4
Acid Washed Kaolin	MEK	18.45	-48.6	-49.6	-51.8	-53

II. Solvent-Polymer Interaction Leading to Dissociation in the Solvent

A. Basic Polymers in Solvents of High Dielectric Constant

In solvents of higher dielectric constant, acid-base interaction between solvent and polymer can lead to charged polymer molecules in solution. If these charged polymer molecules adsorb onto filler surfaces they can provide appreciable zeta-potentials. Basic polymers in acidic solvents of higher dielectric constant become positively charged and tend to increase zeta-potential of fillers. A mechanism of charge transfer of basic polymers in high dielectric constant solvents is shown in Fig. 21.

When PMMA is in solution of acetic anhydride + acetic acid it tends to have positive charge in solution. Fig. 23 shows how kaolin particles in these solvents become more positive in zeta-potential with increasing concentration of PMMA. Adsorption of PMMA onto kaolin from acetic anhydride/acetic acid mixture (Table 10) supports these results, where it is evident that kaolin particles had accepted protons from the solvent, becoming themselves positively charged and leaving the solvent negatively charged.

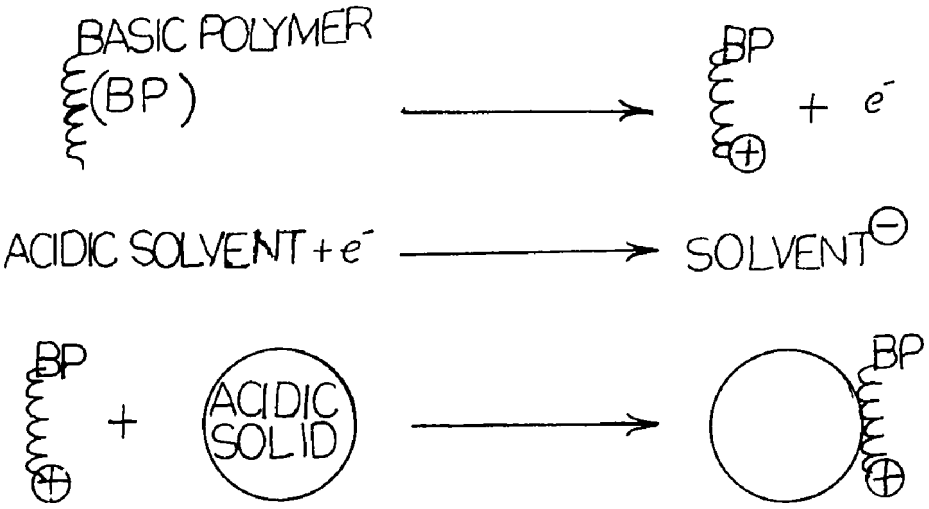

Fig. 21. Mechanism of charge transfer of basic polymers in high dielectric constant solvents.

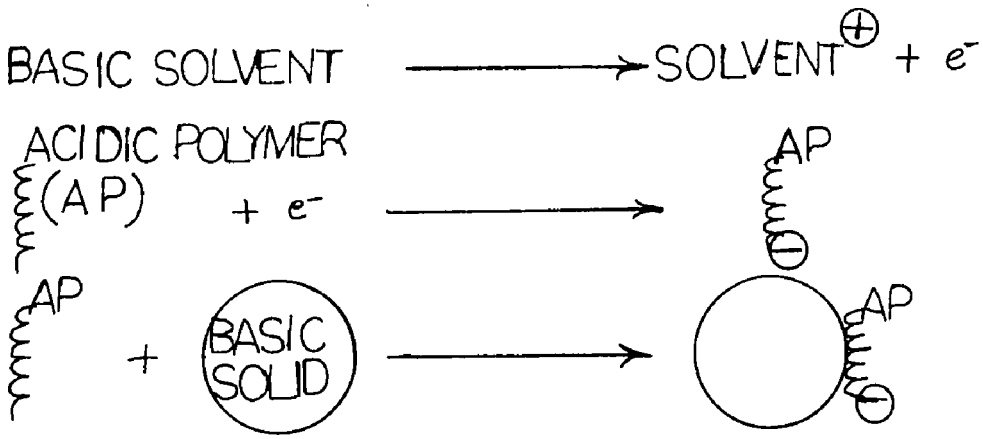

Fig. 22. Mechanism of charge transfer in acidic polymers in high dielectric constant solvents.

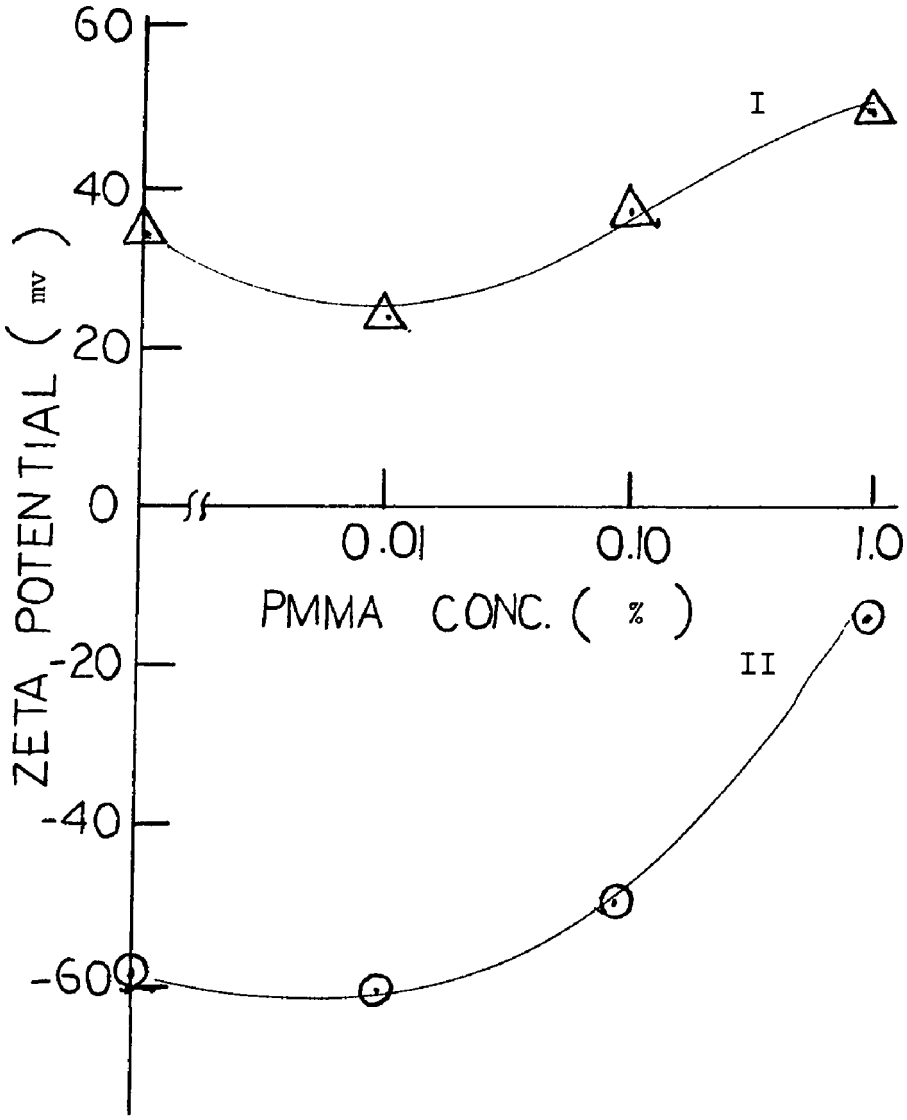

Fig. 23. Zeta potential as a function of concentration of PMMA onto acid washed kaolin from (I) 85% acetic anhydride + 15% acetic acid and (II) acetic anhydride.

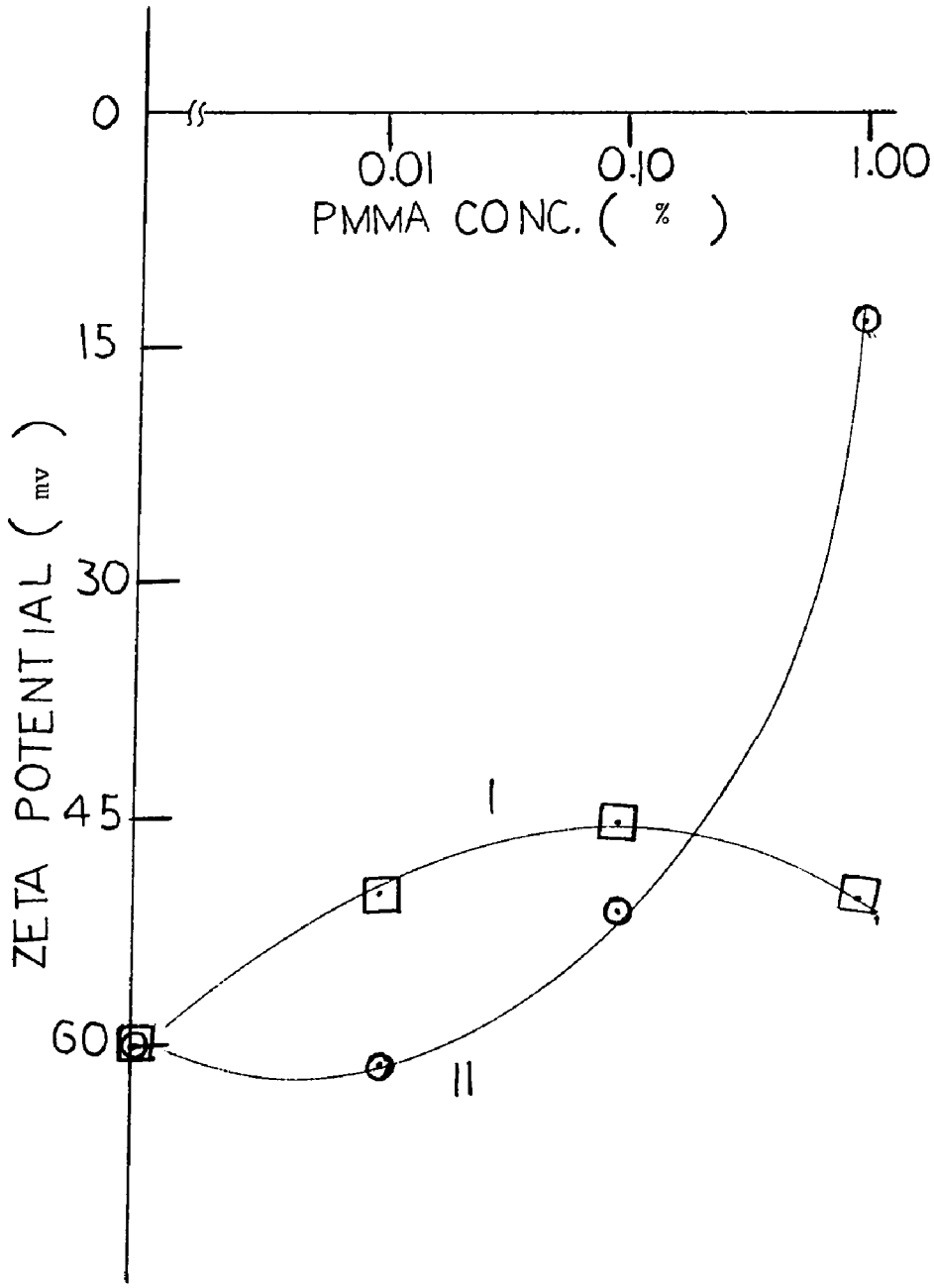

Fig. 24. Zeta potential as a function of concentration of PMMA in acetic anhydride onto (I) calcium carbonate and (II) acid washed kaolin.

Acid-washed kaolin suspension in acetic anhydride shows a negative zeta potential (Table 14). On adding the poly(methyl methacrylate) to this suspension, the basic polymer donates electrons to the solvent and adsorbs to the negatively charged kaolin. This obviously would lead to an increasingly positive charge with higher PMMA concentration. (Fig. 23) Since PMMA donates electrons to acetic anhydride (ε = 20), the positively charged PMMA would then be able to adsorb onto the acidic kaolin. However, when the inorganic solid was the basic $CaCO_3$, no adsorption was observed (Table 10). As a result of this adsorption, an increase in positive zeta-potential on kaolin was found while on $CaCO_3$ there was none.

The effect of acid-base interactions between basic polymers and acidic solids on zeta-potential is illustrated in Fig. 25. When nitrobenzene (ε = 35), a weakly acidic solvent (due to the presence of acidic -NO group and weak basic benzene ring) is used with the basic polymer, Lexan polycarbonate, positively charged PC molecules are expected to be present. Polycarbonate adsorbs onto acid-washed kaolin by means of acid-base interactions, but no adsorption onto calcium carbonate is observed. Kaolin shows an increase in positive zeta-potential with higher polymer concentration while $CaCo_3$

Table 14

Effect of change of PMMA conc. in Acidic and Basic Solvents on Zeta Potential with Acidic and Basic Particles.

PARTICLES	SOLVENT	DIELECTRIC CONSTANT	Zeta Potential at xg PMMA/100 ml Solvent x 0.00	0.01	0.10	1.00
CaCO	Acetic Anhydride (AA)	20	-59	-48	-45	-49
Acid Washed Kaolin	Acetic Anhydride (AA)	20	-59.2	-60.2	-51.2	-13.7
Acid Washed Kaolin	85% Acetic Anhydride 15% Acetic Acid	20	+33.4	-22.6	+37.6	+48.4

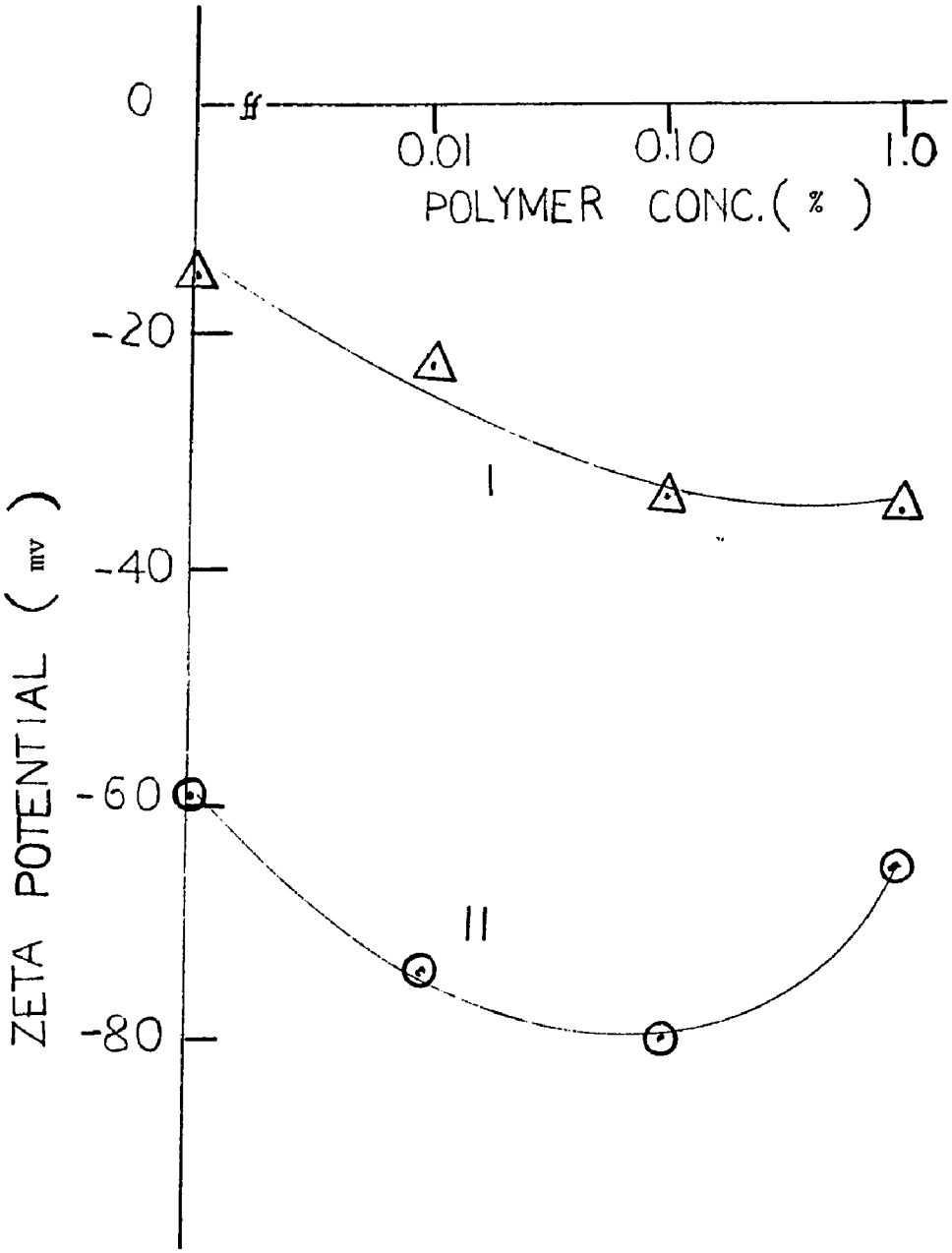

Fig. 25. Zeta potential as a function of polycarbonate concentration in nitrobenzene onto (I) calcium carbonate and (II) acid washed kaolin.

shows very little change, illustrating that the positively charged basic PC molecules adsorbed appreciably onto the acid kaolin but not onto the basic $CaCO_3$.

The adsorption of polycarbonate onto acid washed kaolin from nitrobenzene has led to an increasing zeta-potential toward more positive charge at higher concentrations. But when calcium carbonate was used instead of the kaolin, no adsorption was observed and the zeta-potential showed a slight change, as can be seen in Fig. 25.

B. Acidic Polymers in Solvents of High Dielectric Constant

A possible mechanism of charge transfer in acidic polymers in high dielectric constant solvents is illustrated in Fig. 22. It is proposed that the high dielectric constant has allowed the acidic polymer to accept electrons from the solvent (an electron donor) and to adsorb as a negatively charged polymer onto the particles and making the zeta-potential more negative.

The negatively acidic polymer ions of Cl-PVC in solution adsorbs onto the basic CaO (see Table 11) which makes the zeta-potential more negative. In the absence of Cl-PVC, the positive zeta-potential results from electron-donation from CaO to THF.

We would expect that Cl-PVC would carry negative charges in solution from MEK, but it seems that $CaCO_3$ is not basic enough to adsorb Cl-PVC from MEK (Table 11) and positive trend in zeta-potential is absent.

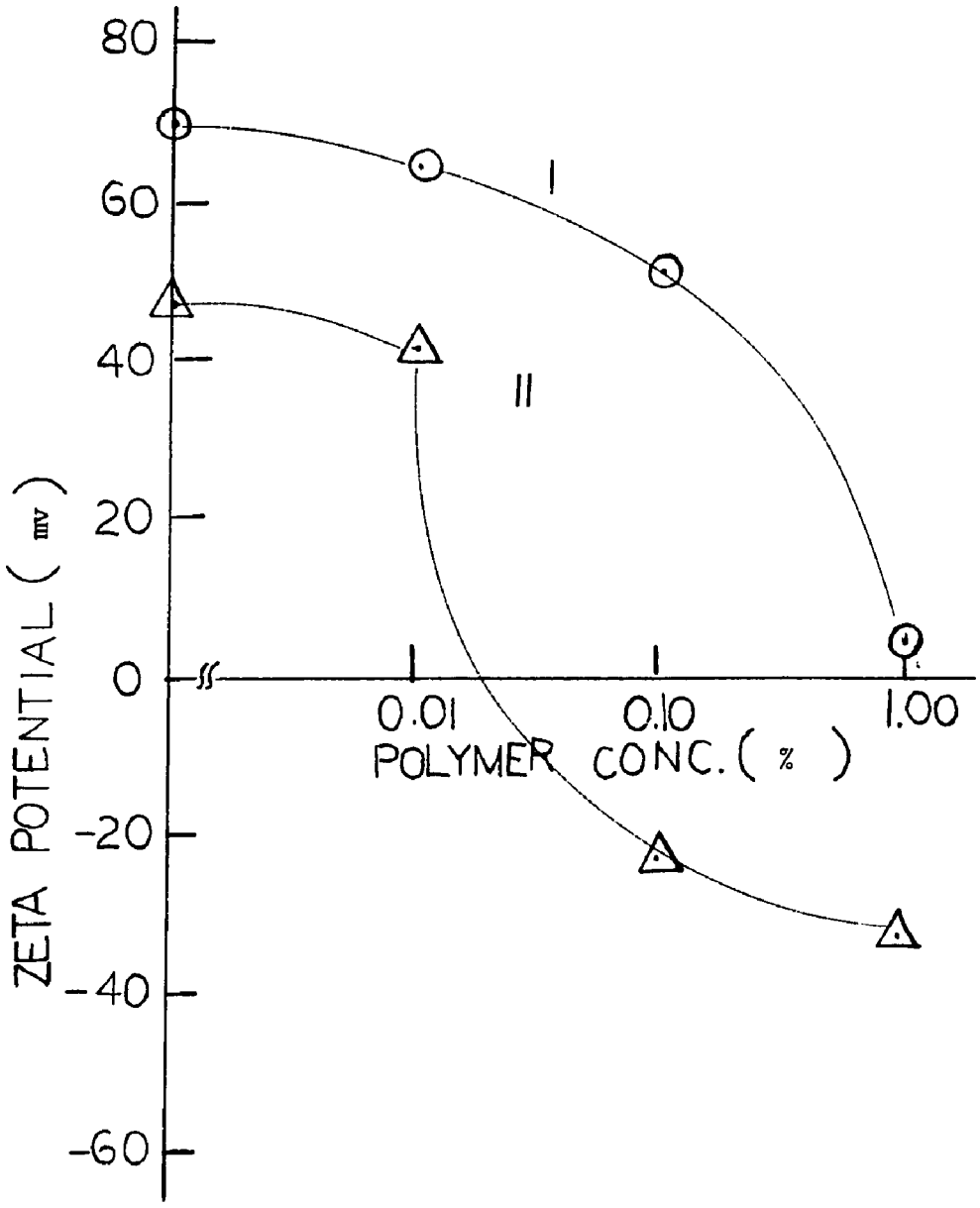

Fig. 26. Zeta potential as a function of concentration of Cl-PVC in methylene chloride onto (I) CaO and (II) $CaCO_3$.

Conclusion

For low dielectric constant solvents charge transfer can occur by acid-base interaction at the surface of the solid. By means of the dynamic adsorption process the incoming polymer molecules will displace those previously adsorbed. These in turn will carry with them the charge which develops on the surface. Under these conditions, any basic dispersant (such as PC) leaves acidic particles negatively charged.

For high dielectric constant solvents charge separation can occur by acid-base interaction in the solvent, i.e., acidic solvents can accept electrons from basic polymers and the resulting basic polymer cations can adsorb on the acidic surfaces and give the particles a positive charge.

In the case of an acidic polymer in basic solvent, the polymer takes an electron and becomes negatively charged. The acidic anionic polymer can adsorb on the surfaces of basic particles and charge them more negatively.

Drago's correlation makes no distinction between proton-donor or electron acceptor acids. We have shown that both types of acids behave about the same in providing charge transfer, which suggests that negatively charged particles have either donated protons or accepted electrons.

Suggestion for Further Studies

The findings of the thermodynamic phenomenon concerning the solvent competition suggest that a chromatographic elution by a series of increasingly acidic or basic solvents could separate and identify polymers.

Stability in non-aqueous systems could be determined by measuring the electrostatic pressure in sedimentation (perhaps with the ultracentrifuge), especially with fine particles of high surface area in solvents of high dielectric constant.

The effect of improved mechanical properties combined with strong adsorption of filled polymers with inorganic materials produce finer dispersions, a case which would be utilized in: (1) Study of surface coatings, solution-masterbatched rubber and mixing fillers into uncured liquids such as polyester, epoxides, phenolics or urethanes. (2) Study of the interface immunity to water penetration which would lead to a greater permanence to adhesive bonds.

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Appendix I

On the Derivation of the E and C Equation

Drago used the variation method[80] in conjunction with simplified Mulliken model wave functions, ψ, to calculate the ground state bond energy of the adduct. The change in energy produced during the interaction of two systems by the partial transfer of electrons from an initially doubled occupied highest filled (ψ_B) to an initially empty orbital (lowest ψ_A) was calculated (i.e., energy of the charge-transfer transition in the electron spectrum). The following integrals were defined:

$$H_B = \int \psi_B \hat{H} \psi_B \, d\tau \qquad \text{I-a}$$

$$H_A = \int \psi_A \hat{H} \psi_A \, d\tau \qquad \text{I-b}$$

$$H_{AB} = \int \psi_A \hat{H} \psi_B \, d\tau \qquad \text{I-c}$$

and $$s = \int \psi_A \psi_B \, d\tau \qquad \text{I-d}$$

In neutral acid-base interaction, where the typical enthalpies of interactions[81] are $\Delta H = 10 \frac{kcal}{mole} (40 \frac{kJ}{mole})$, the amount of charge donated by the base to the acid is fairly small. This would result in new energy states close to the initial ones. Then we would be able to approximate the integrals H_A and H_B by linear espressions as follows:

$$H_A = - \varepsilon_A (1 - \Delta_A q_B) \qquad \text{I-e}$$

$$H_B = - I_B (1 - \Delta_B q_A) \qquad \text{I-f}$$

where Δ_A and Δ_B represent the relative change in energy level per unit charge for the acid and base respectively. q_A is the absolute value of the amount of charge accepted by the acid and for a given adduct equal in magnitude to q_B, the absolute value of the amount of charge donated by the base. ε_A is the electron affinities of the acid, [in the order of 50 kcal/mole (200 kj/mole)].

An equation of the following form was obtained:

$$-\Delta H = 2I_B \, {}_B q_A + (2S^2 H_A H_B)/(H_A - H_B) \qquad \text{I-g}$$

The quantity $I_B \Delta_B q_A$ is about 1-5 kcal/mole (4.18 - 21 kj?mole) but since I_B is in the order of 200-300 kcal/mole (850 - 1300 kJ/mole), $\Delta_B q_A$ must be very small. The second term in the above equation would have a higher contribution from H_B term than from H_A. Thus $(H_A - H_B)$ is largely a property of the base.

When the last term in the above equation (I-g) is replaced by empirical parameters, the $(H_A - H_B)$ term is incorporated into a base parameter, C_B'. If H_A does become large enough to be appreciable for a particular acid, the acid parameter, C_A, can be empirically adjusted to compensate.

Hence, product function for a selected value of $H_B >> H_A$ could reproduce $(H_A - H_B)$.

If S^2 can also be represented by a product function, the above equation would be written in a form which would be easily converted to the E and C form:

$$-\Delta H = (I_B \Delta_B)(2q_A) + S_A C'_A \; S_B C'_B \qquad \text{I-h}$$

$$= E_B E_A + C_A C_B \qquad \text{I-i}$$

The term $E_B E_A$ consists only of one center integral approximation which corresponds to an ionic bonding, while the term $C_A C_B$ consists of two center integrals which correspond to a covalency bonding.

q_A would indicate the extent to which a given acid perturbs the energy of the electrons that are on the base. It is not a constant, and it varies with the donor. But since the charge transfer is very small, the product $E_A E_B$ would empirically compensate for inconsistance of q_A in the parametrization of the acid and the base. In other words, the product $E_A E_B$ is corrected for this effect by appropriate adjustment of the E_B parameter.

Appendix II

Table 15

Values of ΔH^{ab} for Solvents Used for Adsorption of PMMA onto SiO_2, Utilizing Drago's Equation ($-\Delta H^{AB} = C_A C_B + E_A E_B$).*

Acidic Model	C_A	E_A	Basic Solvents	C_B	E_B	$-\Delta H^{ab}$ (kJ/mole)
BuOH	0.612	4.162	THF	8.711	1.995	13.63
BuOH	0.612	4.162	1,4 Dioxane	4.855	2.224	12.23
BuOH	0.612	4.162	Benzene	2.856	0.224	2.68

Basic Model	C_B	E_B	Acidic Solvents	C_A	E_A	$-\Delta H^{ab}$ (kJ/mole)
EtAC	3.549	1.989	CH_2Cl_2	0.020	3.386	6.81
EtAC	3.549	1.989	$CH\ Cl_3$	0.306	6.752	14.52

*C_A, E_A, C_B and E_B are expressin in $kJ/mole)^{\frac{1}{2}}$.

Appendix II

Table 16

Adsorption of PMMA onto $CaCO_3$ and Modified SiO_2, and Cl-PVC onto SiO_2 from Acidic, Basic and Neutral Solvent.

Solvent	PMMA Adsorption ($10^4 g/m^2$)		Cl-PVC Adsorption ($10^4 g/m^2$)
	SiO_2(modified)	$CaCO_3$($6m^2/g$)	SiO_2($380m^2/g$)
THF	0.2	0.0	0.0
1,4 Dioxane	0.4	0.0	0.0
Benzene	1.3	0.2	0.0
CCl_4	5.0	0.3	0.0
CH_2Cl_2	8.4	0.0	0.0
$CHCl_3$	1.9	0.0	0.0

Appendix II

Table 17

Intrinsic Viscosity, Adsorption Values of PMMA onto SiO_2 and ΔH^{ab} Values

Solvent	Dielectric Constant ε_{20}	Solubility Parameter, $\sqrt{cal/ml}$	$(\sqrt{J/ml})$	$-\Delta H^{ab}$, (kJ/mole)	PMMA	
					Intrinsic Viscosity [η] dℓ/g	Adsorption onto SiO $10^4 g/m^2$. (Å)
THF	7.88	9.9	(20.2)	13.63	1.1	0.40 (0.33)
1,4 Dioxane	2.20	10.0	(20.4)	12.23	1.11	1.30 (1.08)
Benzene	2.284	9.15	(18.70)	2.68	1.20	5.95 (4.42)
CCl_4	2.238	8.6	(17.60)	--	0.23	12.30 (10.25)
CH_2Cl_2	9.08	9.7	(19.80)	6.81	1.01	4.80 (3.83)
$CHCl_3$	4.81	9.3	(19)	14.52	1.69	0.93 (0.75)

Appendix II

Table 18

Values of ΔH^{ab} for Solvents Used for Adsorption of Cl-PVC onto $CaCO_3$, Utilizing Drago's Four Parameters* Equation ($-\Delta H^{ab} = C_A C_B + E_A E_B$).

Acidic Model	C_A	E_A	Basic Solvents	C_B	E_B	$-\Delta H^{ab}$ (kJ/mole)
$CHCl_3$	0.306	6.752	THF	8.711	1.995	16.136
$CHCl_3$	0.306	6.752	P-Dioxane	4.855	2.224	16.502
$CHCl_3$	0.306	6.752	Benzene	2.856	0.224	2.998
Basic Model			**Acidic Solvents**	C_A	E_A	$-\Delta H^{ab}$ (kJ/mole)
EtAc	3.549	1.989	CH_2Cl_2	0.020	3.386	6.81
EtAc	3.549	1.989	$CHCl_3$	0.306	6.752	14.52

*C_A, E_A, C_B and E_B are expressed in $(kJ/mole)^{1/2}$

Appendix III

Sample Calculation of Values of Electrophorific Mobilities U_{SL} and Zeta Potentials ζ.

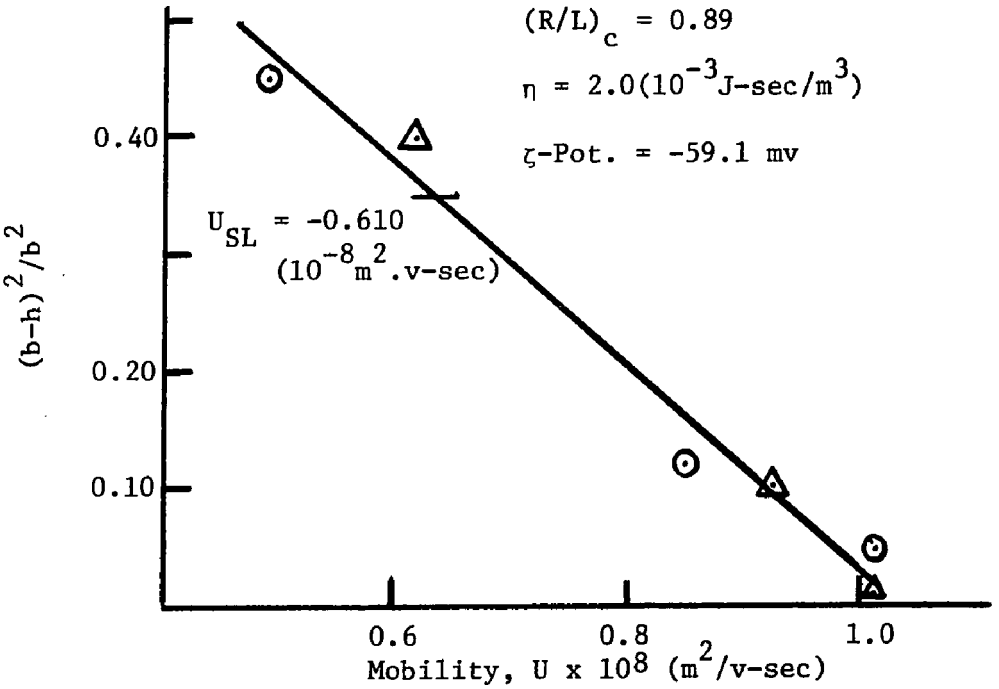

Fig. 27. Mobility, U of Acid Washed Kaolin Particles in Nitrobenzene as a fn of $(b-h)^2/b^2$

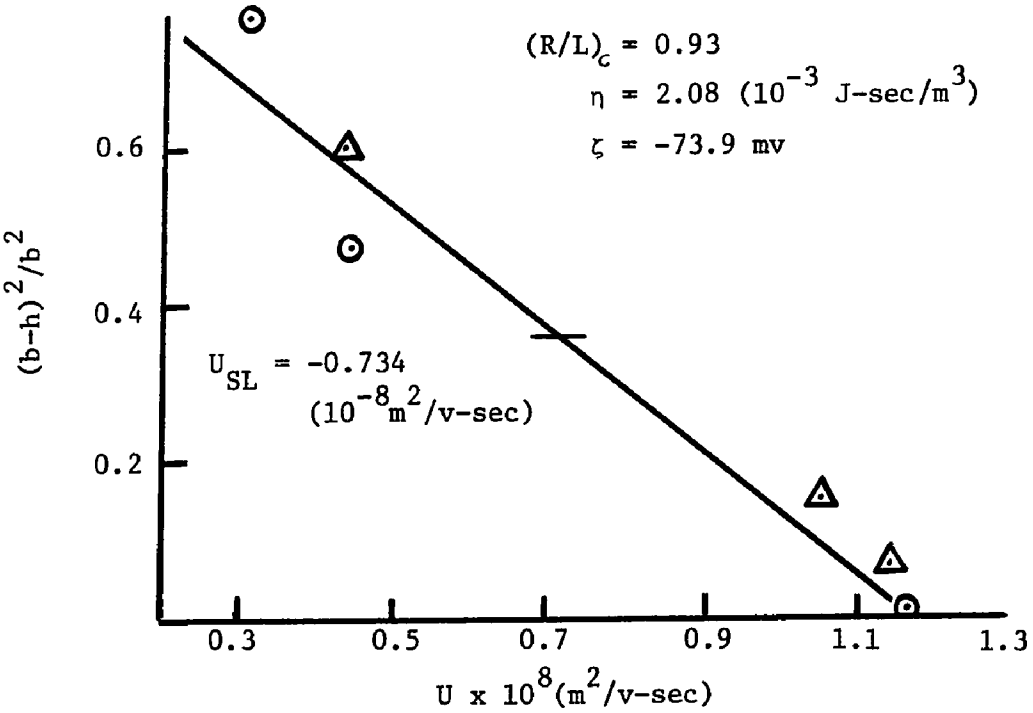

Fig. 28. Mobility, U of Acid Washed Kaolin Particles in (0.01%PC/Nitrobenzene) as a fn of $(b-h)^2/b^2$

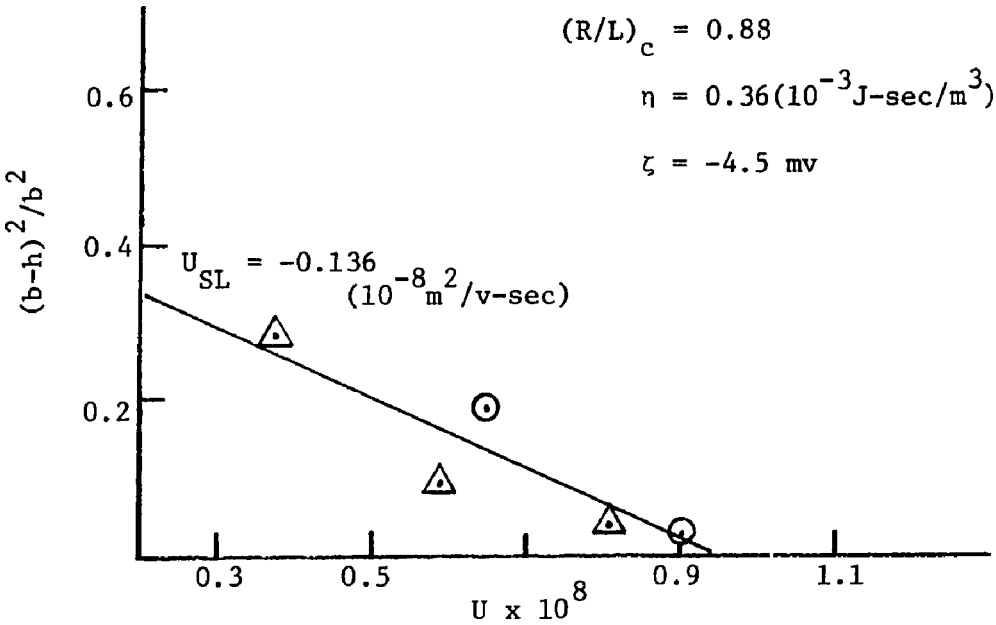

Fig. 29. Mobility, U, of $CaCo_3$ particles in MEK, as a fn of $(b-h)^2/b^2$.

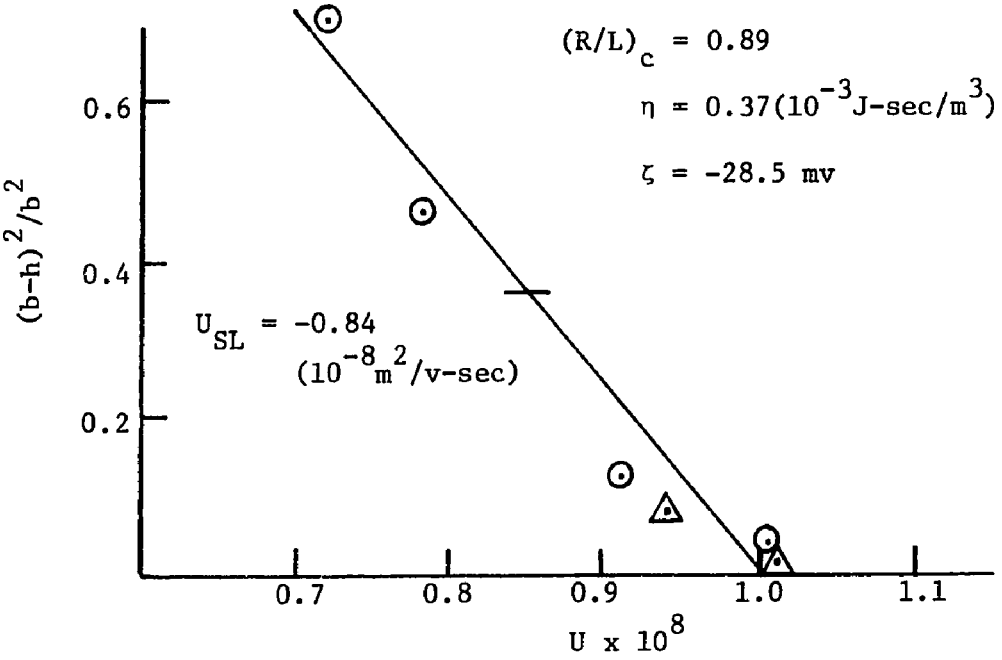

Fig. 30. Mobility, U, of $CaCo_3$ particles in (0.01% Cl-PVC /MEK) as a fn of $(b-h)^2/b^2$.

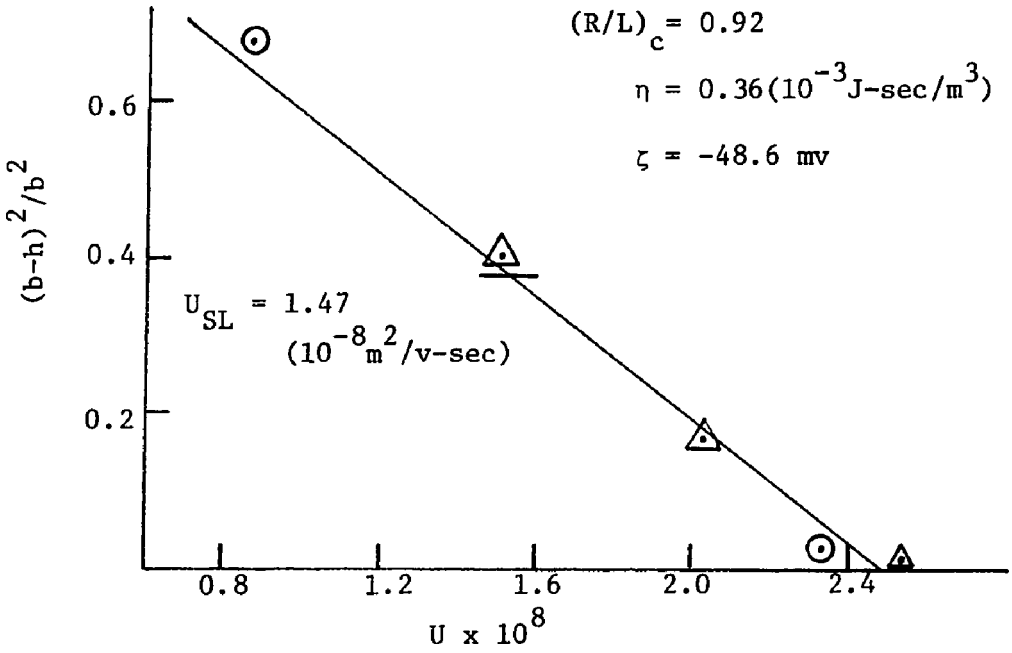

Fig. 31. Mobility, U, of Kaolin particles in MEK, as a fn of $(b-h)^2/b^2$.

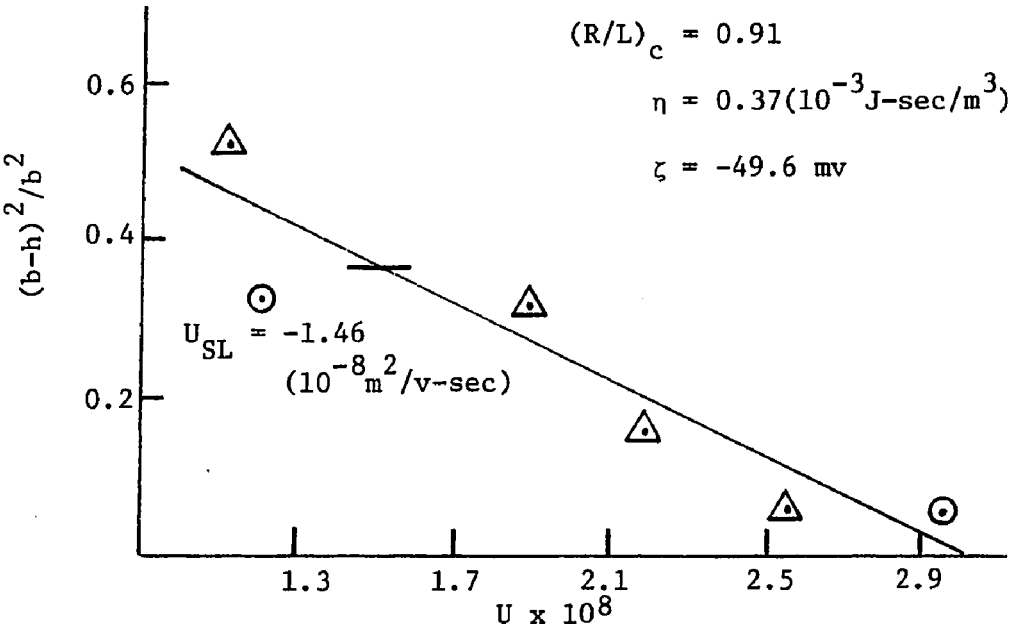

Fig. 32. Mobility, U, of Kaolin particles in (0.01% Cl-PVC/MEK) as a fn of $(b-h)^2/b^2$.

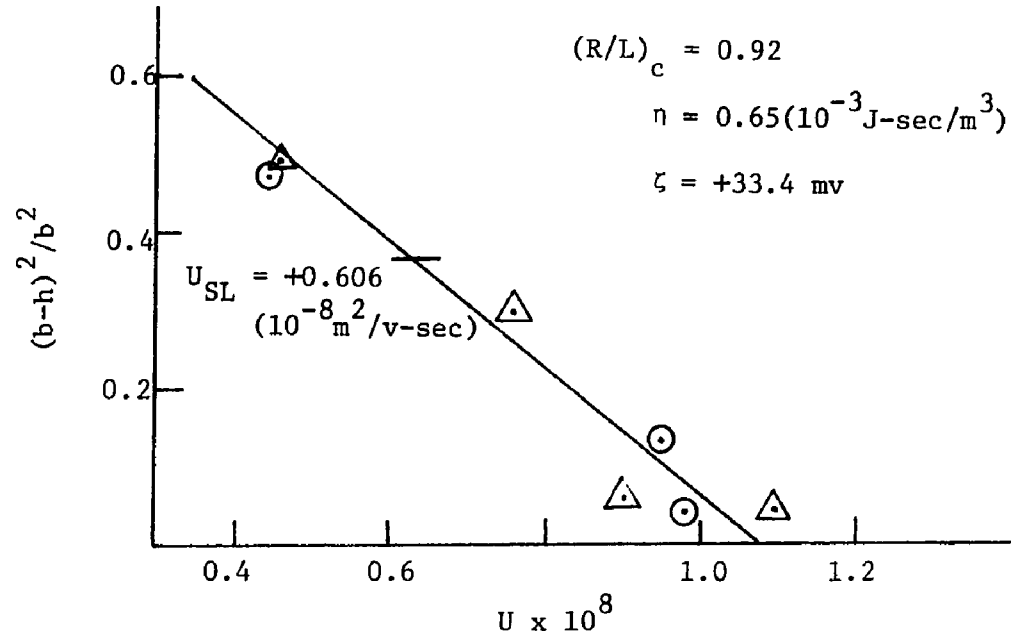

Fig. 33. Mobility, U, of Acid Washed Kaolin Particles in (85% AA + 15% HoAc) as a fn of $(b-h)^2/b^2$.

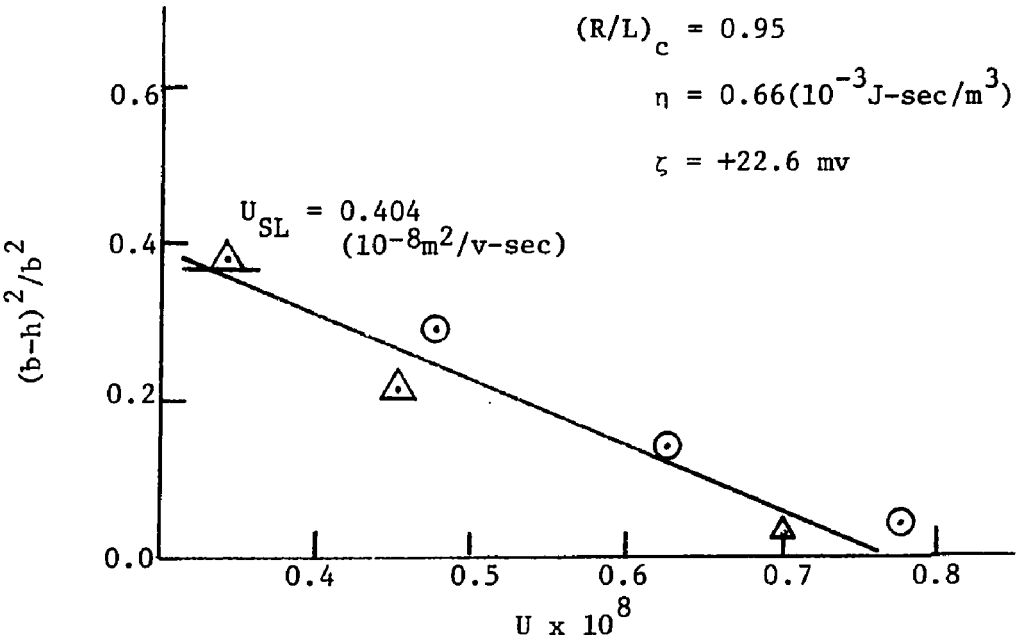

Fig. 34. Mobility, U, of Acid Washed Kaolin Particles in (0.01% PMMA/85% AA +15% HoAc) as a fn of $(b-h)^2/b^2$.

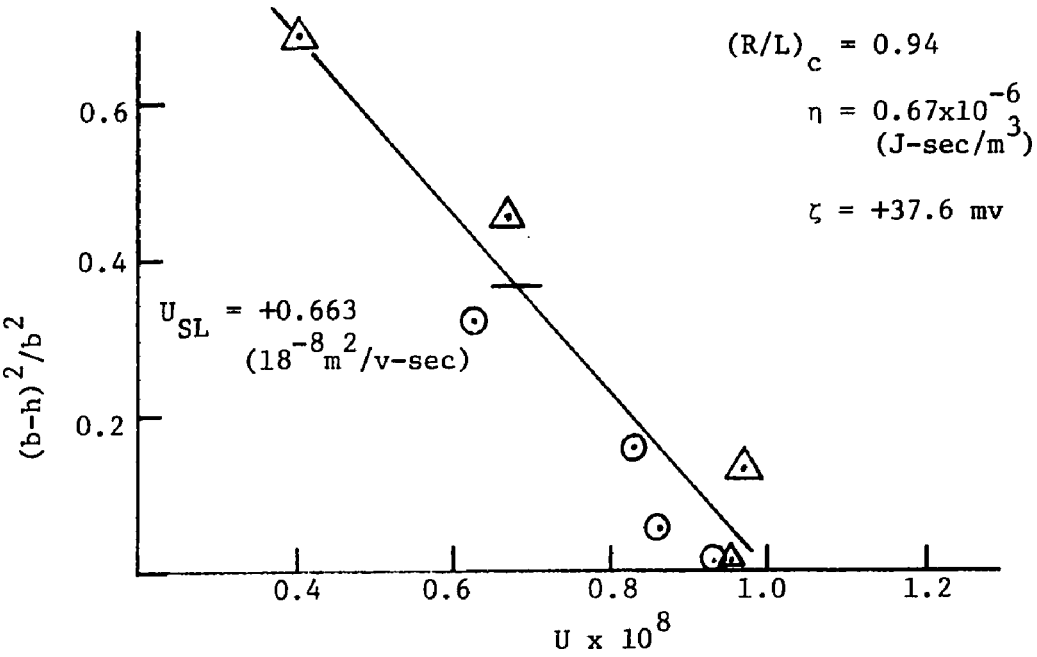

Fig. 35. Mobility, U, of Acid Washed Kaolin Particles in (0.10% PMMA/85% AA + 15% HoAc) as a fn of $(b-h)^2/b^2$.

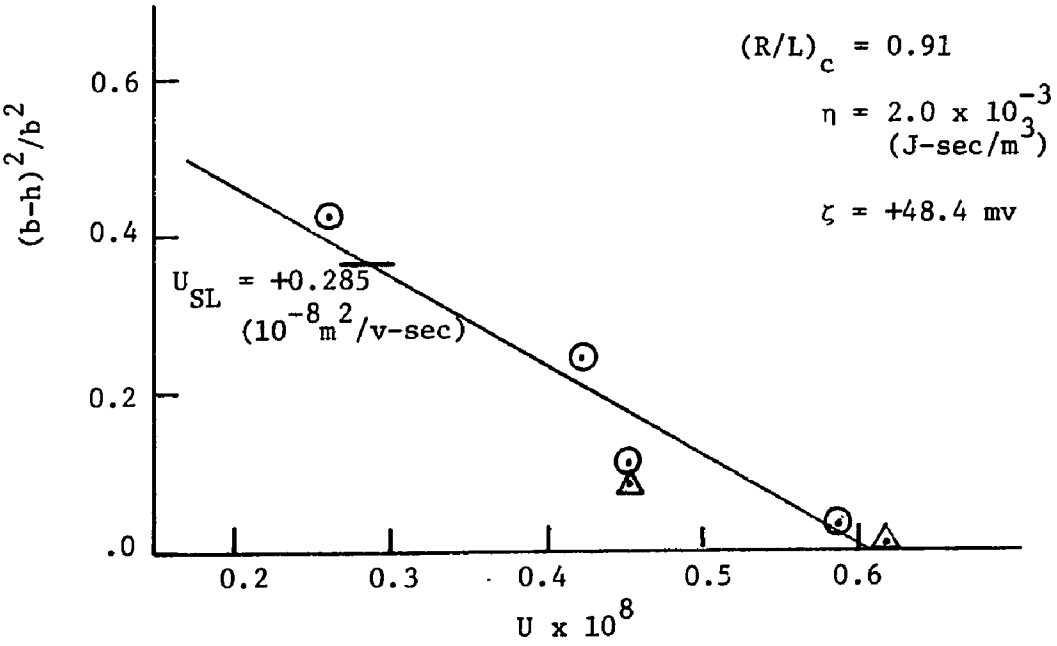

Fig. 36. Mobility, U, of Acid Washed Kaolin Particles in (1.0% PMMA/85% AA + 15% HoAc) as a fn of $(b-h)^2/b^2$.

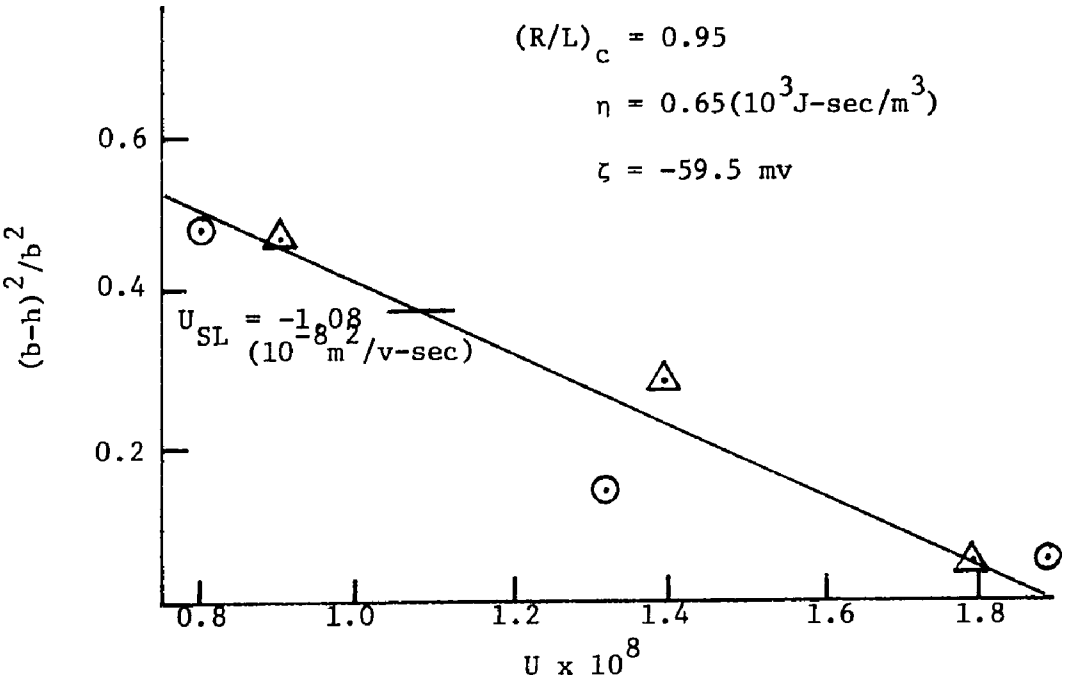

Fig. 37. Mobility of Acid Washed Kaolin Particles in Acetic Anhydride as a fn of $(b-h)^2/b^2$

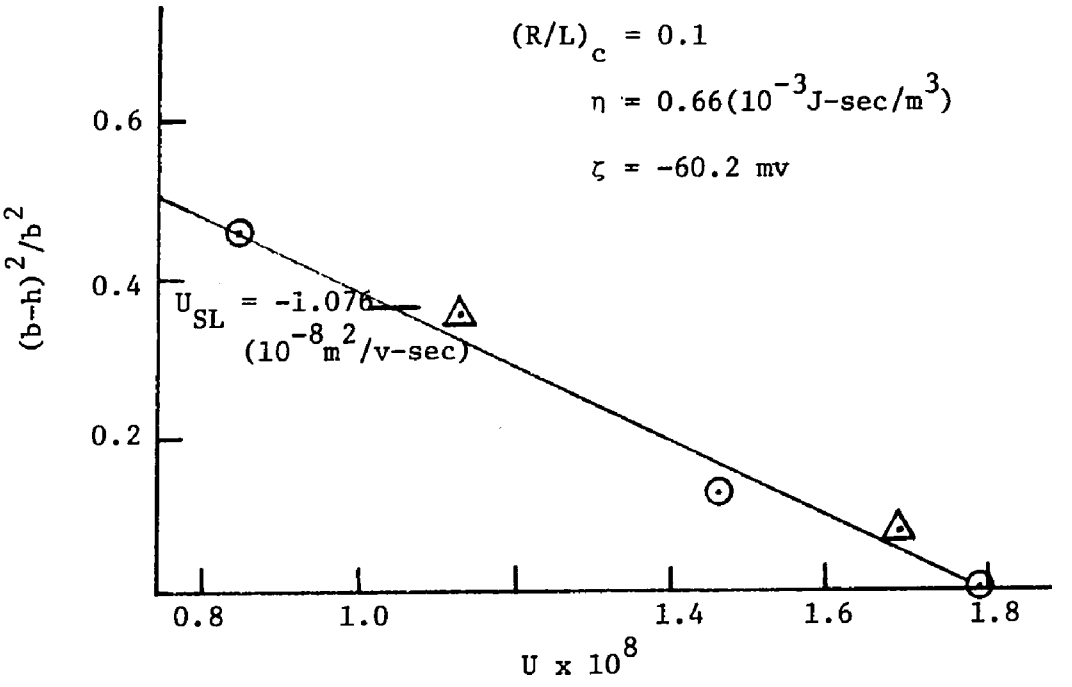

Fig. 38. Mobility of Acid Washed Kaolin Particles in (0.01% PMMA/Acetic Anhydride) as a fn of $(b-h)^2/b^2$.

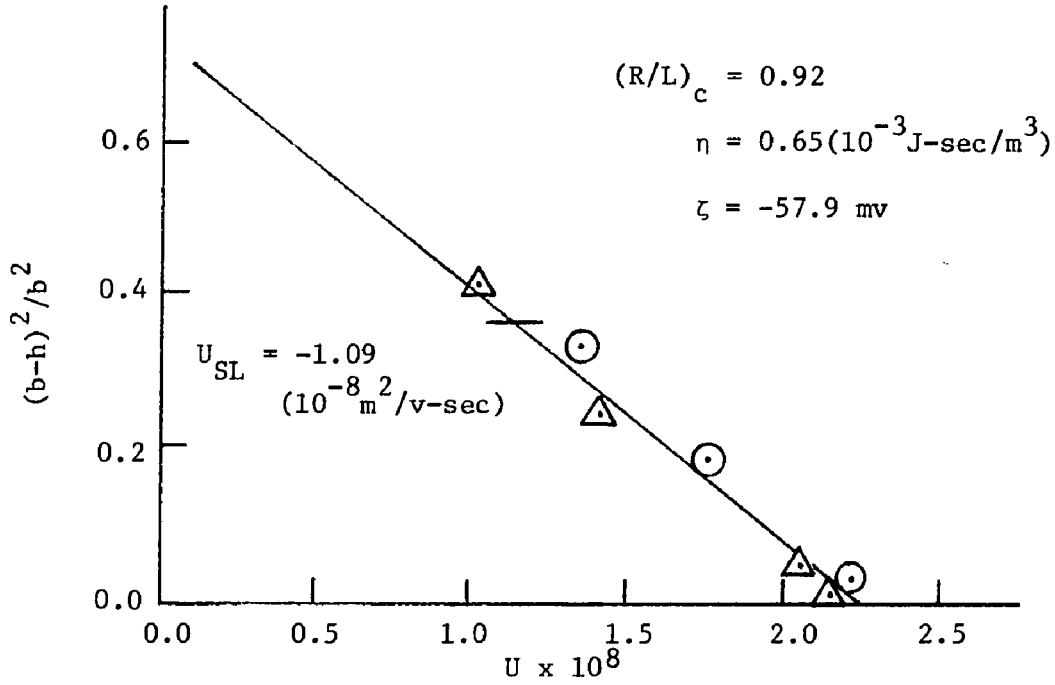

Fig. 39. Mobility, U, of $CaCo_3$ Particles in Acetic Anhydride as a fn of $(b-h)^2/b^2$.

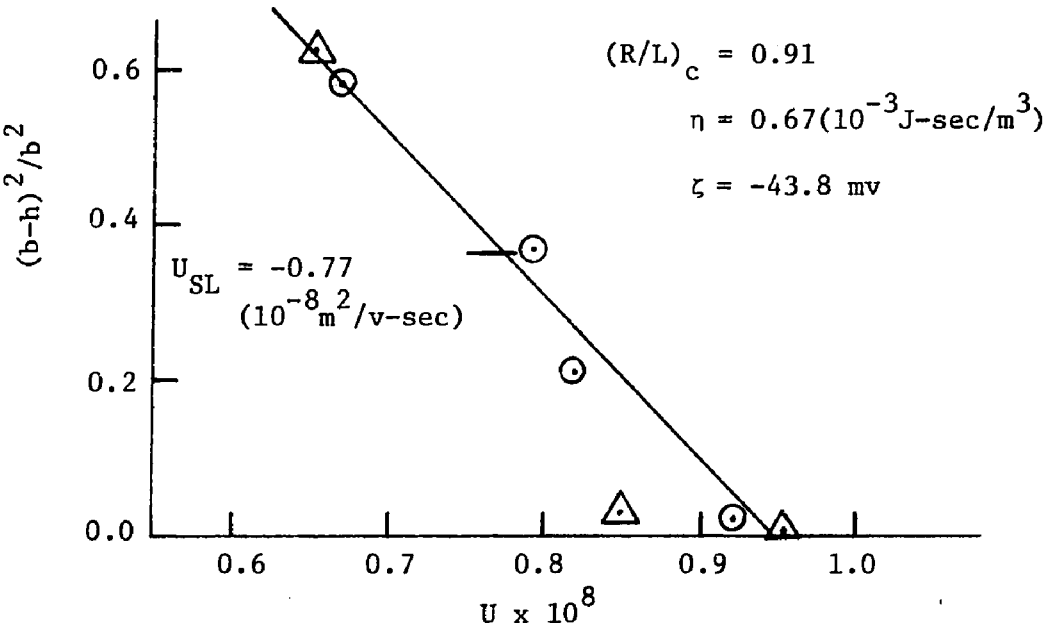

Fig. 40. Mobility, U, of $CaCo_3$ Particles in (0.01% PMMA in Acetic Anhydride) as fn of $(b-h)^2/b^2$.

VITA

The author was born May 6, 1940, in Cairo, Egypt, the son of Mr. and Mrs. Ahmed Mostafa.

He attended Shobra High School in Cairo, graduating in 1958. He received his Bachelor of Science in chemistry and geology from Ain-Shames University in Cairo in 1964.

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Mr. Mostafa taught chemistry at Bon Pastier French school and worked as a chemist in the Chemical Department of the Ministry of Industry in Cairo before coming to the United States. He taught school at Barnesville, Georgia, and was head of the science department for two years at Doane Academy, a boys' preparatory school at Burlington, N.J.

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Mr. Mostafa is married to the former Roselyn Midboe of Fosston, Minnesota.