

Heat of Dilution of Polymer Solutions. Part I. Polystyrene-Toluene System †

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A calorimeter based on a design by McGlashan has been used to measure the heat of dilution of non-polar polymer-solvent systems. The influence of concentration and molecular weight of polystyrene on the heat of dilution with toluene has been examined in detail by use of monodisperse polymers with molecular weights from 900 to 98,000. The concentration-dependence of χ_H , the apparent enthalpy parameter, shows characteristics similar to those which have been reported for more polar systems. The concentration-independent enthalpy parameter χ_1 varies from -0.32 to -0.02 with increasing molecular weight. The excess and residual entropy of dilution parameters have been calculated and an attempt made to interpret the results.

LIGHT-SCATTERING photometry and osmometry are widely used techniques for measuring the free energy of dilution of polymer solutions. If these measurements are carried out at different temperatures, one can obtain a quantitative value for the enthalpy of dilution. The unambiguous assignment of an enthalpic and entropic contribution to the mixing of a polymer and solvent would aid the understanding of the molecular nature of polymer solutions.¹ However, the absolute magnitude of the enthalpic contribution derived by differentiation of free-energy data with respect to temperature is notoriously inaccurate.²

Calorimetric methods of obtaining enthalpic data on polymer solutions are, in principle, superior to more conventional solution property measurements, although less frequently used because of experimental difficulties. It is possible to measure the heat of solution of a polymer sample in a large excess of solvent, which would effectively yield a value of ΔH_m^∞ , the heat of solution of the polymer per mole of repeat unit, at infinite dilution. The long dissolution time characteristic of solid polymers in contact with solvents limits this type of measurement to Tian-Calvet microcalorimeters,³ which measure very small heat effects over prolonged periods. There are

other and more serious limitations to the usefulness of heat of solution measurements, namely that unless the temperature at which the heat of solution is measured is above the glass transition temperature of the polymer, there will be an exothermic effect due to the dissolution of the glass,^{4,5} and also, if the polymer is not completely amorphous, the heat of solution will depend upon the degree of crystallinity of the polymer.^{6,7}

Although measurement of heats of dilution circumvent the difficulties inherent in measuring the heats of solution, there have been few systematic studies of the heats of dilution of polymer solutions and those are mainly of polar systems.⁸⁻¹² The dilution of a polar system gives an exothermic heat of dilution several magnitudes larger than the effect in a non-polar system. The scarcity of data of non-polar polymer-solvent systems can probably be explained in terms of the general difficulty of achieving sufficient sensitivity and reproducibility to measure the small heat effects encountered. This is unfortunate, because the bulk of polymer solution theory appertains to non-polar systems.

The most frequent assumption in the theory of the heats of mixing of polymers with solvents is that the nearest-neighbour interactions between polymer molecules and solvent molecules are proportional to the

† This paper was presented in part at the Autumn Meeting of the Chemical Society, at the University of Keele, September 24-26, 1968.

¹ G. V. Schulz and H. Doll, *Z. Elektrochem.*, 1952, **56**, 248.

² M. L. McGlashan, 'Experimental Thermochemistry,' ed. H. A. Skinner, Interscience Publ. Inc., New York, 1961, vol. 2, ch. 15.

³ G. Delmas, D. Patterson, and T. Somcynsky, *J. Polymer Sci.*, 1962, **57**, 79.

⁴ U. Bianchi, E. Pedemonte, and C. Rossi, *Makromol. Chem.*, 1966, **92**, 114.

⁵ B. J. Cottam, J. M. G. Cowie, and S. Bywater, *Makromol. Chem.*, 1965, **86**, 116.

⁶ S. Maron and F. Filisko, *Polymer Preprints*, 1968, **9**, 909.

⁷ H. P. Schreiber and M. H. Waldman, *J. Polymer Sci.*, 1967, **A2**, **5**, 555.

⁸ P. Meares, *Trans. Faraday Soc.*, 1951, **47**, 699; Von W. Bruns, F. Mehdorn, K. Mirus, and K. Ueberreiter, *Kolloid-Z. Z. Polym.*, 1968, **224**, 17; K. Amaya and R. Fujishiro, *Bull. Chem. Soc. Japan*, 1956, **29**, 830; H. J. L. Schuurmans and J. J. Hermans, *J. Phys. Chem.*, 1957, **61**, 1496.

⁹ K. Amaya and R. Fujishiro, *Bull. Chem. Soc. Japan*, 1956, **29**, 361.

¹⁰ A. Kagemoto, S. Murakami, and R. Fujishiro, *Bull. Chem. Soc. Japan*, 1967, **40**, 11.

¹¹ A. Kagemoto, S. Murakami, and R. Fujishiro, *Makromol. Chem.*, 1967, **105**, 154.

¹² H. Daoust and A. Hade, *Polymer*, 1968, **9**, 47.

volume fractions of the components,⁹ which leads to an expression (1) for the partial molar heat of dilution of the solvent $\Delta\bar{H}_1$, where ϕ is the volume fraction of polymer

$$\Delta\bar{H}_1 = RT\chi_H\phi^2 \quad (1)$$

in solution, χ_H is the apparent enthalpy parameter, and $RT\chi_H$ represents the difference in molar enthalpy of solvent surrounded by pure polymer compared with pure solvent.^{13a} Integration of equation (1) to obtain an expression for ΔH_d , the integral heat of dilution gives¹⁴ equation (2) where ϕ_1 , ϕ_2 are the volume fractions of polymer in solution, before and after dilution, respectively, and Δn is the number of moles of solvent added.

$$\Delta H_d = RT\phi_1\phi_2\Delta n\chi_H \quad (2)$$

It has been found that equation (2) does not satisfactorily represent the concentration-dependence of the integral heat of dilution,¹⁴ and it has been shown that a power-series expansion for the concentration-dependence of the apparent enthalpy parameter may be used¹⁵

$$\chi_H = \chi_1 + \chi_2\phi + \chi_3\phi^2 \quad (3)$$

where χ_1 , χ_2 , $\chi_3 \dots$ are the first, second, third, etc., enthalpy parameters. It is convenient to consider the first two terms in the expansion, ignoring third and higher enthalpy parameters, whereby it can be shown that the integral heat of dilution may be expressed as (4).

$$\Delta H_d = RT\phi_1\phi_2\Delta n\{\chi_1 + \chi_2(\phi_1 + \phi_2)/2\} \quad (4)$$

χ_H as determined by insertion of experimental results in equation (2) should, if this analysis is correct, give a straight line when plotted against $(\phi_1 + \phi_2)/2$ of slope χ_2 and intercept χ_1 . The concentration-independent enthalpy parameter χ_1 is equivalent to the parameter κ introduced in the dilute solution theory of Flory, and used extensively in the literature relating to polymer solutions.¹³ The difference in the chemical potential between the pure solvent and the solvent in a polymer solution, $-\Delta\mu_1$, may be determined by measuring the osmotic pressure of that solution, and using equation (5).

$$\frac{\pi}{\bar{V}_1} = -\Delta\mu_1 \quad (5)$$

Here π is the osmotic pressure, \bar{V}_1 the partial molar volume of the solvent. The chemical potential may be split into ideal and excess terms, (6), where $\Delta\mu_1^I$ and

$$\Delta\mu_1 = \Delta\mu_1^I + \Delta\mu_1^E \quad (6)$$

$\Delta\mu_1^E$ represent ideal and excess chemical potential, respectively. $\Delta\mu_1^I$ is given by the usual equation (7) for the ideal chemical potential, where x_1 is the

$$\Delta\mu_1^I = -RT \ln x_1 \quad (7)$$

¹³ P. J. Flory, 'Principles of Polymer Chemistry,' Cornell Univ. Press, New York, 1953, (a) ch. XII; (b) ch. XIV.

¹⁴ A. Kagemoto, S. Murakami, and R. Fujishiro, *Bull. Chem. Soc. Japan*, 1966, **39**, 15.

mole fraction solvent of and $\Delta\mu_1^I$, by the Flory-Huggins lattice theory, is expressed as equation (8)

$$\Delta\mu_1^E = -RT\{(\frac{1}{2} - \chi)\phi^2 + \phi^3/3 + \dots\} \quad (8)$$

where χ is the interaction parameter characteristic of nearest-neighbour interactions. Ignoring terms in ϕ^3 and higher we may approximate the excess chemical potential of the solvent by equation (9). The term

$$\Delta\mu_1^E \approx RT(\chi - \frac{1}{2})\phi^2 \quad (9)$$

$(\chi - \frac{1}{2})$ can be identified with the parameters κ and ψ derived from the Flory dilute solution theory, *i.e.*, equation (10). Equations (11a and b) show the relation-

$$\chi - \frac{1}{2} = \kappa - \psi \quad (10)$$

$$\Delta\bar{H}_1 = RT\kappa\phi^2 \quad (11a)$$

$$\Delta\bar{S}_1 = R\psi\phi^2 \quad (11b)$$

ships of κ and ψ to the partial molar enthalpy and entropy of dilution, respectively. It has been shown¹⁶ that the chemical potential of the solvent can be split up in an alternative way as in (12) where $\Delta\mu_1^O$ is the chemical

$$\Delta\mu_1 = \Delta\mu_1^O + \Delta\mu_1^R \quad (12)$$

potential due to combinational, *i.e.*, donfiguration contributions and $\Delta\mu_1^R$ is the chemical potential due to non-combinational effects, known as the residual chemical potential. $\Delta\mu_1^R$ is to be thought of as being due solely to nearest-neighbour effects. Since χ is the parameter characteristic of nearest-neighbour effects, it may be related to $\Delta\mu_1^R$ by equation (13)

$$\Delta\mu_1^R = RT\chi\phi^2 \quad (13)$$

and on splitting χ into enthalpic and entropic components by analogy with equation (11) we see that χ is given by equation (14) where $\Delta\bar{S}_1^R$ is given by equation (15), $\Delta\bar{S}_1^R$ being the residual partial-molar

$$\chi = \kappa - (\psi - \frac{1}{2}) \quad (14)$$

$$\Delta\bar{S}_1^R = R(\psi - \frac{1}{2})\phi^2 \quad (15)$$

entropy due to nearest-neighbour interactions. It should be remembered that the accuracy of this analysis rests upon the assumptions of the Flory-Huggins lattice theories in predicting that the portion of the excess chemical potential attributable to configurational or combinational effects is given by $-RT\phi^2/2$. Unfortunately there is no experimental method of distinguishing between entropic effects caused by nearest-neighbour interactions and those caused by configurational or combination effects.

In this paper we examine the heat of dilution of the

¹⁵ T. A. Orofino and P. J. Flory, *J. Chem. Phys.*, 1957, **25**, 1067; M. A. Kabayama and H. Daoust, *J. Phys. Chem.*, 1958, **62**, 1127; M. Senez and H. Daoust, *Canad. J. Chem.*, 1962, **40**, 734.

¹⁶ P. J. Flory, J. L. Ellenson, and B. E. Eichinger, *Macromolecules*, 1968, **1**, 279.

polystyrene-toluene system. There is conflicting information in the literature for this system,^{14,17-20} and there has been no systematic study of the influence of molecular weight and concentration on the heat of dilution. It was felt that such measurements would help substantiate some current developments in polymer solution theory.

EXPERIMENTAL

The criteria used for selecting a suitable apparatus to measure the heats of dilution were as follows: (a) The polymer solution should be mixed efficiently with the solvent (and quickly, in the case of a pseudo-adiabatic calorimeter). This is frequently difficult with polymer solutions because of viscosity. (b) The heating induced by stirring of the contents of the calorimeter should be minimal consistent with (a). (c) The solution and the solvent should be mixed in the absence of vapour-space. This is a point which has received much attention for the mixing of low-molecular weight liquids,² but has been ignored by many workers using polymer solutions. For low-concentration polymer solutions, the difference in vapour-pressure between the solution and the solvent is small but this is not so for polymer solutions where the volume fraction of polymer is as high as 0.4. An additional complication is that vigorous mixing will cause evaporation of the solvent into the vapour space and re-equilibration may be slow.²¹

A calorimeter based on the design by Larkin and McGlashan²² was found to be the simplest and most successful for our purposes of several calorimeters examined, in that criteria (a), (b), and (c) were fully satisfied. The general technique of filling the calorimeter with mercury and loading with polymer solution and solvent followed that described by Larkin and McGlashan. We followed the technique of Morcom and Travers²³ of enclosing the cell in a close-fitting polystyrene jacket which was then placed in a silvered Dewar vessel fitted with a rubber bung containing water-tight conduits for the electrical circuits. The calorimeter was immersed in a water-bath controlled thermostatically to better than $\pm 0.001^\circ$ at 30° . The three thermistors (Messrs. Standard Telephones and Cables Limited, Footscragg, Sidcup, Kent, Type M52) which had resistances of about 370 ohms each at 30° were connected in series to give a total resistance of about 1100 ohms at 30° , forming one arm of a Wheatstone's bridge circuit with fixed resistances of 10 ohms and 100 ohms and a variable resistance, in the appropriate positions. This bridge circuit provided near-optimum conditions for the D.C. amplifier used, (D.C. Microvolt amplifier type 9290, Messrs. Guildline Instruments Limited, Smiths Falls, Ontario, Canada), an extremely high-sensitivity chopper amplifier with internal noise level $\pm 0.0017 \mu\text{v}$. The bridge current of 10 ma gave a rate of self-heating in the thermistors of 8.93×10^{-6} watt. A Hitachi-Perkin Elmer 165 pen recorder was connected to the amplifier output. A chart speed of 10 mm./min. was used. The heating circuit for calibration was again similar to that used by Larkin and McGlashan. The time of heating was measured with an electrical stop-clock, with

an accuracy of ± 0.01 sec. The whole apparatus was maintained in an environment thermostatted at a convenient temperature between 24° and 27° to $\pm 0.5^\circ$ dependent on the ambient temperature, to prevent inaccuracies due to thermal e.m.f.s in the bridge or change in resistance values with temperature. The general experimental methods for measuring the heat of dilution followed those described previously for heats of mixing²² with the following exceptions: (i) The dilution of polystyrene in toluene was exothermic; therefore, the technique of simultaneous heating during mixing which can be used in an endothermic dilution experiment could not be used. This gave rise to some uncertainty in the extrapolations used for compensation of heat losses, and so was a source of error; (ii) when the calorimeter was stirred once every 4 sec. four stirs were found to be sufficient to ensure complete mixing, verified by the fact that a stirring calibration could be repeated without giving a different value to that for the first calibration; an estimation of the total uncertainty introduced for

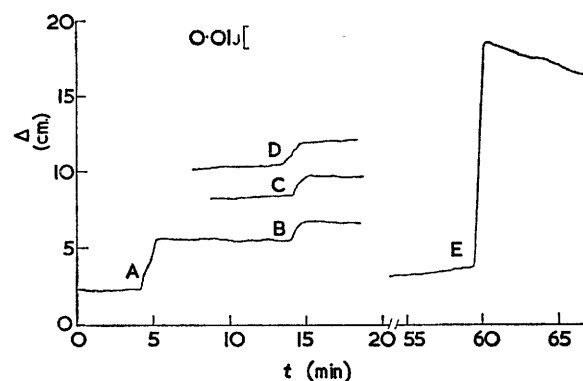


FIGURE 1 Pen-recorder deflection, Δ , plotted against time for a typical experiment. A, exothermic mixing; B, C, D, repeated stirring corrections; E, calibration

ΔH_d , the integral heat of dilution gave a value of $(\pm 0.001\text{J})$, hence a maximum error of $\pm 12\%$ for small values of ΔH_d .

A typical trace is shown in Figure 1 for a mixing followed by repeated stirring calibrations and heating calibration.

Materials.—AnalaR toluene was purified by the usual methods,²⁴ followed by refluxing over molten sodium and distillation twice through a 30-plate fractionating column, discarding generous head and tail fractions each time. A reflux ratio of 10 : 1 was used. The product was stored over calcium hydride. The density, d_4^{30} , of the toluene was $0.85765 \text{ g. ml}^{-1}$ (lit.,²⁴ 0.85769). The polymer samples (Table 1) were commercial monodisperse polystyrenes supplied by Messrs. Pressure Chemicals Limited, 3419 Smallman Street, Pittsburgh, Pennsylvania 15201, or by Messrs. Waters Associate, 61 Fountain Street, Framingham, Massachusetts, U.S.A. The polymers were purified by reprecipitation twice using the benzene (solvent)–methanol (non-solvent) system and then freeze-dried from benzene solution under vacuum. The samples were finally dried in a vacuum oven at 60° overnight. However, several

¹⁷ H. Tompa, *J. Polymer Sci.*, 1952, **8**, 51.

¹⁸ G. V. Schulz and A. Horbach, *Z. phys. Chem. (Frankfurt)*, 1959, **22**, 377.

¹⁹ K. Amaya and R. Fujishiro, *Bull. Chem. Soc. Japan*, 1956, **29**, 270.

²⁰ K. Amaya and R. Fujishiro, *Bull. Chem. Soc. Japan*, 1958, **31**, 19.

²¹ M. L. McGlashan, *J. Pure Appl. Chem.*, 1964, **8**, 157.

²² J. A. Larkin and M. L. McGlashan, *J. Chem. Soc.*, 1961, 3425.

²³ K. W. Morcom and D. N. Travers, *Trans. Faraday Soc.*, 1965, **61**, 230.

²⁴ Ed. A. Weissburger, 'Technique of Organic Chemistry,' Wiley, New York, 1958, vol. VII.

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polymer samples which were used without reprecipitation and freeze-drying but with oven drying gave results in good agreement with the reprecipitated samples. The most concentrated polymer solutions were made in 5 ml. graduated flasks at 30°, and the more dilute solutions were

TABLE I

Origin, molecular weights, and apparent densities in solution at 30° of polystyrene samples

	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	d_2 (g. cm. ⁻³)
Pressure Chemicals Co.	900	990	1.10	1.017
Waters Associate	4600	5000	1.09	1.025
Pressure Chemicals Co.	10,900	10,500	1.04	1.069
Waters Associate	19,650	19,850	1.01	1.033
Waters Associate	96,200	98,200	1.02	1.043

made up by diluting the concentrated solutions by weight in 2 ml. capped sample tubes, volume additivity being assumed. The apparent densities in solution at 30° were determined (Table I) and used for all necessary calculations.

RESULTS

An attempt has been made to analyse our experimental results in terms of equation (2) by plotting ΔH_d against $RT\phi_1\phi_2\Delta n$, which should give a straight line passing through the origin with slope χ_H if χ_H is independent of concentration. Figure 2 shows an example of the results which were obtained with polymer of \bar{M}_n of 4600. The curve demonstrates that the enthalpy parameter is not independent of concentration. The shape of the curve is comparable with those obtained for similar plots for other polymer-solvent systems by Kagemoto *et al.*^{10,11,14} On plotting χ_H as determined from equation (2) against $(\phi_1 + \phi_2)/2$, according to equation (4), as the molecular weight of the polymer is increased, we observe a greater deviation from linearity

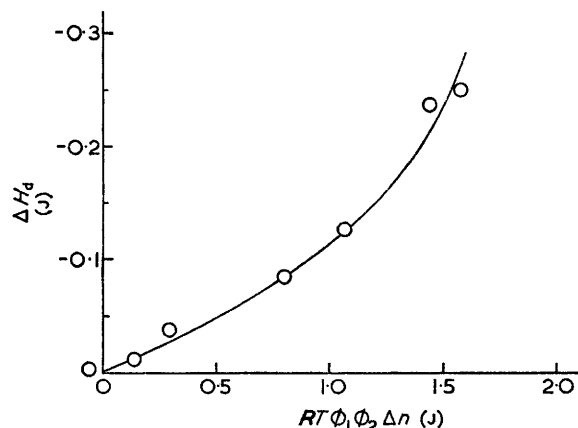


FIGURE 2 The integral heat of dilution plotted against $RT\phi_1\phi_2\Delta n$, for polystyrene of $\bar{M}_n = 4600$, in toluene

(Figure 3). It is thought that the results are best represented by the smooth curves drawn, and the intercepts on the χ_H axis, although subject to the errors of extrapolation, give values of χ_1 (or κ), the concentration-independent enthalpy parameter. Several of the low average volume fraction results for the polymer of \bar{M}_n 900 seem anomalous, in relation to the rest of the data. The continuous line A represents an extrapolation which correlates with the concentration-dependence observed for the higher molecular weight samples. However, there is no reason to suspect

the accuracy of the experimental data because the system is more exothermic on dilution than at higher volume fractions and, in principle, more accurately measured; hence it is possible that the concentration-dependence is represented by the broken curve A'. This sharp increase of apparent enthalpy parameter has been noted before, but

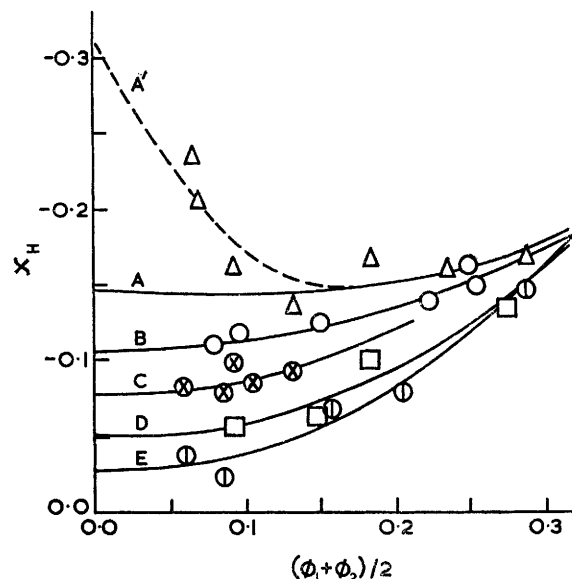


FIGURE 3 The apparent enthalpy parameter plotted against average volume fraction, for polystyrene in toluene
Values of \bar{M}_n : A' and A, 900; B, 4600; C, 10,900; D, 19,650; and E, 96,200

only with a more polar system, poly(methyl methacrylate)-benzene.¹²

DISCUSSION

There has been no systematic study of the variation of the concentration-independent enthalpy parameter with molecular weight for polystyrene-toluene. The only reported value of χ_1 is that obtained by Kagemoto, Murakami, and Fujishiro,¹⁴ using a calorimetric technique, of -0.08 with polymer of \bar{M}_n 25,400 at 25°. The experimental data showed considerable scatter when χ_H was plotted against $(\phi_1 + \phi_2)/2$ and the least-squares method was employed to obtain a straight line and hence χ_1 . All reported calorimetric determinations have yielded negative values of χ_H . Our results are consistent with this finding.

The only work in which polymer of more than one molecular weight has been used is that of Schulz and Horbach,¹⁸ who obtained a value of χ_H of -0.032 for an average volume fraction of about 0.075 with polymer of \bar{M}_n 11,000 at 23°. Within experimental error the χ_H values quoted for polymers of \bar{M}_n 237,000 and 580,000 are identical to that for the lower molecular weight sample. Tompa quotes χ_H as -0.16 , which is an average value for dilutions with average volume fraction, $(\phi_1 + \phi_2)/2$, ranging from 0.3 to 0.19 with polymer of \bar{M}_n 3328 at 25°. Amaya and Fujishiro¹⁹ quote a value for χ_H , of -0.24 to -0.27 for a \bar{M}_n of 28,600 at 25°. These

values were obtained by averaging results over an average volume fraction varying from 0.14 to 0.048 and showed no consistent variation with concentration. There is thus general agreement on the order of magnitude of the apparent enthalpy parameter for this system, but it is difficult to make absolute comparisons of molecular weight effects, since \bar{M}_w/\bar{M}_n for the polymer samples used in any previous calorimetric determinations has not been stated.

There have been many determinations of the concentration-independent enthalpy parameter by osmotic pressure and light-scattering determinations on polystyrene-toluene solutions at different temperatures. These yield values of χ_1 which are subject to the normal errors of differentiation of free-energy data with respect to temperature and the scatter of results obtained by different authors is considerable. Bawn and Wajid²⁵ obtain a value of -0.007 by osmotic pressure measurements over a temperature range of $25-55^\circ$ with a \bar{M}_n of 248,000. Schik, Doty, and Zimm²⁶ obtain -0.17 over a temperature range of $27-69^\circ$ with a \bar{M}_n of 524,000 whereas Schulz and Hellfritz²⁷ obtain values of -0.030 and -0.036 for \bar{M}_n 's of 247,000 and 580,000, respectively, at 23° . It is possible to obtain χ_1 values from intrinsic viscosities and their temperature coefficients^{13b} and Cragg, Dumitru, and Simkins²⁸ obtain a value of $+0.06$. The values of χ_1 obtained from viscosity measurements are open to some doubt.

Schulz, Baumann, and Darskus²⁹ have shown that the variation of second virial coefficient with molecular weight for the polystyrene-toluene system can be represented (an athermal system, to which the above closely approximates, being assumed) by equation (16)

$$A_2 = (\bar{V}_{sp}/M_{mon})(\pi a/4d)h(z) \quad (16)$$

where \bar{V}_{sp} is the partial specific volume of the polymer, M_{mon} the molecular weight of the monomer unit, a is its length in the chain (2.54 \AA for vinyl polymers), and d is the averaged diameter of the wormlike chain molecule. The function $h(z)$ contains a configurational effect, because the concentration of segments in the neighbourhood of a segment is not identical with the average concentration of segments in the solution, which can be represented by the equations suggested by Casassa.³⁰ The extensive measurements of the second virial coefficient by light-scattering and osmotic measurements scatter around the theoretical value by $\pm 15\%$, which may be considered acceptable in view of the experimental errors likely to be involved. Values of A_2 have, therefore, been taken as given by the theoretical curve derived by Schulz and values of the $(\chi_1 - \psi)$ excess free energy of mixing parameter calculated by use of equation (17)

$$A_2 = -(\chi_1 - \psi)/\bar{V}_1 d_2^2 \quad (17)$$

where d_2 is the density of the polymer in the solution (Table 2) and \bar{V}_1 is the partial molar volume of the solvent which may be assumed to be equal to the molar volume without appreciable error (107.43 ml.). The values of ψ and $(\psi - \frac{1}{2})$ can then be calculated (Table 2).

TABLE 2

Variation of thermodynamic parameters with molecular weight for polystyrene-toluene

\bar{M}_n	$10^4 A_2$ (g. ⁻² cm. ³ mole)	$10^2(\chi_1 - \psi)$	$10^2\chi_1$	$10^2\psi$	$10^2(\psi - \frac{1}{2})$
900	16.44	-18.28	-14.6	4.68	-45.32
4600	11.52	-13.01	-10.6	2.41	-47.59
10,900	8.81	-10.82	-7.9	2.92	-47.08
19,650	7.70	-8.83	-5.2	3.63	-46.37
96,200	5.37	-6.27	-3.0	3.27	-46.73

It is useful to plot the variation of excess free energy of dilution parameters, $(\chi_1 - \psi)$, and heat of dilution parameter, χ_1 , and excess enthalpy of dilution parameter, ψ , against $\log_{10} \bar{M}_n$, to display their molecular weight dependence (Figure 4). $(\chi_1 - \psi)$ increases with increasing molecular weight reflecting the reduced

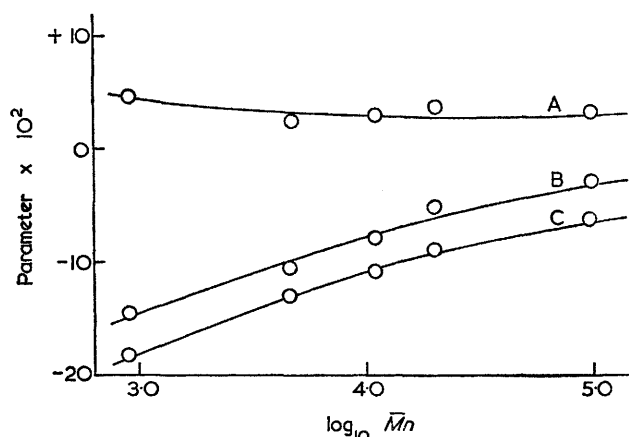


FIGURE 4 The parameters ψ , χ_1 , and $(\chi_1 - \psi)$ plotted against $\log_{10} \bar{M}_n$: curves A, B, and C, respectively

solubility expected with polymers of increasing molecular weight. This increase is closely paralleled by the experimentally determined χ_1 , heat of dilution parameter, which leads to a positive, approximately constant value for the excess entropy of dilution parameter, ψ , of magnitude considerably less than 0.5. A value of 0.5 would be expected on the basis of the rigid lattice theory of polymer solutions where it is assumed there is no nearest-neighbour effect. The low value of ψ may be attributable to specific nearest-neighbour interactions thus giving the large negative values of $(\psi - \frac{1}{2})$ (Table 2), which may be naively interpreted as being attributable to some ordered arrangement of solvent molecules with respect to the polymer chain.

²⁵ C. E. H. Bawn and M. A. Wajid, *J. Polymer Sci.*, 1954, **12**, 109.

²⁶ M. J. Schik, P. Doty, and B. H. Zimm, *J. Amer. Chem. Soc.*, 1953, **72**, 530.

²⁷ G. V. Schulz and H. Hellfritz, *Z. Elektrochem.*, 1953, **57**, 835.

²⁸ L. H. Cragg, E. T. Dumitru, and J. E. Simkins, *J. Amer. Chem. Soc.*, 1952, **74**, 1977.

²⁹ G. V. Schulz, H. Baumann, and R. Darskus, *J. Phys. Chem.*, 1966, **70**, 3647.

³⁰ E. F. Casassa, *J. Chem. Phys.*, 1959, **31**, 800.

The results in Figure 3 indicate that the heat of dilution of the polystyrene-toluene system should become increasingly exothermic with decreasing molecular weight. Measurement of the heat of mixing at 30° of toluene and ethylbenzene (ethylbenzene may be considered as representing one unit in a polystyrene chain) produces a value of χ_1 of about -0.02 with a similar analysis of the data to that used for dilution measurements.³¹ It has been said that ethylbenzene is not as good a low molecular weight model of the polystyrene chain as 1,3-diphenylbutane.³² The concept of a low molecular weight analogue of a polymer chain is in itself questionable. It would be expected that the heat of dilution of a non-polar polymer in a non-polar solvent would produce an endothermic effect when only non-polar dispersion forces exist between molecules, by analogy with the results obtained from mixing non-polar low molecular weight liquids. It has been observed, however, that non-polar polymers may dissolve in non-polar solvents with evolution of heat.³ This cannot be satisfactorily explained on the van Laar theory of the heat of mixing of non-polar molecules,^{33,34} which leads to an equation for the heat of mixing given as (18) where ΔH_m is the heat of

$$\Delta H_m = V_m(\delta_A - \delta_B)^2 \phi_A \phi_B \quad (18)$$

mixing, V_m the volume of solution, δ_A and δ_B the solubility parameters of components A and B, respectively, and ϕ_A and ϕ_B the volume fractions of components A and B, respectively. The solubility parameter δ is defined as follows in equation (19) where ΔE^{vap} and V denote the energy of complete vaporisation per c.c. and the molar volume respectively of the substance. Hildebrand and

$$\delta = \{\Delta E^{vap}/V\}^{1/2} \quad (19)$$

Scott³⁴ have examined the physical basis for the assumption of equation (18) and have concluded that the van Laar postulate is justified when considering the mixing of relatively non-polar molecules, and this is found by experiment to apply to the heats of mixing of most non-polar low molecular weight compounds to a first approximation. The most serious assumption made in the above approach is that there should be no net change in volume in the mixing process for non-polar mixtures. If there is a change in volume there will be a contribution (20) to the experimentally measured enthalpy change at constant pressure $(\Delta H_m)_p$

$$(\Delta H_m)_p = (\Delta U_m)_v + T \left(\frac{\partial P}{\partial T} \right)_v (\Delta V_m)_p + \quad (20)$$

where $(\Delta U_m)_v$ is the heat of mixing at constant volume (*i.e.*, is given by the theoretical equation (18)) and

$(\Delta V_m)_p$ is the change in volume at constant pressure. Equation (20) may be approximated by (21) where P_i

$$(\Delta H_m)_p \simeq (\Delta U_m)_v + P_i(\Delta V_m)_p \quad (21)$$

is the internal pressure of the solution. Estimates of the value of P_i and literature values of $(\Delta V_m)_p$ suggest that for the mixing of toluene with ethylbenzene the $(\Delta U_m)_v$ values approximate to zero which would be predicted on the basis of equation (18). This suggests that the heat of dilution of polystyrene in toluene is also exothermic as a result of volume contraction. The measurement of volume changes on dilution are naturally more difficult to measure than volume changes on mixing. We are trying to measure the volume change on dilution for this system and preliminary results indicate a contraction on dilution, which when multiplied by the internal pressure P_i of toluene gives a quantity having the same order of magnitude as ΔH_d . A further consequence is that the rigid lattice prediction of $\psi = 0.5$ is no longer valid. It is instructive that negative volume changes are predicted for mixing or diluting non-polar polymeric and non-polar monomeric molecules by the theories of Prigogine³⁵ and Flory¹⁶ where attention is drawn to the difference in thermal coefficients of expansion between the polymer and monomeric species. These theories take into account the fact that two lattice sites containing segments of a chain molecule joined by a covalent bond will not separate much compared with two sites occupied by solvent molecules held by weak dispersion forces. When mixing occurs, the spacing between the solvent molecules is decreased to fit the solvent and polymer together on the same solution lattice leading to a negative contribution to the heat of mixing.³⁶ Both the Prigogine and Flory theories contain interaction parameters characteristic of contacts between a polymer segment and a solvent molecule which cannot be predicted, only deduced empirically from experiment. The Prigogine theory, as interpreted by Patterson *et al.*,³ suggest that the enthalpy parameter may be split into two components, one resulting from nearest-neighbour interactions χ_N , and the other, χ_p , from the difference in size of the two lattices characterising the solvent and the polymer. Then equation (22) is obtained, where χ_p is given by equation (23), where B is a constant, and

$$\chi_1 = \chi_N + \chi_p \quad (22)$$

$$\chi_p = \frac{-BT}{R} \left(\frac{2}{3} - \frac{1}{r_p} \right)^2 \quad (23)$$

r_p is the number of monomer units in the polymer chain. Since B must be positive on the Prigogine theory, our data will not fit an equation of the type (24) unless χ_N is

$$\chi_1 = \chi_N - \frac{BT}{R} \left(\frac{2}{3} - \frac{1}{r_p} \right)^2 \quad (24)$$

³¹ G. Lewis and A. F. Johnson, unpublished results.

³² J. Biros, K. Sole, and J. Pouchly, *Faserforsch. Textiltech.*, **1964**, **15**, 608.

³³ J. J. van Laar and R. Lorenz, *Z. anorg. Chem.*, **1925**, **146**, 42.

³⁴ J. Hildebrand and R. Scott, 'The Solubility of Non-Electrolytes,' 3rd edn., Reinhold Publishing Corp., New York, 1949.

³⁵ I. Prigogine, 'The Molecular Theory of Solutions,' North Holland Publishing Co., Amsterdam, and Interscience Publishers, New York, 1957, chs. 16 and 17.

³⁶ G. Delmas and D. Patterson, *Offic. Dig. Canad. Soc. Paint Technol.*, **1962**, **34**, 677.

a quantity which becomes more positive with molecular weight. This would mean that the interaction between interior polymer segments and solvent is more unfavourable than the interaction between chain ends and solvent, since a high molecular weight polymer has a relatively greater number of interior segments than a low molecular weight polymer. This finding may be contrasted with the results of the heats of mixing of polyisobutylene with various n-alkanes by Patterson *et al.*³ as analysed by Flory *et al.*¹⁶ in which it is found that the interactions of terminal groups make a greater positive contribution to the heat of mixing than the midchain groups.

The concentration-dependence of the apparent enthalpy parameter (Figure 3) is quite marked, and not a

linear function of the average volume fraction. This suggests that the concentration-dependence of χ_H cannot be represented by using only two terms in equation (3). There is a definite decrease in χ_H as the average volume fraction is increased, which is difficult to explain with the information available. It is noteworthy that a value of χ_2 of -0.94 has been obtained by Kagemoto *et al.* on the basis of experimental results showing considerable scatter.¹⁴

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