Determination of the interaction parameter *g* by inverse gas chromatography: an additional experimental test of the classic lattice model

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(Received 21 December 1988; accepted 20 January 1989)

Inverse gas chromatography measurements on narrow polystyrene samples of different molecular weights have been interpreted in terms of the classic lattice model. The analysis includes a rather complex temperature dependence of the interaction parameter, g, different from the usual Flory–Huggins prediction, which only allows a linear dependence on $1/T$. The extension of the simple model supplies an adequate description of the data, giving the enthalpic and entropic contributions of the interaction parameter at infinite dilution, g^{∞}. The different coefficients of the new temperature dependence have been determined from experimental data obtained by using chromatographic columns packed with polystyrene samples of different molecular weights, where different molecular probes have been injected. The influence of the molecular weight on these coefficients has also been studied.

(Keywords: interaction parameter; inverse gas chromatography; polystyrene; lattice model)

INTRODUCTION

In spite of continuous references to the rigid lattice model of polymer solutions, the model has been the subject of much criticism. However, recent literature contains some papers which continue to investigate the limits of its applicability[1,2], particularly from the point of view of its predictive power, given its simplicity compared with other more sophisticated models.

The starting point for binary polymer–solvent systems is the Gibbs mixing function, ΔG_m, which can be written, without approximations as

$$\frac{\Delta G_m}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + N g \phi_1 \phi_2 \qquad (1)$$

for a mixture of n_1 moles of solvent and n_2 moles of polymer with a single mass M_2. In equation (1)

$$N = n_1 + n_2 \qquad (2)$$

$$\phi_1 = n_1/N \qquad (3)$$

$$\phi_2 = n_2 m_2/N \qquad (4)$$

where m_2 is

$$m_2 = v_{sp,2} M_2/V_1 \qquad (5)$$

with $v_{sp,2}$ and V_1 the specific volume of the polymer and the molar volume of the solvent, respectively. The parameter g is the interaction function in terms of the interchange energy, related to the classical interaction parameter, defined on the basis of the solvent chemical potential, by means of the equation

$$\chi = g - \phi_1 \frac{\partial g}{\partial \phi_2} \qquad (6)$$

Experimental data have suggested that the interpretation of g and χ as a free energy is preferable.

There is little question today about the advantages of gas–liquid chromatography (g.l.c.) for measurements of many physicochemical properties[3]. Activity and partition coefficient data derived from the g.l.c. method do in fact agree to well within the experimental errors arising with more traditional or static apparatus of various designs. Application of the g.l.c. technique to polymer solutions represents a quite natural extension of studies of these kinds. This technique, which is also called inverse gas chromatography (i.g.c.), provides solvent activity coefficients at infinite dilution of the solvent. Consequently $\phi_1 \rightarrow 0$, and according to equation (6),

$$\chi^{\infty} \rightarrow g^{\infty}$$

where the superscript ∞ indicates the infinite dilution of the solvent. Comparative studies of i.g.c. and static methods[4,5] have shown that the i.g.c. method is in fact capable of sufficient precision and accuracy to be of value in the measurement of thermodynamic properties of polymer solution.

In this paper, we summarize experimental data on the interaction parameter measured for different molecular weights of atactic polystyrene (PS) and different solvents,

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0032-3861/89/081493-05$03.00
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as determined by i.g.c. Data at different temperatures have been interpreted as far as the rigid lattice model would permit.

EXPERIMENTAL

The atactic polystyrene (PS) samples were obtained from the Pressure Chemical Co. Their molecular weight distributions had specifically low polydispersities. A wider distribution sample, provided by Arrahona S.A., Barcelona, Spain, with a polydispersity index of 3.1 ($\bar{M}_z = 385\,200$, $\bar{M}_w = 178\,000$, $\bar{M}_n = 56\,500$) has also been used to clarify the polydispersity influence on the thermodynamic parameters determined in this paper.

All the solutes were chromatoquality or reagent grade and were used without further purification.

In every column, the polymer was deposited onto Chromosorb W (AW-DMCS treated, 80/100 mesh) from a chloroform solution by continuous stirring and slow evaporation of the solvent. The coated support was dried *in vacuo* at 333 K in order to remove the last traces of chloroform. Afterwards, the coated support was packed in a stainless steel column by applying a vacuum to one end. Glass wool was used to block the ends of the columns. The columns were 100 cm long and the loadings oscillated between 7 and 9% (w/w).

The gas chromatographic measurements were taken with a Sygma 300 Perkin–Elmer gas chromatograph equipped with a flame ionization detector. The column temperature was controlled to ± 0.1 K over the measured temperature range. Nitrogen was used as the carrier gas. Methane, as a non-interacting marker, was used to correct the dead volume in the column and the retention time was directly measured with the aid of an Olivetti M-24 microcomputer, provided with a CHROM+ card and appropriate software. A minimum of four measurements was taken for every molecular probe and for each temperature in all columns. Pressures at inlet and outlet of the column, read from a mercury manometer, were used to compute corrected retention volumes by the usual procedures. Flow rates were measured from the end of the column with a bubble flowmeter and the value was maintained at $5\,\mathrm{ml\,min^{-1}}$. More details can be found elsewhere[6].

The molecular probes, including a small amount of the methane marker, were injected manually with a $10\,\mu$l Hamilton syringe ($<0.01\,\mu$l). The columns were conditioned at temperatures above T_g for ≈ 48 h before use, while N_2 was flushed through the column in order that it should reach an equilibrium.

RESULTS AND DISCUSSION

From gas–liquid chromatographic experiments, the specific retention volume V_g^o can be calculated[7] from the equation

$$V_g^o = \frac{273.16 \times t_N F j}{T_c w_L} \tag{7}$$

where t_N is the net retention time of the solvent, w_L the weight of the polymer in the column, j the James–Martin correction factor for gas compressibility, T_c the column temperature and F the flow rate of the carrier gas at 273 K and 1 atm (10^5 Pa).

The interaction parameter at infinite dilution ($\phi_1 \to 0$), where g and χ become identical, can be calculated in the following way:

$$g^\infty \equiv \chi^\infty = \ln\left(\frac{273.16 \times R v_{sp,2}}{P_1^o V_g^o V_1}\right) - \left(1 - \frac{V_1}{M_2 v_{sp,2}}\right) - \frac{(B_{11} - V_1)P_1^o}{RT} \tag{8}$$

where M_2, V_g^o, V_1 and $v_{sp,2}$ have been previously defined, P_1^o is the vapour pressure of the solvent and B_{11} its second virial coefficient.

Results for χ^∞ have been obtained for the probes n-butanone, chloroform, toluene, n-propanol, chlorobenzene and n-decane in a range of temperatures between 393 and 473 K.

In all cases $\chi^\infty (\equiv g^\infty)$ exhibited a parabolic behaviour, which could be seen totally or partially, as shown in *Figure 1*, which illustrates three different examples obtained with different solvents and molecular weights.

Such parabolic T-dependence can be explained on the lattice model basis, in spite of the original Flory–Huggins formulation, which only allowed for a linear dependence of χ on $1/T$. This temperature dependence has often given grounds for objections against the model, because of its alleged incapability of describing the existence of both lower and upper critical solution temperature (LCST and UCST). This experimental occurrence of UCST and LCST is consistent with a parabolic dependence of χ on T as shown by our samples in *Figure 1*.

However, as Koningsveld[8] has demonstrated, this criticism of the lattice model is not justified. On revising some fundamental thermodynamic relations we can write

$$\Delta H = \int \Delta C_p \mathrm{d}T \tag{9a}$$

$$\Delta S = \int (\Delta C_p / T) \mathrm{d}T \tag{9b}$$

where ΔH, ΔS and ΔC_p are the enthalpy, entropy and specific heat changes occurring upon mixing.

The specific heat at constant pressure C_p of a liquid is known to be dependent on the temperature. In addition, ΔC_p must be expected to vary with concentration:

$$\Delta C_p = (c_0 + c_1 T)\phi_1 \phi_2 \tag{10}$$

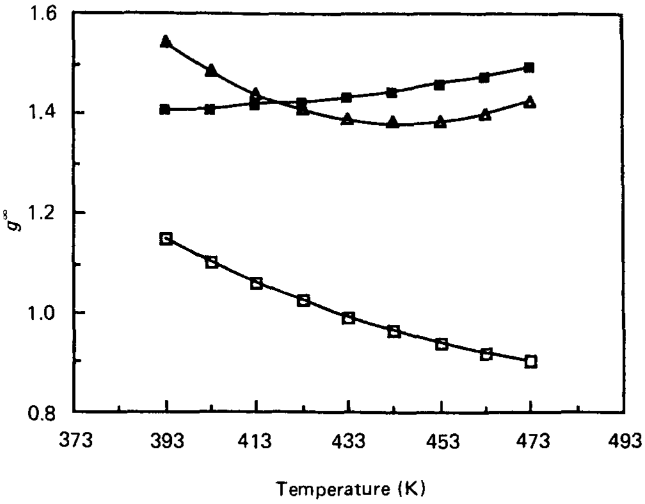

Figure 1 Variation of the interaction parameter at infinite dilution, g^∞, with temperature for (△) PS9000/n-propanol, (□) PS35000/2-butanone and (■) PS9000/chloroform systems

Equations (9a), (9b) and (10) together with equation (1) can be used to obtain a new expression for $g(T)$. And so, it is possible to write

$$g = g_a + g_b/T + g_c T + g_d \ln T \qquad (11)$$

where g_a and g_b are integration constants and

$$g_c = -c_1/2NR, \qquad g_d = -c_0/NR$$

In conclusion, g^∞ (or χ^∞), as g, can be expressed as a more complex function of temperature than $1/T$. Equation (11) is qualitatively consistent with the experimental data provided by i.g.c. similar to those shown in *Figure 1*.

Other $g(T)$ functions can be theoretically derived in the framework of the rigid lattice model, as Staverman[9] and Koningsveld and Kleintjens[10] among others have demonstrated.

Nowadays it is accepted that the major reason for the dependence of g on concentration arises from the disparity in size and shape of the solvent molecules and the polymer segments.

According to an idea of Staverman[9], it is possible to write g as

$$g = B(T)/(1-\gamma\phi_2) \qquad (12)$$

from his expression for the enthalpy of mixing. In equation (12) $B(T)$ resumes the temperature dependence

$$B(T) = B_0 + B_1/T \qquad (13)$$

and

$$\gamma = 1 - \sigma_2/\sigma_1 \qquad (14)$$

where σ_2/σ_1 is the ratio of the surface areas of polymer segments and solvent molecules, calculable from Bondi's radii[11], The ratio σ_2/σ_1 is identical in meaning to s_2/s_1 in the free-volume models, such as the equation of state theory[12] or the Sanchez–Lacombe[13] model.

However, if we apply this set of equations to the experimental data of various systems, it is revealed[7] that a new empirical adjusting parameter C is needed. At high ϕ_2 calculated and measured binodals, spinodals and χ *versus* ϕ_2 curves illustrate that this empirical parameter depends on the temperature

$$C = a_1 + a_2 T \qquad (15)$$

Consequently

$$g = \frac{B(T)}{(1-\gamma\phi_2)} + a_1 + a_2 T \qquad (16a)$$

or

$$g = \frac{B_0 + B_1/T}{(1-\gamma\phi_2)} + a_1 + a_2 T \qquad (16b)$$

which gives a new g–T dependence, also consistent with the experimental data provided by i.g.c.

Following a first approximation given by Koningsveld[8], we have separated g^∞ into two contributions: g_H^∞ related to the $B(T)$ term and an entropic contribution g_S^∞. Then,

$$g^\infty = g_H^\infty + g_S^\infty \qquad (17)$$

g_H^∞ and consequently g_S^∞ are also available from i.g.c. measurements. In the framework of the i.g.c. theory, the excess partial molar heat of mixing $\overline{\Delta H}_1^\infty$ can be calculated as[14]

$$\overline{\Delta H}_1^\infty = R\left(\frac{\partial \ln \Omega_1^\infty}{\partial(1/T)}\right) \qquad (18)$$

where Ω_1^∞ is an activity coefficient at infinite dilution, defined in terms of the weight fraction

$$a_1^\infty = \Omega_1^\infty w_1 \qquad (19)$$

and calculable from i.g.c. measurements:

$$\ln \Omega_1^\infty = \ln\left(\frac{273.16 \times R}{P_1^0 V_g^0 M_1}\right) - \frac{P_1^0(B_{11} - V_1)}{RT} \qquad (20)$$

Consequently, from equations (18) and (20),

$$\overline{\Delta H}_1^\infty = -R\left(\frac{\partial \ln P_1^0}{\partial(1/T)} + \frac{\partial \ln V_g}{\partial(1/T)}\right) \qquad (21)$$

The term on the left-hand side of equation (21) is the heat of vaporization of the pure solvent:

$$\Delta H^V = -R\partial \ln P_1^0/\partial(1/T) \qquad (22)$$

On the other hand, the retention volume V_g^0 is related to the free energy of vaporization from the solution ΔG (Reference 14):

$$\Delta G' = RT \ln V_g^0 \qquad (23)$$

Consequently, the heat of vaporization from the solution will be

$$\frac{\partial(\Delta G'/T)}{\partial(1/T)} = R\frac{\partial \ln V_g^0}{\partial(1/T)} \qquad (24)$$

and the heat of solution will be

$$\Delta H_S = -R\frac{\partial \ln V_g^0}{\partial(1/T)} \qquad (25)$$

From these last equations

$$\overline{\Delta H}_1^\infty = \Delta H_V + \Delta H_S \qquad (26)$$

Even in recent years, i.g.c. has been claimed to be a useful method for calculating experimental values of ΔH_V and consequently the solubility parameters of the solvents introduced in the i.g.c. columns[15]. The authors of Reference 15 verify the agreement between the data calculated from V_g^0 and estimations from the Clausius–Clapeyron equation. A close inspection of equations (20)–(25) shows that V_g^0 does not really affect ΔH_V. It is only a direct consequence of the P_1^0 values introduced in the calculations.

Values of $\overline{\Delta H}_1^\infty$ for the different molecular weights and solvents at different temperatures have been calculated using equation (18). From $\overline{\Delta H}_1^\infty$, g_H^∞ interpreted as the reduced residual molar enthalpy of mixing at infinite dilution, can be estimated as

$$g_H^\infty = \overline{\Delta H}_1^\infty/\mathrm{RT} \qquad (\phi_2 = 1) \qquad (27)$$

From g_H^∞ and g^∞, the value of g_S^∞ is calculable with the aid of equation (17).

Figures 2 and *3* show the dependence of these two parameters on temperature for a narrow PS sample of $\overline{M}_w = 47\,500$. Similar behaviour has been observed at the other molecular weights.

From such linear correlation, the behaviour of g^∞ seems to follow equation (16b) and consequently the different coefficients of this equation can be easily determined.

The original lattice model treatment introduced χ as a parameter independent of molar mass. The dependence of χ on molar mass was observed in early measurements, especially in the dilute regime ($\phi_1 \rightarrow 1$) and was

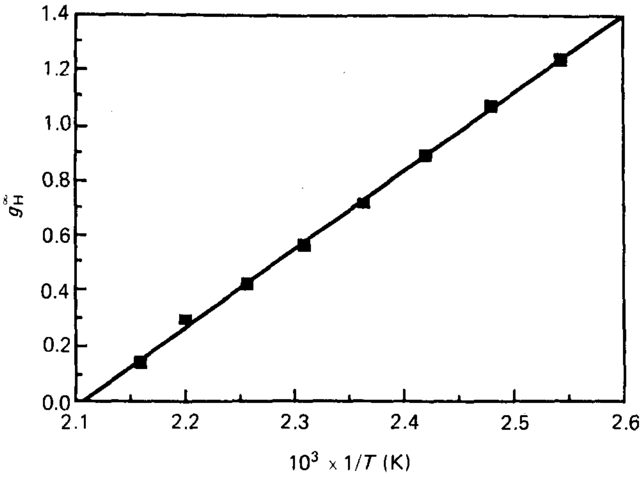

Figure 2 Dependence of the parameter g_H^∞ on temperature in the PS ($\bar{M}_w = 47\,500$)/toluene system

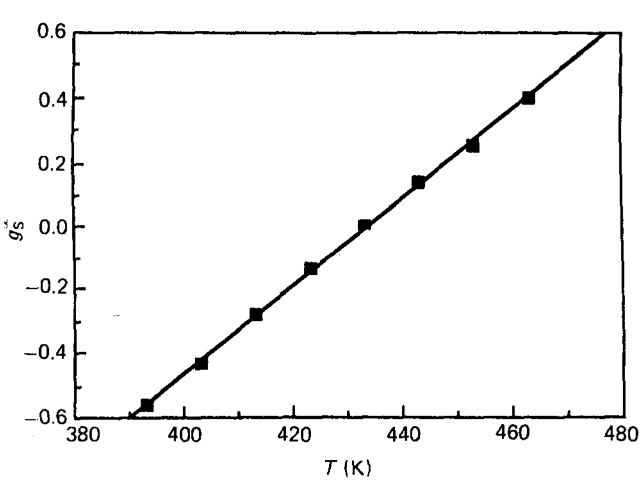

Figure 3 Dependence of the parameter g_S^∞ on temperature in the PS ($\bar{M}_w = 47\,500$)/toluene system

successfully attributed to the non-uniform density in dilute polymer solutions through the so-called excluded volume theories[16]. Some years ago, Staverman[17] considered the influence of molecular weight on the g parameter in the concentrated regime. This influence arises from the effect of the chains bending back on themselves. Originally developed for athermal solutions, the theory is being developed for other situations[18]. Consequently, experimental data of the molecular weight dependence of the g parameter on the concentrated regime, where molecules overlap extensively, may be interesting in testing such predictions.

Data for g^∞ show a complex relationship with molecular weight. According to our data from i.g.c. measurements, they would appear to pass through a maximum near a molecular weight of 10^5. Some experimental difficulties inherent in i.g.c. measurement may be the cause of such behaviour and further experimental work will have to be done to confirm this dependence. Variables such as flow rate, column loading or the support nature can affect the measurements and the dependence of g on molecular weights.

However, there is a clear conclusion arising from our study: in spite of previous evidence[1] about the molecular weight dependence of the coefficients a_1 and a_2 in equation (15) (g_S^∞ and C have been treated identically), our data reveal that a_2 is independent of molecular weight. Results have been conclusive in all the different molecular probes investigated. *Table 1* gives the results corresponding to the good solvent chloroform and the poor solvent 2-butanone.

The polystyrene/toluene system is very interesting. Data for other molecular weight standards, expressed in the form of linear relationships of the specific retention volumes against the inverse of the temperature have been found in the literature[19,20]. From these data we have recalculated the thermodynamic parameters, using the same values for all the characteristic magnitudes of the polymer and the probes. Results from these two sources and our own data show surprisingly good agreement, from which it is possible to draw conclusions on both the reproducibility of the technique in obtaining such data and the independence of the a_2 coefficient on the molecular weight. *Table 2* summarizes data for B_0, B_1, a_1 and a_2 in the PS/toluene system.

Both B_1 and a_1 seem to be molecular weight dependent and show a maximum and a minimum, respectively, in the intermediate range of molecular weight. However, more data on other polymers with molecular weight standards and interlaboratory comparisons are needed to clarify these dependences. But it is clear that i.g.c. provides interesting data in a concentration range not widely studied. Moreover, the molecular weight influence on g seems to be well founded and should be taken into account in experimental comparisons or specific uses of i.g.c., such as the calculation of polymer–polymer interaction parameters from data of retention times of the probes in columns coated with pure components and the mixture.

A final comment is in order about the effect of the polydispersity on the molecular weight dependence of

Table 1 a_2 values (see equation (15)) for the systems PS/chloroform and PS/2-butanone

	a_2	
Molecular weight	Chloroform	Butanone
9000	0.0126	0.0151
35000	0.0127	0.0151
47500	0.0125	0.0153
90100	0.0128	0.0153

Table 2 Temperature coefficients of g_H^∞ and g_S^∞ at different molecular weights for the PS/toluene system ($\sigma_2/\sigma_1 = 0.92$)

$10^{-3}\bar{M}_w$	B_0	B_1	a_1	a_2	Ref.
2.2	−5.44	2300	−5.36	0.0140	19
4.0	−5.45	2500	−5.63	0.0140	19
9.0	−5.60	2325	−5.41	0.0139	This work
17.5	−5.44	2381	−5.49	0.0140	19
35.0	−5.54	2588	−5.85	0.0137	This work
47.5	−5.54	2629	−5.95	0.0137	This work
82.1	−5.56	2498	−5.61	0.0136	20
90.1	−5.46	2480	−5.86	0.0140	This work
107.0	−5.44	2414	−5.49	0.0140	19
1800.0	−5.44	2250	−5.20	0.0140	19
177.9[a]	−5.63	2195	−5.05	0.0140	This work

[a] Polydisperse sample

such a parameter. For our polydisperse sample, the interaction function g^{∞} exhibits a peculiar dependence on temperature, closer to the very low molecular weight standards than to others of similar average molecular weights. If we follow the suggestion[1] of using $\overline{M}_w{}^2/\overline{M}_z$ instead of the molecular weight of the sample, this value is seen to be 82 300. Even with this value, B_0, B_1 and a_2 are not consistent with the other values in *Table 2*. However, a_2 remains constant once again, irrespective of the polydispersity of the sample.

Error analysis

The reliability of the V_g° values, based on repeated measurements was within 1–2%. The precision on g^{∞}, as estimated also from repeated measurements, was better than 5%. The uncertainty in $\overline{\Delta H_1^{\infty}}$ values (4%) refers to standard errors in the slope, as given by the least-squares analysis. The estimated errors are probe dependent, the measured magnitudes being less accurate with low-boiling solvents.

ACKNOWLEDGEMENT

We are very grateful to the Fondo Nacional para la Investigación Científica y Técnica for their financial support of this research (Project number PB86-0257). One member of our team (C.U.) would also like to thank the Spanish Ministerio de Educación y Ciencia for a grant award.

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