Determination of thermodynamic data for the interaction of aliphatic alcohols with poly(styrene-*co*-divinylbenzene) using inverse gas chromatography

Roman Sanetra, Bożena N. Kolarz* and Andrzej Włochowicz
Textile Institute, Technical University of Łódź, Bielsko-Biała, Findera 32, 43-300 Bielsko-Biała, Poland
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The thermodynamic functions of mixing, the weight fraction activity coefficients at infinite dilution and the Flory–Huggins interaction parameters were determined for systems of normal aliphatic alcohols (C_1–C_6) interacting with poly(styrene-*co*-divinylbenzene) (5, 10 and 20 wt% divinylbenzene). The Hildebrand solubility parameters δ_2 of the copolymers were calculated. The values obtained directly from the free energy of mixing were found to agree best with literature data. In the range 455–480 K they were 14.8, 15.7 and 17.8 $MPa^{1/2}$, respectively, for the copolymers crosslinked with 5, 10 and 20 wt% of divinylbenzene.

(Keywords: poly(styrene-*co*-divinylbenzene); thermodynamic data; solubility parameters)

INTRODUCTION

Inverse gas chromatography (i.g.c.) is widely used to characterize linear polymers. It provides much quantitative data on polymer–solvent interactions as well as on the structure of polymers in the condensed state. In general, the method consists of coating an inert material with the polymer to be studied and recording the so-called retention diagram. Such a diagram obtained for a selected solvent is used as a source of information about the polymer itself and about polymer–solvent interactions. Unfortunately, as shown by Braun and Guillet[1], the kind of material used as polymer support may considerably affect retention diagrams.

In our i.g.c. studies on poly(styrene-*co*-divinylbenzene) no additional supporting material was needed. The crosslinked polymer as such was used as the column filling. The supermolecular structure of the polymer fixed at the synthesis stage was thus preserved. Aliphatic C_1–C_5 alcohols were used as molecular probes. In such systems the absorption equilibrium was at temperatures as high as about 100°C above T_g (cf. ref. 2).

In this work, the thermodynamic parameters of the system poly(styrene-*co*-divinylbenzene)–aliphatic alcohols are calculated from the absorption parts of i.g.c. retention diagrams. Since the polymers are insoluble, such data are hard to obtain by other methods.

EXPERIMENTAL

Materials

The styrene–divinylbenzene copolymers (St-DVB) were obtained in suspension under the conditions described elsewhere[3–6].

The composition of each copolymer is coded in its symbol, as in the following example. The symbol HT 19 0.5/10 means that monomers were diluted with a heptane–toluene mixture 1:9, by volume, and the initial fraction of monomers was 0.5. The number following the slash is the crosslinking degree of the copolymer, i.e. the weight per cent of divinylbenzene (DVB) in the St-DVB mixture. The characteristics of the copolymers used have been presented elsewhere[2].

The alcohols, methanol (C_1), propanol (C_3), butanol (C_4) and pentanol (C_5), used as sorbates (probes) were all chromatographic standards supplied by PolyScience Co. (USA) or POCh (Poland). Ethanol (C_2) was of PA grade. In each injection, 0.5 μl of an alcohol was used.

Procedure

The copolymers in the form of 0.1 ± 0.02 mm diameter beads were placed into stainless-steel columns ($\frac{1}{8}$ inch internal diameter, 1 m length). Retention diagrams were recorded on a Varian instrument as described before[2].

DATA TREATMENT

The specific retention volume V_g was calculated as:

$$V_g = \frac{273.2 t_R F}{T_k w} I \qquad (1)$$

where t_R is the net retention time, w is the weight of copolymer, F is the flow rate of carrier gas at 273 K, T_k is the column temperature and I is the factor which corrects for gas compressibility:

$$I = \tfrac{3}{2}\{[(p_i/p_o)^2 - 1]/[(p_i/p_o)^3 - 1]\} \qquad (2)$$

(p_i and p_o are the inlet and outlet carrier gas pressures respectively).

The partial molar free energy of sorption ΔG_1^s was

* Institute of Organic and Polymer Technology, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

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calculated from the relation

$$\Delta G_1^s = -RT \ln(M_1 V_g/273R) \quad (3)$$

where M_1 is the molar mass of the solute and RT has its usual meaning.

The molar enthalpy of sorption ΔH_1^s was of the form form

$$\Delta H_1^s = -R\frac{\partial \ln V_g}{\partial(1/T)} \quad (4)$$

and the entropy was calculated as

$$\Delta S_1^s = (\Delta H_1^s - \Delta G^s{}_1)/T \quad (5)$$

The alcohol vapour pressure was estimated using the Antoine equation[7]:

$$\log p_1^\circ = A - \frac{B}{T_k + C} \quad (6)$$

where A, B and C are constants.

The weight fraction activity coefficient of sorbates at infinite dilution $(a_1/w_1)^\infty$ was calculated from the expression

$$\ln(a_1/w_1)^\infty = \ln(273.2R/p_1^\circ V_g M_1) - \frac{p_1^\circ/B_{11} - V_1}{RT} \quad (7)$$

where M_1 and V_1 are the molar mass and volume, respectively, and B_{11} is the second virial coefficient of the sorbate. The values of B_{11} were evaluated from the equation of corresponding states[7]:

$$\frac{B_{11}}{V_c} = 0.430 - 0.886\frac{T_c}{T} - 0.694\left(\frac{T_c}{T}\right)^2 - 0.0375(n-1)\left(\frac{T_c}{T}\right)^{4.5} \quad (8)$$

where the critical quantities have the subscript 'c' and n is the number of carbon atoms in the sorbate molecules.

For polymers of high molecular weight, the reduced Flory free energy parameter χ at unit volume fraction of polymer is closely related to $\ln(a_1/w_1)^\infty$, since the former is given by (cf. equation (7))

$$\chi = \ln\left(\frac{273.2Rv_2}{p_1^\circ V_g V_1}\right) - \frac{p_1^\circ(B_{11} - V_1)}{RT} - 1 \quad (9)$$

where v_2 is the volume fraction of polymer.

The partial molar heat of mixing $\Delta\bar{H}_1^\infty$ at infinite dilution is given by

$$\Delta\bar{H}_1^\infty = R\frac{\partial(a_1/w_1)^\infty}{\partial(1/T)} \quad (10)$$

Consequently, the partial molar free energy of mixing $\Delta\bar{G}_1^\infty$ is

$$\Delta\bar{G}_1^\infty = RT \ln(a_1/w_1) \quad (11)$$

The molar enthalpy of vaporization of a solute can be calculated from the difference

$$\Delta H_v = \Delta\bar{H}_1^\infty - \Delta H_1^s \quad (12)$$

Assuming no volume change associated with mixing of polymer with solute in the chromatographic experiments, it seems justifiable to take:

$$\Delta\bar{H}_1^\infty = V_1(\delta_1 - \delta_2)^2 \quad (13)$$

where δ_1 and δ_2 are the Hildebrand solubility parameters. Thus, δ_2 can be found as the slope of a plot of δ_1 vs. $(\Delta\bar{H}_1^\infty/V_1)^{1/2}$.

Similarly, assuming no pressure difference upon mixing, one obtains

$$\Delta\bar{G}_1^\infty = V_1(\delta_1 - \delta_2)^2 \quad (14)$$

A third possibility is to combine the Hildebrand–Scatchard and Flory–Huggins theories to obtain

$$\chi = \frac{V_1}{RT}(\delta_1 - \delta_2)^2 \quad (15)$$

which can be rearranged to

$$\frac{\delta_1^2}{RT} - \frac{\chi}{V_1} = \frac{2\delta_2\delta_1}{RT} - \frac{\delta_2^2}{RT} \quad (16)$$

The term on the left-hand side can be calculated with the aid of equation (9) and plotted against δ_1 for different sorbates to yield $2\delta_2/RT$ as the slope.

RESULTS AND DISCUSSION

The thermodynamic parameters of sorption calculated for the copolymers include contributions from the processes of the transfer of a sorbate molecule to the adsorbed phase and of its penetration inside the copolymer. The values of the thermodynamic functions (for sorption and mixing) are shown in *Table 1*. They agree well with the values found by Schuster *et al.*[8] for the systems polystyrene/hydrocarbons. The relationships between the thermodynamic functions of sorption and the molecular weight of alcohol probes are roughly linear (cf. *Figure 1*).

The changes in the thermodynamic function of mixing are shown in *Figure 2* for the copolymers crosslinked with 5 and 20 wt% DVB. The changes in the free energy of mixing are small, but the molar enthalpy of mixing changes more markedly. It is highest for C_3 alcohols (5 wt% DVB) and C_4 alcohols (20 wt% DVB).

The molar enthalpies of vaporization (ΔH_v) calculated from equation (12) (*Table 1*) are smaller than that reported by Zado *et al.*[9] for the highly crosslinked polymer, Poropak Q.

The weight fraction activity coefficient at infinite dilution may be regarded as a measure of the interactions between polymer and aliphatic alcohols. The values of $(a_1/w_1)^\infty$ decrease with increasing temperature for all copolymer–alcohol pairs (*Table 2*). The magnitudes of the activity coefficients measured in this work do not deviate from those reported for polystyrene–ethanol[10,11] or, generally, for polystyrene–bad solvent systems[7].

Table 1 The values of thermodynamic functions for sorption and mixing (kJ mol^{-1})

	HT 19 0.5/5 at 445 K			HT 9 0.5/10 at 480 K			HT 19 0.5/20 at 480 K		
	ΔG_1^s	$-\Delta H_1^s$	$-T\Delta S_1^s$	ΔG_1^s	$-\Delta H_1^s$	$-T\Delta S_1^s$	ΔG_1^s	$-\Delta H_1^s$	$-T\Delta S_1^s$
1	14.5	12.7	27.2	17.4	17.9	35.3	16.2	13.4	29.6
2	14.1	16.0	30.1	–	–	–	15.7	16.8	32.5
3	10.4	8.8	19.2	14.0	16.9	29.8	14.0	11.9	25.8
4	8.1	5.7	13.8	11.6	16.0	27.6	12.4	11.7	24.1
5	–	–	–	10.0	15.1	25.1	11.1	8.5	19.6
	$\Delta \bar{G}_1^\infty$	$\Delta \bar{H}_1^\infty$	ΔH_v	$\Delta \bar{G}_1^\infty$	$\Delta \bar{H}_1^\infty$	ΔH_v	$\Delta \bar{G}_1^\infty$	$\Delta \bar{H}_1^\infty$	ΔH_v
1	12.4	11.9	24.6	12.8	10.3	28.2	11.6	14.6	28.0
2	13.0	17.0	33.0	–	–	–	12.3	13.8	30.6
3	10.7	22.6	31.4	12.5	10.2	26.0	12.5	17.2	28.0
4	11.2	22.0	27.7	12.2	17.0	33.0	13.1	25.9	32.6
5	–	–	–	13.6	16.0	31.2	14.7	22.2	30.7

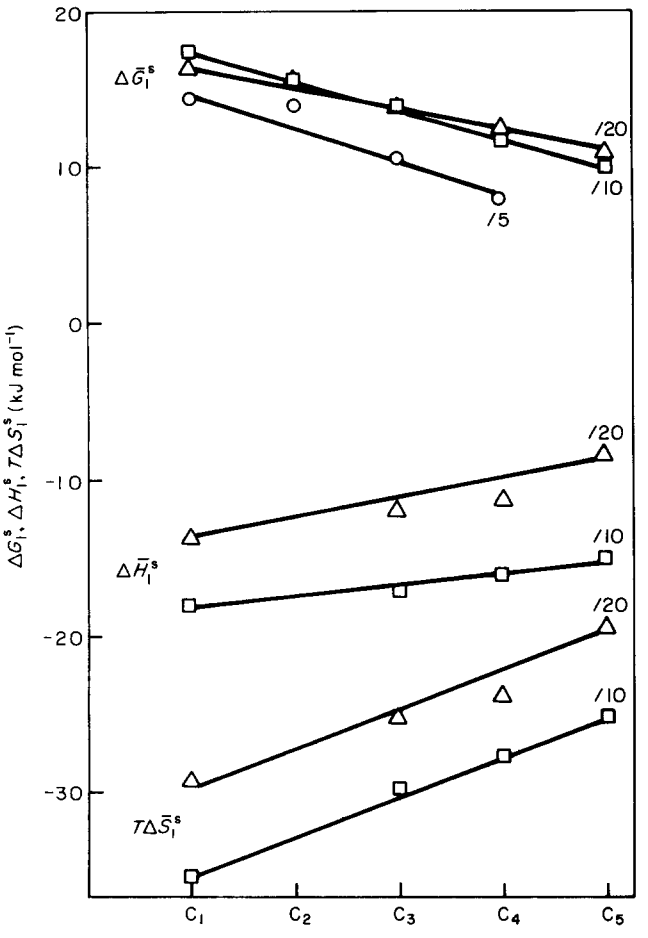

Figure 1 Thermodynamic functions of sorption *versus* the number of CH_2 groups in aliphatic alcohols (10 and 20 wt% DVB, 480 K; 5 wt% DVB, 455 K)

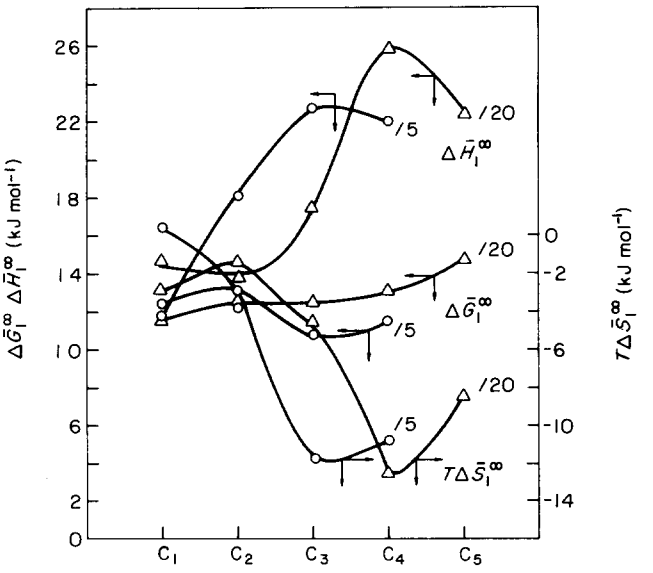

Figure 2 Thermodynamic functions of mixing *versus* the number of CH_2 groups in aliphatic alcohols (20 wt% DVB, 480 K; 5 wt% DVB, 455 K)

The effect of degree of crosslinking on the values of $(a_1/w_1)^\infty$ has been discussed before[12].

The dependence of the χ parameter on temperature and degree of crosslinking has been found to be similar to that for $(a_1/w_1)^\infty$ (*Figure 3*). The values of χ are high, as usual for polymer–non-solvent systems. The dependence of χ on temperature is non-linear. A similar non-linear character of the relationship between an entropic term χ_s or a parameter χ^* (calculated from the equation of state) and temperature was observed by Fernandez-Berridi *et al.*[13,14] for poly(ethylene oxide)–alcohol pairs. It is possible that the non-linearity is due to specific interactions of copolymers with C_3–C_4 alcohols, which were discussed before[2]. The values of χ are plotted against δ_1 in *Figure 4*. In the whole temperature range there is a minimum in χ for δ_1 corresponding to C_3 ($\delta_1 = 24.3$ MPa$^{1/2}$).

The values of the free energy of mixing calculated from the activity coefficient (equation (11)) are plotted against solubility parameters of alcohol probes in *Figure 5*. The plots are non-linear with minima for C_3 too. As suggested before[2], the minima might result from superimposed effects of polymer–solvent interactions and the accessibility of the inhomogeneous gel.

Since the amount of sorbate introduced into the chromatographic column was very small, it seemed

Table 2 The temperature dependence of the weight fraction activity coefficient $(a_1/w_1)^\infty$ of alcohols at infinite dilution

Temperature (K)	HT 19 0.5/5					HT 19 0.5/10					HT 19 0.5/20				
	C_1	C_2	C_3	C_4	C_5	C_1	C_2	C_3	C_4	C_5	C_1	C_2	C_3	C_4	C_5
445	28.3	34.0	24.7	20.8	21.0										
455	27.0	30.7	21.1	18.8		29.1	38.9	31.5	37.6	37.7					
460											21.8	26.6	36.2	41.6	52.5
465	25.0		19.1	16.1		27.5		24.4	26.3	35.5					
470											20.1	23.1	29.2	33.3	44.1
475						25.0		23.7	22.5	30.4					
480						25.0		23.2	21.0	29.9	18.5	21.9	22.9	26.5	39.6

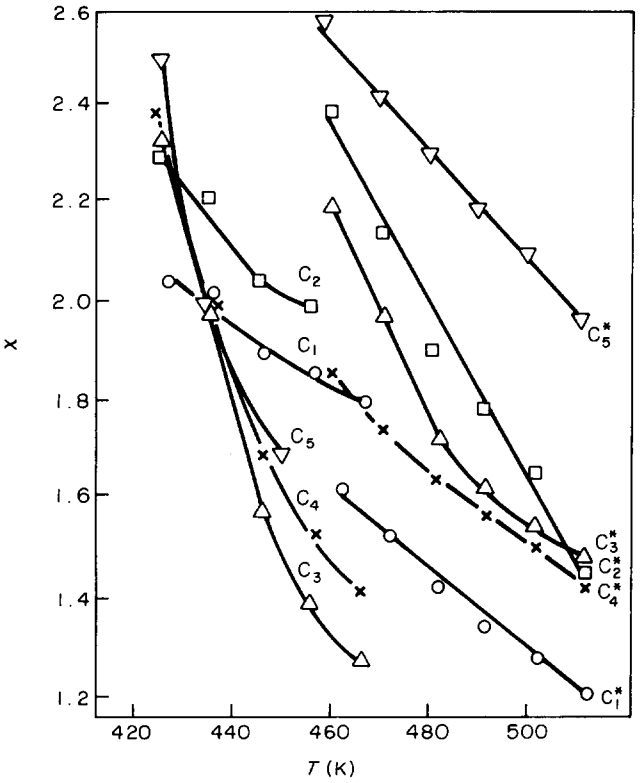

Figure 3 The temperature dependence of the Flory–Huggins parameter χ for the systems poly(styrene-*co*-divinylbenzene)–aliphatic alcohols (20 wt% DVB, C*; 5 wt% DVB, C)

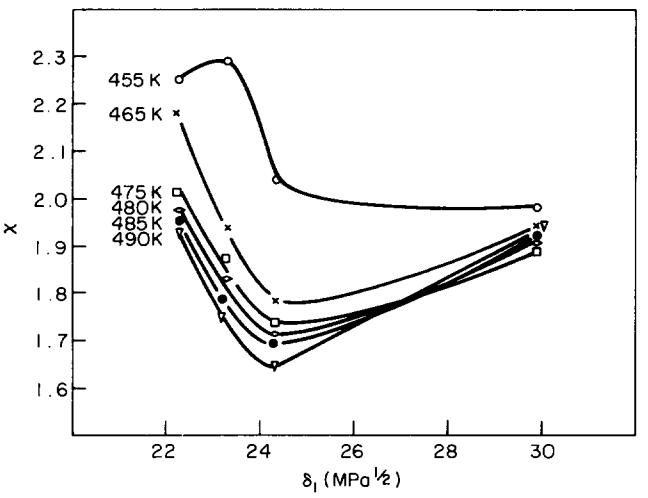

Figure 4 The correlation between the Flory–Huggins parameter χ and the solubility parameters δ_1 for aliphatic alcohols at the temperatures specified (HT 19 0.5/10)

reasonable to assume a zero change in volume upon mixing the sorbate with the polymer. A value of δ_2 can thus be calculated from equation (13), at $\Delta\bar{H}_1^\infty = 0$. The term $\delta_1^2 - \Delta\bar{G}_1^\infty/V_1$, where $\Delta\bar{G}_1^\infty$ was calculated from equation (11), is plotted against the solubility parameter of alcohols δ_1 in *Figure 6*. The slope again corresponds to δ_2.

The third way of evaluating δ_2 is to use equation (16) (cf. *Table 3*).

It is known that the solubility parameters decrease with temperature[7,13]. Hence, the values in rows 1 and 3 of *Table 3* are evidently too high (the temperature range is 455–480 K). The reported values of δ_2 for polystyrene and styrene–divinylbenzene copolymers are 17.4–18.6 at 298 K.[15]

Values of δ_2 comparable to the reported ones were obtained from $\Delta\bar{G}_1^\infty$ (row 2, *Table 3*) using equation (14) (cf. *Figure 6*). The use of $\Delta\bar{G}_1^\infty$ for calculating δ_2 was also

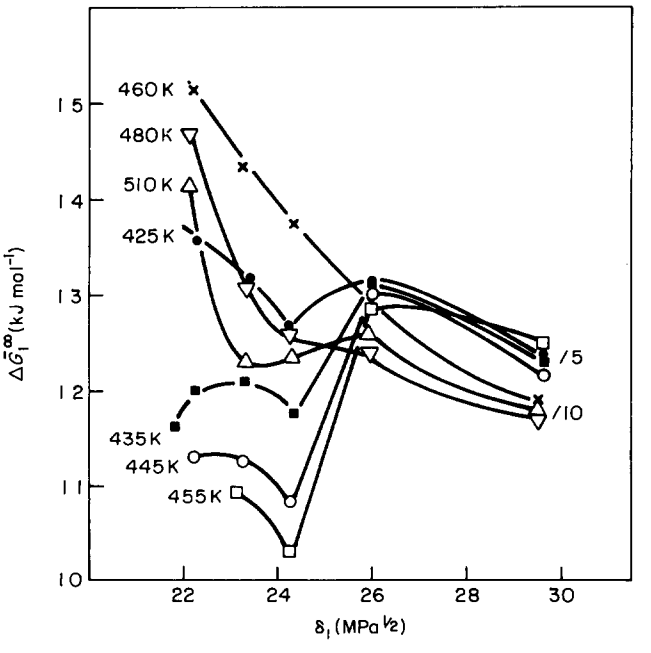

Figure 5 The partial molar free energy of mixing $\Delta\bar{G}_1^\infty$ as a function of solubility parameters δ_1 of alcohols at the temperatures specified

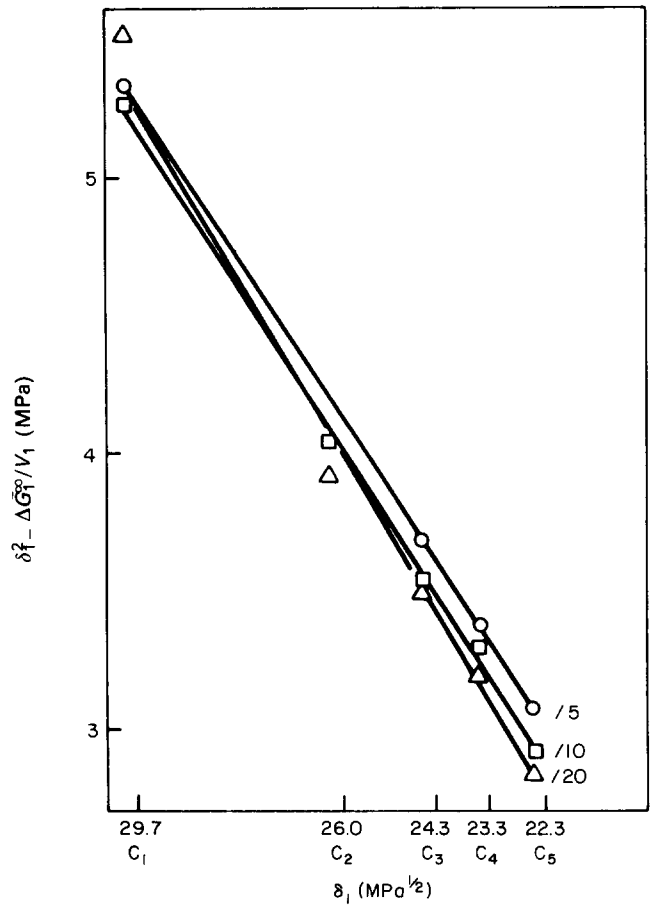

Figure 6 The estimation of the solubility parameters δ_2 of poly(styrene-*co*-divinylbenzene) from the partial molar free energy of mixing $\Delta\bar{G}_1^{\infty}$

suggested by DiPaola-Baranyi *et al.*[7] who, following Scott[16], questioned the approach in which the volume changes on mixing were neglected.

As pointed out by Ito and Guillet[17] and by Fernandez-Berridi *et al.*[13], the too high volumes of δ_2 obtained by using equation (15) might be due to a contribution of entropic terms.

CONCLUSIONS

By using the i.g.c. method, it is possible to evaluate a number of thermodynamic parameters for the interaction of poly(styrene-*co*-divinylbenzene) with aliphatic alcohols in a broad range of temperature. The values of $(a_1/w_1)^{\infty}$, χ and δ_2 are sensitive measures of these interactions, and show that the strength of the interactions increases with degree of crosslinking of the copolymers and for the series of normal alcohols has a maximum for propyl or butyl alcohol.

The solubility parameters δ_2 for the copolymers calculated from the values of free energy of mixing $\Delta\bar{G}_1^{\infty}$ seem to be most reliable. They deviate the least from those determined using other methods.

Table 3 The Hildebrand solubility parameters ($MPa^{1/2}$) for poly(styrene-*co*-divinylbenzene) estimated using different equations (455–480 K)

Equation	HT 19 0.5/5	HT 19 0.5/10	HT 19 0.5/20
(13)	20.0	19.6	20.2
(14)	14.8	15.7	17.8
(15)	19.8	20.1	22.3

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