

Thermodynamic Study of Polymer–Solvent Systems by Reversed-Flow Gas Chromatography

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Synopsis

Reversed-flow gas chromatography, a new method for studying heterogeneous catalysis, diffusion, adsorption, evaporation, and other related phenomena, is now applied to the determination of activity of the solvent in a polymer–solvent system in the whole range of polymer concentration, as well as for the calculation of excess partial molar thermodynamic functions of mixing. The systems used were polystyrene in cyclohexane, polyvinylacetate in cyclohexanone and polyvinylpyrrolidone in methanol. In the first system, which was studied in detail, weight fraction activity coefficients (a_1/w_1) at several temperatures (333.8–348.1 K) and various polymer concentrations (0.020–0.131 g/g) were determined. From the latter parameters weight fraction activity coefficients at infinite dilution (a_1/w_1) $^\infty$ were computed. Flory–Huggins interaction parameters x and solubility parameters δ_2 were also determined. Finally, the thermodynamic parameters found by the present method are compared with those determined by other techniques or calculated theoretically.

INTRODUCTION

The activity of the solvent in a polymer–solvent system may be determined by a number of techniques such as light scattering, osmotic pressure, intrinsic viscosity, and inverse gas chromatography. The unique feature of the intrinsic viscosity technique is that it only generates information in the limiting case of infinite dilution of the polymer. Inverse gas chromatography, on the other hand, provides information at the other extreme of infinite dilution of the probe molecule.

In this work we present for the first time a new chromatographic method, called reversed-flow gas chromatography (r.f.g.c.) for the thermodynamic study of polymer–solvent systems in the whole range of polymer concentration.

Reversed-flow gas chromatography is really a sampling technique and consists in reversing the direction of flow of the carrier gas from time to time. If the carrier gas contains other gases at certain concentrations, recorded by the detector system of the chromatograph, each flow reversal creates perturbations on the chromatographic elution curve, having the form of extra peaks (“sample peaks”).

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If the concentration of a constituent in the flowing gas depends on a rate process, taking place within the chromatographic column, then, by reversing the flow, one performs a sampling of the process, for example, of a sufficiently slow chemical reaction, or the slow diffusion of the vapors of a liquid into the carrier gas. Using suitable mathematical analysis, equations are derived by means of which the rate coefficient of the slow process responsible for the sample peaks is determined.

This method has been used to determine gas diffusion coefficients in binary and ternary mixtures,¹⁻³ adsorption equilibrium constants,⁴ molecular diameters and critical volumes in gases,⁵ Lennard-Jones parameters,⁶ mass transfer coefficients on solid adsorbents,⁷ rates of drying of catalysts,⁸ and recently, activity coefficients,⁹ as well as mass-transfer coefficients for the evaporation of pure liquids¹⁰ or mixtures of liquids with water,¹¹ together with the diffusion coefficients of their vapors into the carrier gas.

The experimental setup for measuring activity coefficients is illustrated in Figure 1. A long diffusion column of length L , at the end of which the polymer solution or the pure solvent is placed, is connected perpendicularly to the

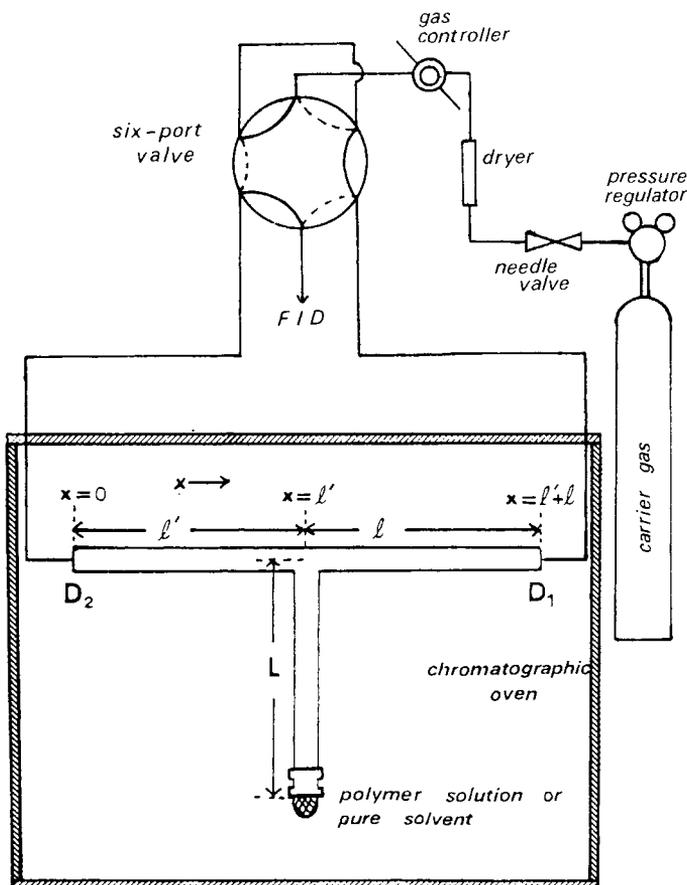


Fig. 1. Experimental setup for the thermodynamic study of polymer-solvent systems by the reversed-flow gas chromatography method.

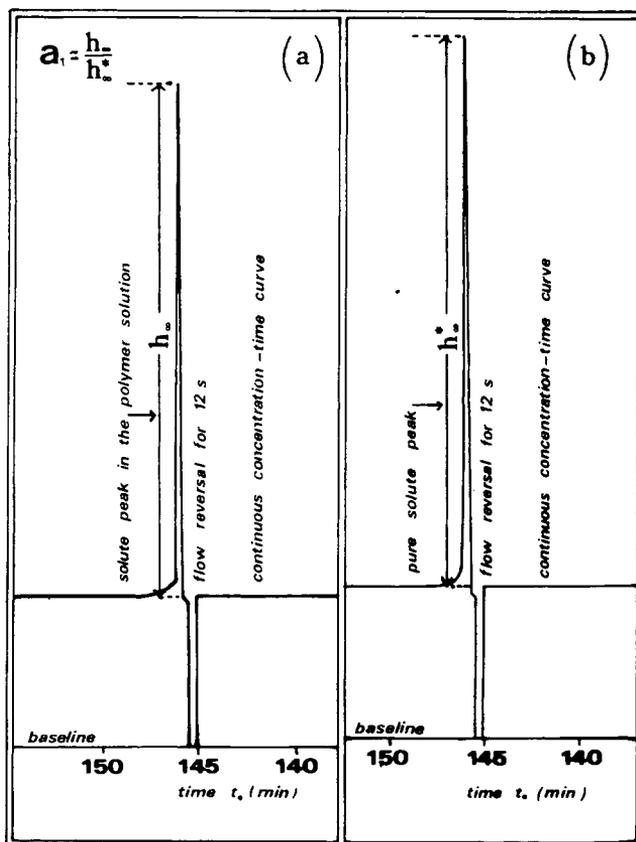


Fig. 2. Two reversed-flow chromatograms, showing (a) the maximum peak for the diffusion of cyclohexane vapor from the polystyrene-cyclohexane solution into the carrier gas helium. The temperature was 348.1 K, the pressure 1 atm and the carrier flow rate $\dot{V} = 0.6 \text{ cm}^3 \text{ s}^{-1}$ and (b) the maximum peak for the diffusion of pure cyclohexane vapor into the carrier gas helium.

midpoint of a "sample column," of length $l' + l$, both placed inside the oven of a chromatograph. The two ends D_1 and D_2 of the sampling column are connected to the carrier gas inlet and the flame-ionization detector, via a six-port valve, as shown. When we switch the valve from one position (—) to the other (---), we inverse the direction of the carrier gas through the sampling column, resulting in the presence of "sample peaks" in the recorder line (see Fig. 2).

EXPERIMENTAL

Materials

The polymers employed were polystyrene (PS) of molecular weight $M_w = 150,000$, polyvinylacetate (PVA) of $M_w = 45,000$, and polyvinylpyrrolidone (PVP) of $M_w = 44,000$. All these polymers were products of BDH Chemicals Ltd.

The solvents used (cyclohexane, cyclohexanone, and methanol) were all from Merck (Uvasol grade). The carrier gas was helium of 99.99% purity from Linde (Greece).

Instrumentation and Procedure

The experimental setup for the thermodynamic study of polymer-solvent systems is shown in Figure 1. Lengths of $L = 112$ cm for the diffusion column and $l' + l = 100 + 100$ cm for the sampling column were used. All of the columns were 1/4-in. empty stainless-steel chromatographic tubes of 4 mm I.D. At the end of the diffusion column a 5-cm glass tube of the same diameter, containing the polymer solution or the pure solvent, was connected by means of a simple 1/4-in. union. Packing of the column of length $l + l'$ was unnecessary because there was not a separation problem.

About 20 min after placing the polymer solution or the pure solvent at the end of the diffusion column, an asymmetric concentration-time curve for the vapor of the pure solvent or the solvent in the polymer solution was recorded, rising continuously, and approaching a limiting plateau. During the rise period, and also when the plateau was reached, flow reversals for 12 s were effected by means of the six-port valve. When the gas is restored to its original direction, sample peaks were recorded (cf. Fig. 2) corresponding to various times t_0 from the beginning. The velocity of the carrier gas helium was constant and equal to $0.6 \text{ cm}^3 \text{ s}^{-1}$, while the pressure drop along column $l' + l$ was negligible. The measurements were repeated three times at each temperature.

In order to obtain homogeneous polymer solutions, the following technique was used, based on an idea of Scholte.¹² Into one glass tube of sufficient length a weighted amount of the polymer and certain volume of the solvent were placed. Then the glass tube was closed, by melting its upper part, and finally the tube was placed into an oven of high temperature (340–370 K) for 1–5 days, shaking the polymer solution from time to time. Cutting the glass tube at the desired point, the polymer solution was ready for its placement at the end of the diffusion column.

THEORETICAL

As it has been shown previously,^{2,9,13} the infinity maximum height, h_∞ , of a sample peak in r.f.g.c. is given by the relation

$$h_\infty \approx 2c_0(l', t_0) \quad (1)$$

In the last equation $c_0(l', t_0)$ is the solute concentration at $x = l'$ and the time t_0 measured from the moment of placing the polymer solution or the pure solvent at the bottom of column L to the last backward reversal of gas flow.

The concentration of the solute at equilibrium, c_0 , is given by the expression⁹

$$c_0 = \frac{vh_\infty}{2} \left(\frac{L}{D} + \frac{1}{k_c} \right) \quad (2)$$

where v is the linear velocity of the carrier gas, D is the diffusion coefficient of the solute vapor into the carrier gas, and k_c the rate coefficient for solute evaporation. Since the parameters D and k_c can be determined as described elsewhere,¹⁰ the value of the concentration c_0 in equilibrium with the liquid bulk phase may be also computed.

If we perform experiments with polymer solutions, which give us c_0 , and with pure solvents, which give us c_0^* then the ratio c_0/c_0^* is equal to P/P^* and that gives the activity a_1 of the solvent in the polymer solution, assuming that the deviation of the solvent vapor from ideal behavior is small. Then we can write

$$a_1 = \frac{c_0}{c_0^*} = \frac{h_\infty(L/D + 1/k_c)}{h_\infty^*(L/D^* + 1/k_c^*)} = \frac{h_\infty}{h_\infty^*} \quad (3)$$

where h_∞ and h_∞^* are the maximum heights of the solvent peaks in the polymer solution and the pure state, respectively. The approximation in eq. (3) was based on the assumption that D and k_c are the same when the solvent is either pure or in the polymer solution. This assumption was verified experimentally.

Equation (3) shows that, in order to find the activity of the solvent a_1 , in a polymer solution, one must perform two experiments, one with the pure solvent and the other with the polymer solution. The only experimental parameters, as eq. (3) shows, are the infinite values h_∞ and h_∞^* for the solvent peak heights.

In polymer solution thermodynamic it is useful to consider the ratio of the activity a_1 to weight fraction of the probe solvent, w_1 . Thus,

$$\frac{a_1}{w_1} = \frac{h_\infty}{h_\infty^* w_1} \quad (4)$$

So we can calculate the weight fraction activity coefficient of the solvent, a_1/w_1 , in a polymer-solvent system and then the excess partial molar free energies of mixing, $\Delta\bar{G}_1$, by the equation¹⁴

$$\Delta\bar{G}_1 = RT \ln(a_1/w_1) = \Delta\bar{H}_1 - T\Delta\bar{S}_1 \quad (5)$$

The last equation shows that a plot of $\ln(a_1/w_1)$ vs. $1/T$ gives a straight line with slope equal to $\Delta\bar{H}_1/R$ from which the excess heat of mixing, $\Delta\bar{H}_1$, at each solvent concentration, can be determined and with intercept equal to $-\Delta\bar{S}_1/R$, from which the excess entropy of mixing, $\Delta\bar{S}_1$, at each solvent concentration, can be also computed.

The partial molar free energies of mixing at infinite dilution of the solvent, $\Delta\bar{G}_1^\infty$, were computed by extrapolation of the $\Delta\bar{G}_1$ values found at various w_1 to the w_1 zero value. From the $\Delta\bar{G}_1^\infty$ values, the weight fraction activity coefficients at infinite dilution, $(a_1/w_1)^\infty$ were computed via eq. (5). It must be pointed out that it is difficult to choose a function which allows the representation of activity or free energy of mixing data covering a wide concentration

range. The following equation,^{12,14}

$$\ln\left(\frac{a_1}{w_1}\right)^\infty = \frac{\Delta\bar{G}_1^\infty}{RT} = \ln(1 - w_2) + w_2\left(1 - \frac{1}{r}\right) + xw_2^2 \quad (6)$$

where w_2 is the weight fraction of the polymer in the solution and r is the degree of polymerization, i.e., the ratio of the number-average molar volume of the polymer to the molar volume of the solvent, shows that the variation of $\Delta\bar{G}_1$ with w_1 is approximately linear in the range $0.2 < w_1 < 1.0$. On the other hand, previous work¹⁵ showed that this variation is approximately linear in the whole range of w_1 . Supposing that the variation of $\Delta\bar{G}_1$ with w_1 is approximately linear in the whole range of w_1 , one can calculate $\Delta\bar{G}_1^\infty$ corresponding to infinite solvent dilution, and from these weight fraction activity coefficients at infinite dilution, interaction parameters, and finally solubility parameters. If the latter parameters are close to those found by other workers or calculated theoretically from empirical equations, one can conclude that in the conditions under consideration the linear dependence of $\Delta\bar{G}_1$ on w_1 is a relatively good approximation. However, we must take into account that this result can be affected by a large error due to the inherent difficulties in extrapolating from 0.884 (for the PS-cyclohexane system), 0.767 (for the PVA-cyclohexanone system), and 0.634 (for the PVP-methanol system) to zero. Of course, more work covering wider range of w_1 is necessary in order to find the exact function describing the variation of $\Delta\bar{G}_1$ with w_1 .

For high molecular weight the link between $(a_1/w_1)^\infty$ and the interaction parameter x is given for unit volume fraction of the polymer by¹⁴

$$x = \ln(a_1/w_1)^\infty - 1 + \ln(v_2/v_1) \quad (7)$$

In eq. (7), v_1 and v_2 are the specific volumes of the solvent probe (1) and the polymer (2), respectively.

Replacing volume fractions by segment fractions and the specific volumes v_1 and v_2 by the characteristic specific volumes v_1^* and v_2^* , the interaction parameter based on segment fractions x^* , is related to $(a_1/w_1)^\infty$ through an equation similar to eq. (7):

$$x^* = \ln(a_1/w_1)^\infty - 1 + \ln(v_2^*/v_1^*) \quad (8)$$

v^* parameters are related to v parameters by the equation of state parameters defined by

$$\bar{v} = v/v^* = [(4\alpha T + 3)/(3\alpha T + 3)]^3 \quad (9)$$

where α is the thermal expansion coefficient of the component indicated by the subscript. This is usually defined by

$$\alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P \quad (10)$$

RESULTS AND DISCUSSION

Weight Fraction Activity Coefficients and Partial Molar Thermodynamic Functions of Mixing

In Table I the values of the weight fraction activity coefficients, a_1/w_1 , determined via eq. (4), and the partial molar free energies of mixing, $\Delta\bar{G}_1$ for the polystyrene in cyclohexane at various temperatures and solvent concentration are given. It can be seen from this table that the a_1/w_1 values (or the $\Delta\bar{G}_1$ values) increase with decreasing w_1 in all temperatures. The variation of $\Delta\bar{G}_1$ with w_1 at constant temperature is due to the variation of solubility of polymer with w_1 . As the w_1 increases, the solubility of polymer increases, thus decreasing the excess free energy of mixing $\Delta\bar{G}_1$. Such a variation was also observed previously.¹⁶

In all w_1 cases, the weight fraction activity coefficients decrease with increasing temperature, suggesting that the solubility of the cyclohexane in the polystyrene increases accordingly.

In Table II the partial molar heats and entropies of mixing for the polystyrene-cyclohexane system, determined via eq. (5), at various w_1 are given. It can be seen that all the partial molar heats of mixing are certainly positive and small in accordance with previous results,¹⁷ but further conclusions seem to be unwarranted. From the plots of $\ln(a_1/w_1)$ vs. $1/T$ the heats and entropies of mixing were determined at various solvent concentrations. Such a plot is shown in Figure 3.

By the procedure described in the theoretical section the infinite dilution partial molar free energies of mixing, $\Delta\bar{G}_1^\infty$, and the weight fraction activity coefficients at infinite dilution, $(a_1/w_1)^\infty$, for the polystyrene-cyclohexane system were determined. These parameters are given in Table III. For comparison purposes, some values of $(a_1/w_1)^\infty$ calculated from eq. (7) are also

TABLE I
Weight Fraction Activity Coefficients, a_1/w_1 , and Partial Molar Free Energies of Mixing, $\Delta\bar{G}_1$, of Cyclohexane in Polystyrene at Various Temperatures and Solute (Cyclohexane) Weight Fractions w_1

T (K)	w_1	a_1/w_1	$\Delta\bar{G}_1$ (J mol ⁻¹)
333.8	0.980	0.913	-252.60
	0.961	1.013	35.85
	0.924	1.091	241.71
	0.884	1.115	302.09
338.5	0.980	0.924	-222.45
	0.961	1.024	66.75
	0.924	1.099	265.67
	0.884	1.115	306.35
342.9	0.980	0.904	-287.73
	0.961	0.996	-11.43
	0.924	1.085	232.57
	0.884	1.073	200.87
348.1	0.980	0.852	-463.55
	0.961	0.975	-73.27
	0.924	1.002	5.78
	0.884	1.052	146.71

TABLE II
 Partial Molar Heats and Entropies of Mixing for the Polystyrene–Cyclohexane
 System at Various Solute Weight Fractions

w_1	$\Delta \bar{H}_1$ (kJ mol ⁻¹)	$\Delta \bar{S}_1$ (J mol ⁻¹ K ⁻¹)
0.980	4.72	14.67
0.961	2.90	8.50
0.924	5.54	15.70
0.884	4.33	11.99
Mean values	4.37	12.72

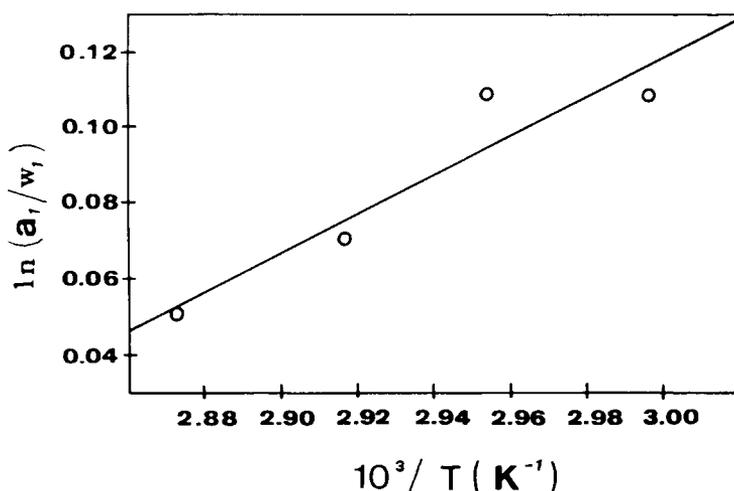


Fig. 3. Plot of $\ln(a_1/w_1)$ vs. $1/T$ for the polystyrene (PS)–cyclohexane system at $w_1 = 0.884$.

TABLE III
 Infinite Dilution Partial Molar Free Energies of Mixing, $\Delta \bar{G}_1^\infty$ and
 Weight Fraction Activity Coefficients at Infinite Dilution, $(a_1/w_1)^\infty$,
 of Cyclohexane in Polystyrene at Several Temperatures

T (K)	$\Delta \bar{G}_1^\infty$ (kJ mol ⁻¹)	$(a_1/w_1)^\infty$	
		This work	Calculated ^a
333.8	5.164	6.43	6.44
338.5	4.930	5.77	6.47
342.9	4.614	5.05	6.50
348.1	5.030	5.69	6.54
	Mean value	5.74	6.49

^a Calculated from Eq. (7) (as x the most common value of 0.5 was used).

given in the same table. It is seen that the experimental values of $(a_1/w_1)^\infty$, determined by the proposed methodology of r.f.g.c., are in some temperatures in excellent agreement with those calculated from eq. (7), while in the rest have a relatively big error. This error, as it was pointed out in the theoretical section, may be due either to the nonlinearity of the plot of $\Delta \bar{G}_1$ vs. w_1

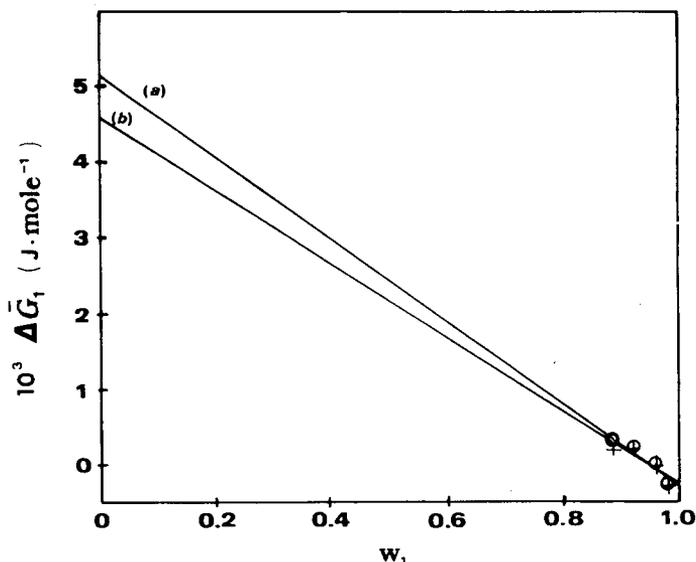


Fig. 4. Plots of $\Delta\bar{G}_1$ vs. w_1 : (a) PS-cyclohexane at 333.8 K; (b) PS-cyclohexane at 342.9 K.

(cf. Fig. 4) in the whole range of w_1 or/and to the inherent difficulties in extrapolating from 0.884 to 0.

In general, the activity data presented in Table III, for the polystyrene-cyclohexane system, indicate that r.f.g.c. can be applied successfully to the determination of weight fraction activity coefficients not only in the limiting case of infinite dilution of the polymer, but also in the other extreme of infinite dilution of the probe molecule.

The infinite dilution partial molar free energies of mixing and the weight fraction activity coefficients at infinite dilution for the polyvinylacetate/cyclohexanone and polyvinylpyrrolidone/methanol systems at a constant temperature are given in Table IV. The $(a_1/w_1)^\infty$ value for the PVP-methanol system is too low, a general indication of solvent-polymer good miscibility.

Interaction Parameters

The interaction parameters x and x^* for the polystyrene-cyclohexane system are determined from eqs. (7) and (8), respectively. The necessary values of v and v^* for both components of the mixture are given in Table V. The values of x and x^* are summarized in Table VI together with some literature data. It is seen that the experimental x and x^* values are in some cases

TABLE IV
Infinite Dilution Partial Molar Free Energies of Mixing and Weight Fraction Activity Coefficients at Infinite Dilution for the PVA-Cyclohexanone and PVP-Methanol Systems

System	T (K)	w_1 (range)	$\Delta\bar{G}_1^\infty$ (kJ mol ⁻¹)	$(a_1/w_1)^\infty$
PVC-Cyclohexanone	343.5	0.767 < w_1 < 0.902	4.847	5.46
PVP-methanol	333.0	0.634 < w_1 < 0.837	2.285	2.28

TABLE V
Equation-of-State Data and Characteristic Parameters of Cyclohexane and Polystyrene at Various Temperatures

T (K)	Cyclohexane ($\alpha = 1.217 \times 10^{-3} \text{ K}^{-1}$)				Polystyrene ($\alpha = 5.74 \times 10^{-4} \text{ K}^{-1}$)			
	v_1 ($\text{cm}^3 \text{ g}^{-1}$)	\bar{v}_1	v_1^* ($\text{cm}^3 \text{ g}^{-1}$)	V_1 ($\text{cm}^3 \text{ mol}^{-1}$)	v_2 ($\text{cm}^3 \text{ g}^{-1}$)	\bar{v}_2	v_2^* ($\text{cm}^3 \text{ g}^{-1}$)	
333.8	1.3688	1.3176	1.0389	115.19	0.9528	1.1696	0.8146	
338.5	1.3796	1.3211	1.0443	116.10	0.9554	1.1717	0.8154	
342.9	1.3899	1.3243	1.0495	116.97	0.9579	1.1736	0.8162	
348.1	1.4022	1.3281	1.0558	118.0	0.9607	1.1759	0.8170	

TABLE VI
Reduced Free Energy Parameters x and x^* for the Cyclohexane-Polystyrene
System at Various Temperatures

T (K)	x		x^*	
	This work	Literature	This work	Literature
333.8	0.499	0.474 ^{15 a} (433 K) 0.534 ^{17 a} (476 K)	0.618	0.715 ^{15 a} (433 K)
338.5	0.384	0.508 ^{12 a} (303 K)	0.504	
342.9	0.246	0.5 ^{18 a} (298 K)	0.367	
348.1	0.360		0.482	
Mean values	0.372		0.493	

^a Values found in Refs. 12, 15, 17, and 18 at the temperatures given in parentheses.

relatively close to those found by other workers.^{12, 15, 17, 18} This suggests that the assumption of the linear dependence of $\Delta\bar{G}_1$ on w_1 on the whole range of w_1 may be a relatively good approximation.

Plot of x against temperature for the PS-cyclohexane system is shown in Figure 5. It is evident that the plot shows a positive minimum and curvature which remains positive throughout the range of temperatures investigated. This fact was also observed previously.¹⁹ A partial explanation of the exhibition of minimum in x vs. T plot is given by Patterson.²⁰ They expressed x as a sum of two terms. The first term, which is positive, represents the contact energy dissimilarity and decreases with increasing temperature, while the second term, reflecting the free volume dissimilarity, increases without limit.

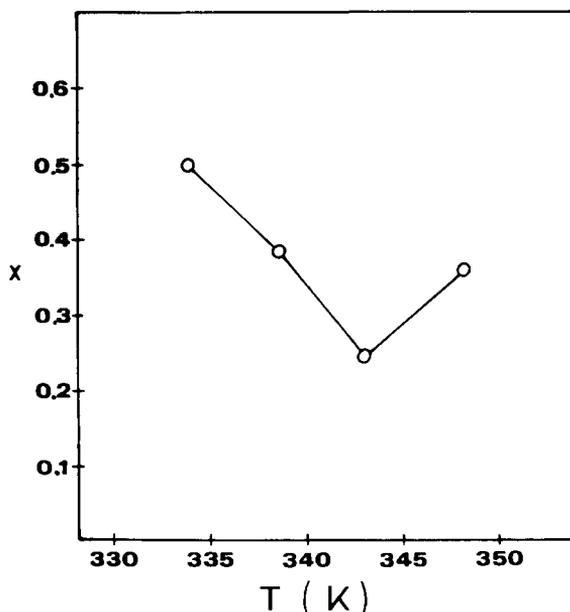


Fig. 5. Plot of x against temperature for the PS-cyclohexane system.

From the infinite dilution weight fraction activity coefficients given in Table IV, the x parameters for the PVC-cyclohexanone and PVP-methanol systems were computed via eq. (7). They were found 0.48 and -0.65 , respectively. The first value is very close to those given in literature¹⁸ showing that the assumption of linear dependence of $\Delta\bar{G}_1$ on w_1 is a good approximation. On the other hand, this assumption seems not to be valid in the second system.

Solubility Parameter

Supposing that the solubility parameter δ_2 of the polystyrene in cyclohexane is constant in the working temperature range ($333.8 < T < 348.1$ K), an average value of the parameter δ_2 at 340.8 K (the mean temperature of the working temperature range) may be evaluated by the DiPaola-Baranyi and Guillet equation¹⁷

$$\frac{\delta_1^2}{RT} - \frac{x}{V_1} = \frac{2\delta_2}{RT}\delta_1 - \frac{\delta_2^2}{RT} \quad (11)$$

In eq. (11) δ_1 is the solubility parameter, and V_1 the molar volume of the solute probe both referred to the same temperature. The δ_1 values at various temperatures were obtained by interpolating the values given in Ref. 17 to the selected temperatures.

Equation (11) shows that a plot of $\delta_1^2/RT - x/V_1$ vs. δ_1 should yield a straight line with a slope of $2\delta_2/RT$ and an intercept of $-\delta_2^2/RT$. This is illustrated in Figure 6. The δ_2 values so obtained (cf. Table VII) are slightly different, depending on whether they have been obtained from the intercept or the slope. The values found at 340.8 K are close to those given in literature.^{17,18}

Correction of the Activities Due to the Variation of Mass Transfer Coefficient with the Solvent Weight Fraction

The correct value of a_1 is calculated from eq. (3). For this reason the k_c and D values must be determined as follows: The height, h , from the ending baseline of each sample peak, produced by a short flow reversal in r.f.g.c., is given by

$$h = \frac{2k_c D c_0}{v(k_c L + D)} \left\{ 1 - \exp \left[- \frac{2(k_c L + D)t_0}{L^2} \right] \right\} \quad (12)$$

Modification of eq. (12) leads to two approximate solutions, one for short and one for long times.¹¹ The latter approximation is

$$\ln(h_\infty - h) = \ln h_\infty - [2(k_c L + D)/L^2] t_0 \quad (13)$$

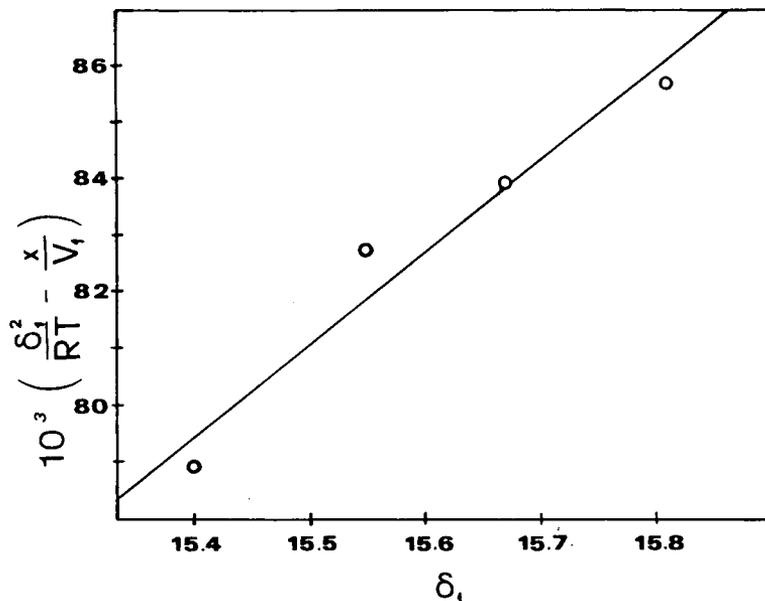


Fig. 6. Estimation of solubility parameter (δ_2) of the polystyrene at 340.8 K from the x parameters.

TABLE VII
Solubility Parameters of Cyclohexane at Several Temperatures and Polystyrene at 340.8 K

T (K)	δ_1^* (J cm^{-3}) ^{1/2}	δ_2 (J cm^{-3}) ^{1/2}		Literature ^{17,18}
		Found		
		Slope of eq. (11)	Intercept of eq. (11)	
333.8	15.81	22.97	21.96	14.5 < δ_2 < 21.1
338.5	15.67			
342.9	15.55			
348.1	15.40			

^aThe δ_1 values were found by interpolating the values of Ref. 17 to the selected temperatures.

while the short-time approximation is

$$\ln \left[h \left(\frac{L}{2t_0^{1/2} + k_c t_0^{1/2}} \right) \right] = \ln \left[\frac{4k_c c_0}{v} \left(\frac{D}{\pi} \right)^{1/2} \right] - \frac{L^2}{4D} \frac{1}{t_0} \quad (14)$$

where h_∞ is the infinity maximum value for the peak height.

Equation (13) shows that a plot of $\ln(h_\infty - h)$ vs. t_0 should be linear, and from the slope $-2(k_c L + D)/L^2$ a first-approximation value of k_c can be calculated from the known value of L and a theoretical calculated value of D . This value of k_c can be used to plot the data at short times according to eq. (14). A plot of the left-hand side of eq. (14) vs. $1/t_0$ should be linear, from the slope of which a first experimental value for D is found. This can be used with

the slope found from the plot of eq. (13) to calculate a better approximation of the k_c value and this in turn is used to replot eq. (14) for a better approximation of the D value. These iterations can be continued until no significant changes in the values of k_c and D result, but it is not usually necessary to go beyond the first iteration.

CONCLUSIONS

Polymer-solvent interactions were investigated using the new technique of reversed-flow gas chromatography. This method is closer to a static than to a GC technique. No real chromatography is performed. Only GC instrumentation is used to sample the space at $x = l'$ (cf. Fig. 1). The method is simple and can be carried out with a conventional gas chromatograph. There is a little doubt that additional experiments would be required to account fully for the exceptional features exhibited by reversed-flow gas chromatography studying polymer-solvent systems.

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