Low Polymer-solvent Interaction. Solubility And Heat Of Solution Of Polyindene.

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LOW POLYMER - SOLVENT INTERACTION. SOLUBILITY AND HEAT OF SOLUTION OF POLYINDENE

By

Jack Vanderryn

A DISSERTATION
Presented to the Graduate Faculty
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Doctor of Philosophy

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This dissertation is respectfully submitted to the Graduate Faculty of Lehigh University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Jack Vanderryn

Jack Vanderryn

Approved and recommended for acceptance as a dissertation in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

April 20, 1955
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CHAPTER I

INTRODUCTION

The interaction between polymers and solvents or plasticizers is of great theoretical importance and practical significance. An understanding of the behavior of polymer-solvent systems furthers our understanding of the fundamental nature of solutions. The widespread application of polymeric systems in industry emphasizes the need for basic information concerning the behavior of such systems.

The physical chemical behavior of polymer-solvent systems has received a great deal of attention in recent years (for example, references 1, 5, 7, 10, 11, 12, 15, 18, 19, 31, 33, 37, 50, 62). A large portion of these investigations have centered around studies of the thermodynamic properties of high polymer solutions, especially those of polystyrene and rubber. However, additional data is still needed for a complete understanding of the behavior of high polymer systems. Correlations of the results of different experimental techniques such as solution viscosity, vapor pressure, critical miscibility, and heat of solution are still incomplete. Nevertheless, considerable advances in the field of solubility and solution chemistry have been made. On the other hand, the behavior of low molecular weight polymer solutions has not received much attention in spite of the importance of low molecular weight polymers, as evidenced by their wide use in the manufacture of such products as varnishes, mastic tile, coating compositions, and rubber products.

Solutions of low polymers have not received much attention yet they are the connecting link between ordinary small molecule solutions and high polymer solutions; both of these latter solutions have received much attention. The large number of repeating units in a high polymer molecule has made possible the application of statistical thermodynamic methods to their solutions with a moderate degree of success. Practically no work has been done to test the applicability of the results of statistical theory to solutions of low polymers. On the other hand, it must be pointed out that our understanding of the behavior of relatively "simple" solutions of small molecules is still quite incomplete, especially if one or both of the components contains polar groups. For instance, no quantitative relationship has ever been proposed for the heat of mixing of nonelectrolytes when the heat is exothermic.

The present study was undertaken to study the nature of the interaction of a low molecular weight polyindene type polymer with solvents or plasticizers. It was desired to test the applicability of thermodynamic solubility and heat of solution relationships proposed for high polymer systems to solutions of low polymers. Solubility relationships of this polyindene polymer whose molecular weight distribution and viscosity characteristics were previously investigated in this laboratory (43, 44, 71) were determined in a wide variety of organic solvents and with low polymers.

The measurement of solubility and critical composition were done first to give an insight into the type of interactions which occur in this type of polymer solution. These measurements were then followed by precise determination of the heat of solution of the polymer in the various solvents to reveal some of the quantitative thermodynamic characteristics of the interaction.

The heats of solution of the polyindene polymer were determined in twenty one different solvents: cyclohexane, 1-nitropropane, nitrobenzene, ethyl acetate, methyl ethyl ketone, benzene, ethyl benzene, n-butyl chloride, n-heptyl chloride, chlorobenzene, bromobenzene, carbon tetrachloride, chloroform, methyl chloroform, s-tetrachloroethane, pyridine, dimethyl aniline, n-butyl amine, anisole, ethyl benzoate, and benzonitrile. Intrinsic viscosities were determined in several of these solvents in order to ascertain the extent of "uncurling" of the polymer molecules in solution. Heats of solution in chloroform, chlorobenzene, and 1-nitropropane of four different molecular weight fractions of the polymer were also determined.

The observed behavior of the polymer-solvent systems was compared with (1) the behavior expected from theoretical considerations, and (2) the behavior of high polymer-solvent systems reported in the literature. The observed heats of solution are explained on the basis of the thermodynamic state of the polymer and of the structure and chemical nature of the solvents.

Theory related to heat of mixing - Hildebrand and Scott (27) have summarized much of the theory and experimental work relating to the interactions of nonelectrolytes, including polymers. Although noncrystalline polymers, such as used in this study, have the appearance of solids, thermodynamically they are liquids (see also Chapter V). Thus the problem of the energy of mixing of a polymer in a solvent is essentially the problem of the energy of mixing of two liquids. Scatchard (53) has shown* that the energy of mixing of a nonpolar binary mixture may be expressed as:

$$\Delta E^M = (N_1 V_1 + N_2 V_2)\left[\left(\frac{\Delta E_1^V}{V_1}\right)^{1/2} - \left(\frac{\Delta E_2^V}{V_2}\right)^{1/2}\right]^2 \varphi_1 \varphi_2 , \qquad (1)$$

and the partial molal energy of mixing for component 1 is then:

$$\left(\frac{\partial(\Delta E^V)}{\partial N_1}\right)_{N_2} = \overline{\Delta E}_1^M = \varphi_2^2 V_1 \left[\left(\frac{\Delta E_1^V}{V_1}\right)^{1/2} - \left(\frac{\Delta E_2^V}{V_2}\right)^{1/2}\right]^2 , \qquad (2)$$

where** N indicates the number of moles, V is the molar volume, φ is the volume fraction and ΔE^V is the molar energy of vaporization. Subscript 1 always refers to the solvent and subscript 2 refers to the solute. Equation 1 was derived by calculating the cohesive energy of a

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* The derivation and assumptions of this, and subsequent equations are given in Appendix III.

** A glossary of symbols is given in Appendix I.

a mole of liquid mixture using the following assumptions: (1) the distribution of the molecules in position and in orientation is random; (2) the change in volume on mixing, ΔV^M, at constant pressure is zero; and, (3) the mutual energy of the two molecules depends only upon the distance between them and their relative orientation. Equation 1 was also derived by Hildebrand and Wood (28) by integrating the intermolecular potentials between pairs throughout the liquid making use of the continuous distribution function.

The quantity $\frac{\Delta E^V}{V}$, the energy of vaporization per cc., is sometimes called the cohesive energy density. This function can be taken as a measure of the internal pressure and it plays an important role in the theory of solutions. The symbol δ, termed the solubility parameter, has been defined in terms of $\frac{\Delta E^V}{V}$ according to the equation:

$$\delta = \left(\frac{\Delta E^v}{V}\right)^{1/2} . \tag{3}$$

If the volume change on mixing is zero then the energy of mixing may be identified with the heat of mixing since $\Delta H = \Delta E + P\Delta V$. Because the term $(N_1V_1 + N_2V_2)$ is equal to the volume of the mixture, Equation 1 may be rewritten:

$$\Delta H^M \simeq \Delta E^M = V_m(\delta_1 - \delta_2)^2 \varphi_1 \varphi_2 = V_m(\delta_1 - \delta_2)^2 \varphi_2(1-\varphi_2) , \tag{4}$$

or

$$\Delta H^M \simeq \Delta E^M = V_m B \varphi_2(1-\varphi_2) , \tag{5}$$

where V_m is the volume of the mixture and

$$B = (\delta_1 - \delta_2)^2 \tag{6}$$

The partial molal quantity is given by the expression:

$$\left(\frac{\partial(\Delta H)}{\partial N_1}\right)_{N_2} = \overline{\Delta H_1} = V_1 B \varphi_1^2 \tag{7}$$

According to Equation 5 a plot of $\frac{\Delta H^M}{V_m}$ vs. $\varphi_2(1-\varphi_2)$ should give a straight line with slope B. Since B is a squared term it must always be a positive number and thus this theory predicts that the heat of mixing two nonpolar nonelectrolytes must be endothermic. However, when there is specific interaction between two species in solution, the experimental value of B is not given by Equation 6 but becomes more complex and often negative. Equation 5 may still be applicable even though ΔH^M is negative.

The validity of Equation 5 has been tested by several investigators (8, 35, 36, 38, 39, 54, 67, 68) using calorimetric methods and simple binary mixtures such as benzene, carbon tetrachloride, and cyclohexane. The equation was found to be valid for nonpolar mixtures and for some polar mixtures. Ferry, Gee, and Treloar (14) measured the heat of solution of dihydromyrcene and squalene (low molecular liquid homologues of natural rubber) with a series of solvents and showed that Equation 5 is obeyed with considerable accuracy; only acetone and chloroform showed considerable deviations. Newing (42) measured the heat of mixing of solutions of silicones (mol. wt. 1140 to 15,700) in benzene and found that the value of B increased linearly with increasing silicone concentration. Daoust and Rinfret (9) measured the heat of solution at low concentrations of polyvinyl acetate (mol. wt. 85,000 - 135,000) in several common organic solvents and found relatively good agreement with Equation 5 when heats of mixing were endothermic although the value of B tended to decrease with increasing polymer concentration. However, they found that B values went through a maximum for the exothermic solvents ethylene chloride and s-tetrachloroethane. Daoust and Rinfret explain their exothermic heats of mixing by postulating solvation of the "basic" carbonyl oxygen of polyvinylacetate by the "acidic" solvent molecules such as chloroform and ethylene chloride. Staverman and Dekking (60) found that the description of the heat of mixing by Equation 5 is not satisfactory for solutions of polymethylmethacrylate in trichloroethylene and acetone due to the polar nature of the solutions.

The heats of solution of polystyrene have been determined by several investigators (24, 26, 51, 63) who found surprisingly high exothermic values for certain solvents. Hellfritz (26) and von Günner and Schulz (24) showed that the heat of solution of polystyrene became more exothermic with increasing molecular weight.

In the present study the validity and applicability of Equations 5 and 6 in the low concentration range for solutions of polyindene has been tested. The variation of the heat of solution with molecular weight has been investigated and the results compared with those for polystyrene (24). A quantitative explanation of these results is given. The observed differences of heats of solution in different solvents is explained on the basis of the chemical nature and structure of the solvent.

Theory related to solubility - It has been shown (27) that the entropy of mixing for any structure in which the molecules of one component can be interchanged with those of the second component without altering the structure, is given by the expression:

$$\Delta S^M = -R\left(N_1 \ln \frac{N_1}{N_1+N_2} + N_2 \ln \frac{N_2}{N_1+N_2}\right) = -R\left(N_1 \ln x_1 + N_2 \ln x_2\right), \quad (8)$$

where x refers to the mole fraction. For components having different molar volumes the expression becomes:

$$\Delta S^M = -R\left(N_1 \ln \varphi_1 + N_2 \ln \varphi_2\right) . \quad (9)$$

Equations 8 and 9 can be referred to as configurational entropies and do not take into account any local order which might exist in the mixture. Equation 8 leads to a partial molal entropy of:

$$\overline{\Delta S}_1^{\,i} = -R \ln x_1 . \quad (10)$$

Since $\Delta F^M = \Delta H^M - T\Delta S^M$ we can combine Equations 5 and 8 to get:

$$\Delta F^M = RT\left(N_1 \ln x_1 + N_2 \ln x_2\right) + V_m B \varphi_2 (1-\varphi_2) , \quad (11)$$

and

$$\overline{\Delta F}_1 = RT \ln x_1 + V_1 B \varphi_2^2 . \quad (12)$$

Flory (16) and Huggins (29) have expanded this treatment to include binary mixtures for components having different molar volumes.

Their equation for $\overline{\Delta F_1}$ becomes:

$$\overline{\Delta F_1} = RT\ln\varphi_1 + RT\left(1-\frac{1}{X}\right)\varphi_2 + BV_1\varphi_2^2 \quad , \tag{13}$$

and for $\overline{\Delta S_1}^n$:

$$\overline{\Delta S_1}^n = -R\left[\ln\varphi_1 + \left(1-\frac{1}{X}\right)\varphi_2\right] \quad , \tag{14}$$

where $X = \frac{V_2}{V_1}$. The superscript n is used following the notation of Shultz and Flory (58) to indicate a "normal" entropy of dilution as opposed to the "ideal" entropy of dilution (Equation 10, superscript i) for a mixture of molecules of equal size.

Inspection of Equation 11 shows that if B = O, ΔF^M will always be negative, resulting in complete miscibility. As the (positive) value of B is increased, or as the solubility parameters of the two components become more dissimilar, the mutual solubilities will decrease. The solubility parameter of a solute can be calculated from the solubility curve using the following equation:

$$RT_c = \frac{2x_1x_2V_1^2V_2^2}{(x_1V_1+x_2V_2)^3}B \quad , \tag{15}$$

where T_c is the critical solution temperature and the x's indicate mole fractions at T_c. In order to have unmixing at no lower than 25°C, in the case of two liquids with equal molal volumes of 100 cc., B would have to be at least 11.5.

Flory (16) has shown that the critical condition for incipient separation into two phases occurs when:

$$B\ (\text{critical}) = \frac{RT}{2V_1}\left(1+X^{1/2}\right)^2 \quad , \tag{16}$$

and that the critical composition, $\varphi_{2,c}$, is given by the expression:

$$\varphi_{2,c} = \frac{1}{1+X^{1/2}} \quad . \qquad (17)$$

The critical composition is the concentration at which phase separation first appears on passage to the two phase region.

In Table I are listed some representative values for B (critical) and $\varphi_{2,c}$ at various values of X.

Table I

B AND $\varphi_{2,c}$ AS A FUNCTION OF X AT 300° K
$V_1 = 100$

X	B (critical)	$B^{1/2}$	φ_2 (critical)
1	11.88	3.45	0.500
2	8.65	2.94	0.414
4	6.68	2.58	0.333
7	5.64	2.37	0.274
10	5.15	2.27	0.240
100	3.59	1.89	0.091
1000	3.16	1.78	0.031

Inspection of Table I shows that the solubility curve has its maximum at 0.5 volume fraction for equal molal volumes and shifts to lower polymer concentrations as the molecular weight of the polymer is increased. Several investigators have tested the applicability of Equation 17 and have found both critical compositions larger than those predicted (57) and smaller (49). Part of the present study was concerned with testing the applicability of Equation 17 to a low molecular weight polymer in several solvents.

If we solve Equation 16 it is found that a high polymer (V_2 =100, 000) is soluble in solvents (V_1= 100) which satisfy the following conditions:

$$(\delta_2 - 0.89) < \delta_1 < (\delta_2 + 0.89) \quad , \qquad (18)$$

whereas for liquids of equal molal volumes:

$$(\delta_2 - 1.73) < \delta_1 < (\delta_2 + 1.73) \quad . \qquad (19)$$

Thus a polymer is soluble over a much smaller range of solvents than a corresponding low molecular weight compound. Since the solubility parameter for a polymer can not be determined from the energy of vaporization it can be determined (1) by applying Equation 15, or (2) by testing its solubility in a series of solvents having different solubility parameters. These procedures have been applied in the present study.

Solubility data are a necessary preliminary to heat of solution measurements because a qualitative understanding of interactions must be reached before quantitative heat measurements are made.

Intrinsic Viscosity of Dilute Solutions - In an energetically unfavorable solvent (at low polymer concentration) polymer segments will attract each other and thus will tend to reduce polymer-solvent contacts. The favoring of polymer-polymer contacts will cause the curling up of the polymer molecules in such solutions. Polymer-solvent contacts are preferred in an energetically more favorable solvent and thus the polymer molecules will tend to uncurl and form a chain type structure in solution. In this type of solution the molecule will be extended and thus will offer more resistance to flow. Therefore its solution viscosity will be higher than that of a curled-up molecule. These predictions have been substantiated by several investigators (2, 9, 56). Intrinsic viscosity thus gives us an indication of the relative shape of the molecule in solution.

This study was thus undertaken in order to investigate certain aspects of the behavior of low polymer solutions. Comparisons with the behavior of high polymer solutions are made. Critical composition and solubility relationships were investigated in a wide variety of organic solvents. Heats of solution in twenty one different solvents at low polymer concentration were measured. The variation of the heat of solution with molecular weight was measured in three different solvents. Intrinsic viscosity measurements were then correlated with the heats of solution. Finally, the results were compared with present theory and experimental data.

CHAPTER II

EXPERIMENTAL

The materials and methods used to measure solubility, heats of solution, intrinsic viscosity, and vapor pressure are discussed in the following section.

Polymers and Solvents

Polymers - The four polymers used in this study were low molecular weight synthetic resins*. They included two coumarone-indene, one modified polystyrene, and one modified methyl styrene resin. Some of the pertinent properties of these polymers are given in Tables II and III.

Resins I and II were identical to those used by Pieski (43)** except that different samples were used which may have slight variations in properties. Resin IV is the same sample as used by Pieski and the molecular weight fractions prepared by him were used in the present study for solubility and heat of solution measurements. The molecular weight and softening points of these fractions are listed in Table IV. The three highest molecular weight fractions are "solids" having a density of 1.09 g./cc. whereas the X-5 fraction is a viscous, tacky liquid having a density of 1.25 g./cc. The four unfractionated resins all have

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* Manufactured by Pennsylvania Industrial Chem. Corp.

** Resins I, II, and IV correspond to Pieski's numbers II, IV, and II respectively.

Table II

PROPERTIES OF POLYMERS

Material	Type	Mol. Wt.	Method	Softening Pt. °C[2]	Iodine No.	Aniline Point[4]
Resin I	coumarone-indene	769	1	100	55	60° C
		1023	2			
		765	3			
Resin II	modified polystyrene	914	1	115	--	19
		2868	2			
		973	3			
Resin III	mod. methyl styrene	645	1	100	135	∠10
Resin IV	(coumarone)-indene	749	1	105	41	60
		1023	2	86[3]		
		765	3			

Methods: 1 Cryoscopic
2 Weight Average; calculated from data of Pieski (43)
3 Number Average: calculated from data of Pieski (43)

[2] Ring and Ball
[3] Capillary Method
[4] Solution temperature of equal weights of aniline and sample

Table III

CHEMICAL ANALYSIS OF RESINS I AND IV

Material	%C	%H	%O
Resin I	87.4	8.8	3.8
Resin IV	91.5	7.9	0.6
Polyindene ($C_{63}H_{56}$)	93.1	6.9	0

Table IV

MOLECULAR WEIGHTS AND SOFTENING POINTS OF FRACTIONS

Fraction Number	Molecular Weight (Cryoscopic)	Softening Point (Capillary)
X-1	1790	162 °C.
X-2	1350	135
X-3	842	94
X-4	401	27

densities very close to 1.09 g./cc. Resins I and IV are similar except that they were manufactured at different times and thus vary somewhat in their properties. The chemical analysis shows that Resin IV contains little or no coumarone since the oxygen content is quite low. Thus it will be referred to as a polyindene polymer.

Resins I and IV largely consist of polymers of indene and methyl indene. Resin II is a mixture of about 75% low molecular weight polystyrene and 25% polyindene, each polymerized separately. The chief constituents of Resin III were isomers of methyl styrene with small amounts of triolefins and straight chain compounds also present. The infrared spectra of these polymers are presented in Figures 20-23, Appendix IV.

Solvents - The organic solvents used in the solubility studies were reagent grade chemicals, dried over anhydrous $MgSO_4$. The solvents used for the heat of solution measurements were dried over $MgSO_4$ and distilled. The benzene was washed with concentrated sulfuric acid, dried over sodium, and distilled.

The mineral oil was a standard blend* of paraffin hydrocarbons adjusted to an aniline point of 102°C. This is the standard aniline point used in many laboratories to test solubility properties of the type of resins used in this study.

Experimental Techniques of Measuring Solubility, Heats of Solution, and Intrinsic Viscosity

Solubility - Solubility of the resins and mixtures of resins in mineral oil was determined by heating a weighed sample of the resin (or resins) and oil in a four inch test tube in a glycerol bath until solution was effected. The bath was then cooled slowly with the thermometer immersed in the solution until a definite separation or "cloud" was evident with stirring. In order to facilitate the detection of the precipitation temperature the sample tube was illuminated by a conventional microscope illuminator. This method has been widely used (17, 41, 45-49) to determine phase equilibria of high polymer-solvent systems and has been found to give satisfactory and reproducible results. The precipitation temperature thus obtained is assumed to be that of a system substantially at equilibrium. This is substantiated by the experimental observation that the "cloud" disappears almost immediately if the sample at the precipitation temperature is slowly reheated. Flory (17) has claimed reproducibility to ± 0.1°; in this study the uncertainty in the precipitation

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*Prepared by blending 65 parts of Nujol with 35 parts of No. 415 oil (Magie Brothers, Chicago) temperature in most determinations was ± 0.2°. The greater uncertainty is due to the fact that the change of light transmission with temperature is less abrupt for low molecular weight materials than for high molecular weight materials (4). Thus the "cloud point" is not quite as sharp. At concentrations greater than 0.15 volume fraction the uncertainly rose to as much as ± 1.0°.

Solubility in all other solvents was determined in a similar manner except that sample tubes were reweighed after the determination if a volatile solvent was used in order to determine the amount of solvent lost by evaporation. In most cases this effect was very small.

Heats of Solution - The thermistor calorimeter which was used to measure the heats of solution has been described previously (69, 72). Sample bulbs were blown from 8 mm. Pyrex tubing. Finely powdered resin was weighed into the bulbs which were then sealed off and placed in the sample holder of the calorimeter. 200 ml. of organic solvent at a temperature below 26° C was added to the Dewar flask. The calorimeter was then assembled and allowed to equilibrate in the air bath for at least one hour. Time-resistance readings were then taken every minute until a constant rating period of not greater than 0.0020 ohms* per minute was attained. The sample bulb was then broken under the liquid and time-resistance readings were continued until a constant

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* Temperature coefficient of resistance of thermistor is -4 ohms/degree C.

final rating period was attained. A typical time-resistance diagram and calculation is shown in Figure 24, Appendix V. Calibrations were made each time by measuring the resistance change caused by a known amount of electrical energy introduced by the heater. An electric timer was used to determine the length of time the heater was on.

The calculated calorimeter error, excluding the heat of breaking, was about ± 2% (69). Blank runs were made to determine the heat effect produced in the breaking of the sample bulb. The heat of breaking was about -0.02 calories for solvents boiling above 100° C. For more volatile solvents the average heat of breaking was +0.25 calories. In this case the reproducibility was not very good, the average deviation being 0.04 cal. This relatively large deviation is in agreement with the results of Bartell and Suggitt (3). A longer time was needed to attain equilibrium after breaking the sample bulb in the case of the volatile solvent.

All heat of solution measurements were made between 26.0 and 26.2° C (± 0.005). About two hundred separate heat of solution measurements were made in this study.

Intrinsic Viscosities - Solution viscosities were measured at 24.98 ± 0.03° C. using an Ostwald-Fenske No. 50 viscometer with approximately 0.40 mm. diameter capillary having a flow time of 158.9 seconds for benzene. Concentrations of approximately 0.5, 1.0, and 1.5 grams of resin per 100 ml. of solvent were used. Separate solutions were prepared for each concentration and allowed to stand at least 24 hours after they were prepared before any measurements were made. Extreme care was taken to remove all dust and dirt particles. Solutions were filtered twice before each determination and the viscometer was cleaned with cleaning solution after each run. Solutions were transferred to the viscometer using a 10 ml. pipette after preliminary equilibration at 25.00°C.

Vapor pressure - Preliminary vapor pressure measurements were made of benzene solutions of Resin IV using the apparatus depicted in Figure 25, Appendix VI. Measurements were made at 26.2°C. The manometer levels were read with a cathatometer. Samples of polymer and benzene were weighed into the sample tube and the solution degassed by freezing and melting under vacuum several times (at higher polymer concentrations the solution did not freeze). Concentrations were changed by distilling off the benzene under vacuum. To attain higher concentrations samples were also heated. Concentrations were determined by weighing the sample tube after each determination. The apparatus was allowed to come to equilibrium at least one hour before readings were taken. The time required to reach equilibrium increased markedly as the polymer concentration was increased.

CHAPTER III

SOLUBILITY OF POLYMER-MINERAL OIL SYSTEMS

The precipitation temperatures of Resin I (coumarone-indene) and Resin II (modified polystyrene) in mineral oil were determined at resin concentrations from about 1 to 80% as shown in Figure 1. Resin III was completely soluble in mineral oil at all concentrations. Figure I also indicates the usual behavior for a polymer-solvent system (57) where $\varphi_{2,c}$ occurs at a value much less than 0.5.

The precipitation temperatures of three-component mixtures of Resins I, II, and III with mineral oil were determined and the results plotted on triangular coordinates. These results are shown in Figures 2, 3, and 4 plotted as isotherms at various temperatures. The numbers on the isotherms indicate the temperature. The resins are all completely soluble in each other at all concentrations.

The curves indicate that Resin I is much more soluble in mineral oil than Resin II. Mixtures of Resin I and III with mineral oil show regular changes in solubility; the precipitation temperature decreased regularly as the ratio of Resin III to Resin I is increased. In contrast to this, systems containing Resin II maintain a constant precipitation temperature as the ratio Resin II/Resin I or Resin II/Resin III is decreased until a low concentration of Resin II is attained.

Figure 1

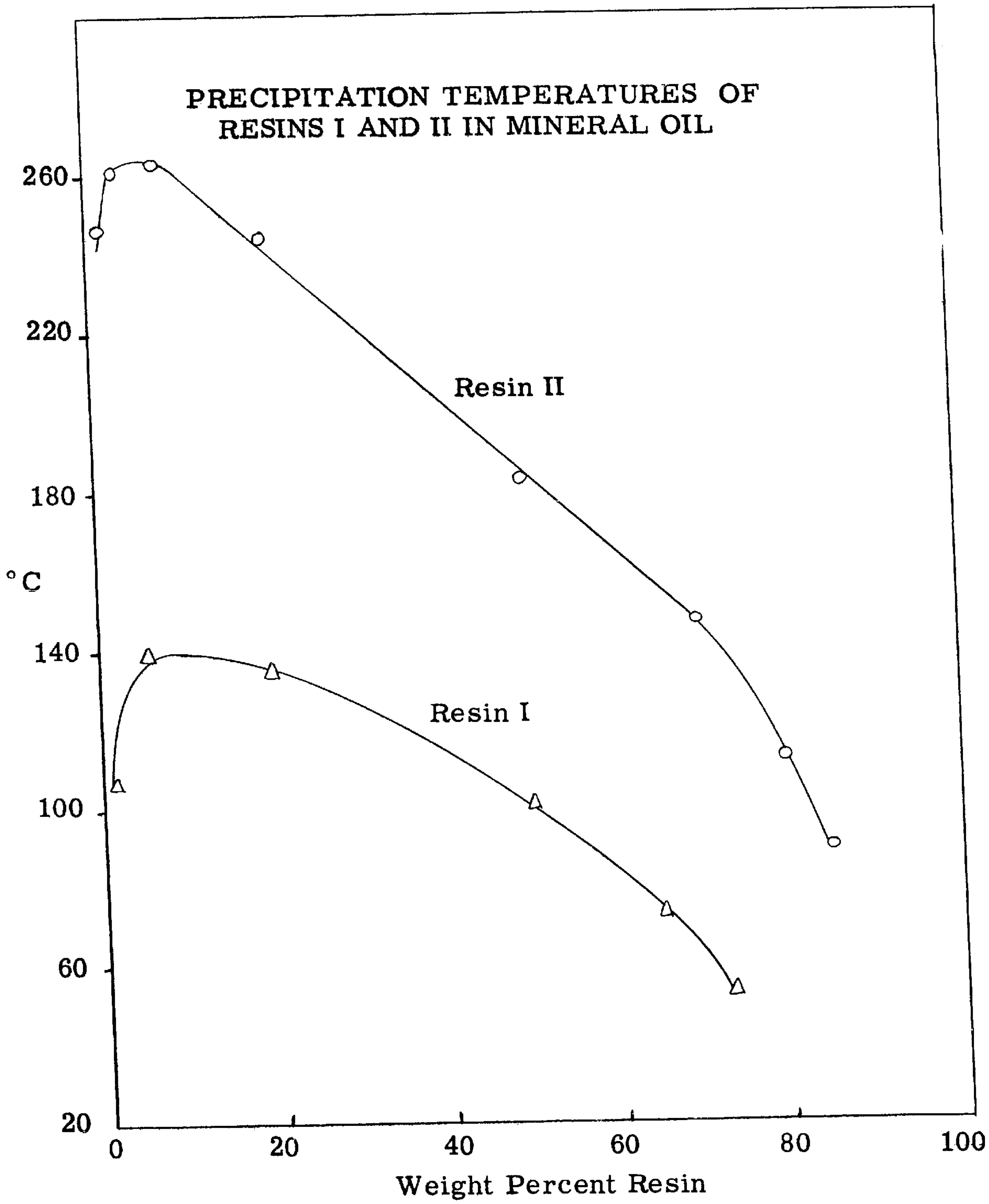

PRECIPITATION TEMPERATURES OF RESINS I AND II IN MINERAL OIL
Resin II
Resin I
°C
260
220
180
140
100
60
20
0
20
40
60
80
100
Weight Percent Resin

Figure 2

PRECIPITATION TEMPERATURES OF RESIN I - RESIN III - MINERAL OIL SYSTEM

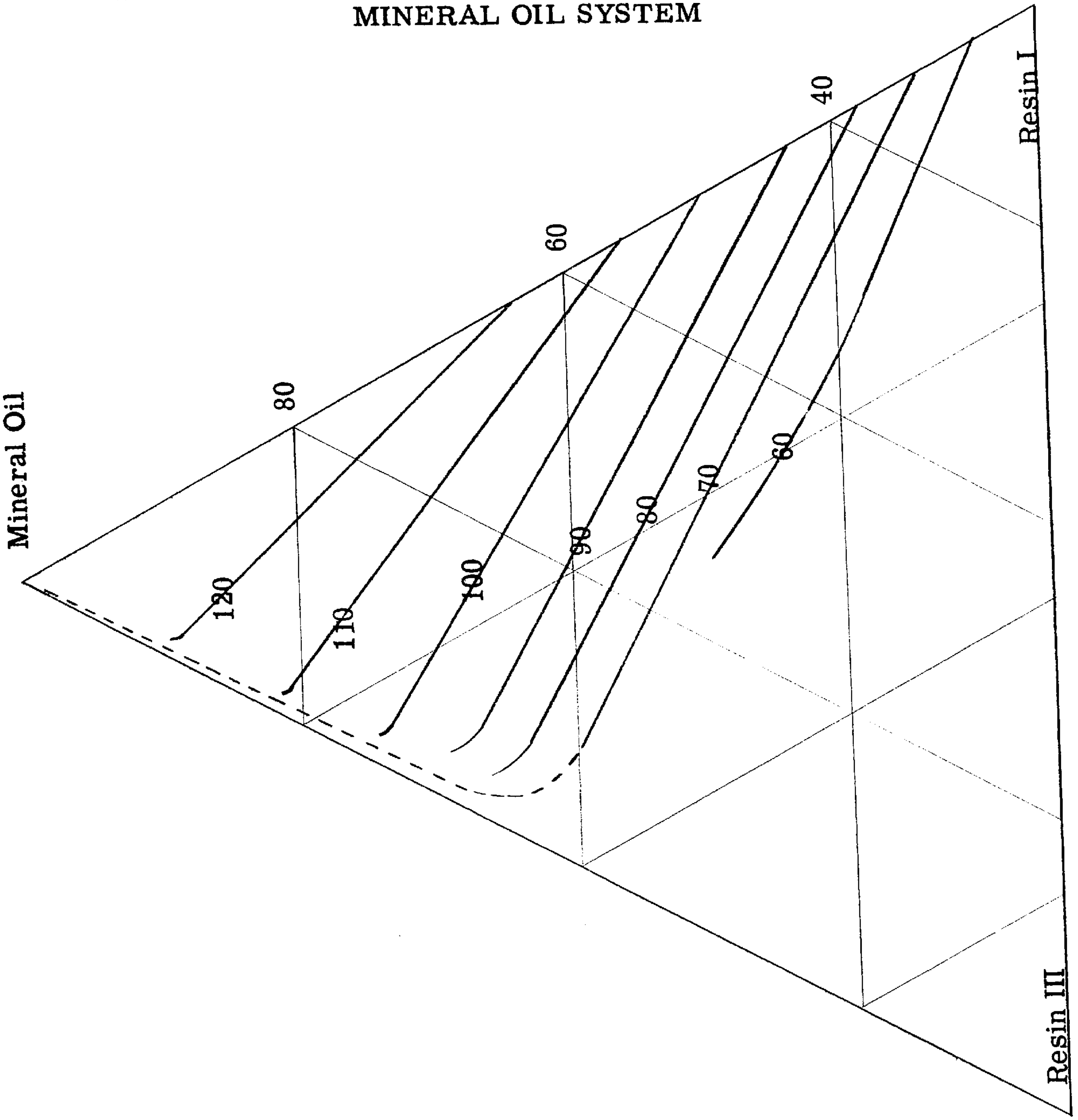


Figure 3

PRECIPITATION TEMPERATURES OF RESIN I – RESIN II – MINERAL OIL SYSTEM

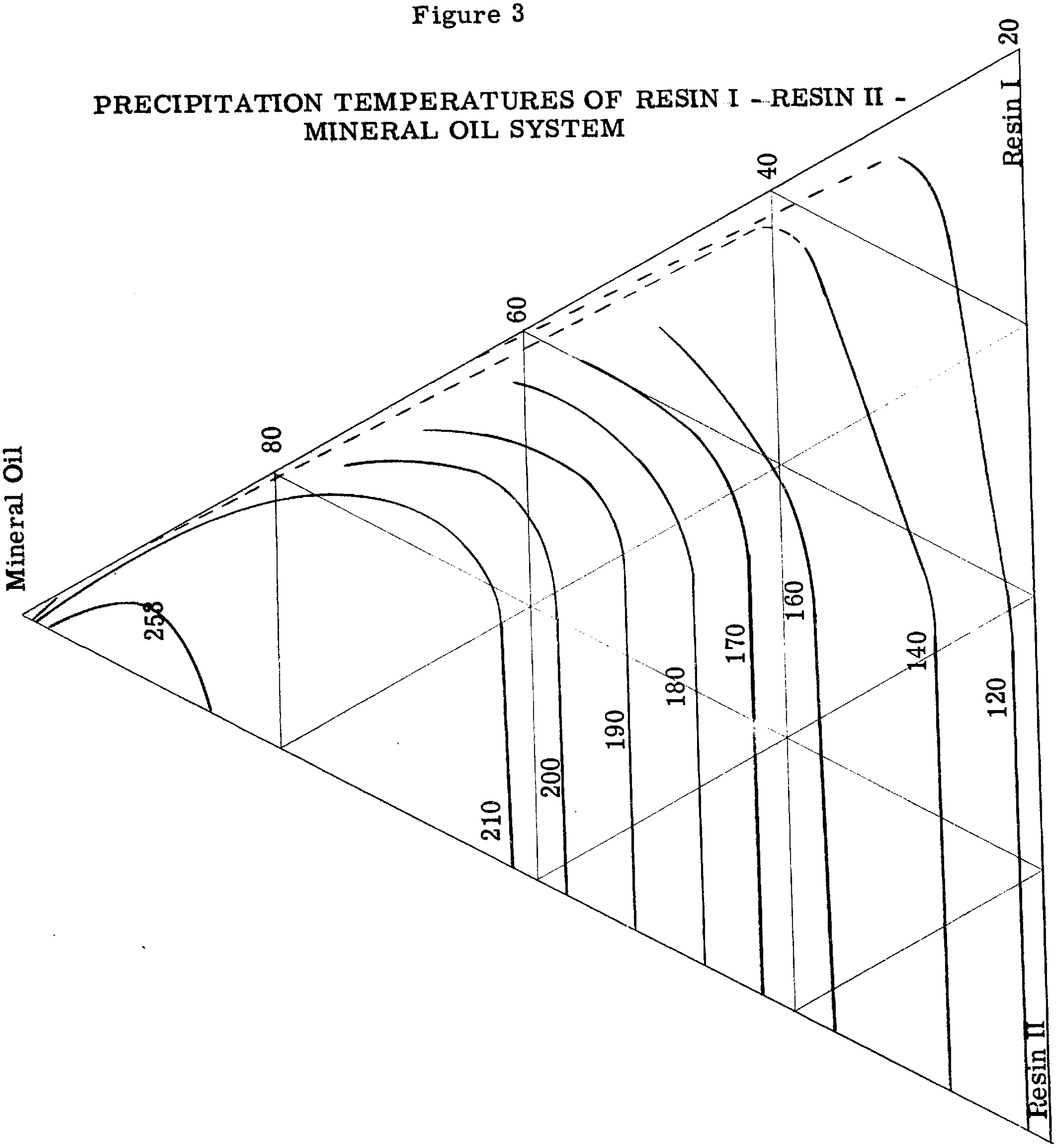
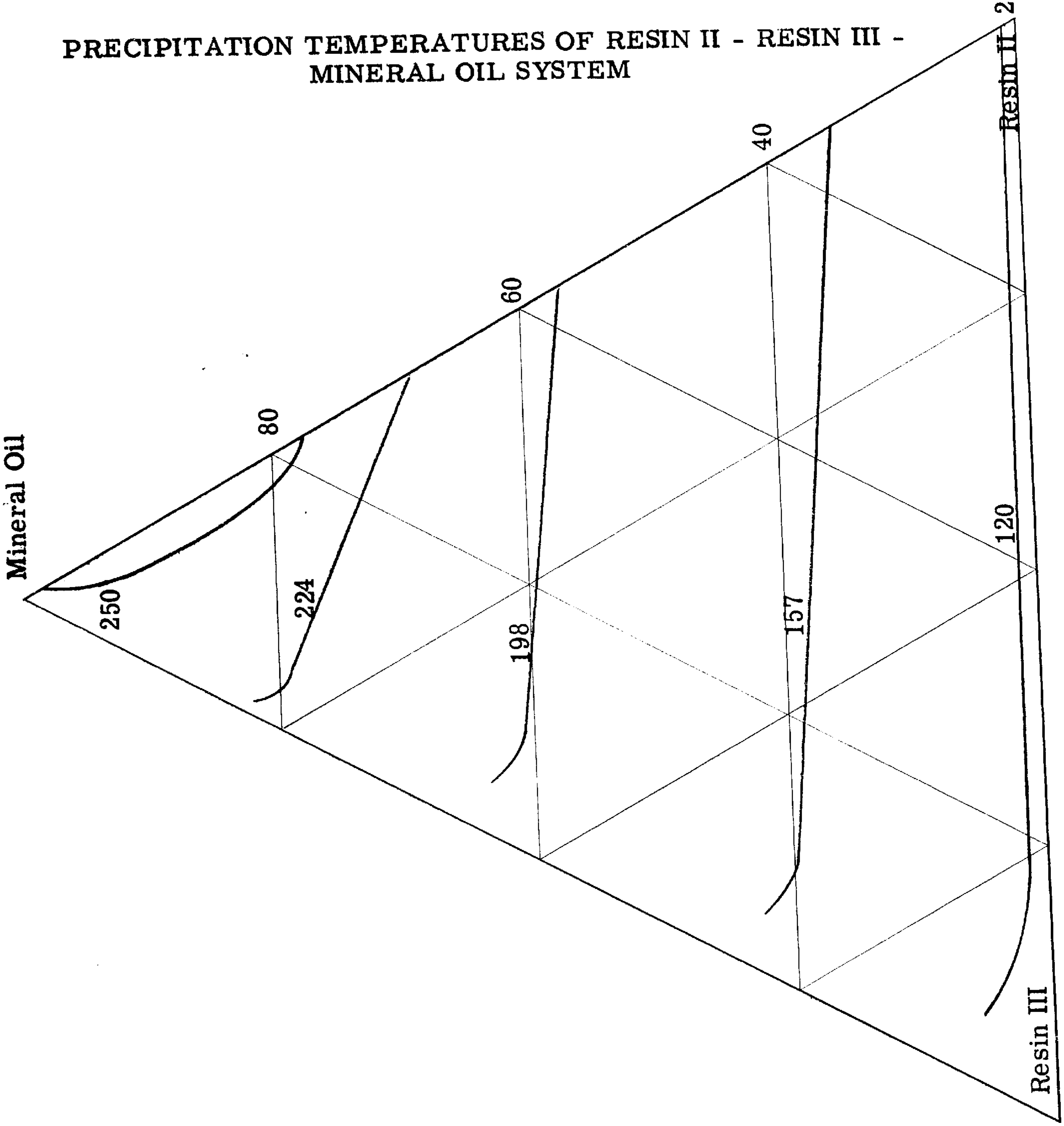


Figure 4

PRECIPITATION TEMPERATURES OF RESIN II - RESIN III - MINERAL OIL SYSTEM



The phase diagram for the system Resin I - Resin III - mineral oil, shown in Figure 2, exhibits a close similarity to the phase relationships for the system polystyrene - toluene - normal paraffin hydrocarbon studied by Powers (45, 47). The comparison indicates that Resin III exhibits a behavior similar to toluene which is the solvent in Powers' system. This analogy seems reasonable since Resin III is completely soluble in mineral oil. Further analysis shows, however, that the critical resin composition is not appreciably increased (as it is with toluene) as Resin III is added to either Resin I-mineral oil or Resin II-mineral oil mixtures. This finding is emphasized in Figures 5 and 6 where the results are redrawn by plotting precipitation temperatures against resin concentration at various ratios of Resin III to mineral oil. The numbers on the curves indicate the percentages of Resin III in the mineral oil - Resin III mixtures.

At a Resin III content of 40%, Resin I-mineral oil mixtures were soluble in all proportions above 50° C. Complete miscibility above 20° C at all concentrations occurs when the Resin III content is 50% or greater. Exact data for this system below 50° C are not shown. The high viscosity of the mixtures below 50° C makes the determination of precise precipitation temperatures difficult. Figure ~~6~~ 5 indicates that the critical resin composition is only increased from 5 to 8% as the percentage of Resin III is increased. This indicates that Resin III is a relatively poor solvent for Resin II-mineral oil mixtures even though

Figure 5

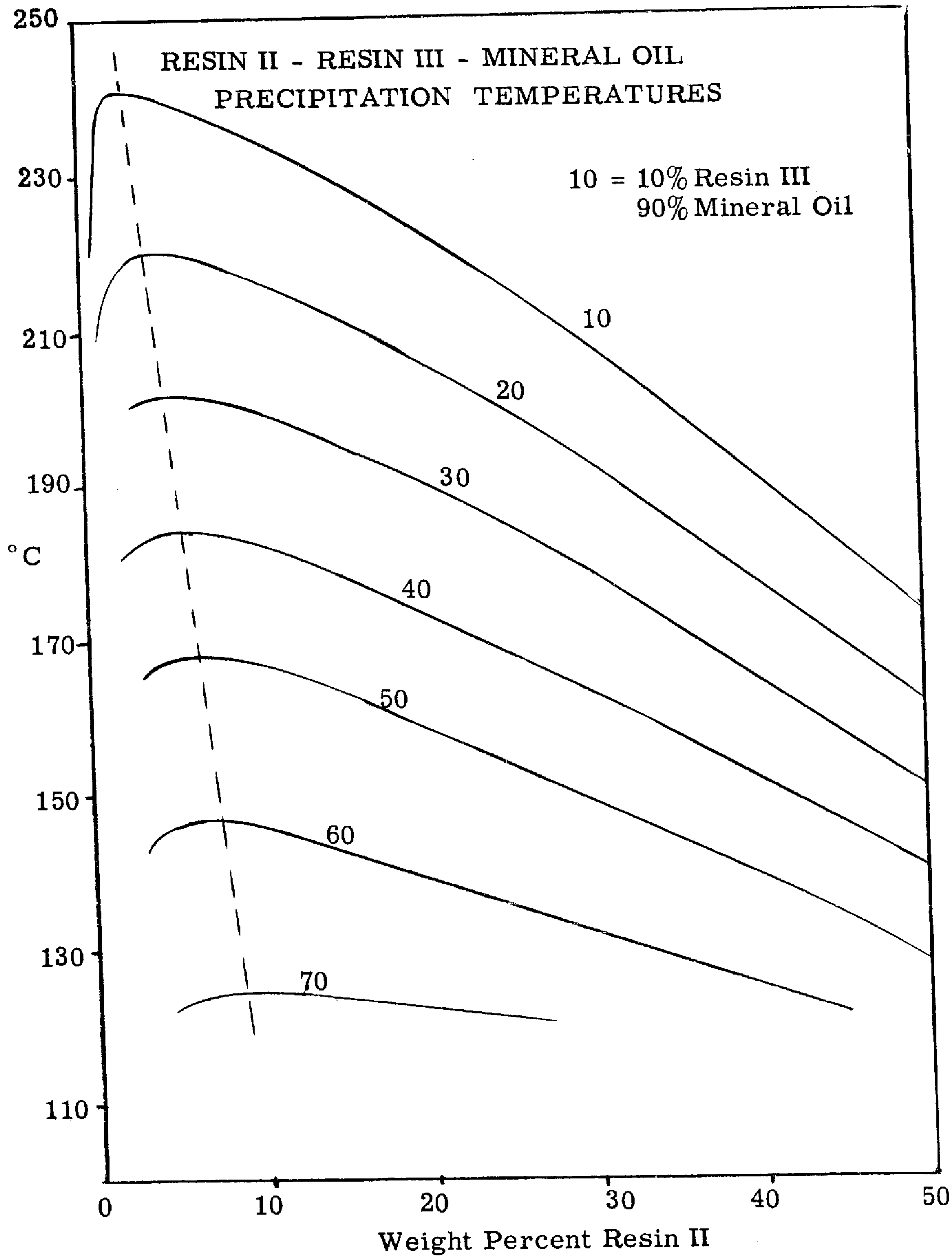
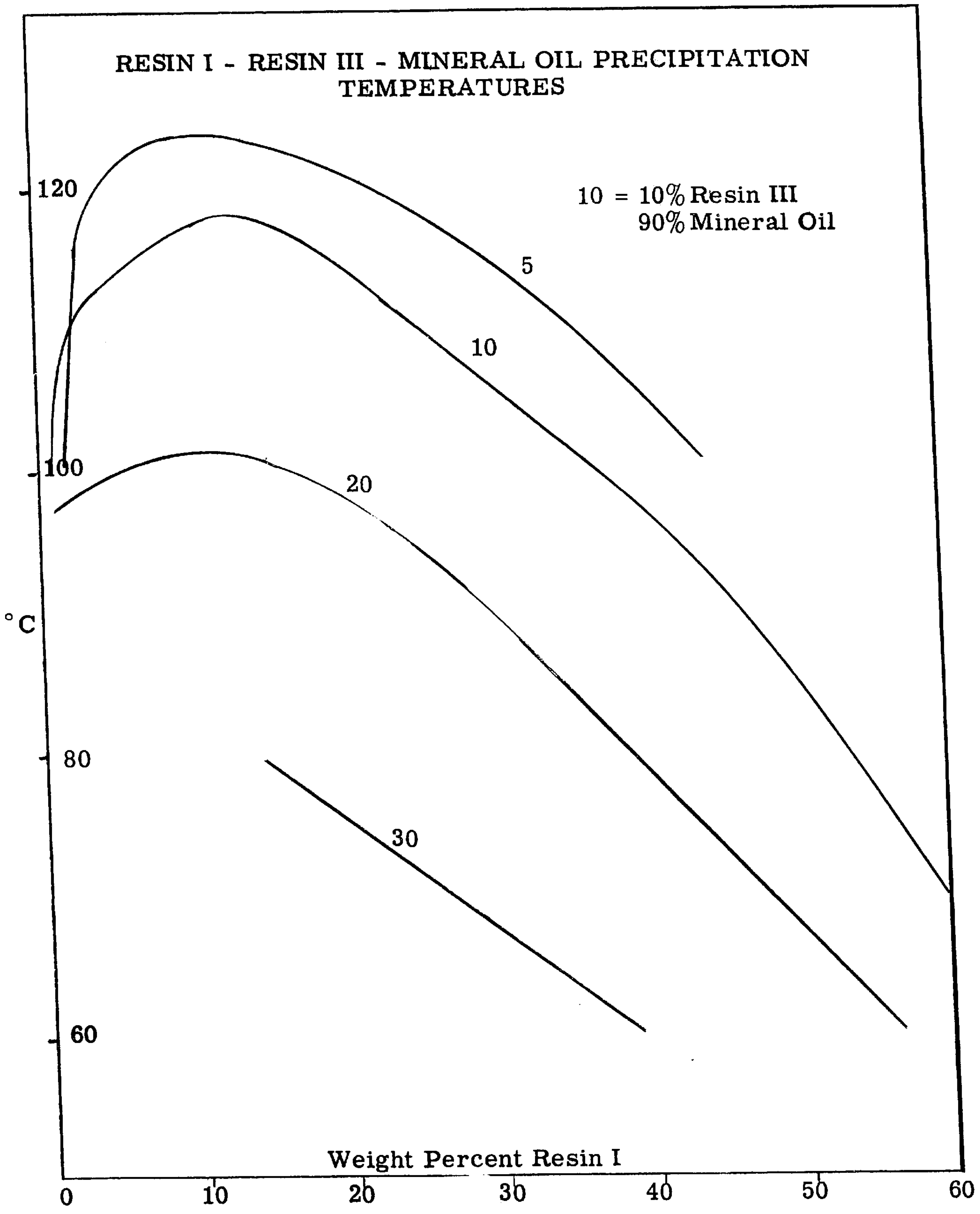

RESIN II - RESIN III - MINERAL OIL
PRECIPITATION TEMPERATURES
10 = 10% Resin III
90% Mineral Oil
10
20
30
40
50
60
70
250
230
210
190
170
150
130
110
°C
0
10
20
30
40
50
Weight Percent Resin II

Figure 6


RESIN I - RESIN III - MINERAL OIL PRECIPITATION TEMPERATURES
10 = 10% Resin III
90% Mineral Oil
5
10
20
30
120
100
80
60
°C
Weight Percent Resin I
0
10
20
30
40
50
60

it is miscible in all proportions with the components individually.

Resin II appears to superimpose its insolubility on mixtures of Resin I or III and mineral oil. In other words, Resin II controls the precipitation temperature of the system. This superposition is attributed to the fact that Resin II contains a high molecular weight fraction which greatly influences its solubility characteristics. Mixtures of Resin I and III with mineral oil show a regular change in solubility because their molecular weight distribution curves are quite similar. The enhanced solubility of Resin III in mineral oil is attributed in part to increased content of unsaturates in this resin* as indicated by its high iodine number.

These preliminary studies point up several important observations, namely:

1. The precipitation temperature, or solubility, of an unfractionated polymer is principally controlled by the highest molecular weight fraction.

2. The solubility curves for the low polymers used in this study exhibit critical compositions at unusually low polymer concentrations. In this respect they act like polymers of much high molecular weight.

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* Effect of unsaturation on solubility is further discussed on page 46.

3. A polymer, e. g. Resin III, although it is completely miscible in the system, does not act like a true solvent because it does not appreciably change the critical composition.

4. Although several polymers (i. e. Resins I, II, and III) have solubility parameters which are almost identical (see Chapter IV) their quantitative solubilities in a particular system may be quite different.

CHAPTER IV

SOLUBILITY OF POLYMERS IN PURE ORGANIC SOLVENTS

A. Determination of Solubility Parameters of Polymers

The solubility of Resins I, III, and IV were determined in a wide variety of organic solvents. The type of solubility curve obtained is essentially the same as that presented in Figure 1. The maxima in the solubility curves show some differences in the critical composition. The critical composition varies from about 0.5 to 0.1 depending on the nature of the solvent. The types of cruves obtained are discussed in more detail in the next section.

Solubility of Resins I, III, and IV were determined at 20 weight percent by the methods previously discussed. These data are given in Tables V and VI. Table V lists data for solvents whose solubility parameters are known. Due to the fact that heats of vaporization for some compounds have not been determined, and so are not available in the literature, solubility parameters for many common solvents and plasticizers are not known. Solubilities of Resins I, II, and IV have been determined in several of these solvents in order to provide a wider range of data. Results obtained with these solvents are listed in Table VI. In comparison with the data for these polymers, Gauger and Breston (20) have qualitatively determined the solubility of indene and coumarone monomers. They found them to be com-

Table V

SOLUBILITY OF RESINS I, III, and IV

20% by weight resin

Solvent	δ solvent	Resin I	Resin III	Resin IV
n-hexane	7.3	i	i	i
n-heptane	7.4	i	i	i
ethyl ether	7.4	s	s	s
n-octane	7.55	i	i	i
n-octadecane	8.2	180	136	170
cyclohexane	8.2	78	i	s
dimethyl aniline	8.4	s	s	s
benzonitrile	8.4	s	s	s
n-butyl chloride	8.4	s	s	s
methyl chloroform	8.5	s	s	s
carbon tetrachloride	8.6	s	s	s
ethyl benzene	8.8	s	s	s
ethyl acetate	9.1	s	s	s
benzene	9.15	s	s	s
chloroform	9.3	s	s	s
methyl ethyl ketone	9.3	s	s	s
dibutyl phthalate	9.3	s	s	s
chlorobenzene	9.5	s	s	s
nitrobenzene	10.0	s	s	s
carbon disulfide	10.0	s	s	s
pyridine	10.7	s	s	s
1-nitropropane	10.7	s	s	s
aniline	10.73	65	s	65
n-amyl alcohol	10.9	106	46	83
nitroethane	11.1	54	82	50
n-butyl alcohol	11.4	110	84	102
cyclohexanol	11.4	s	s	s
acetonitrile	11.9	i	i	i
nitromethane	12.6	i	i	i
methyl alcohol	14.5	i	i	i

---

s = soluble above 5°C
i = insoluble at boiling point of solvent
Temperature indicates precipitation temperature, °C

pletely miscible with most common solvents, such as alcohols, ethers, ketones, naphthas, pyridine, carbon disulfide, carbon tetrachloride, and chloroform. Partial miscibility was found with some of the glycols, amines, and ethanol amines. The indene type polymers used in this study were completely miscible with esters, ketones, and many of the common solvents such as benzene, carbon tetrachloride, pyridine, and chloroform. Partial miscibility was found with the paraffin hydrocarbons, the alcohols, nitromethane, nitroethane, and aniline.

The solubility parameter for Resin I was calculated from the data given in Table V using the relationships between B, δ_1 , and δ_2 as expressed in Equations 16-19. This procedure gave a value of approximately 9.4 for the solubility parameter of Resin I. The solubility parameter of Resin IV is about the same or slightly lower even though inspection of the data show~~n~~s that it is somewhat more soluble than Resin I. The decreased solubility of Resin I is tentatively attributed to its higher oxygen content. The solubility parameter for Resin III is probably slightly lower than 9.4 because of its increased solubility in octadecane (δ_1 = 8.2) and its decreased solubility in nitroethane (δ_1 = 11.1). The parameter for polystyrene (mol. wt. 90,000) was determined by Edelson (13) to be 9.2 using the same procedure as above; this value approximates the value for Resin II since it has been shown that the solubility parameter of a polymer is not

Table VI

SOLUBILITY OF RESINS I, III, AND IV

20% by weight resin

Solvent	Resin I	Resin III	Resin IV
methyl aniline	s	s	s
morpholine	16	10	s
acetic acid	i	i	i
propionic acid	100	s	s
n-butyl amine	29	s	s
2-ethyl hexyl amine	79	s	23
2-ethyl hexyl alcohol	90	-1	67
hexylene glycol	i[2]	139	137
methyl benzyl alcohol	s	s	s
tributyl phosphate	s	s	s
tributyl citrate	s	s	s
butoxy ethyl stearate	s	s	s
methyl cyclohexyl stearate	s	s	s
methoxy ethyl oleate	s	s	s

s = soluble above 5°C
i = insoluble at boiling point of solvent
Temperature indicates precipitation temperature, °C
[2] insoluble at 160°C

dependent on its molecular weight and does not appreciably differ from its monomer.

The solubility parameters of the four polymers used in this study thus do not differ appreciably. This is not surprising since we know that there is considerable chemical similarity among the four polymers.

The relation between critical solution temperature, critical composition (expressed as mole fractions), and solubility parameters is given by Equation 15. The solubility of Resins I and IV in aniline has been determined over a wide range of concentrations. The solubility curves thus obtained are presented in Figure 7. The solubility parameter was calculated from these data using Equation 15. The value for both Resins I and IV was found to be 8.9. The agreement of this value with the value determined above (9.4) is good, especially considering the fact that aniline is a hydrogen-bonding solvent. The solubility parameters of Resins I and IV check well with that for indene which may be considered their monomeric model*. The solubility parameter for indene is 9.1.

B. Critical Composition

The theoretical value for the critical composition is given by Equation 17. In the early stages of this work it was noticed that the critical composition for some of the polymer solutions was much smaller than predicted by theory (see Figure 1.) Table VII lists the systems studied, their experimental and theoretical critical compositions, and their critical solution temperatures. The solubility curves obtained are presented in Figures 8, 9, and 10. Figure 8 also includes data on n-dodecane and n-heptane to indicate the influence of paraffin

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* Indane is perhaps a better monomeric model for polyindene but data for the calculation of its solubility parameter was not available. Value for indene calculated from the heat of vaporization (44).

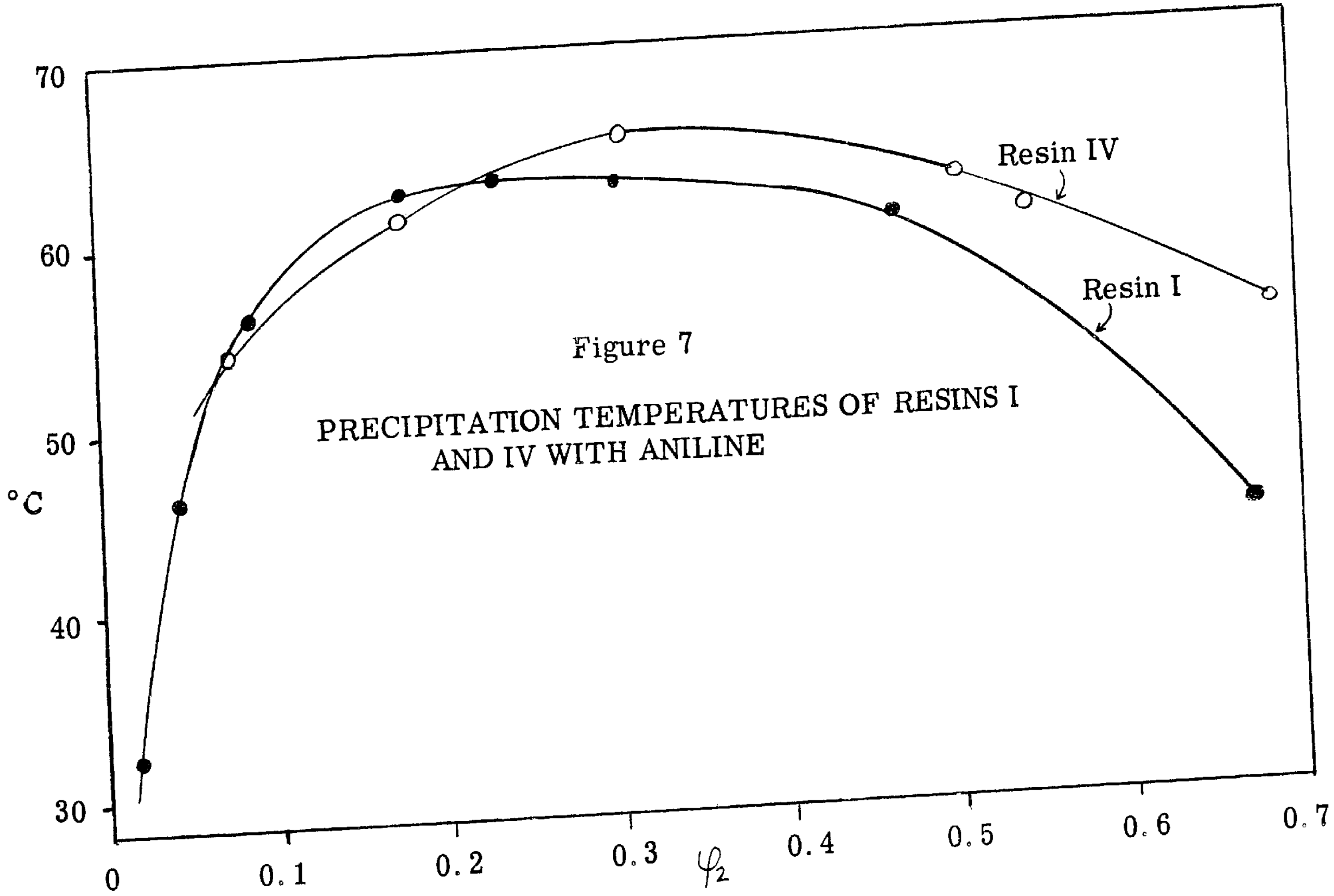


Figure 7

PRECIPITATION TEMPERATURES OF RESINS I AND IV WITH ANILINE

Table VII

CRITICAL COMPOSITIONS OF POLYMER-SOLVENT SYSTEMS

Solvent	Solute	φ_2 (critical) calculated	φ_2 (critical) exptl.	t_c, °C
Aniline	Resin I	0.265	0.25	63
Aniline	Resin IV	0.265	0.34	65
Nitroethane	Resin IV	0.242	0.24	53
Octadecane	Resin I	0.41	0.08	180
Octadecane	Resin IV	0.41	0.12	170
Octadecene-1	Resin IV	0.41	0.12	122
Amyl Alcohol	Fraction X-1	0.204	0.116	113.5
Amyl Alcohol	Fraction X-2	0.228	0.095	90
Amyl Alcohol	Fraction X-3	0.272	0.135	57.5
Amyl Alcohol	Fraction X-5	0.352	0.116	18
Amyl Alcohol	Resin IV	0.284	0.118	85
4 Pentenol-1	Fraction X-1	0.204	0.116	85.5
4 Pentenol-1	Fraction X-3	0.272	0.15	27
Heptyl Alcohol	Fraction X-1	0.227	0.131	115
Heptyl Alcohol	Fraction X-2	0.253	0.097	96
Heptyl Alcohol	Fraction X-3	0.300	0.135	58.6
Heptyl Alcohol	Fraction X-5	0.383	0.113	17

Figure 8

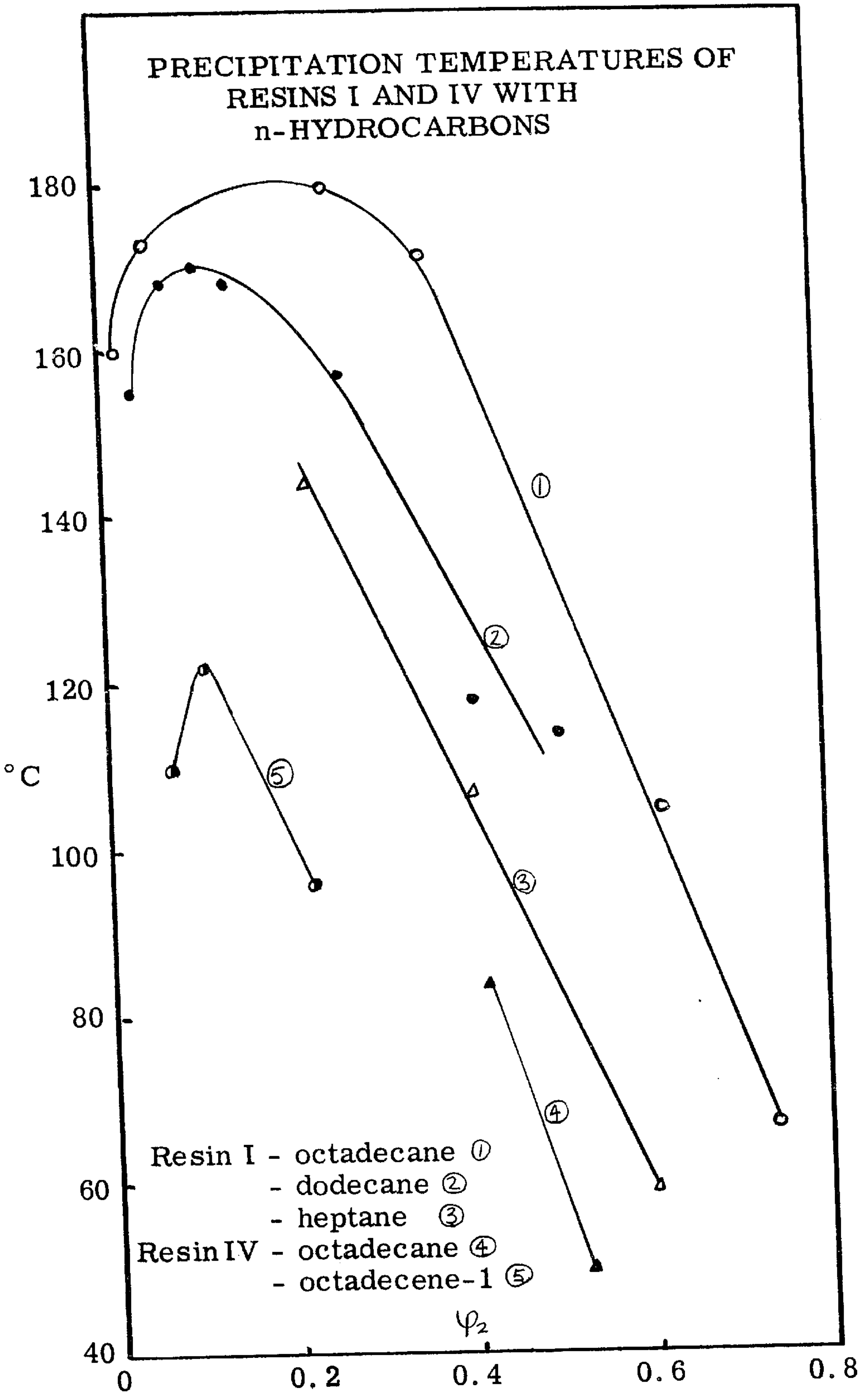

PRECIPITATION TEMPERATURES OF RESINS I AND IV WITH n-HYDROCARBONS
180
160
140
120
100
80
60
40
°C
0
0.2
0.4
0.6
0.8
φ_2
①
②
③
④
⑤
Resin I - octadecane ①
- dodecane ②
- heptane ③
Resin IV - octadecane ④
- octadecene-1 ⑤

Figure 9

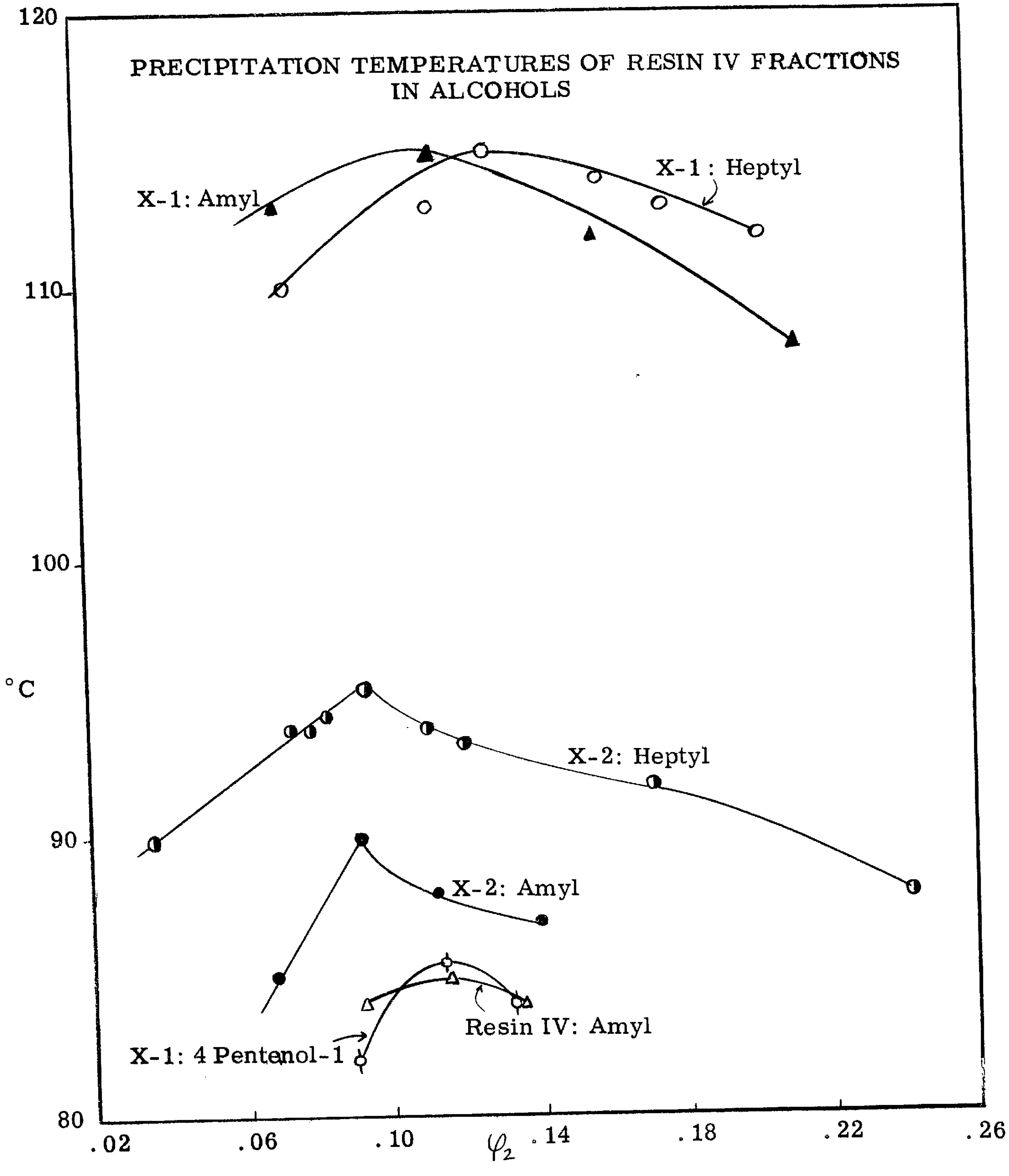
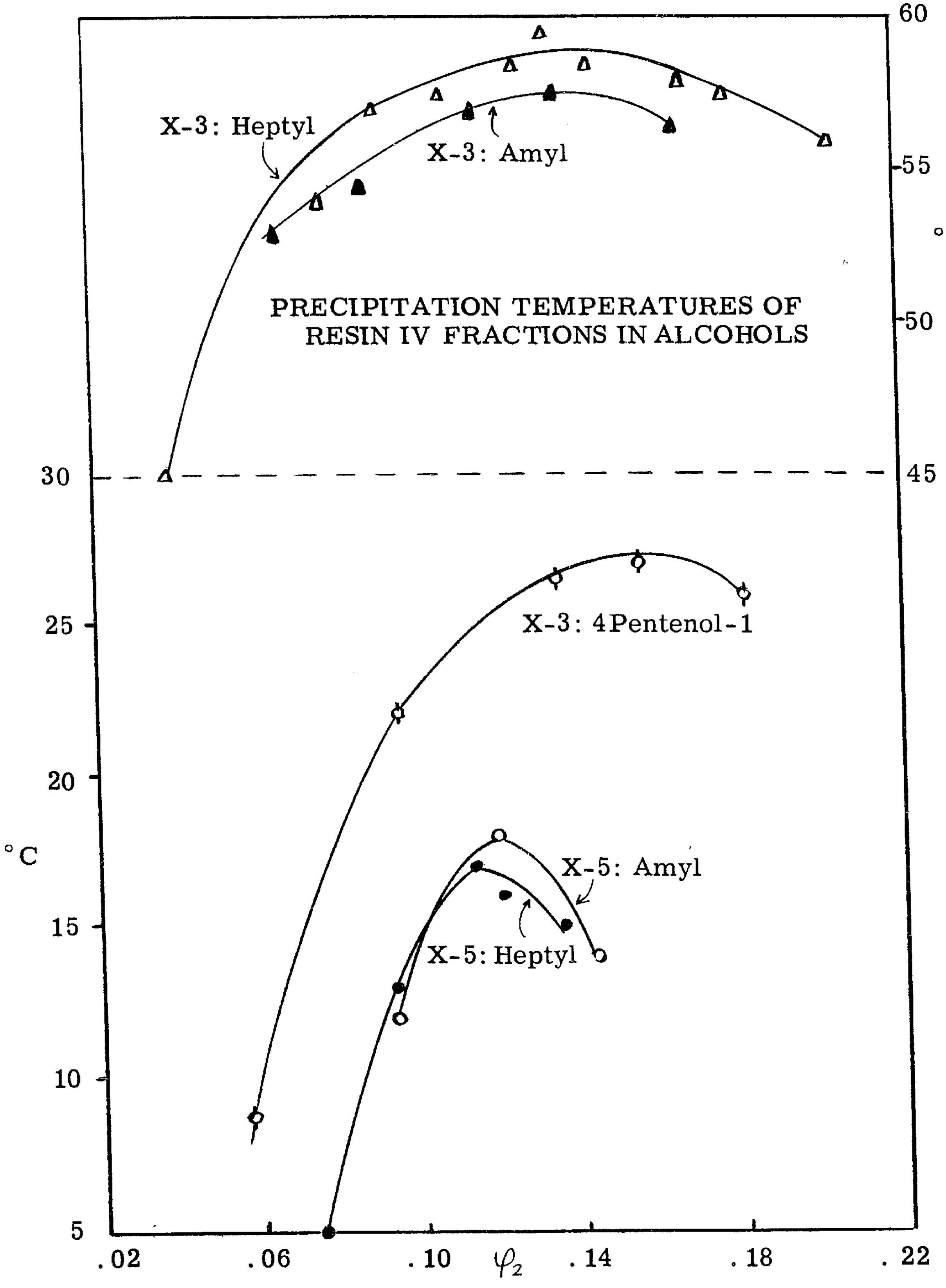

PRECIPITATION TEMPERATURES OF RESIN IV FRACTIONS IN ALCOHOLS
120
110
100
90
80
°C
.02
.06
.10
.14
.18
.22
.26
φ_2
X-1: Amyl
X-1 : Heptyl
X-2: Heptyl
X-2: Amyl
Resin IV: Amyl
X-1: 4 Pentenol-1

Figure 10


PRECIPITATION TEMPERATURES OF RESIN IV FRACTIONS IN ALCOHOLS
X-3: Heptyl
X-3: Amyl
X-3: 4Pentenol-1
X-5: Amyl
X-5: Heptyl
°C
°C
60
55
50
45
30
25
20
15
10
5
.02
.06
.10
φ_2
.14
.18
.22

chain length on solubility. The shorter chain compounds are more similar to the polymers in structure and thus are better solvents than long chain paraffins. The solubility data of Powers (45-48) on polyindene and polystyrene is in agreement with these results. (This increased solubility with decreasing chain length cannot be explained on the basis of solubility parameters because the solubility parameters of the paraffins, calculated from heats of vaporization, approach the value for the polymer as the chain length is increased. A further study of this problem might indicate that there is a decrease in the volume on mixing when a short chain paraffin is used or that the entropy of mixing is greater in the case of the short chain paraffin).

Except for aniline and nitroethane all the experimental values for the critical composition are considerably lower than theoretically predicted. Preliminary investigations show that the critical compositions of Resin I are also less than the theoretical value in n-butyl alcohol, 2-ethyl hexyl alcohol, propionic acid, n-butyl amine, 2-ethyl hexyl amine, and hexyl ether. Inspection of Table VII shows that the poorer the solvent, i.e., the higher the critical solution temperature for the polymer-solvent system, the greater the deviation from the predicted critical composition. The highest critical solution temperature is exhibited by the long chain paraffin whereas the lowest critical solution temperature is exhibited by an aromatic derivative. The relation between the structure of the polymer and that of the solvent thus seems to have an effect on the critical composition.

The molecular weight of the individual fractions in this low molecular weight range did not appear to have any well-defined effect on the critical composition although, according to Equation 17, the lower molecular weight fraction should exhibit a higher critical composition. This implies that it is the chemical nature of the solvent-solute interaction which is important in determining the critical compositions of very low molecular weight polymers and not the molecular weight of the solute as theoretically predicted. Thus it appears that Equation 17 is not valid for these low polymer - solvent systems.

The discrepancies between the theoretical and calculated values of the critical composition may be analyzed from a qualitative viewpoint. Richards (49) has indicated that the low values for the critical composition of polyethylene are probably due to an entropy of mixing. Clustering may also occur in the polymer near the critical solution temperature. The concept that clustering leads to a lower value for $\Delta \overline{S}_1$, has been theoretically supported by Miller (40). Scatchard, Wood, and Mochel (55) have shown that the methanol - benzene system shows a negative excess entropy of mixing at high methanol (considered the solvent) concentrations.

To support the view that the entropy of mixing in the alcohols is low, or lower than that obtained with high polymers, values for the entropy and heat parameters of the Resin IV - alcohols systems can be calculated from the solubility data of the fractions of Resin IV (Table VII). The entropy and heat parameters ψ_{12} and κ_{12} are related to the critical solution temperature, T_c, by the equation (57):

$$\frac{1}{T_c} = \left(\frac{1}{\Theta_{12}}\right)\left[1+\left(\frac{1}{\psi_{12}}\right)\left(\frac{1}{X^{1/2}}+\frac{1}{2X}\right)\right], \tag{20}$$

where Θ_{12} is the critical solution temperature for infinite molecular weight (infinite X). The entropy and heat parameters are related to B by the equation:

$$\frac{BV_1}{RT} = \frac{1}{2} - \left(\psi_{12} - \kappa_{12}\right) = \frac{1}{2} - \psi_{12} + \frac{\psi_{12}\Theta_{12}}{T}, \tag{21}$$

ψ_{12} and κ_{12} are such that:

$$\overline{\Delta H_1} = RT\kappa_{12}\varphi_2^2 = R\psi_{12}\Theta_{12}\varphi_2^2, \tag{22}$$

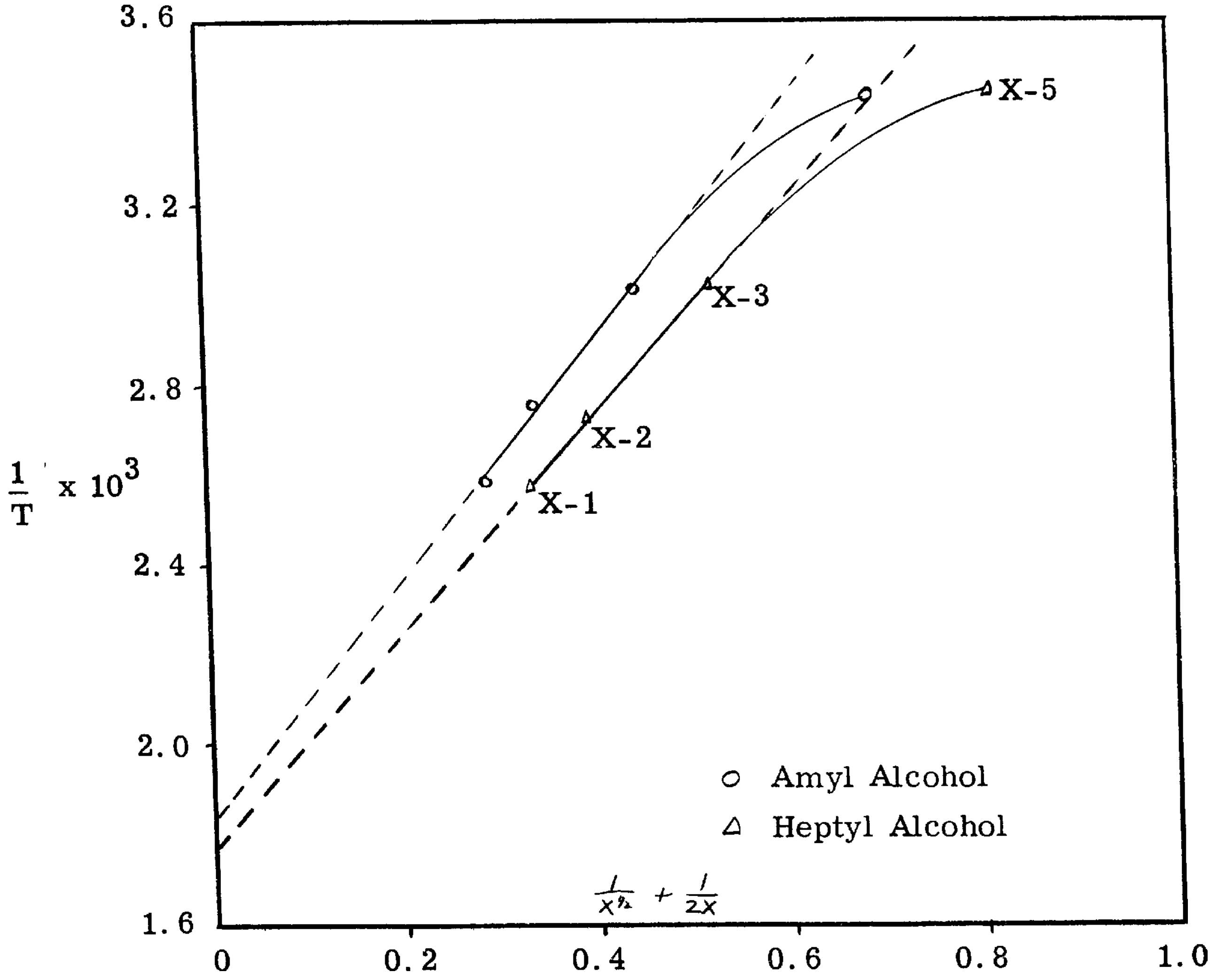
$$\overline{\Delta S_1} = R\psi_{12}\varphi_2^2. \tag{23}$$

The configurational entropy of dilution, $\overline{\Delta S_1^m}$, for a binary mixture in which the local interactions make no contribution to the entropy is given by Equation 14.

Figure 11 shows a plot of $\frac{1}{T_c}$ vs $\frac{1}{X^{1/2}}+\frac{1}{2X}$ for the fractions of Resin IV in amyl and heptyl alcohol. Following the theoretical

Figure 11

RECIPROCAL CRITICAL PRECIPITATION TEMPERATURES vs. $\frac{1}{X^{1/2}} + \frac{1}{2X}$ FOR RESIN IV FRACTIONS IN AMYL AND HEPTYL ALCOHOL



prediction, the data give a straight line plot with the exception of the lowest molecular weight fraction. The reason for this deviation from the straight line for the lowest molecular weight fraction is related to the second-order transition temperature of the fraction and is discussed in Chapter VI B. The Θ_{12} and Ψ_{12} values were obtained from the intercepts and slopes of the graph. Table VIII lists the interaction parameters of the Resin IV-alcohol systems along with the parameters for the polystyrene - octyl alcohol system given by Shultz and Flory (58).

Table VIII

THERMODYNAMIC PARAMETERS FROM PRECIPITATION DATA ON POLYMER-ALCOHOL MIXTURES

Component 1	Component 2	Θ_{12}(°K)	Ψ_{12}	K_{12}	$R\Psi_{12}\Theta_{12}$* (cal.)	B, 25°C
Amyl Alcohol	Resin IV	548	0.674	1.24	731	5.83
Heptyl Alcohol	Resin IV	562	0.742	1.40	826	4.85
Octyl Alcohol	Polystyrene	474	1.30	2.05	1225	4.69

---

* $R\Psi_{12}\Theta_{12} = \lim(\varphi_2 \to 1)\ \overline{\Delta H_1}$ is the amount of heat absorbed by a system when one mole of component 1 is dissolved in an infinite amount of component 2.

The entropy parameter, Ψ_{12} , should be approximately 1/2 if we consider only the configurational entropy and disregard first neighbor interactions. Shultz and Flory (58) have attributed the high values of ψ_{12} for the polystyrene-octyl alcohol system to the high degree of local order in the pure liquid alcohol. The entropy parameter for the Resin IV systems is considerably lower than that for the high molecular weight polystyrene even though there is little or no difference between the pure liquid solvents. Thus the low polymer systems show a lower entropy of dilution than the high polymer system. This finding is even more striking when it is noted that the theoretical treatment requires that the entropy of dilution should be greater the lower the molecular weight of the polymer. The high entropy parameter of the polystyrene system may mean that the high polymer has a greater tendency to break up the associated structure of the alcohol than the lower polymer.

The values for $\overline{\Delta S}_1$ for simple liquid systems cannot be determined from precipitation data of different molecular weight fractions. This means that we can only compare $\overline{\Delta S}_1$ values for high or low polymers and have no comparison for monomer mixtures using this method.

It has been pointed out previously that the straight chain hydrocarbons are very poor solvents and thus there may be clustering of the solute molecules in solution which leads to a lower entropy of mixing. The number of statistically distinguishable configurations in a mixture of polymer and a long-chain solvent such as octadecane is less than the number in a mixture with a smaller molecule (i. e. nitroethane) or with a solvent more similar in structure to the polymer (i. e. aniline) and thus yields a lower entropy of solution. Unfortunately the critical solution temperature for lower paraffins such as n-dodecane and n-heptane could not be determined because it falls above the boiling point of the solvent (see Figure 8). The values for the thermodynamic functions such as ΔF^M and ΔH^M are needed in order to make a more complete analysis.

C. Effect of Unsaturation

Inspection of Table VIII and Figures 8 and 9 shows that the introduction of one double bond in the solvent molecule markedly increases the solubility of the polymer although it does not increase the critical composition. The difference in solubility between saturated and unsaturated compounds has been attributed (27) to the increased bond polarizability of the carbon to carbon double bond as compared to the single bond. Comparison may be made to the introduction of a functional group into the hydrocarbon chain which markedly increases the solubility. For instance, Resin IV has limited solubility in n-heptane but is infinitely soluble in n-heptyl chloride. Further discussion of this effect will be found in chapter V B.

CHAPTER V

HEATS OF SOLUTION; INTRINSIC VISCOSITIES

A. Results

Unfractionated Polymer - Heats of solution of Resin IV were measured as described in chapter II. The results for most of the solvents (cyclohexane, 1-nitropropane, nitrobenzene, ethyl acetate, methyl ethyl ketone, benzene, methyl chloroform, carbon tetrachloride, bromobenzene, chlorobenzene, butyl chloride, s-tetrachloroethane, chloroform, and butyl amine) are presented in Figures 12-14 plotting integral heat of solution in cal./g. of polymer versus volume fraction, φ_2 , of polymer. φ_2 has been used instead of $\varphi_2(1-\varphi_2)$ because in this concentration range $\varphi_2 \simeq \varphi_2(1-\varphi_2)$. The pertinent data for all the solvents which were used are listed in Table IX giving average values for the heat of solution per gram, per base mole (monomer unit), B values for Equation 5 taken from the slopes of the curves of Figures 12-14, $\overline{\Delta H_2}$, dipole moments and solubility parameters for the solvents, and calculated B values assuming a solubility parameter of 9.15 for Resin IV. The value 9.15 was chosen since it is the average of two values: (1) calculated from the solubility in aniline, and (2) estimated from solubility in a variety of organic solvents. The average value coincides with the parameter for benzene. This result

Figure 12

HEAT OF SOLUTION OF POLYINDENE

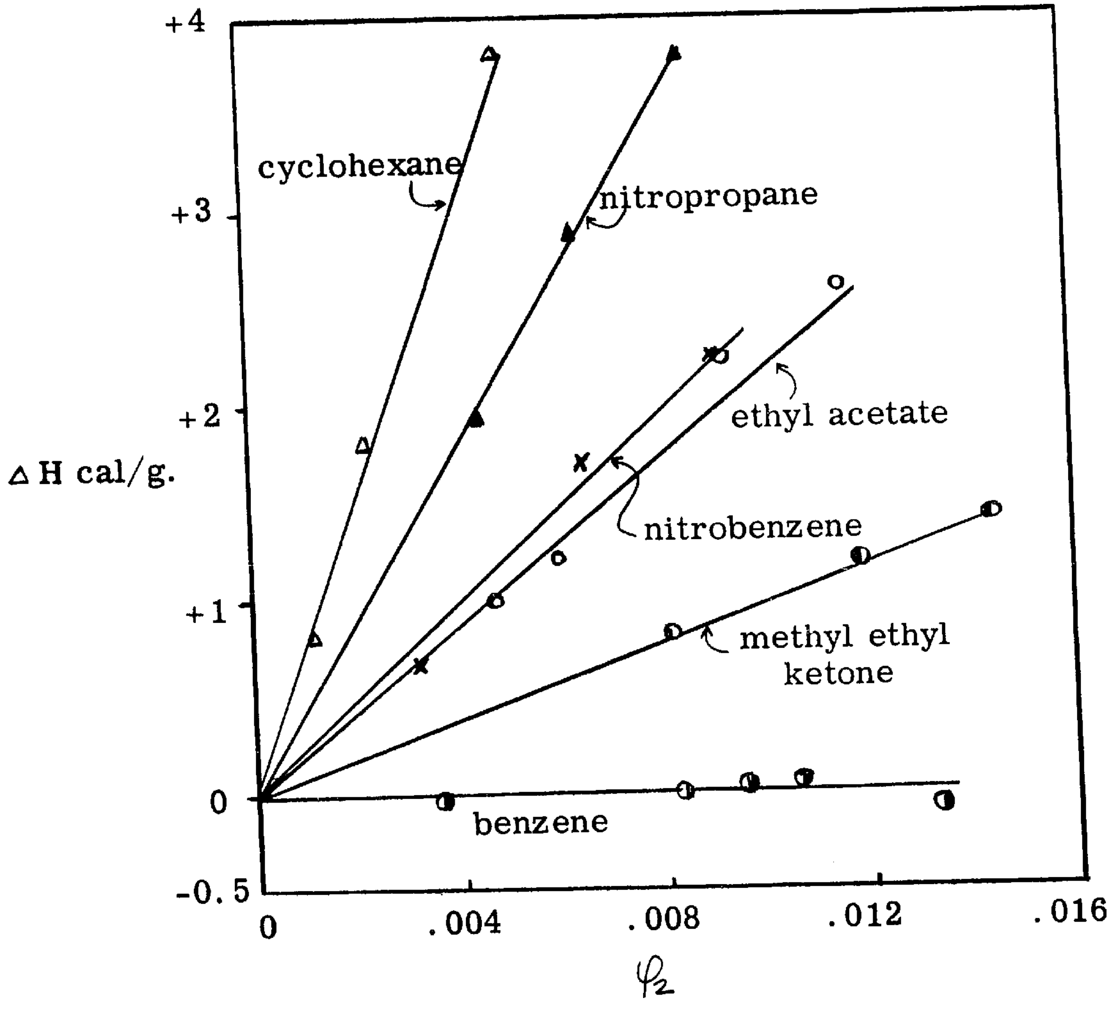


Figure 13

HEAT OF SOLUTION OF POLYINDENE

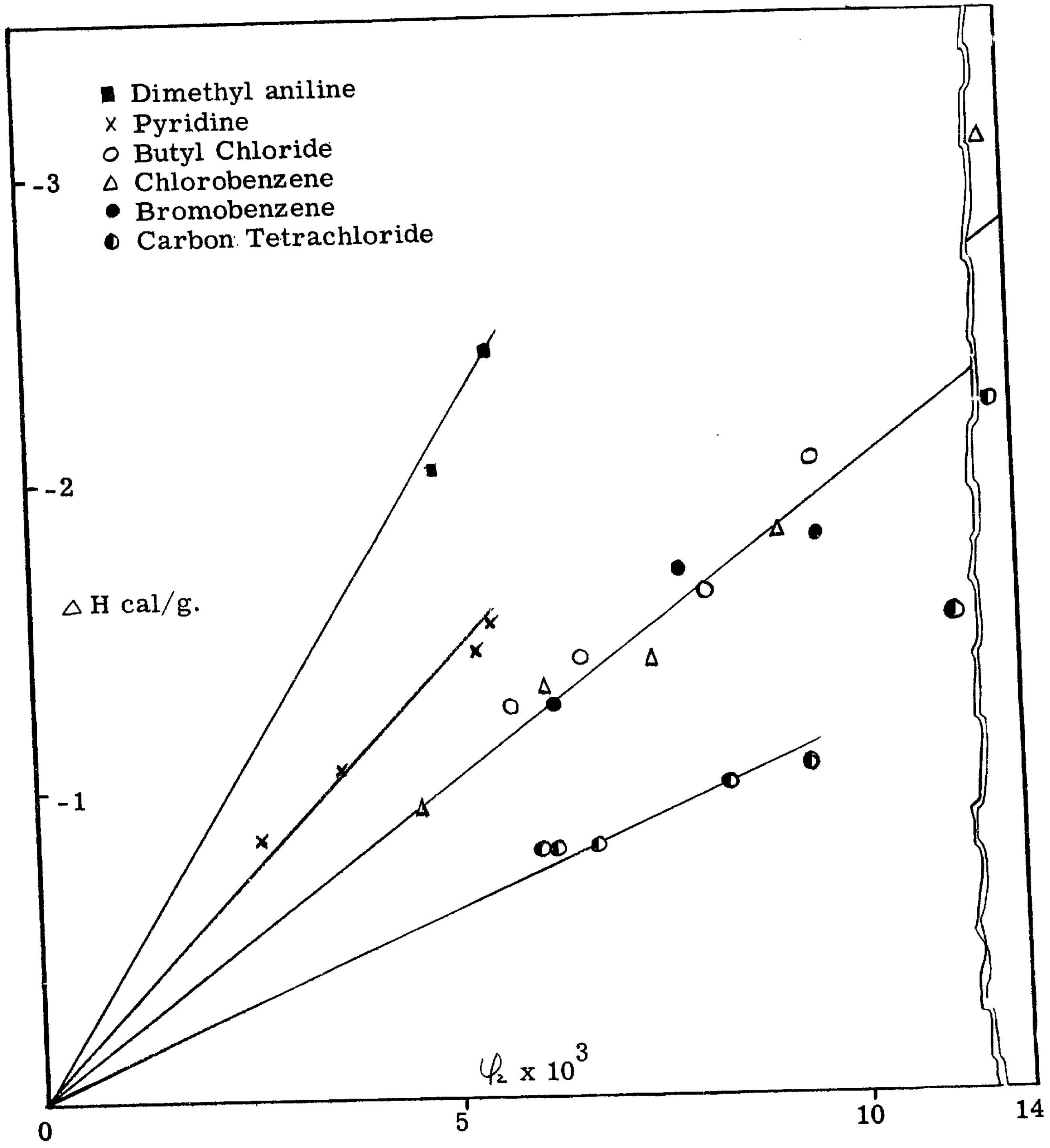


Figure 14

HEAT OF SOLUTION OF POLYINDENE

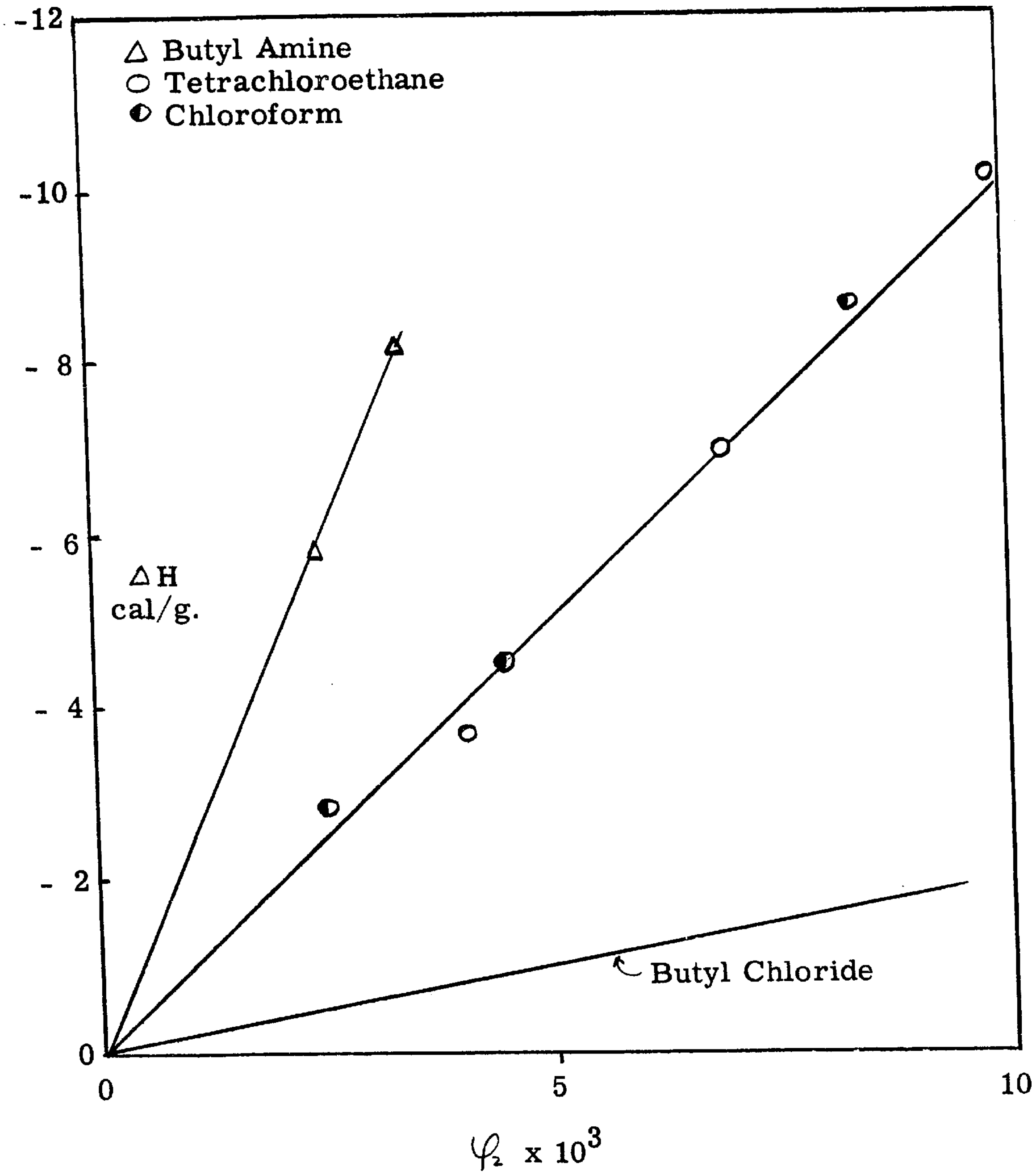


Table IX

HEATS OF SOLUTION OF RESIN IV (POLYINDENE)

Solvent	Dipole Moment	δ_1	ΔH/g cal.	ΔH/base mole cal.	B expt'l	B calc.	$\overline{H}_2$ cal.
Cyclohexane	0	8.2	3.52	407	3.96	0.9	410
1-Nitropropane	3.3	10.7	2.01	232	2.22	2.4	302
Nitrobenzene	4.1	10.0	1.09	127	1.25	0.7	197
Ethyl Acetate	1.8	9.1	1.00	116	1.14	0	135
Anisole	1.35	(8.5)	0.49	57	0.5	0.4	73
Methyl Ethyl Ketone	2.8	9.3	0.46	53	0.5	0.02	55
n-Heptyl Chloride	1.85	---	0.36	42	0.4	---	48
Benzene	0	9.15	-0.01	-1	0	0	-1.4
Ethyl Benzoate	1.8	(7.8)	-0.16	-19	-0.2	1.8	-25
Ethyl Benzene	0.5	8.8	-0.33	-39	-0.37	0.1	-43
Methyl Chloroform	1.6	8.5	-0.42	-48	-0.44	0.4	-83
Carbon Tetrachloride	0	8.6	-0.59*	-68*	-0.63	0.3	-142
Bromobenzene	1.7	(8.9)	-0.92	-107	-1.01	0.06	-205
Chlorobenzene	1.7	9.5	-0.93	-108	-1.01	0.1	-155
Butyl Chloride	2.0	(8.4)	-0.96	-112	-1.06	0.6	-128
Benzonitrile	4.1	8.4	-1.04	-121	-1.1	0.6	-155
Pyridine	2.2	10.7	-1.61	-187	-1.42	2.4	-237
Dimethyl aniline	1.6	(8.4)	-1.95	-226	-2.1	0.6	-280
s-Tetrachloroethane	1.6	(9.7)	-4.48	-519	-4.9	0.3	-1073
Chloroform	1.0	9.3	-4.80	-558	-5.2	0.02	-1072
Butyl Amine	1.3	---	-11.3	-1300	-12.0	---	(-1250)

---

*Average of all values

Values in brackets indicate approximate values is in agreement with the Hildebrand equation since the heat of solution in benzene is approximately zero. Individual results for each heat of solution determination are listed in Appendix II.

The heat of solution per gram or per base mole was constant (average deviation in ΔH/gram was 5%) over the concentration range used in this study. On a mole fraction basis the solutions were extremely dilute, e. g., the highest concentration which was used (methyl ethyl ketone, run No. 24) corresponded to a polymer mole fraction of 1.91×10^{-3}. Higher concentrations were not used in this study because of (1) the difficulty of rapidly dissolving the polymer, (2) the high viscosity of the resulting mixture, and (3) the physical limitations of the calorimeter.

Intrinsic viscosities for solutions of unfractionated Resin IV in benzene, ethyl acetate, 1-nitropropane, carbon tetrachloride, and chlorobenzene were determined as described in chapter II. Precise measurements were difficult to obtain because (1) the intrinsic viscosities were extremely low (which is to be expected for such low molecular weight polymers), and (2) the value for η_{sp}/c appeared to pass through a minimum for the exothermic solvents at concentrations of about 1 g./100 ml. The minimum in the η_{sp}/c vs. c curve appears to agree with the results of Streeter and Boyer (61) for solutions of polystyrene in toluene. This effect was not further investigated in the present study. The best values for the intrinsic viscosity, $[\eta]$, are listed in Table X along with the B values obtained from the heat of solution measurements. Figure 15 illustrates the relation between B and $[\eta]$. A preliminary measurement on the viscosity of Resin IV in s-tetrachloroethane (having a B value of -4.9) indicated that η for this solution would not be greater than that for chlorobenzene.

Table X

INTRINSIC VISCOSITIES

Solvent	B	$[\eta]$
Chlorobenzene	-1.01	0.056
Carbon Tetrachloride	-0.63	0.054
Benzene	0	0.032
Ethyl Acetate	1.14	0.027
1-Nitropropane	2.22	0.026

Fractionated Polymer - The heats of solution of Resin IV fractions X-1, X-2, X-3, and X-5 in chloroform, chlorobenzene, and 1-nitropropane were measured and the values in cal./g. are listed in Table XI. The value for the unfractionated resin is listed for comparison.

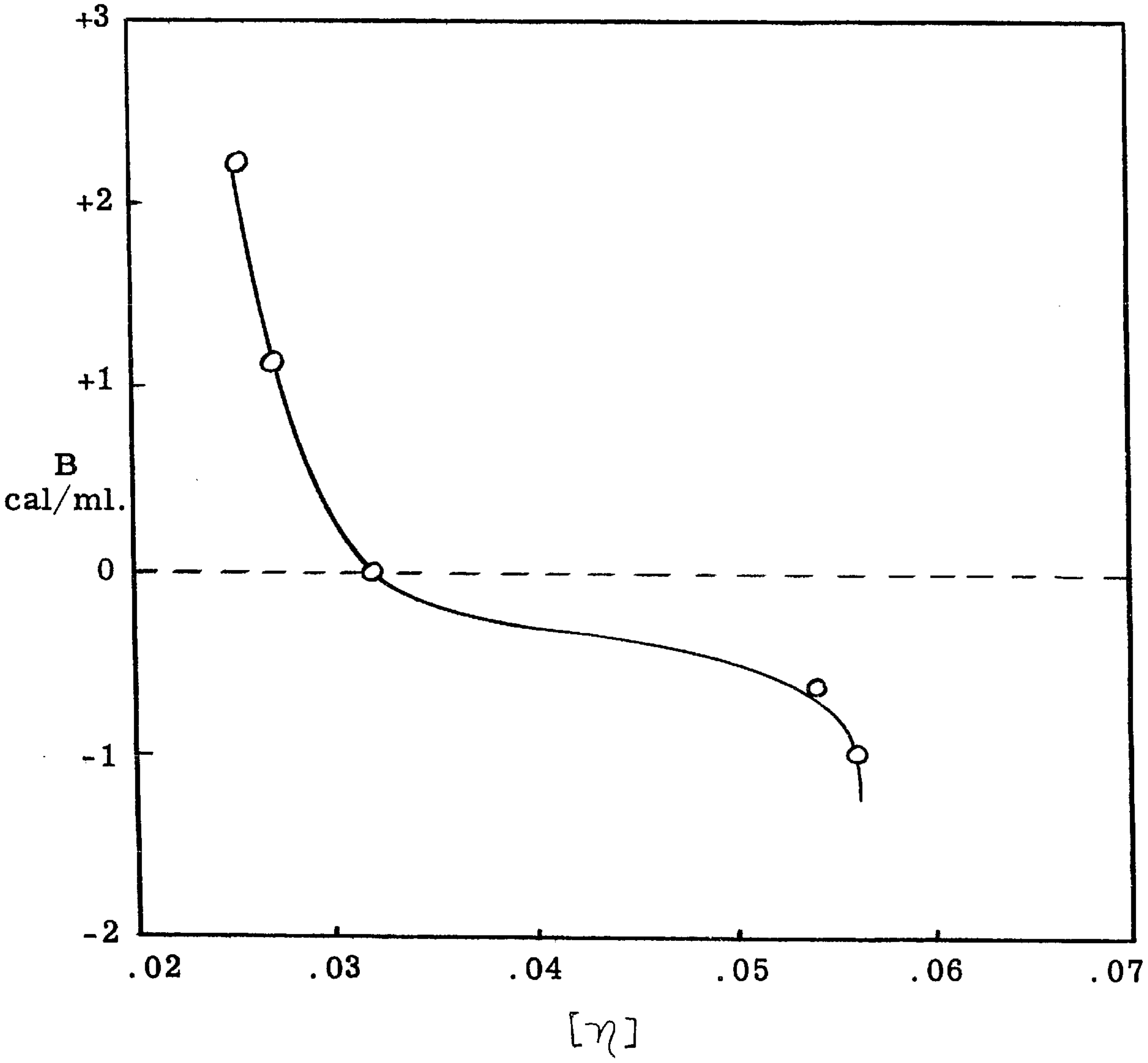
Table XI

HEATS OF SOLUTION OF RESIN IV FRACTIONS
(heats in cal./g.)

Fraction	Solvent Chloroform	 Chlorobenzene	 1-Nitropropane
X-1	-13.5	-11.0	-9.6
X-2	-11.3	- 8.0	-5.7
X-3	- 3.7	- 1.0	1.2
X-5	- 4.6	- 0.3	1.3
Resin IV	- 4.80	- 0.93	2.01

Figure 15

HEAT OF SOLUTION vs. INTRINSIC VISCOSITY



B. Discussion of Heats of Solution

Figures 12, 13, and 14 show that within the limits of experimental error the integral heat of solution varies linearly with the volume fraction of polymer as predicted by Equation 5. The only exception to this is carbon tetrachloride above .01 volume fraction of polymer. Inspection of Table IX shows however that the experimental value of B is not at all in agreement with the theoretical value as predicted from the solubility parameters by Equation 6. The experimental positive values of B are, in general, larger than the predicted theoretical values. Meares (38) and Vold (65) investigating mixtures of small molecules, also have obtained positive B values larger than predicted by theory. Negative B values (i.e., exothermic heats) do not occur according to Hildebrand's theory.

The graph of B values versus intrinsic viscosity in Figure 15 indicates that the polymer molecules tend to uncurl in the solvents which are exothermic and remain in a compact form in the endothermic solvents. The shape of the curve is almost identical to that obtained by Daoust and Rinfret (9) for solutions of polyvinylacetate. The curve also shows that the maximum intrinsic viscosity, and thus the maximum length of the polymer chain, is attained at relatively small exothermic heats of solution. A larger exothermic heat does not tend to increase further the length of the molecule in solution and thus the increased exothermicity of solvents such as chloroform is not due to physical effects but must result from chemical interactions. Similarly, at low endothermic heats the polymer molecule tends to curl up; larger endothermic heats do not cause further curling of the molecule.

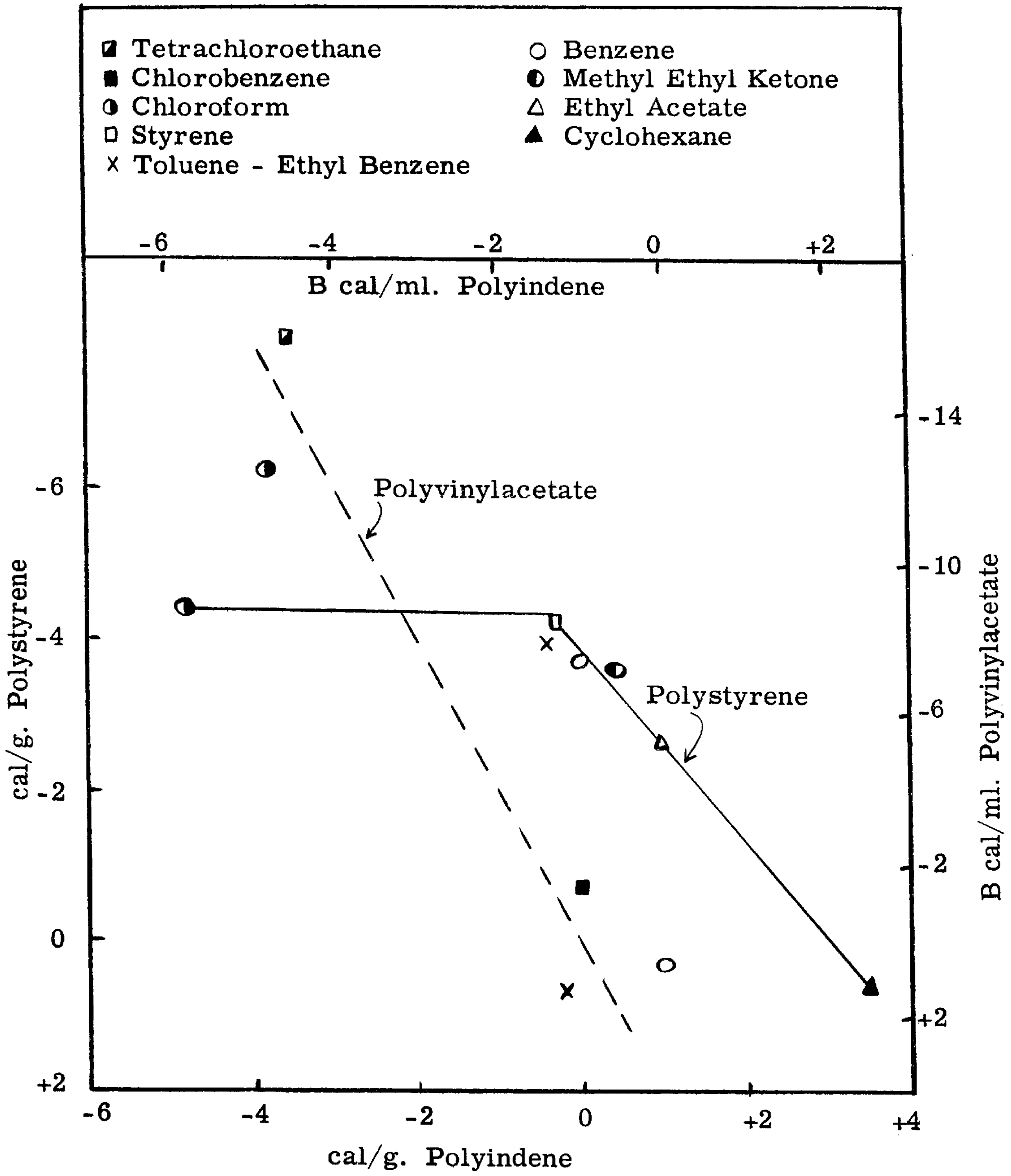
Several reasons have been proposed for the occurrence of exothermic heats of solution. The usual cause is given as the occurrence of specific interactions in the mixture such as solvation effects, i. e., a strong attraction between solute and solvent. For example, the exothermic heats of solution of polyvinylacetate in chloroform have been explained on the basis of "acid-base" interaction between the "acid" hydrogen of the chloroform and the "basic" carbonyl oxygen of the polymer. The presence of this type of interaction in such molecules has been substantiated by solubility (70) and infrared studies (21). No functional groups as such exist in the polyindene (Resin IV) molecule and thus such a straightforward explanation cannot be offered.

However, it is instructive to compare the results of Hellfritz (26) on the heat of solution of polystyrene and those of Daoust and Rinfret (9) on polyvinylacetate with the results obtained in this study. In Figure 16 the results obtained by Hellfritz and Daoust and Rinfret are plotted versus the results obtained in this study for solvents which were common to both studies. In both

Figure 16

HEATS OF SOLUTION

POLYINDENE vs. POLYSTYRENE AND POLYVINYLACETATE



cases the values for toluene were compared to the values for ethyl benzene obtained in this study. The units were used as they were reported in the literature; Δ H per gram for polystyrene and B values for polyvinylacetate. Inspection of Figure 16 shows that there is a regular relationship between the heats of solution of polystyrene and polyindene except for chloroform. The heat of solution of polyindene in chloroform is much more exothermic than would be expected from the polystyrene data. On the other hand, the chloroform (and s-tetrachloroethane) data for polyvinylacetate and polyindene seem to follow the regular relationship. This comparison suggests that there is a similarity in the mechanism of the interaction of chloroform (and s-tetrachloroethane) with low molecular weight polyindene and with polyvinylacetate. This mechanism does not operate in the case of polystyrene (mol. wt. 20,000).

An inspection of the values for the heats of solution of polyindene in chloroform, s-tetrachloroethane, methyl chloroform, and carbon tetrachloride indicates that the compounds containing "acid" hydrogens (chloroform and s-tetrachloroethane) bring about high exothermic heats while carbon tetrachloride and methyl chloroform, which contain no "acid" hydrogen atoms, exhibit markedly lower exothermic heats of solution. The "basic", or electron donor groups which must be present for interaction with the acid hydrogen exist in the form of terminal double bonds in the polyindene molecule (polyindene contains one terminal double bond per molecule) which are believed to be more avialable for interaction than the π electrons in the benzene ring. Polystyrene of a high molecular weight has very few terminal double bonds and thus does not exhibit this interaction. Thus it is believed that the high exothermic heats of solution of Resin IV in chloroform and s-tetrachloroethane can be explained on the basis of "acid-base" interaction. The dipole moment of the solvent is not important since s-tetrachloroethane and methyl chloroform have the same dipole moment (1. 6) while that of chloroform is lower (1. 0).

The indene or polyindene molecule is unusual in that it may be considered to be amphoteric in nature. The basic nature of polyindene has been discussed above on the basis of double bonds acting as electron donors. It has been shown (30) that the three carbon system of indene exhibits prototropy, or mobile-hydrogen tautomerism. This is primarily a base - catalyzed reaction and a complex is formed between the base (nitrogen atom) and a hydrogen atom. This mechanism is a possible explanation for the high exothermic heat of solution obtained with butyl amine, the strongest base use in this study, and the relatively lower exothermic heats obtained with pyridine and dimethyl aniline (which also can only function as bases).

The experimental heats of solution for most of the other solvents can be qualitatively explained on the basis of structure and the chemical nature of the solvent molecules. Cyclohexane exhibits a high endothermic heat of solution. This molecule has no polar groups available for solvent-solute interaction and is not easily polarized. It is a poor solvent for the type of polymer used in this study (see Table V) because it is a paraffin hydrocarbon (see also Chapter III and IV), and thus energy must be supplied in order to bring about the solution process. On the other hand, benzene is very similar in structure to the polymer, has a highly polarizable conjugated double bond structure and yet no polar groups, and has a solubility parameter equal to that of the polymer. Thus it is not surprising that the solution process is athermal.

The molecules which contain oxygen all exhibit endothermic or very low exothermic heats. These compounds are not strongly "acidic" or "basic", in some cases may exhibit some association in the pure liquid state, have relatively high dipole moments (especially the nitro compounds and methyl ethyl ketone), and have large polar groups. Steric effects and the fact that both the oxygens and the polymer are electron donors would thus prevent polymer-solvent interaction. Within this group of solvents the influence of the aromatic versus aliphatic structure is evident. In the pairs nitrobenzene-nitropropane and ethyl benzoate-ethyl acetate, the aromatic derivative exhibits a lower endothermic heat because of structure similarity to the polymer. The importance of the length of the aliphatic chain is evident by comparing the value for heptyl chloride which exhibits a low endothermic heat while butyl chloride is exothermic.

Most polymers show a decrease in partial specific volume on solution (22) which means that a decrease in volume occurs in dissolving the polymer. Thermodynamically it can be shown that the heat of solution at constant pressure (the experimental heat of solution) may be more exothermic than the heat of solution at constant volume if there is a decrease in volume on mixing. This contraction in volume may serve to show why exothermic heats are obtained in certain cases (e.g. chloro-, bromo-, and ethyl benzene, carbon tetrachloride, and butyl chloride). These solvents all might be expected to show a decrease in volume on mixing due to the fact that they are either similar in structure to the polymer or relatively small molecules which would lead to an efficient packing of the molecules in the solution. Unfortunately no data is available for the partial specific volumes of polyindene. However, the <u>cause</u> for the change in volume (if any occurs) is still explained by the previous observations regarding acid-base interactions, structure, and chemical nature of the solvent.

Effect of molecular weight - The increasing exothermic heats of solution with increasing molecular weight may be explained by considering the state of the polymer at room temperature. Almost all amorphous polymers exhibit an increase in the coefficient of thermal expansion at a definite temperature. This temperature is commonly called the second-order transition temperature, T_m. It is believed that it is the contribution of changing liquid structure to the thermodynamic properties which is absent at low temperatures and results in the drop in the coefficient of expansion. Kauzmann (32) has given a complete review of the nature of second-order transitions. A polymer below its second-order transition temperature is in a thermodynamically unstable state (59) and can be considered a super-cooled liquid. When the polymer is placed in solution, in effect the transition temperature is lowered, which liberates the excess free energy of the unstable state. In other words the polymer is in a higher energy state in the bulk "solid" than it is in solution.

Ueberreiter and Kanig (64) have shown that the second-order transition temperature of polystyrene varies lineraly with the degree of polymerization P, according to the equation:

$$\frac{1}{T_m} = a + \frac{b}{P} \tag{24}$$

where a and b are constants. Von Günner and Schulz (24) have recently applied this concept quantitatively and have developed the following equation:

$$W_E = -\Delta C_p (T_m - T) \quad , \tag{25}$$

where Δc_p is the difference in heat capacity of the polymer above and below T_m and W_E is the heat due to the free energy released when the polymer is placed in solution and is thus a heat term due to a "physical" step in the solution process. Substitution of Equation 24 in Equation 25 gives

$$W_E = -\frac{\Delta C_p}{a}\left(\frac{P}{P + b/a}\right) + T\Delta C_p \ . \tag{26}$$

The heat of solution below T_m, ΔH is given by

$$\Delta H = W_E + W_W \quad , \tag{27}$$

where W_W is the chemical interaction energy between polymer and solvent and should be similar to that between monomer and solvent. Substitution of Equation 26 into Equation 27 gives:

$$\Delta H = -\frac{\Delta C_p}{a}\left(\frac{P}{P + b/a}\right) + T\Delta C_p + W_W \ . \tag{28}$$

Thus the heat of solution of a polymer below its transition point is composed of a physical (W_E) and a chemical (W_W) heat term. Above T_m the heat of solution is given by

$$\Delta H = W_W \ . \tag{29}$$

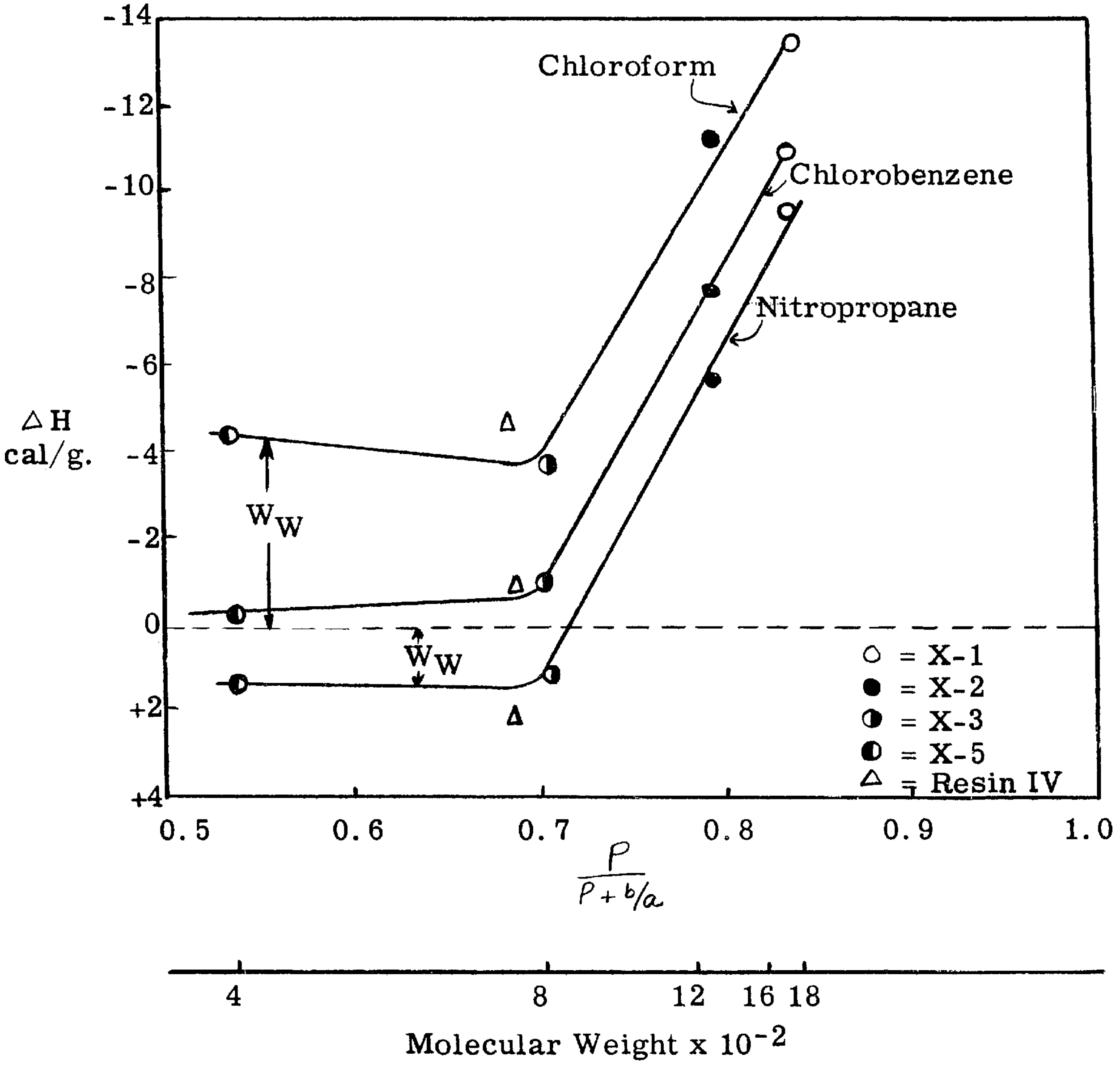
A preliminary test of this theory by von Günner and Schulz (24) has shown that for polystyrene over a range of P values of

30 to 100 a plot of ΔH versus $\frac{P}{P + b/a}$ gives a series of parallel lines for different solvents. The values for the constants a, b, and Δc_p for polystyrene were available from the literature. The value for b/a was 1.91. The values of these constants are not available for the polymer used in this study.

In comparison with polystyrene (mol. wt. circa. 100,000), polyindene (mol. wt. 750) has the same second-order transition temperature (82° C) for a much lower molecular weight. This contrast indicates that the polyindene molecule has a much more sterically hindered structure than polystyrene. This conclusion may be supported by two facts, namely (1) the activation energy for viscous flow of Resin IV is unusually high (43, 44), and (2) the infrared spectra of the polymers used in this study show very few characteristic peaks in comparison to the monomer (see Appendix III), indicating an extremely hindered structure. Thus it would be expected that the value of Δc_p and b/a for Resin IV would be greater than those for polystyrene. On this assumption the values of ΔH for the different fractions (Table XI) were plotted against $\frac{P}{P + b/a}$ assuming a value of 2.98 for b/a. The result is shown in Figure 17. If the value of b/a used by von Günner and Schulz is used, the graphs have the same general appearance except for a shift to the right on the $\frac{P}{P + b/a}$ axis.

Figure 17

HEAT OF SOLUTION vs. MOLECULAR WEIGHT



The results of this procedure are very striking and are excellent experimental evidence for support of the theory. Inspection of Figure 17 shows that the curves obtained for the three solvents are parallel lines drawn through the data for the three highest molecular weight fractions and level off sharply for the lowest molecular weight fraction. Since the lowest molecular weight fraction is a viscous liquid, more dense than the higher molecular weight fractions (this could not be so unless the fraction was above its second-order transition temperature) its second-order transition temperature must be below room temperature. This is also supported by the fact that the values for T_m are usually below the values of the ring and ball melting point of the polymer. Table IV shows shows the melting points of the fractions; fraction X-5 has a melting point of 27 °C while the other fractions have melting points of 95°C and higher.

Equation 29 must thus be used for the heat of solution of the lowest fraction while Equation 28 applies to the higher molecular weight fractions. Thus the chemical interaction energy, W_W, is obtained as indicated in Figure 17 and it is shown that the results obtained for the heats of solution of the unfractionated polymer (Resin IV) are a measure only of the chemical interaction energy. The break of the curve in Figure 17 at a molecular weight of about 800 corresponds to the break in the heat of activation of viscous flow curve obtained by Pieski (43, 71) for Resin IV.

The fact that the lowest molecular weight fraction is above T_m also explains why its critical solution temperature is higher than would normally be expected (see Figure 11). As previously stated, a polymer above T_m should be less soluble than the same polymer below T_m because the polymer above T_m is not in a metastable state and thus does not have any excess free energy to release on going into solution.

It has thus been shown that the theory of the "solid" state of polymers explains the change in heat of solution with molecular weight and is able to differentiate between the physical and chemical contributions to the heat of solution. The theory also explains the apparent anomaly of the low solubility of the lowest molecular weight fraction used in this study.

CHAPTER VI

VAPOR PRESSURE

Preliminary vapor pressure measurements were made on the Resin IV - benzene system using the apparatus described in chapter II and Appendix VI. The results of the measurements are listed in Table XII and plotted as p/p_0 vs. mole fraction of polymer in Figure 18. Columns 4, 5, and 6 in Table XII were calculated from the following equations:

$$\overline{\Delta F_1} = -RT \ln p/p_0 \tag{30}$$

$$\overline{\Delta S_1} \text{ exptl.} = -R \ln p/p_0 \ ; \ \overline{\Delta H_1} = 0 \tag{31}$$

$$\overline{\Delta S_1^{\sim}} \text{ calc.} = -R\left[\ln \varphi_1 + \left(1 - \frac{1}{X}\right)\varphi_2\right] . \tag{14}$$

The $\overline{\Delta S_1^{\sim}}$ and $\overline{\Delta S_1}$ values are plotted versus concentration in Figure 19.

Inspection of the data shows that the agreement between theoretical and experimental partial molal entropies is very good (assuming the heat of solution to be zero over the entire concentration range). The agreement of these results with those of Newing (42) on benzene solutions of polydimethylsiloxane (calculated from vapor pressure and heat of solution) is very striking. The partial molal entropies calculated from vapor pressure data of the low polymers

Table XII

VAPOR PRESSURES OF RESIN IV - BENZENE SYSTEM

Mole fraction Polymer	φ_2	P/P_0	ΔF (cal.)	$\overline{\Delta S}_1$, exptl.	$\overline{\Delta S}_1^{\sim}$ calc.
0.773	0.962	0.03	-2087	6.94	4.84
0.640	0.929	0.147	-1141	3.80	3.65
0.524	0.891	0.238	- 854	2.84	2.87
0.378	0.818	0.420	- 516	1.72	1.97
0.348	0.798	0.480	- 437	1.45	1.80
0.255	0.717	0.586	- 318	1.06	1.27
0.165	0.595	0.746	- 174	0.58	0.77
0.157	0.580	0.767	- 158	0.52	0.72
0.097	0.444	0.895	- 66	0.22	0.40
0.003	0.023	0.991	- 5.4	0.018	0.0067

(i. e. this study and Newing's work) seem to be in much better agreement with theory than those for high polymers (15). The experimental high polymer $\overline{\Delta S}_1$ values are less than the theoretical values. It is to be noted, however, that the partial molal entropy values for high polymers reported in the literature (15) were calculated from the temperature coefficient of the activity. Thus calorimetric data has not been used to calculate partial molal entropies for high polymeric systems.

Figure 18

VAPOR PRESSURE vs. COMPOSITION OF RESIN IV - BENZENE SYSTEM

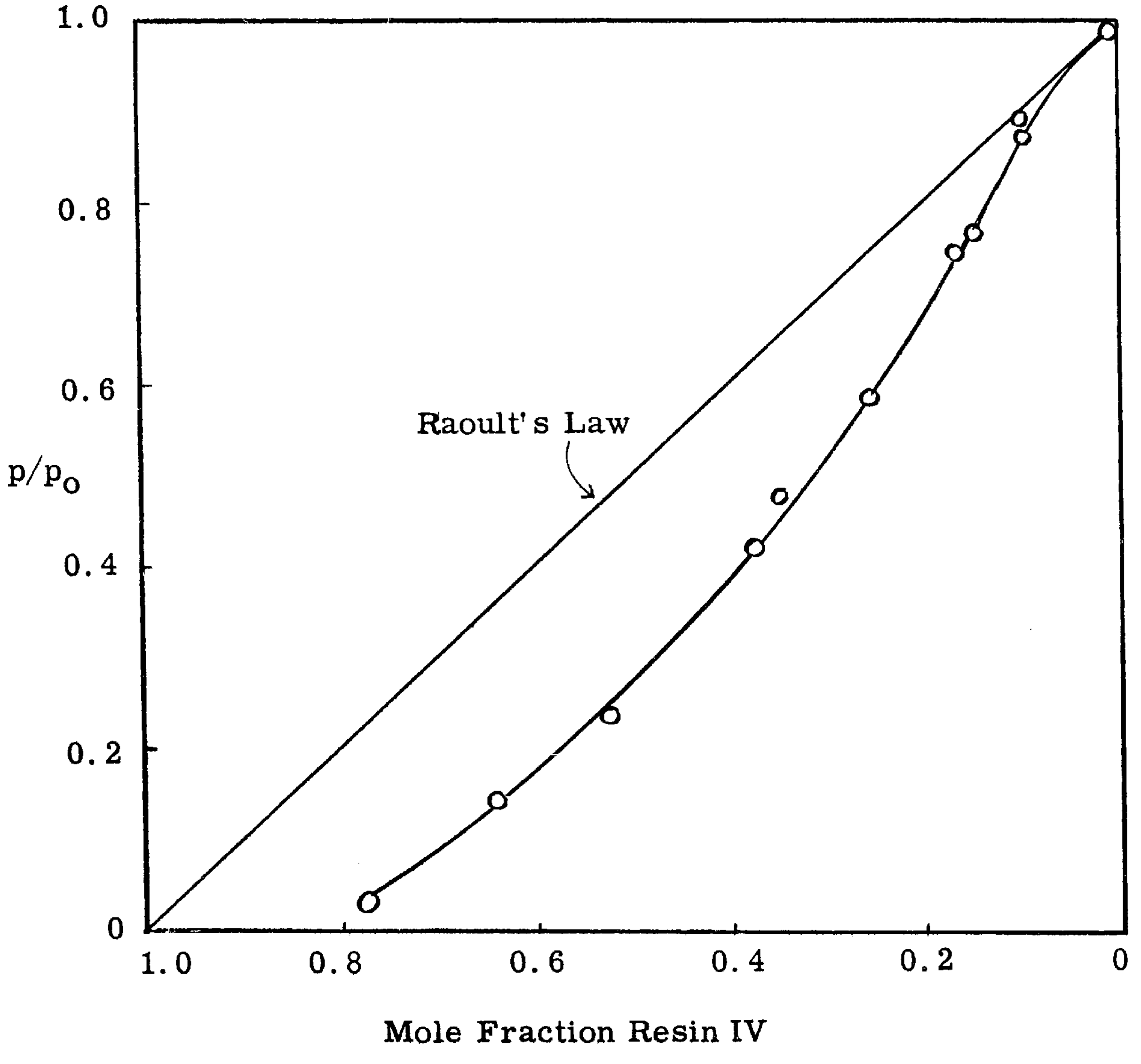
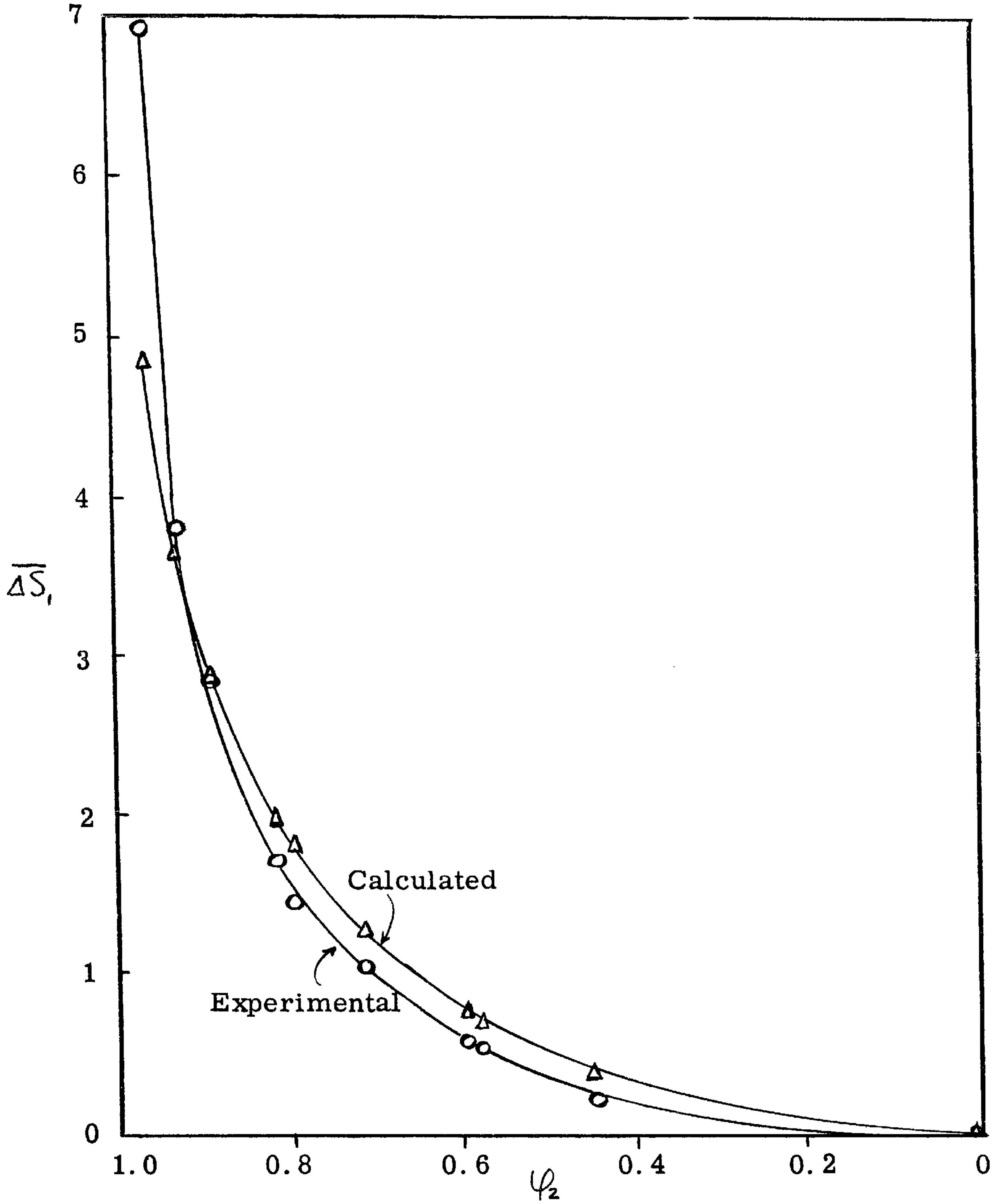


Figure 19

PARTIAL MOLAL ENTROPY OF BENZENE IN RESIN IV - BENZENE SYSTEM



Good agreement with the theoretical partial molal entropies has been shown for two types of low polymer solutions (Newing (42) and this study) where calorimetric and vapor pressure data were used in the calculations. The poor agreement for high polymeric systems may result from inaccuracies in the theoretical treatment of the configurational entropy of dilution. There is thus a strong indication that additional measurements of heats of solution and vapor pressures on high polymer-solvent systems are needed in order to verify the Flory-Huggins equations for partial molal entropy.

SUMMARY

The conclusions reached in this study may be summarized as follows:

1. The heat of solution of a polymer is related to the chemical nature of the solvent-polymer interaction and to the structure similarities and differences between polymer and solvent. The heat of solution also depends on the thermodynamic state of the polymer which, in turn, is related to its molecular weight and structure, and which is reflected in its second-order transition temperature.

2. The Hildebrand-Scatchard equation for the heat of mixing of nonelectrolytes cannot be used to predict heats of solution of low polymers.

3. The heats of solution of low molecular weight polyindene are linear functions of concentration up to a volume fraction of 0.01 in all types of solvents.

4. The intrinsic viscosity measurements indicate that the polymer molecules are extended in an exothermic solvent and curled up in an endothermic solvent. The magnitude of the heat effect is of little importance in influencing the amount of extension or contraction.

5. The partial molal entropy of benzene in the polyindene - benzene system, arrived at from vapor pressure and heat of solution measurements, is in close agreement with the values predicted by the Flory-

Huggins equation. The agreement is better than that for high polymers, and as good as that for many ordinary sized molecules.

6. The entropy parameter of the systems polyindene-amyl alcohol and polyindene-heptyl alcohol, as calculated from critical miscibility data, is about half the value of the parameter for the polystyrene (high mol. wt.) - octyl alcohol system. The difference cannot be explained on the basis of existing theory.

7. The critical composition of low molecular weight polyindene in many solvents is considerably lower than that predicted by theory. The discrepancies are tentatively attributed to an entropy of mixing which is lower than the configurational entropy.

8. The precipitation temperature of a low molecular weight polymer is controlled by its highest molecular weight fraction.

APPENDIX I

Glossary of Symbols

Subscript 1 - refers to solvent

2 - refers to solute

Superscript M - refers to mixing process

V - refers to vaporization

a, b - constants

B - square of difference between solubility parameters

B - interaction constant

Δc_p - difference in heat capacity above and below the second-order transition temperature

δ - solubility parameter

E - energy

φ -volume fraction

$\varphi_{2,c}$ -critical composition of polymer

H - heat, enthalpy

κ_{12} - heat parameter

N - number of moles

$[\eta]$ - intrinsic viscosity

η_{sp} - specific viscosity

P - pressure

P - degree of polymerization

p - vapor pressure above solution

p_o - vapor pressure of pure solvent

R - gas constant

S - entropy

$\overline{\Delta S}^{i}$ - ideal partial molal entropy = - Rlnx

$\overline{\Delta S}^{n}$ - normal partial molal entropy (Equation 14)

ψ_{12} - entropy parameter

T_c - critical solution temperature

T_m - second-order transition temperature

θ_{12} - critical solution temperature at infinite molecular weight

V - molar volume

V_m - volume of mixture in cc.

W_E - physical interaction energy

W_W - chemical interaction energy

x - mole fraction

X - ratio of molar volume of polymer to that of solvent

APPENDIX II

Heat of Solution Determinations of Resin IV

Volume of Solvent: 200 ml.

Sample Wt.	Δ H total	ΔH/g	φ_2
Cyclohexane:			
0.4896 g.	1.858 cal.	3.795 cal.	.00223
0.2631	0.860	3.269	.00120
1.1116	3.870	3.481	.00505
Nitrobenzene:			
0.7195	0.686	0.954	.00327
1.4408	1.73	1.20	.00654
2.0224	2.27	1.21	.00915
1-Nitropropane:			
0.9839	1.94	1.972	.00447
1.4175	2.90	2.046	.00643
1.8916	3.79	2.004	.00856
Ethyl Acetate:			
1.0500	0.984	0.937	.00477
1.3178	1.220	0.926	.00598
2.0502	2.250	1.097	.00927
2.5877	2.660	1.028	.01168

Sample Wt.	Δ H total	Δ H/g.	φ_2
Methyl Ethyl Ketone:			
1.8085	0.873	0.483	.00819
2.6253	1.192	0.454	.0118
3.2054	1.386	0.432	.0144
Anisole:			
0.9881	0.374	0.379	.00449
1.1880	0.717	0.603	.00540
Heptyl Chloride:			
1.2936	0.484	0.374	.00587
0.8965	0.309	0.349	.00403
Carbon Tetrachloride:			
1.3438	-0.786	-0.585	.00610
1.3733	-0.803	-0.585	.00623
1.4916	-0.816	-0.547	.00676
1.8510	-1.018	-0.550	.00838
2.0628	-1.077	-0.522	.00933
2.5003	-1.560	-0.624	.0113
3.0822	-2.253	-0.731	.0139

Sample Wt.	Δ H total	ΔH/g	φ_2
Pyridine:			
0.5819	-1.099	-1.889	.00265
0.8081	-1.324	-1.638	.00368
1.1722	-1.690	-1.442	.00532
1.2234	-1.795	-1.467	.00556
Chloroform:			
0.9909	-4.517	-5.158	.00450
0.5574	-2.875	-4.558	.00254
1.8389	-8.64	-4.70	.00833
Ethyl Benzene:			
1.3827	-0.41	-0.297	.00627
1.7157	-0.505	-0.294	.00777
1.9405	-0.762	-0.393	.00878
2.3951	-0.814	-0.340	.0108
Styrene:			
1.3441	-0.42	-0.31	.0061
Butyl Amine:			
0.7413	-8.4	-11.3	.00337
0.5394[2]	-6.606	-11.2	.00246

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[2] Fraction X-2

Sample Wt.	Δ H total	Δ H/g	φ_2
Benzonitrile:			
1.2113	-1.093	-0.902	.00550
1.2565	-1.648	-1.168	.00570
Ethyl Benzoate:			
1.2832	-0.057	-0.044	.00583
1.1521	-0.31	-0.27	.00523
Methyl Chloroform:			
0.9992	-0.487	-0.487	.00454
1.5985	-0.604	-0.378	.00725
2.2025	-0.850	-0.386	.00996
Dimethyl Aniline:			
1.0744	-2.067	-1.924	.00488
1.2315	-2.446	-1.986	.00559
s-Tetrachloroethane:			
0.8853	-3.71	-4.191	.00403
1.5241	-6.94	-4.552	.00691
2.1792	-10.21	-4.685	.00985

Sample Wt.	Δ H total	Δ H/g	φ_2
Benzene:			
0.8134	-0.06	-0.074	.00370
1.8454	0.00	0.00	.00836
2.0990	0.04	0.019	.00949
2.3460	0.07	0.030	.0106
2.9410	-0.08	-0.027	.0133
Bromobenzene:			
1.3732	-1.254	-0.913	.00623
1.7317	-1.691	-0.976	.00785
2.1026	-1.801	-0.857	.00951
Chlorobenzene:			
1.0118	-0.942	-0.931	.00460
1.3539	-1.324	-0.978	.00614
1.6488	-1.408	-0.854	.00747
2.0038	-1.807	-0.902	.00907
3.0719	-3.09	-1.006	.0138
Butyl Chloride:			
1.2636	-1.257	-0.995	.00574
1.4657	-1.431	-0.976	.00665
1.8101	-1.630	-0.901	.00820
2.1078	-2.056	-0.975	.00953

Heat of Solution of Fractions

Fraction No.	Sample Wt.	ΔH_{total}
Chloroform:		
X-1	0.5693	-7.69
X-2	0.5693	-6.45
X-3	0.5698	-2.12
X-5	0.4153	-1.90
Chlorobenzene:		
X-1	0.5688	-6.205
X-2	0.5704	-4.54
X-3	0.5693	-0.432
X-5	0.4748	-0.159
Nitropropane:		
X-1	0.4959	-4.754
X-2	0.5697	-3.249
X-3	0.5711	0.680
X-5	0.4386	0.568

APPENDIX III

Energy of Mixing (27)

The derivation of Equation 1 involves the assumptions mentioned on page 5 . Assumption 1, that of a random distribution, is the characteristic feature of the theory of regular solutions. At best it is only a good approximation since it ignores the ordering effect of molecular shapes and differences in intermolecular potentials (23, 34, 52). Assumption 3 is that of the additivity of the energies of molecular pairs. While this is not exactly true for dispersion forces, it has proved very successful as the basis for nearly all the theories of liquids and solutions.

The cohesive energy of a liquid mixture is essentially its potential energy E_m, with the opposite sign. Following the treatment of van der Waals (66) the above assumptions permit us to write:

$$-E_m = \frac{c_{11}V_1^2N_1^2 + 2c_{12}V_1V_2N_1N_2 + c_{22}V_2^2N_2^2}{V_1N_1 + V_2N_2} , \qquad \text{(II-I)}$$

where:

$$c_{11} = \frac{-E_1}{V_1} \quad \text{and} \quad c_{22} = -\frac{E_2}{V_2} . \qquad \text{(II-2)}$$

Transforming to volume fractions we obtain:

$$-E_m = (N_1V_1 + N_2V_2)(c_{11}\varphi_1^2 + 2c_{12}\varphi_1\varphi_2 + c_{22}\varphi_2^2) . \qquad \text{(II-3)}$$

The energy of mixing is given by the expression:

$$\Delta E^M = E_m - E_1N_1 - E_2N_2 , \qquad \text{(II-4)}$$

and thus we obtain:

$$\Delta E^M = (N_1V_1 + N_2V_2)(c_{11} + c_{22} - 2c_{12})\varphi_1\varphi_2 ,$$
$$= (N_1V_1 + N_2V_2)(A_{12}\varphi_1\varphi_2) , \qquad \text{(II-5)}$$

where

$$A_{12} = (c_{11} + c_{22} - 2c_{12}) . \qquad \text{(II-6)}$$

If we assume that:

$$c_{12} = (c_{11}c_{22})^{1/2} , \qquad \text{(II-7)}$$

then A_{12} may be written:

$$A_{12} = (c_{11}^{1/2} - c_{22}^{1/2})^2 . \qquad \text{(II-8)}$$

We can identify -E with ΔE^V for liquids at ordinary temperatures and thus we can rewrite Equation II-5:

$$\Delta E^M = (N_1V_1 + N_2V_2)\left[\left(\frac{\Delta E_1^V}{V_1}\right)^{1/2} - \left(\frac{\Delta E_2^V}{V_2}\right)^{1/2}\right]^2 \varphi_1\varphi_2 , \qquad \text{(II-9)}$$

which is identical with Equation 1.

Solubility (16)

Equilibrium between two phases in a binary mixture requires that their compositions φ_2 and φ_2' shall be such that:

$$\overline{\Delta F}_1(\varphi_2) = \overline{\Delta F}_1(\varphi_2') \quad \text{and} \quad \overline{\Delta F}_2(\varphi_2) = \overline{\Delta F}_2(\varphi_2') . \qquad \text{(II-10)}$$

When B = O, $\overline{\Delta F_1}$ decreases continuously as φ_2 increases from zero to unity. When B is sufficiently positive the curve for $\overline{\Delta F_1}$ will possess a maximum and a minimum. We can thus differentiate an expression for $\overline{\Delta F_1}$ such as given by Equation 13 to obtain the critical values for B and φ_2 . Differentiating Equation 13 with respect to φ_2 and equating to zero:

$$KX\varphi_2^2 - (KX - X + 1)\varphi_2 + 1 = 0 \; , \qquad \text{(II-11)}$$

where

$$K = 2BV_1/RT \; . \qquad \text{(II-12)}$$

The solution of II-11 is:

$$\varphi_2 = \frac{KX - (X-1) \pm \left[(KX - X + 1)^2 - 4KX\right]^{1/2}}{2KX} \; . \qquad \text{(II-13)}$$

The critical condition for separation into two phases requires that the maximum and minimum in $\overline{\Delta F_1}$ coincide, i.e., that the two roots of II-13 shall be equal. This occurs when

$$K_{\text{critical}} = \frac{(1+X^{1/2})^2}{X} \; , \qquad \text{(II-14)}$$

or

$$B_{\text{critical}} = \frac{RT}{2V_1}(1+X^{1/2})^2 \; , \qquad \text{(II-15)}$$

which is identical with Equation 16.

Substituting II-14 in II-13 we obtain:

$$\varphi_{2,c} = \frac{1}{1+X^{1/2}} \; , \qquad \text{(II-16)}$$

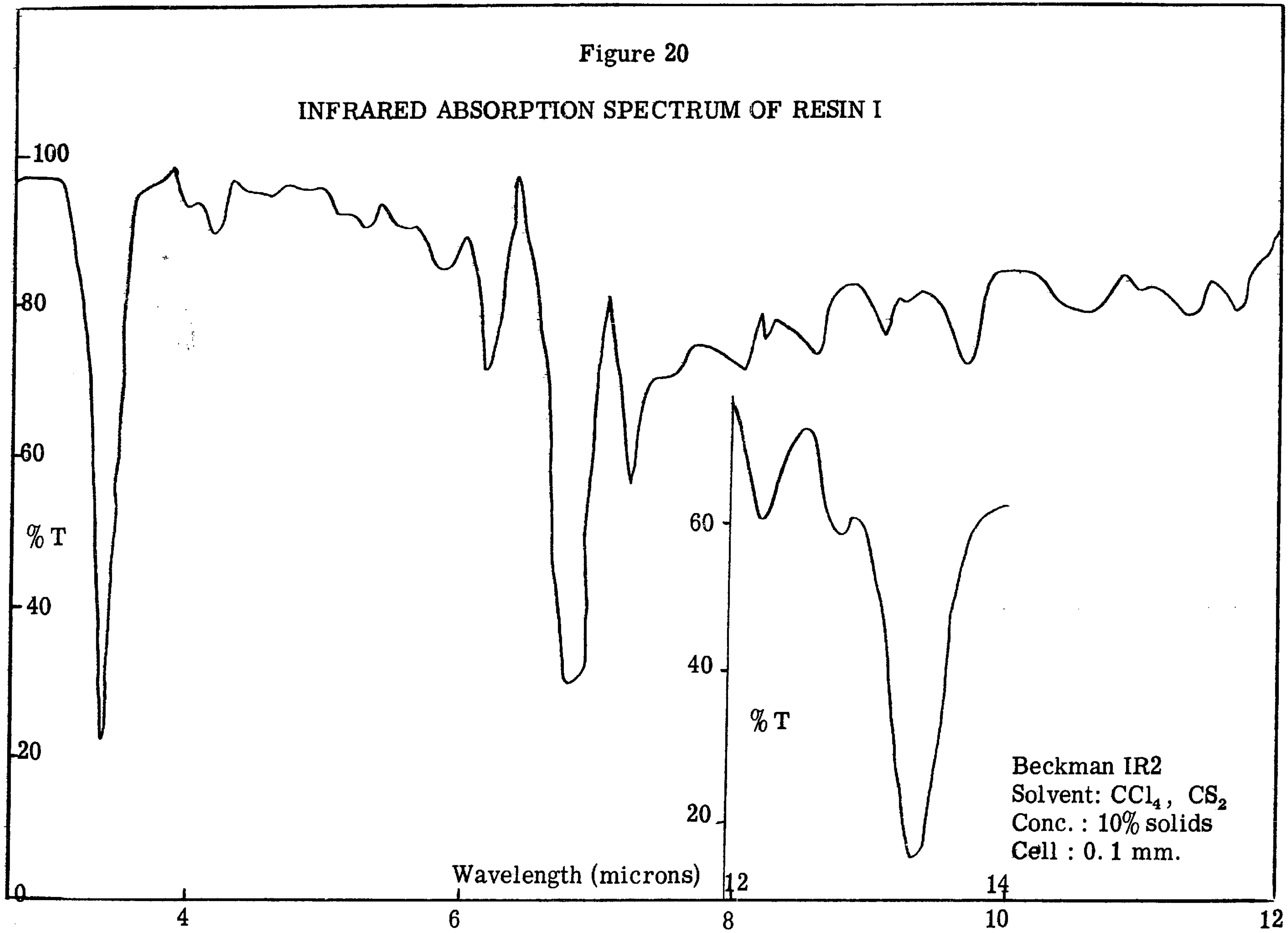
which is identical with Equation 17.

APPENDIX IV

Infrared Absorption Spectra

Figure 20

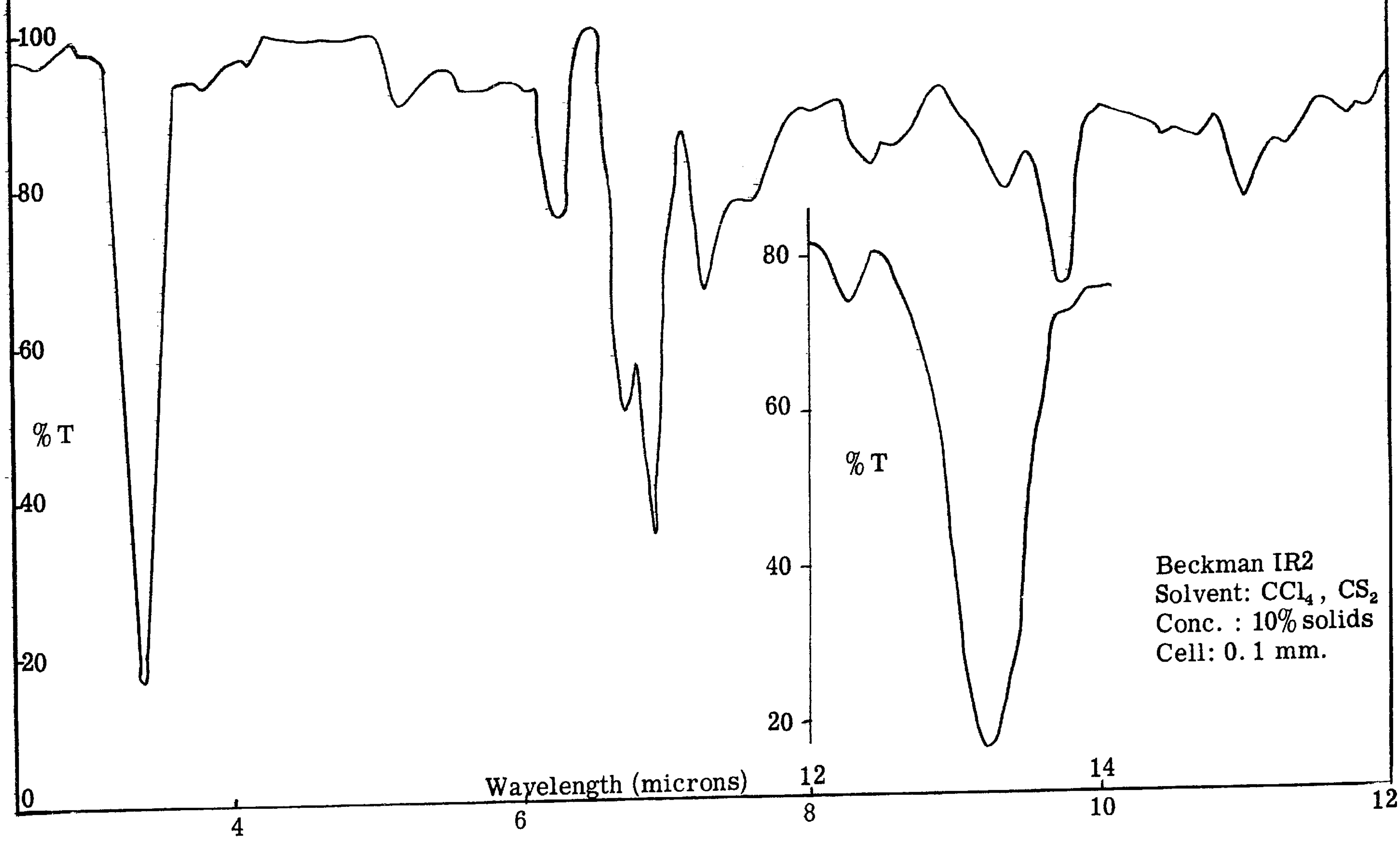
INFRARED ABSORPTION SPECTRUM OF RESIN I



Beckman IR2
Solvent: CCl_4, CS_2
Conc. : 10% solids
Cell : 0. 1 mm.

Figure 21

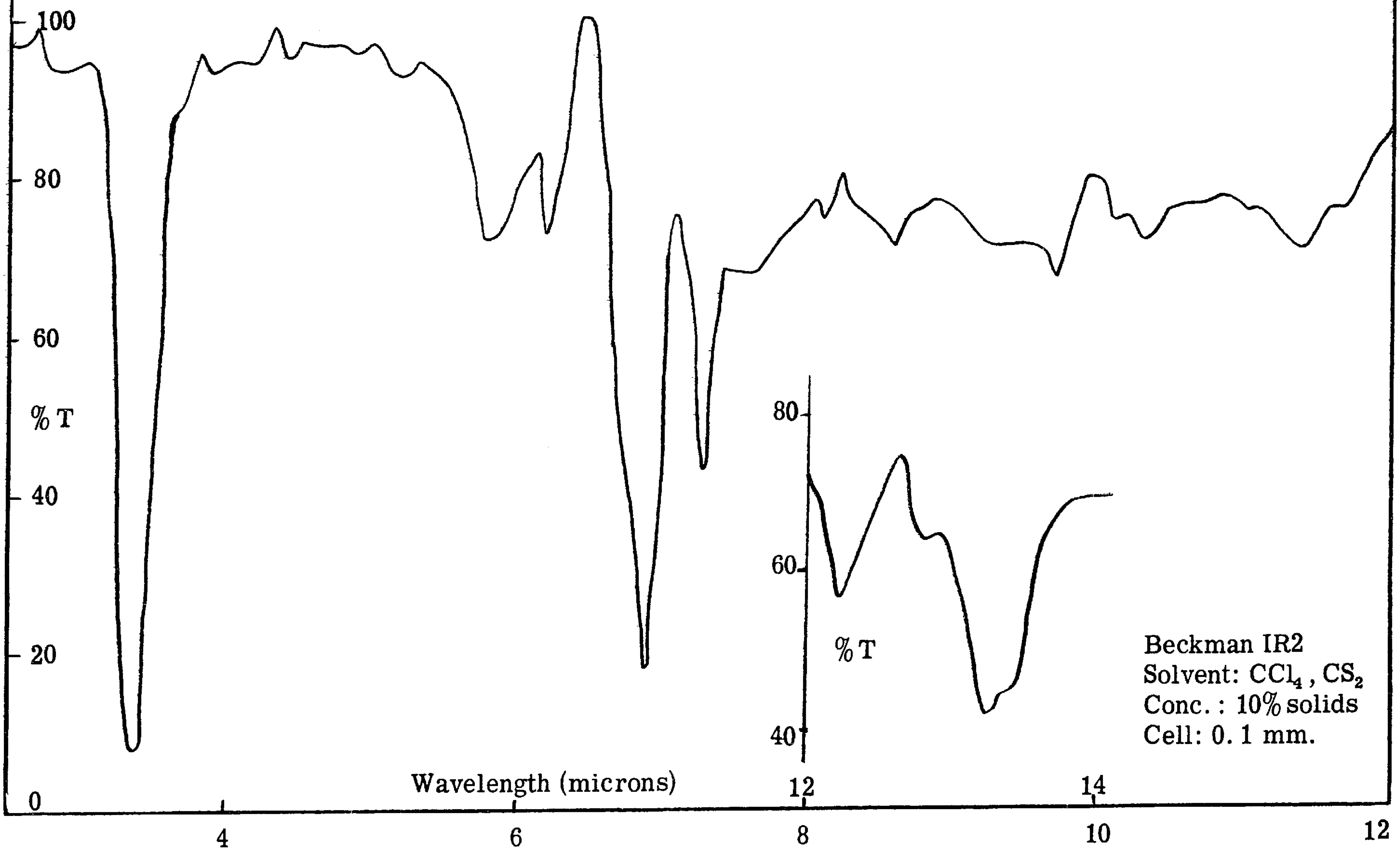
INFRARED ABSORPTION SPECTRUM OF RESIN II



Beckman IR2
Solvent: CCl_4, CS_2
Conc. : 10% solids
Cell: 0. 1 mm.

Figure 22

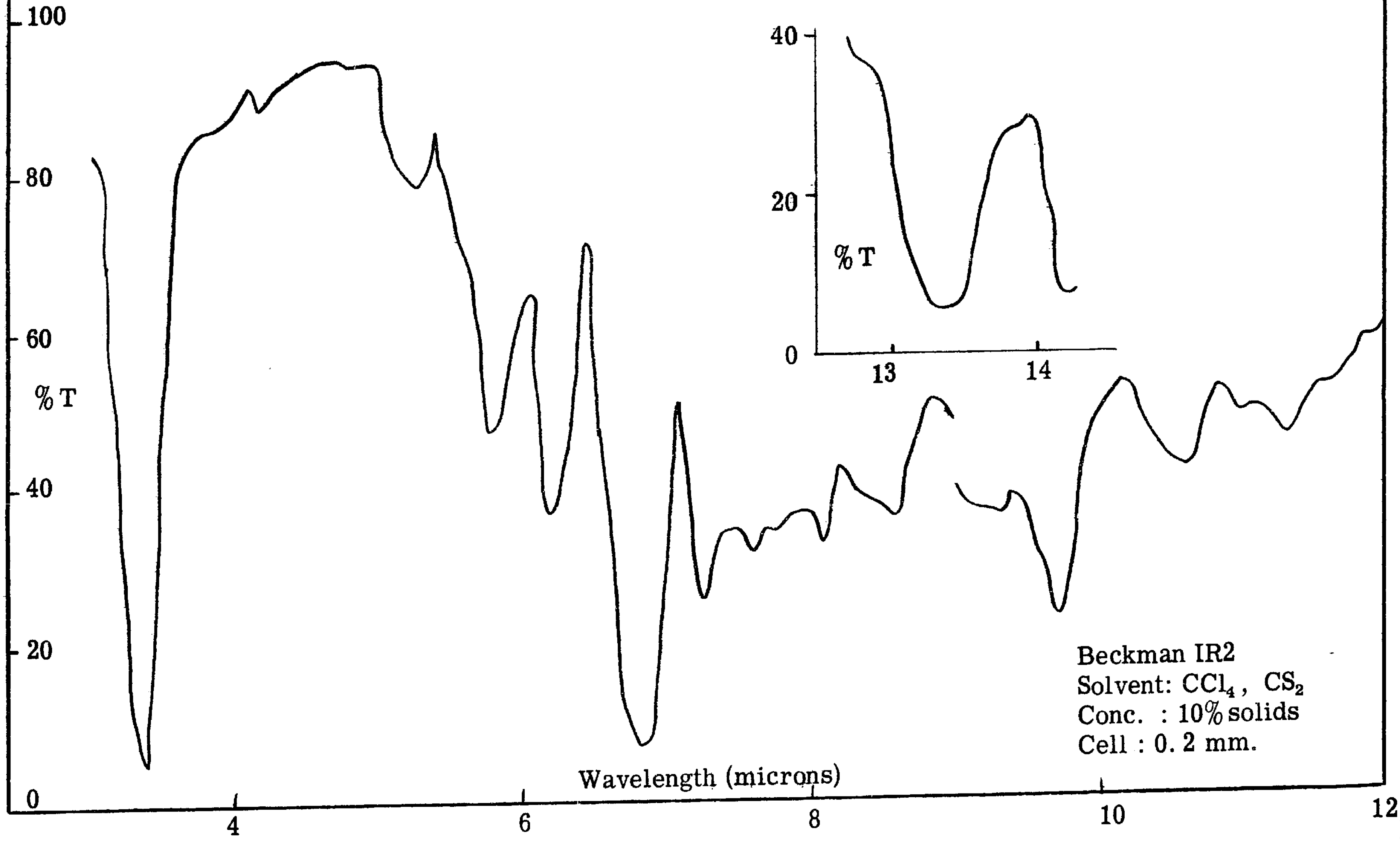
INFRARED ABSORPTION SPECTRUM OF RESIN III



Beckman IR2
Solvent: CCl_4, CS_2
Conc. : 10% solids
Cell: 0. 1 mm.

Figure 23

INFRARED ABSORPTION SPECTRUM OF RESIN IV



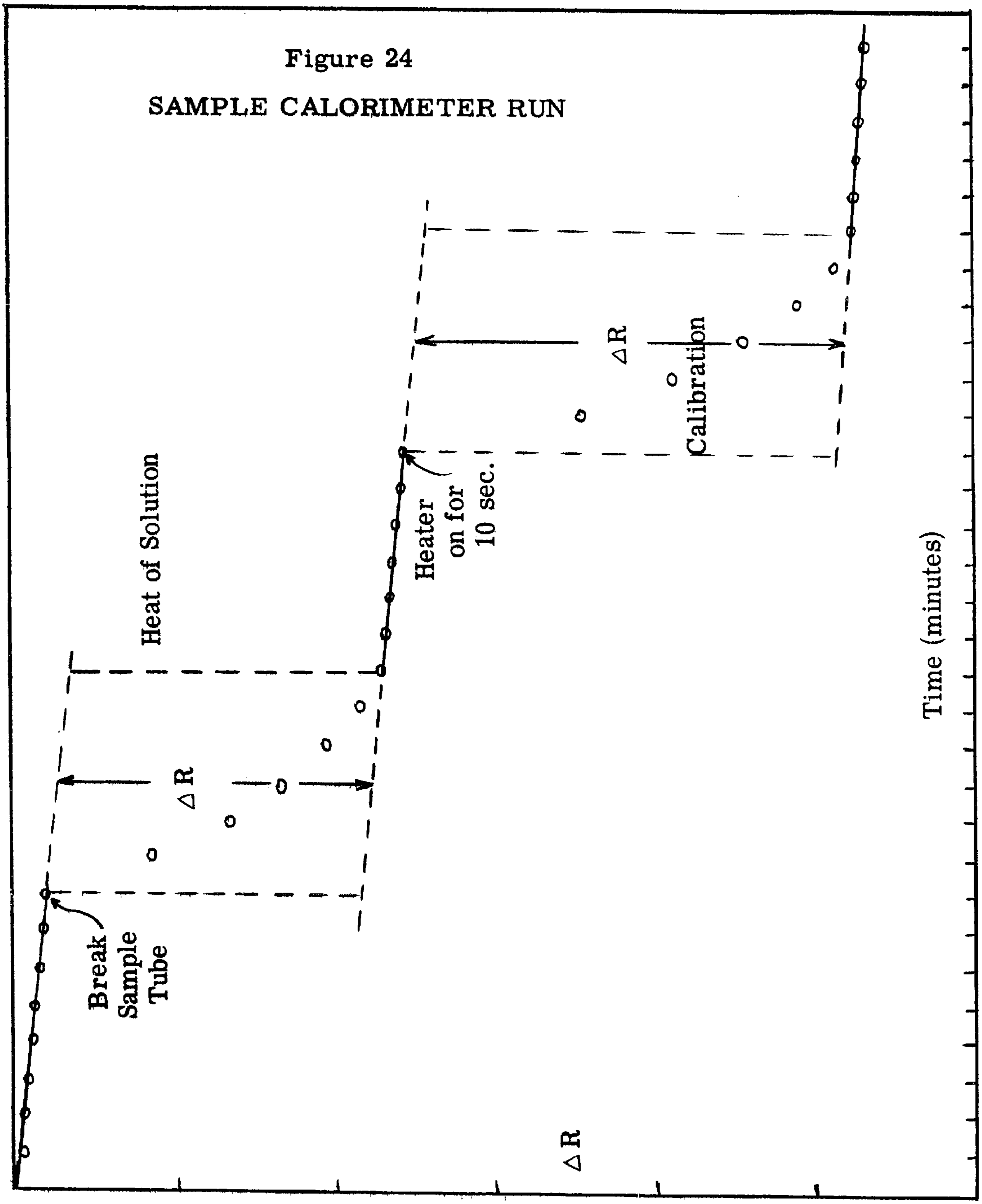
Beckman IR2
Solvent: CCl_4, CS_2
Conc. : 10% solids
Cell : 0. 2 mm.

APPENDIX V

Figure 24 Sample Curve from a Calorimetric Run

Figure 24

SAMPLE CALORIMETER RUN

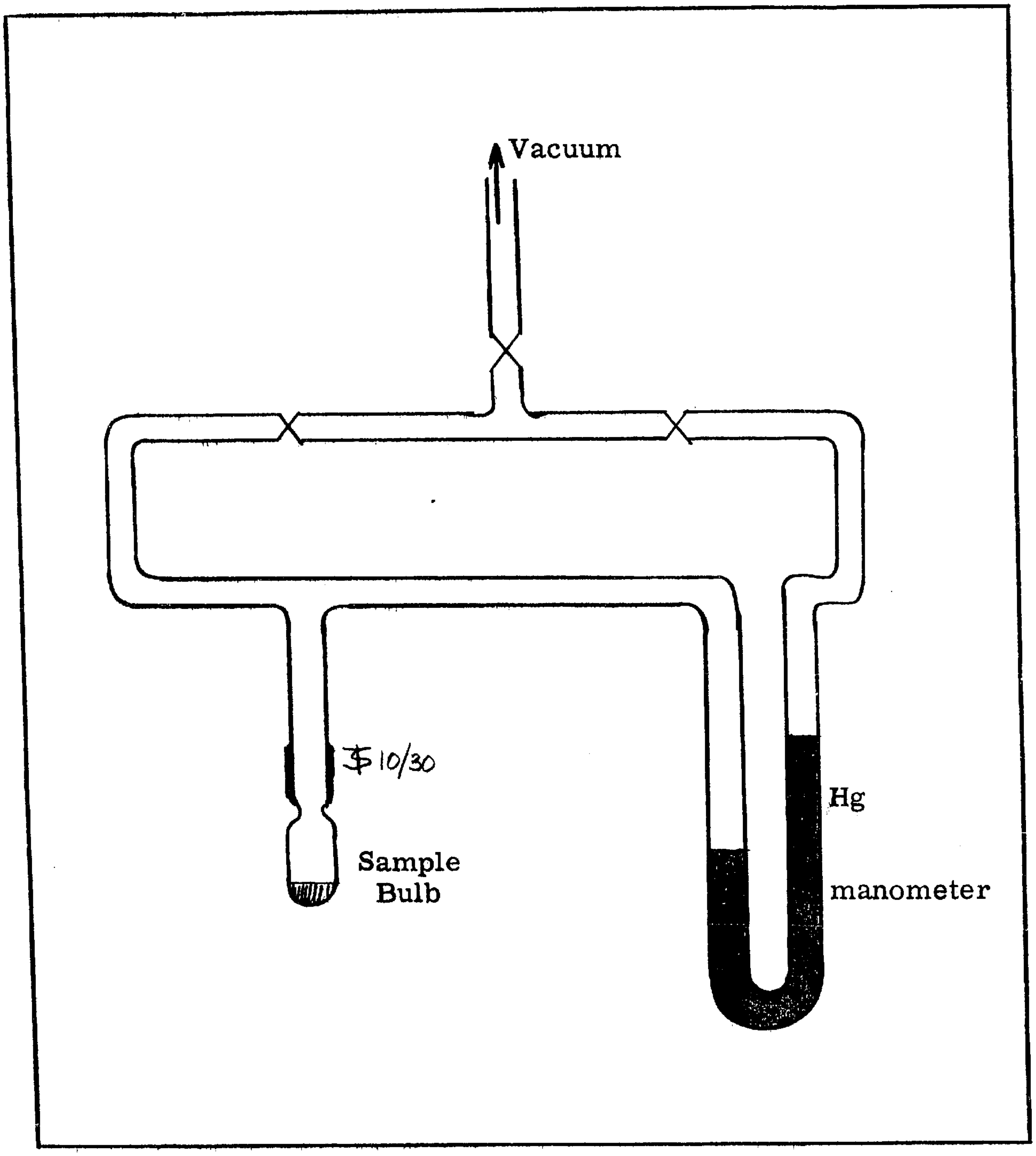


APPENDIX VI

Figure 25 Vapor Pressure Apparatus
Schematic Diagram

Figure 25

VAPOR PRESSURE APPARATUS



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VITA

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