Comparative studies on the use of gas chromatographic and vapour pressure techniques for the determination of the interaction energy parameter

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Comparative studies using gas chromatographic and vapour pressure techniques have been carried out on solutions of poly(vinyl chloride), polystyrene, and poly(methyl methacrylate) in the solvents toluene, methyl ethyl ketone, 1,4 dioxan, tetrahydrofuran and di-n-propyl ether. The values of the corresponding interaction energy parameters (χ_1) are compared and analysed in terms of the Flory–Huggins theory of polymer solutions. The two techniques produced values of χ_1 for a wide range of solvents which were in good agreement with each other, thus substantiating the validity of both methods. Also, the vapour pressure results agreed with the Flory–Huggins theory over an extended range of solute composition. The gas chromatographic method yielded very self-consistent results and proved to be the more rapid technique. It also had the advantage that it could be used without much difficulty over a wider temperature range.

INTRODUCTION

Most of the static methods which have been used for the determination of the interaction energy parameter, χ_1, have proved to be both long and tedious. The most common method is the measurement of vapour pressure which has been used by Gee *et al.*[1–4], Bawn *et al.*[5–7], Nakajima *et al.*[8] and many others[9]. Other methods which have been used with some measure of success include osmotic pressure[10], swelling techniques[2–3, 13–17], optical studies[18–20] and viscosity procedures[21–22]. However, most of these methods necessitate the recording of measurements over long periods of time to ensure the equilibrium necessary for the application of the various thermodynamic equations.

On the other hand some recent studies of gas-liquid chromatography (g.l.c.) have suggested[23–28] that this method is a more rapid and perhaps more consistent means of studying the thermodynamic behaviour of polymer solutions. Patterson *et al.*[23] have studied both straight- and branched-chain polyethylenes using n-decane and n-dodecane as solvents. The values of χ_1 which were obtained from their g.l.c. studies were reported to be in good agreement with those already reported in the literature. In later publications[25] for work involving several other hydrocarbons as solvents a critical comparison was made between values of χ_1 obtained by g.l.c. measurements and the values as determined by osmometry and sorption equilibrium techniques[29]. Good agreement was reported between the two methods. On the other hand no positive correlation could be found when these same g.l.c. results were compared with those obtained by the optical method of Coran and Anagnostopoulos[19]. Summers *et al.*[27] have studied the interaction of poly(dimethyl siloxane) with a variety of hydrocarbon solvents. The χ_1 parameters were found to be in close agreement with those obtained by the static method.

Further experimental comparisons have been reported by Tewari and Schreiber[28] who used rubber–hydrocarbon systems and compared their results with those derived from viscosity and swelling methods. The systems polyisobutylene–benzene/cyclohexane and n-pentane have been studied[31] at different temperatures using the g.l.c. method and comparison made with vapour sorption studies[32,33].

There has been no systematic attempt, however, to compare the g.l.c. method with any of the static methods using the same samples of polymer and employing a sufficiently wide range of solvent types so as to make the comparison of significance. Thus the aim of this present study is to check the usefulness of the g.l.c. method as an alternative to that of vapour pressure for determining values of the interaction energy parameter, χ_1. The solution behaviour of poly(vinyl chloride), polystyrene and poly(methyl methacrylate) is investigated both by vapour pressure and g.l.c. techniques in the solvents toluene, methyl ethyl ketone (MEK), 1,4-dioxan, tetrahydrofuran (THF) and di-n-propyl ether. These systems were deliberately chosen so as to provide a wide range of solution behaviour. The Flory[34]–Huggins[35] equation is used to evaluate the interaction parameter from the vapour pressure measurements, whilst the Patterson expression[23] is used for the g.l.c. data. Both of these equations depend on the lattice-theory concept for their derivation.

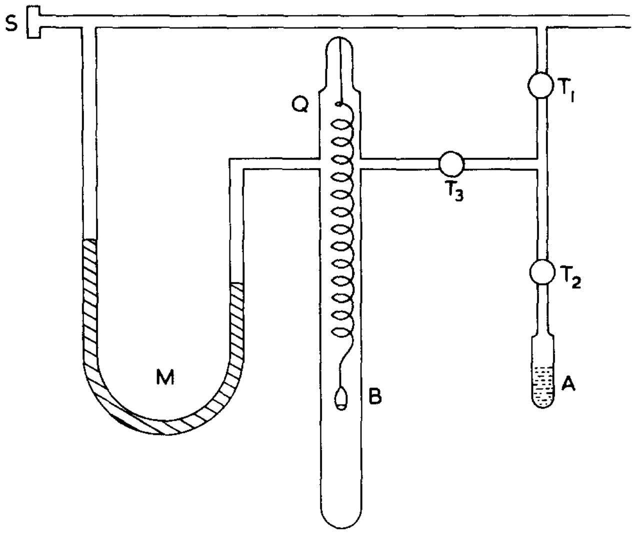

Figure 1 Vapour pressure apparatus. A, Solvent reservoir; B, polymer bulb; M, manometer; Q, quartz spring; S, vacustat; T_1, T_2, T_3, Young's greaseless taps

EXPERIMENTAL

Polymers

Poly(vinyl chloride). The polymer sample was prepared[36] by means of a modified Ziegler–Natta catalyst system, and shown to have an $\bar{M}_n$ value of 3.40×10^4 by means of osmotic pressure measurements. It had a density of 1.413 g/cm^3.

Poly(methyl methacrylate). This polymer was also prepared[37] by using a modified Ziegler–Natta catalyst system, and was found to have an $\bar{M}_n$ value of 1.977×10^4, and a density of 1.184 g/cm^3.

Polystyrene. The polymer sample was supplied by the Pressure Chemical Company, Pittsburgh, USA, and was stated to have an $\bar{M}_n$ value of 1.03×10^4 with an M_w/M_n ratio of 1.06. It had a density of 1.021 g/cm^3.

Solvents

Toluene and methyl ethyl ketone were purified in the same manner. These solvents were dried using ground calcium hydride, refluxed over fresh sodium wire, and then finally fractionated.

Tetrahydrofuran (THF) and di-n-propyl ether were treated with sodium sulphate before fractionation and drying.

1,4-Dioxan was treated with dilute hydrochloric acid to remove any traces of acetaldehyde and glycol acetal before being fractionated using an efficient column and finally dried.

Vapour pressure apparatus

The system, shown in *Figure 1*, was constructed using Young's greaseless taps, T_1, T_2 and T_3. These are more simple to use than either conventional mercury cut-off valves[1,38] or greaseless stopcocks[12]. A is the solvent reservoir, B a glass bulb containing the polymer sample which is attached to the quartz spring Q, and M is a mercury manometer. The whole system was supported inside an insulated wooden box which served as an air thermostat. The front of the box, constructed from Perspex, was removable and afforded easy access. Efficient thermostatic control was achieved by means of an electric fan together with a type TS8 Controller purchased from Sunvic Controls Ltd, London. The temperature fluctuation was found to be less than ±0.3°C.

The manometer, M, was made from wide-bore (1.8 cm) glass tubing so as to minimize the meniscus effect. All the mercury used was triple distilled and filtered twice to ensure high purity.

The quartz springs used were supplied by UKAEA (Harwell) and had the following specifications:

Coil diameter	2 cm
Fibre thickness	0.023 cm
Number of coils/cm	10
Unloaded length	5.8 cm
Average maximum load	0.9 g

The three quartz springs which were employed had extensions of 10.74, 10.39 and 10.22 cm/g. Each spring was calibrated using standard weights and a cathetometer, linear relationships with load being found. A quartz spring was suspended from a hooked glass rod attached to the top of the centre pressure vessel. The bulb containing the polymer sample had an average weight of about 0.3 g.

Vapour pressure determination

The general procedure has been described in an earlier publication[12].

The vapour pressures of pure solvents at the experimental temperature were determined by using the Antoine equation[39]. The constants *A*, *B* and *C* required for this equation were obtained from Fried[40], and others[41,42].

Densities of polymers

Polymer densities were determined by a flotation technique using zinc chloride solutions.

Molecular weights

The osmotic pressure method was used to determine number-average molecular weights.

Gas chromatography system

A dual-column g.l.c. apparatus was used which incorporated a Perkin–Elmer hot-wire thermal conductivity detector. The column temperature was controlled to within ±0.2°C over the entire temperature range 25° to 160°C. Helium was used as the carrier gas so as to minimize the effect of gas–liquid (polymer) interaction[27,43]. Flow rates were varied from 20 to 120 cm^3/min, and were measured by means of a soap-bubble flowmeter at the detector outlet. Care was taken to establish that all retention volumes were independent of the flow rates within the range investigated.

Since the performance of this type of apparatus is dependent on a steady flow of carrier gas this was monitored using a flowmeter and the steadiness of the baseline carefully checked. The inlet pressure was controlled by precision regulators, and measured by means of a mercury manometer. This pressure was kept as low as possible to match the requirements of the various equations which were to be used[27]. The outlet pressure was always atmospheric.

Solvents were injected into the carrier gas stream using a 1 μl syringe. Since equation (3) requires infinite dilution only about 0.2 μl of solvent was used. The infinite dilution conditions were confirmed by the uniformly symmetrical elution peaks which were obtained using this injection procedure[44]. These symmetrical peaks also indicate the attainment of polymer–solvent equilibrium interaction conditions. No dependence of retention time on sample size was observed when the latter was increased by small amounts.

Specific retention volumes, V_g^0, were calculated from the familiar expression of Littlewood *et al.*[45].

Stationary phases and column description

The polymers poly(vinyl chloride), poly(methyl methacrylate) and polystyrene were used as stationary phases, and were coated onto the supports from solutions in THF, MEK and toluene. The coated supports were packed[26] into 0.25 in (o.d.) copper tubing. The exact polymer weights inside the columns were determined by a combustion and ashing method[46]. Details of column composition are given in *Table 1*.

Table 1 Column composition

Polymer	PVC	Polystyrene	Poly(methyl methacrylate)
Supporting material, chromosorb-W:			
Length of column (cm)	180	180	180
Weight of support (g)	10.127	10.325	10.260
Weight of polymer (g)	0.2410	0.5600	0.4897
Weight of polymer (%)	2.380	5.237	4.773
Supporting material, glass beads:			
Length of column (cm)	120	120	–
Weight of support (g)	31.55	32.03	–
Weight of polymer (g)	0.1200	0.1350	–
Weight of polymer (%)	0.380	0.428	–

RESULTS

Vapour pressure results

Tables 2, 3 and *4* contain representative experimental data for the three polymers and the various solvents which were used.

Gas chromatography results

Specific retention volumes were calculated from corrected retention times all of which were averaged from ten runs. Thus the values of V_g^0 which are listed in *Table 5* are average values.

THEORETICAL CONSIDERATIONS

Vapour pressure method

The simple lattice theory as developed by Flory[34] and Huggins[35] relates the chemical potential of the solvent to the interaction energy parameter, χ_1, by means of the equation:

$$\mu_1 - \mu_1^0 = RT[\ln(1 - v_2) + \left(1 - \frac{1}{x}\right)v_2 + \chi_1 v_2^2]$$

$$= RT\ln(P_1/P_1^0) \qquad (1)$$

This equation assumes the behaviour of the solvent vapour to be ideal. μ_1 and μ_1^0 are the chemical potentials of solvent

Table 2 Vapour pressure results for poly(vinyl chloride)

Solvent: tetrahydrofuran Spring extension: 10.74 cm/g Temperature: 42.5°C P_1^0 = 33.270 cmHg w_2 = 0.1024 g		Solvent: di-n-butyl ether Spring extension: 10.39 cm/g Temperature: 42.2°C P_1^0 = 13.750 cmHg w_2 = 0.0764 g		Solvent: 1,4-dioxan Spring extension: 10.22 cm/g Temperature: 42.5°C P_1^0 = 8.600 cmHg w_2 = 0.1024 g		Solvent: toluene Spring extension: 10.22 cm/g Temperature: 43.2°C P_1^0 = 6.845 cmHg w_2 = 0.1500 g	
w_1 (g)	P_1 (cmHg)	w_1 (g)	P_1 (cmHg)	w_1 (g)	P_1 (cmHg)	w_1 (g)	P_1 (cmHg)
0.0060	6.881	0.0030	4.287	0.0113	3.707	0.0090	1.792
0.0093	10.013	0.0040	5.128	0.0264	6.287	0.0117	2.287
0.0240	18.323	0.0060	6.531	0.0333	6.862	0.0186	3.183
0.0381	24.272	0.0080	8.301	0.0380	7.233	0.0225	3.719
0.0631	28.148	0.0090	9.186	0.0441	7.751	0.0303	4.434
0.0807	29.502	0.0110	10.887	0.0495	8.173	0.0326	4.589
0.0959	30.552	0.0130	10.970	0.0590	8.319	0.0800	6.565
0.1129	31.202	0.0150	11.892	0.0776	8.432	0.0911	6.824
0.1429	32.002	0.0210	13.600	0.0848	8.500		
0.2309	33.170						

Table 3 Vapour pressure results for polystyrene

Solvent: toluene Spring extension: 10.22 cm/g Temperature: 48.5°C P_1^0 = 8.650 cmHg w_2 =0.1561 g		Solvent: MEK Spring extension: 10.22 cm/g Temperature: 48.5°C P_1^0 = 25.090 cmHg w_2 = 0.107 g		Solvent: 1,4-dioxan Spring extension: 10.22 cm/g Temperature: 50.0°C P_1^0 = 11.930 cmHg w_2 = 0.1366 g	
w_1 (g)	P_1 (cmHg)	w_1 (g)	P_1 (cmHg)	w_1 (g)	P_1 (cmHg)
0.0132	2.686	0.0062	8.542	0.0078	4.006
0.0188	3.416	0.0095	11.042	0.0122	5.550
0.0247	4.055	0.0107	12.146	0.0186	7.158
0.0300	4.573	0.0267	19.558	0.0207	7.516
0.0351	5.022	0.0416	21.941	0.0350	8.031
0.0455	5.689	0.0527	22.855	0.0600	10.423
0.0708	6.745	0.0640	23.790	0.1115	11.040
0.1452	7.903	0.0793	23.860	0.2093	11.830
0.5119	8.550	0.1106	24.765		

in the solution and pure solvent respectively, P_1 and P_1^0 are the corresponding vapour pressures, and x is the average number of segments per polymer chain.

The volume fraction of polymer, v_2, is given by:

$$v_2 = \frac{w_2}{(M_0/M_1)w_1 + w_2} \qquad (2)$$

where M_0 and M_1 are the molecular weights of polymer repeat unit and solvent respectively, and w_1 and w_2 are the weights of solvent and polymer.

Gas chromatographic method

The experimental g.l.c. data and the interaction energy parameter, χ_1, are linked together by means of equation (3)[23] which also depends on the familiar Flory–Huggins lattice concept[27]:

$$\chi_1 = \ln\left[\frac{273.2KR\tilde{v}_2}{V_g^0 V_1 P_1{}^0}\right] - \left[1 - \frac{V_1}{M_2\tilde{v}_2}\right] - \frac{P_1^0}{RT}\left[B_{11} - V_1\right] \qquad (3)$$

Table 4 Vapour pressure results for poly(methyl methacrylate)

Solvent: toluene	Solvent: MEK
Spring extension: 10.22 cm/g	Spring extension: 10.22 cm/g
Temperature: 48.5°C	Temperature: 48.5°C
P_1^0 = 8.650 cmHg	P_1^0 = 25.090 cmHg
w_2 = 0.1322 g	w_2 = 0.139 g

w_1 (g)	P_1 (cmHg)	w_1 (g)	P_1 (cmHg)
0.0090	2.594	0.0041	5.725
0.0177	4.302	0.0114	9.813
0.0291	5.387	0.0329	18.123
0.0460	6.906	0.0446	20.157
0.0529	7.340	0.0597	21.760
0.0624	7.412	0.0622	22.152
0.0989	8.200	0.0896	23.275
0.1968	8.643	0.1789	24.752

Table 5 Specific retention volumes, V_g^0

	V_g^0 (cm^3/g)		
Polymer	PVC	Polystyrene	Poly(methyl methacrylate)
Tetrahydrofuran	97.4^a	–	–
Di-n-propyl ether	46.63^b	–	–
1,4-Dioxan	233.4^a	255.8^c	
Toluene	222.9^d	438.1^e	312.8^d
Methyl ethyl ketone	–	147.8^e	141.9^e

^{a} Temperature = 42.5°C; ^{b} Temperature = 42.2°C; ^{c} Temperature = 50.0°C; ^{d} Temperature = 43.2°C; ^{e} Temperature = 48.5°C

In this equation $\tilde{v}_2$ is the specific volume of polymer with molecular weight M_2, P_1^0 the vapour pressure of pure solvent at T K and V_1 its molar volume. The second virial coefficient of the solvent in the gas state, B_{11}, was calculated from the corresponding state equation of McGlashan and Potter[47].

DISCUSSION

Comparison of the two methods

The values of the interaction energy parameter, χ_1, for the three polymers, polystyrene, poly(vinyl chloride) and poly(methyl methacrylate) are summarized in *Table 6*. The last column of *Table 6* clearly indicates that the differences between the various values of χ_1 as obtained by the two methods are very small and are thus not considered to be significant, lying as they do well within the limits of experimental error. Whilst the vapour pressure technique has the advantage of being direct and requiring relatively simple apparatus as well as being straightforward in operation, it suffers from a number of disadvantages.

(i) Long periods of time are required to ensure the establishment of time-equilibrium conditions. In particular the time taken to reach equilibrium increases as the solvent vapour pressure increases and the transfer of solvent from the solvent reservoir to the bulb becomes increasingly difficult as the vapour pressure of the solvent approaches saturation.

(ii) This long duration in turn demands quite exacting standards of temperature control which are not too easy to realize when an air thermostat is used.

(iii) The necessary temperature control limits the range of temperature over which the method can be satisfactorily employed.

(iv) In regions of low and high concentration of solvent the experimental errors are necessarily greater due to the difficulty, in the former case, of determining the very small solvent concentrations, and in the latter case, of measuring the vapour pressure of solvent with sufficient accuracy since the value of P_1 is very close to P_1^0.

The g.l.c. method on the other hand is both very rapid and simple in operation, and in practice it can be used over a wider range of temperature thus allowing the dependence of χ_1 on temperature to be more fully investigated. From a practical point of view the main limitation is that the retention volumes should be independent both of sample size (of solvent) and flow rate. However, these conditions can be fairly easily achieved. It should also be realized that this method yields a value for χ_1 only at infinite dilution of solvent. The vapour pressure technique on the other hand

Table 6 Comparative values of χ_1 from vapour pressure and g.l.c. techniques

		Value of χ_1		
Solvent	Polymer	Vapour pressure	G.l.c.	% Difference between vapour pressure method and g.l.c. method
Tetrahydrofuran	Poly(vinyl chloride)	0.556	0.535	+2.1
Di-n-propyl ether	Poly(vinyl chloride)	1.556	1.605	–4.9
1,4-Dioxan	Poly(vinyl chloride)	1.004	0.953	+5.1
1,4-Dioxan	Polystyrene	0.851	0.865	–1.4
Toluene	Poly(vinyl chloride)	1.037	1.011	+2.6
Toluene	Polystyrene	0.402	0.420	–1.8
Toluene	Poly(methyl methacrylate)	0.638	0.611	+2.7
Methyl ethyl ketone	Poly(methyl methacrylate)	0.557	0.518	+4.9
Methyl ethyl ketone	Polystyrene	0.651	0.628	+2.3

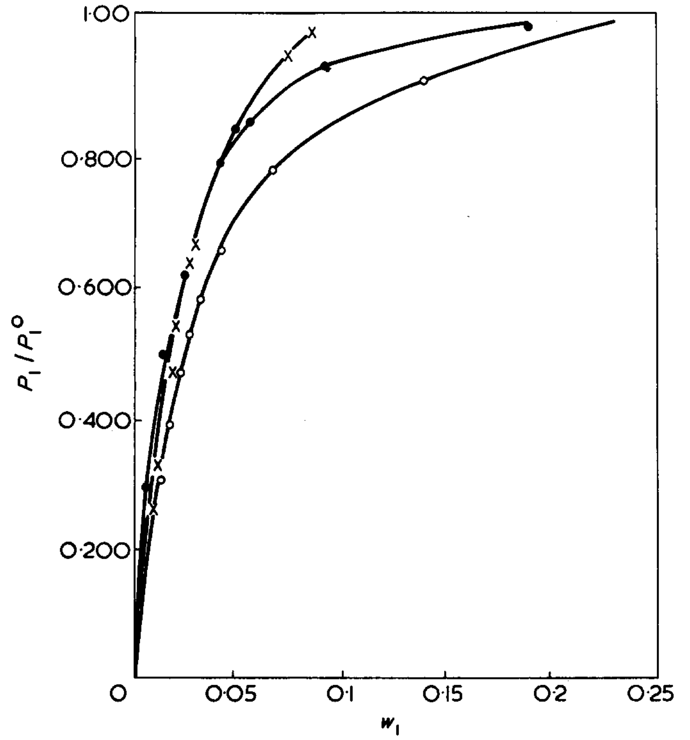

Figure 2 Relative vapour pressure of toluene solutions of polystyrene, poly(methyl methacrylate) and poly(vinyl chloride). Solvent: toluene. ○, Polystyrene; ●, poly(methyl methacrylate); X, poly(vinyl chloride)

affords a convenient method of investigating the dependence of χ_1 on v_1 which is of considerable theoretical importance in assessing the applicability of the Flory–Huggins theory to polymer solutions. Hence both techniques have important applications.

The experimental errors in the vapour pressure technique are mainly concerned with the accuracy of the measurement of the spring extension and of the mercury levels in the manometer where the vibration of the mercury meniscus is the limiting factor. There is also the additional problem of temperature control. An overall error of the order of 5–10% is estimated[48]. The sources of error in the g.l.c. method are also associated with the mercury manometer and temperature fluctuation. These are of the order[48] of 5–8%.

Analysis of vapour pressure results

Since the equations which are used to evaluate χ_1 from vapour pressure and g.l.c. measurements are both derived from the familiar Flory–Huggins lattice theory, any limitations inherent in this theory will apply to both methods, and for this reason it seemed desirable to carry out an analysis of the applicability of the Flory–Huggins theory to the results which had been obtained. The wide variation in solvent and polymer type which has been used makes this comparison of some interest since these were chosen so as to afford a wide variation in thermodynamic solution behaviour. That this is so is evident from an examination of *Figures 2, 3* and *4*. *Figure 2* depicts a plot of P_1 *versus* w_2 for the three polymers in toluene. Polystyrene shows a higher compatibility with this solvent than either poly(vinyl chloride) or poly (methyl methacrylate). On the other hand, *Figure 3* demonstrates that poly(methyl methacrylate) has a higher compatibility with methyl ethyl ketone than does polystyrene. And finally *Figure 4* shows that polystyrene has a higher compatability with 1,4-dioxan than does poly(vinyl chloride).

Since the Flory–Huggins theory predicts that χ_1 should be independent of v_2, plots of χ_1 against values of v_2 were constructed. Representative examples are shown in *Figures 5, 6* and *7*. The resulting plots show either small positive or negative slopes depending on the nature of the solvent, and it is only in the case of solutions of poly(methyl methacrylate) in MEK that there is no deviation from theory over the entire volume fraction range investigated. The results obtained are listed in the captions to *Figures 5, 6* and *7*. These

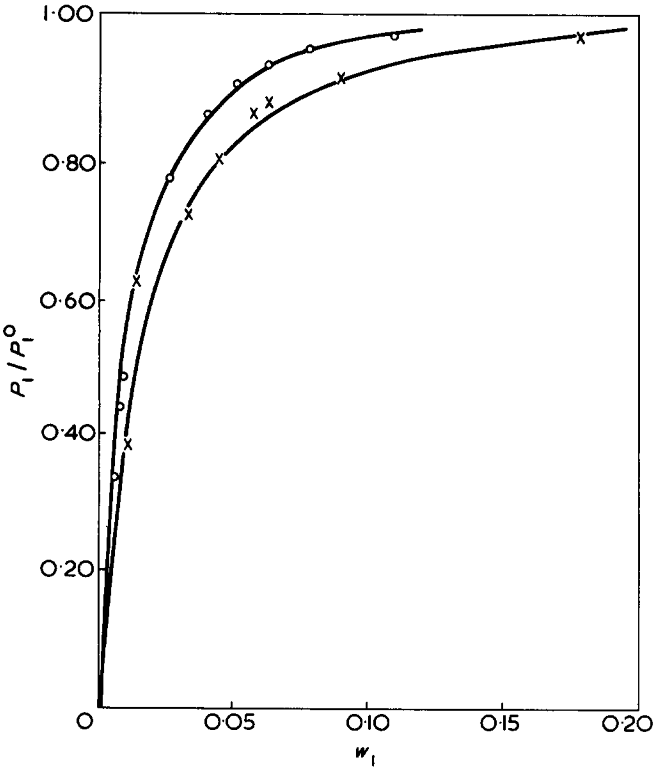

Figure 3 Relative vapour pressure of methyl ethyl ketone solutions of poly(methyl methacrylate) and polystyrene. Solvent: methyl ethyl ketone. ○, Polystyrene; X, poly(methyl methacrylate)

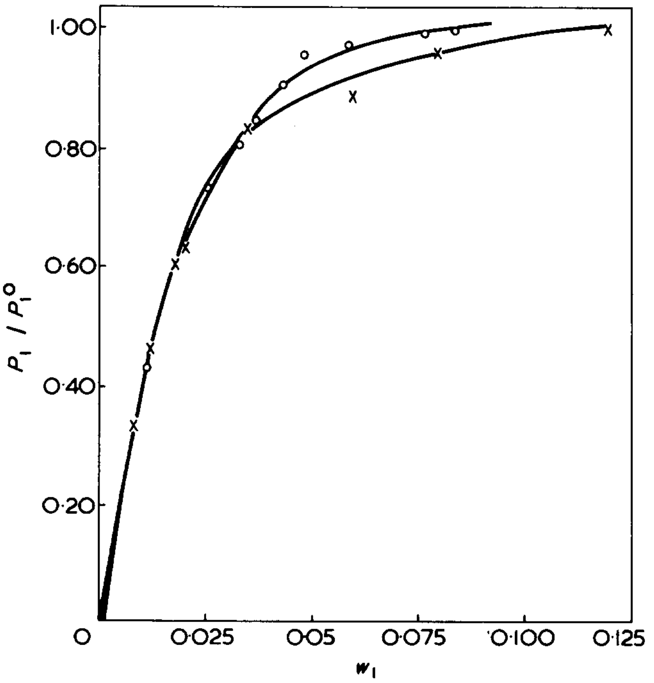

Figure 4 Relative vapour pressure of 1,4-dioxan solutions of polystyrene and poly(vinyl chloride). Solvent: 1,4-dioxan. X, Polystyrene; ○, poly(vinyl chloride)

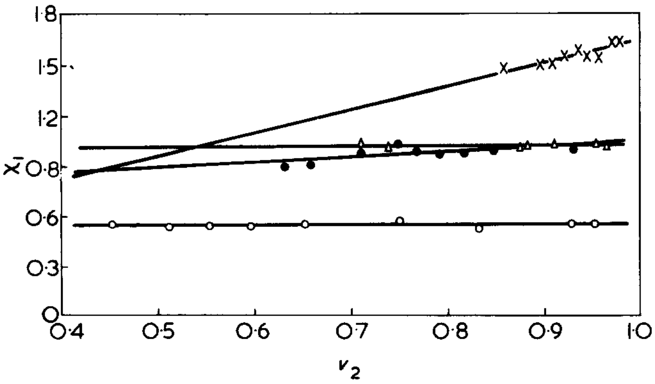

Figure 5 Interaction parameters from the Flory theory. Polymer: poly(vinyl chloride). ○, Tetrahydrofuran (slope = –0.09); ●, 1,4-dioxan (slope = 0.30); △, toluene (slope = +0.03); X, di-n-propyl ether (slope = +1.30)

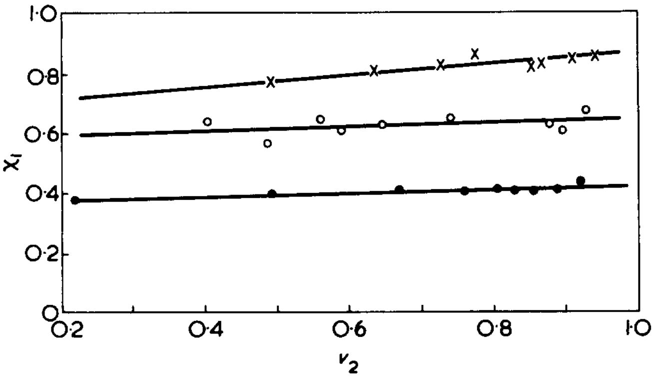

Figure 6 Interaction parameters from the Flory theory. Polymer: polystyrene. ●, Toluene (slope = –0.06); ○, methyl ethyl ketone (slope = –0.07); X, 1,4-dioxan (slope = +0.25)

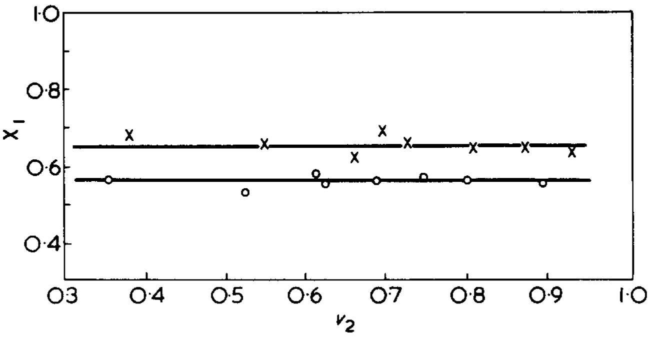

Figure 7 Interaction parameters from the Flory theory. Polymer: poly(methyl methacrylate). ○, Methyl ethyl ketone;(slope = 0.00); X, toluene (slope = +0.06)

deviations are within the experimental error in all cases apart from that of poly(vinyl chloride) where it can be shown that χ_1 is linearly dependent on v_2. This dependence may be due in part to the low compatability of poly(vinyl chloride) with di-n-propyl ether.

A more meaningful plot for demonstrating the validity of the theory is that of $\ln(P_1/P_1^0) - \ln(1 - v_2) - [1 - (1/x)]\, v_2$ *versus* v_2^2. These plots tend to give a rather closer agreement with theory than the corresponding plots of χ_1 *versus* v_2. This is partly due to the increased experimental scatter usually displayed by the latter. For example, the results of Bawn[5] for polystyrene in toluene fall on a good straight line when plots of $\ln(P_1/P_1^0) - \ln(1 - v_2) - [1 - (1/x)]\, v_2$ *versus* v_2^2 are constructed and which only show deviation from theory at higher values of v_2^2, yet the corresponding plots of χ_1, *versus* v_2 show a linear dependence on v_2 with appreciable scatter.

According to equation (1) plots of $\ln(P_1/P_1^0) - \ln(1 - v_2) - [1 - (1/x)]\, v_2$ *versus* the corresponding values of v_2^2 should give linear plots without intercept and with slopes equal to χ_1. When such plots were constructed for the present work (*Figures 8, 9, 10*) most solvent–polymer systems gave either very small positive or negative intercepts. Values of the appropriate intercepts and slopes for these systems are listed in *Table 7*.

Here again solutions of poly(methyl methacrylate) in MEK show an excellent agreement with theory. Although the di-n-propyl ether–poly(vinyl chloride) system gives the poorest results it is still within the experimental error. These results confirm our previous observations that plots of $\ln(P_1/P_1^0) - \ln(1 - v_2) - [1 - (1/x)]v_2$ against v_2^2 are in better agreement with theory than correcponding plots of χ_1 *versus* v_2.

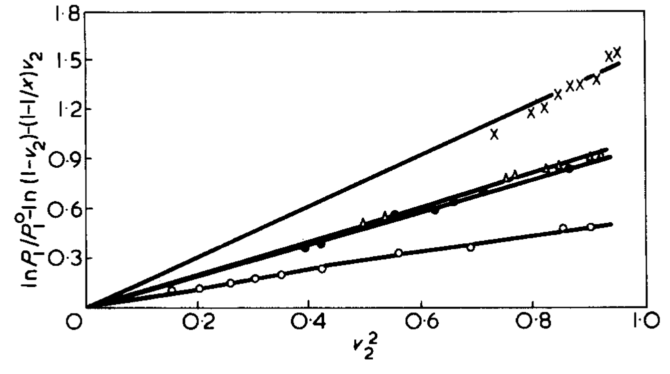

Figure 8 Application of the Flory theory to solutions of poly(vinyl chloride) in tetrahydrofuran, 1,4-dioxan, toluene and di-n-propyl ether. Polymer: poly(vinyl chloride). ○, Tetrahydrofuran; ●, 1,4-dioxan; △, toluene; X, di-n-propyl ether

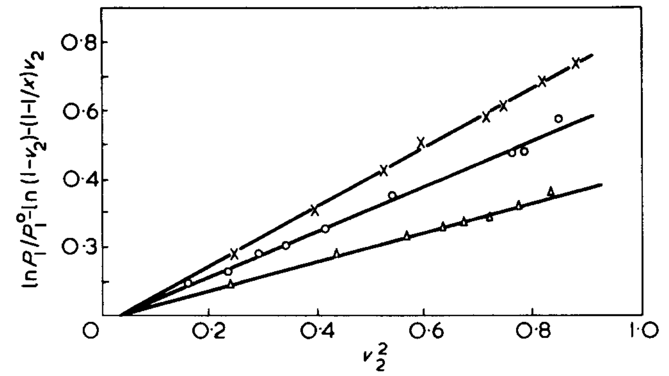

Figure 9 Application of the Flory theory to solutions of polystyrene in toluene, methyl ethyl ketone and 1,4-dioxan. Polymer: polystyrene. △, Toluene; ○, methyl ethyl ketone; X, 1,4-dioxan

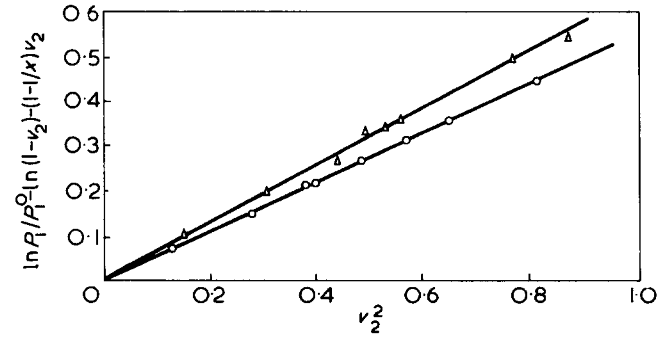

Figure 10 Application ot the Flory theory to solutions of poly (methyl methacrylate) in toluene and methyl ethyi ketone. Polymer: poly(methyl methacrylate). ○, Methyl ethyl ketone; △, toluene

Table 7 Intercepts and slopes for solvent–polymer systems

Solvent	Polymer	Intercept	χ_1
Tetrahydrofuran	Poly(vinyl chloride)	+0.002	0.556
Di-n-propyl ether	Poly(vinyl chloride)	–0.027	1.556
1,4-Dioxan	Poly(vinyl chloride)	–0.017	1.004
1,4-Dioxan	Polystyrene	–0.013	0.851
Toluene	Poly(vinyl chloride)	+0:002	1.037
Toluene	Polystyrene	–0.004	0.402
Toluene	Poly(methyl methacrylate)	+0.004	0.638
Methyl ethyl ketone	Polystyrene	–0.007	0.651
Methyl ethyl ketone	Poly(methyl methacrylate)	0.000	0.557

In conclusion, the two techniques investigated produced values for the interaction energy parameter, χ_1, for polystyrene, poly(vinyl chloride) and poly(methyl methacrylate) in a wide range of different solvent types, which were in good agreement, thus substantiating the validity of both methods. Additionally, the vapour pressure results were found, with the exception of solutions of poly(vinyl chloride) in di-n-propyl ether, to be in good agreement with the Flory–Huggins theory over an extended range of solute composition. The g.l.c. method, however, proved to be a more rapid technique for the determination of χ_1, normally requiring measurements for less than one hour, whereas the vapour pressure procedure may require up to ten days for a single determination of χ_1. There are also experimental difficulties in determining χ_1 at high temperature when using the vapour pressure method. These difficulties do not arise to the same extent with the g.l.c. technique since a more accurate temperature control is more easily maintained.

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