Thermodynamic interactions and characterization of poly(*p*-chlorostyrene) with some aliphatic and aromatic probes by inverse gas chromatography

Ferdane Yılmaz and Özlem Gül Cankurtaran
Department of Chemistry, Yıldız University, 80270, Şişli-Istanbul, Turkey

and Bahattin M. Baysal*
Department of Chemical Engineering and Polymer Research Center, Boğaziçi University, 80815, Bebek-Istanbul, Turkey

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Some thermodynamic quantities were obtained for the interactions of poly(*p*-chlorostyrene) with n-pentane, n-hexane, n-heptane, benzene, toluene, isopropylbenzene and n-propylbenzene by the inverse gas chromatography method in the temperature range 150–170°C. The specific retention volumes (V_g^0), weight fraction activity coefficients of solute probes at infinite dilution (Ω_1^∞), Flory–Huggins thermodynamic interaction parameters (χ_{12}^∞), interaction parameters based on hard-core volumes (χ_{12}^*), effective exchange interaction parameters ($\bar{X}_{12}$) of the equation of state theory, between polymer and solutes are given. The molar enthalpy of sorption ($\Delta\bar{H}^s$), the partial molar heat of mixing at infinite dilution ($\Delta\bar{H}_1^\infty$) and the solubility parameter of polymer (δ_2) were also calculated.

(**Keywords: poly(*p*-chlorostyrene); inverse gas chromatography; polymer–solvent interactions; equation of state parameters**)

INTRODUCTION

The inverse gas chromatography (IGC) method has been used extensively to study the structure of polymers, the interactions of various liquids and gases with polymeric materials and to investigate polymer–polymer miscibility[1–10]. The method is simple, fast, economical and provides valuable thermodynamic information for characterization of polymeric substances.

In this study, we examined the interactions of poly(*p*-chlorostyrene) with aromatic and aliphatic hydrocarbon solute probes using the IGC method. Benzene, toluene, isopropylbenzene and n-propylbenzene were chosen as aromatic and n-pentane, n-hexane, n-heptane as aliphatic solute probes. Among the aromatic solute probes benzene and toluene are good solvents while isopropylbenzene and n-propylbenzene are known as θ solvents[11–15]. On the other hand the aliphatic solvents are non-solvents for poly(*p*-chlorostyrene)[11].

Polymer–solvent interaction parameters and the solubility parameter of the polymer were determined. Experimental results were evaluated according to the equation of state theory.

DATA REDUCTION

The Flory–Huggins polymer–solute interaction parameters, χ_{12}^∞, at infinite dilution of different solutes are defined by the following equation:

$$\chi_{12}^\infty = \ln(273.2Rv_2/V_g^0 p_1^0 V_1) - [1 - (V_1/M_2 v_2)] - (p_1^0/RT)(B_{11} - V_1) \quad (1)$$

where R is the universal gas constant, p_1^0, V_1 and B_{11} are the saturated vapour pressure, liquid molar volume and second virial coefficient of the solute, respectively; v_2 and M_2 are the specific volume and molecular weight of the polymer, respectively; V_g^0 is the specific retention volume of polymer for the solute. The V_g^0 value was determined by applying the classical formulation[1–10,16,17] to the measurements of the retention time and the flow rate of carrier gas. The vapour pressure, p_1^0 was calculated from Antoine's equation[18]. The molar volume of the solute, V_1, was calculated using the following relation[19]:

$$V_1 = V_c/\rho_r \quad (2)$$

where V_c is the critical molar volume and ρ_r is the reduced density of solute given as:

$$\rho_r = 1.20 + (5.565 - 11.03z_c)(1 - T/T_c)^{(0.8z_c + 0.31)} \quad (3)$$

where z_c is the critical compressibility factor.

The molar volumes of the solutes can be obtained from density values at about room temperature given in the literature. The densities at high temperatures such as 160°C may be obtained only by extrapolation of the existing values. The large temperature difference between available and extrapolated values may cause large errors. The method used in this work is very simple and is applicable at all temperatures if the critical values of the solute are known.

B_{11} values of hydrocarbons were computed using the related equations given in the literature[20].

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* To whom correspondence should be addressed

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The molar enthalpy of sorption of the solute absorbed by the polymer, $\Delta\bar{H}^s$, is given by[1]:

$$\Delta\bar{H}^s = -R[\partial(\ln V_g^0)/\partial(1/T)] \qquad (4)$$

where T is the column temperature (K). The average partial molar heat of mixing at infinite dilution of the solute, $\Delta\bar{H}_1^\infty$ is calculated as follows:

$$\Delta\bar{H}_1^\infty = R[\partial(\ln\Omega_1^\infty)/\partial(1/T)] \qquad (5)$$

where Ω_1^∞ is the weight fraction activity coefficient of the solute probe at infinite dilution which is calculated according to the following equation:

$$\ln\Omega_1^\infty = \ln(273.2R/V_g^0 p_1^0 M_1) - (p_1^0/RT)(B_{11} - V_1) \qquad (6)$$

where M_1 is the molecular weight of the solute probe and other symbols are as defined in equation (1).

The measured retention volume has been related to an interaction parameter, χ_{12}^*, of which the hard-core volumes of components in the equation of state theory are replaced by the volumes in equation (1)[2,21]:

$$\chi_{12}^* = \ln(273.2Rv_2^*/V_g^0 \mathrm{V}_1^* p_1^0) - [1 - (V_1^*/M_2 v_2^*)] - (p_1^0/RT)(B_{11} - V_1) \qquad (7)$$

In the equation of state theory, $\tilde{v}$, $\tilde{T}$ and $\tilde{p}$, which are reduced volume, temperature and pressure, respectively, of the system, are ratios of the actual v, T and p to characteristic parameters, v^*, T^* and p^* which can be evaluated from the thermal expansion and pressure coefficients as follows:

$$\tilde{v}^{1/3} = (V/V^*)^{1/3} = [(\alpha T/3)/(1 + \alpha T)] + 1 \qquad (8)$$

$$\tilde{T} = T/T^* = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \qquad (9)$$

$$p^* = \gamma T\tilde{v}^2 \qquad (10)$$

where α is the thermal expansion coefficient defined as:

$$\alpha = (1/V)(\partial V/\partial T)_{p=0} \qquad (11)$$

and γ is the thermal pressure coefficient defined as:

$$\gamma = (\partial p/\partial T)_v \qquad (12)$$

In the Flory formulation of the equation of state theory, the value of χ_{12}^* for infinitely dilute solutions of solute probes is given by[2]:

$$RT\chi_{12}^*/p_1^* V_1^* = \{3\tilde{T}_1 \ln[(\tilde{v}_1^{1/3} - 1)/(\tilde{v}_2^{1/3} - 1)] + \tilde{v}_1^{-1} - \tilde{v}_2^{-1}\} + \bar{X}_{12}/\tilde{v}_2 p_1^* \qquad (13)$$

where subscripts 1 and 2 indicate solute and polymer, respectively. The term inside the square brackets results from the free volume contribution to the mixing process and the term in $\bar{X}_{12}$ results from the energetic contribution. The contact interaction parameter, $\bar{X}_{12}$ is an effective exchange interaction parameter which describes the change in contact energy if a polymer segment in the vicinity of another polymer segment is replaced by a solvent molecule.

EXPERIMENTAL

Materials

Methane was supplied as a standard from Alltech Associates, Inc. All solute probes were purchased from Merck A.G. Benzene and toluene were chromatographic grade, other solvents were analytical reagents and were used without further purification. Poly(*p*-chlorostyrene) was supplied by Polyscience in powder form. Its molecular weight was estimated from intrinsic viscosity in benzene at 30°C as 2.5×10^5 using the following equation[22]:

$$[\eta] = 30.6 \times 10^{-5}\,\mathrm{M}^{0.56} \qquad (14)$$

Chromosorb-W (AW-DMCS-treated, 80/100 mesh) and silane-treated glass wool were obtained from Merck A.G. and Alltech Associates, Inc., respectively.

Instrumentation and procedure

Measurements were run on a Varian 3700 gas chromatograph equipped with flame ionization detectors. Dried nitrogen was used as a carrier gas. The flow rate of nitrogen was controlled by a precision valve and measured by a soap bubble flowmeter with 50 cm^3 volume. Retention times of solute probes were obtained using a Varian 4290 model integrator.

The column was stainless steel tubing, 3.2 mm o.d. and 2 m in length. Polymer was dissolved in benzene and supported on Chromosorb W by gentle mixing and slow evaporation. After drying in a vacuum oven for 3 days at 50°C, the coated support was resieved and then packed into the column. The total loading of polymer on the support was determined as 8.26% by weighing. The ends of the column were loosely plugged with silanized glass wool. The column was conditioned at 170°C and at fast carrier gas flow rate, for 24 h prior to use.

Probes were injected into the columns with 1 μl Hamilton syringes. A portion of solute probe (0.1 μl) was taken into the syringe and flushed into the air. The residual solute was diluted by taking 0.1 μl of air into the syringe. The dilute solute was injected into the column through a silicone rubber septum at the injection port of the chromatograph. At least three consecutive injections were made for each probe at each set of measurements. The retention times were precise and reproducible to ± 0.01 min.

It was observed that the specific retention volumes were affected by the carrier gas flow rate. The specific retention volume data were corrected by extrapolating to zero flow rates. As an example, the data for the poly(*p*-chlorostyrene)/benzene system are given in *Figure 1*.

Calculation of equation of state parameters

The thermal expansion coefficients, α, of solutes were calculated using equations (2), (3) and (11). The α values of cyclohexane, benzene, ethylbenzene, n-hexane and methyl ethyl ketone were obtained by using the above-mentioned method of calculation. For these compounds, the calculated α values deviate only about 5% from literature data[23–26] for the temperature range 20–70°C. However, we have preferred the above-mentioned method because α depends on temperature and α values were not available at 160°C for all solutes used in this work.

The equation of state parameters $\tilde{v}_1$, V_1^* and T_1 were calculated using equations (8) and (9). The reduced volume, $\tilde{v}_2$ of the poly(*p*-chlorostyrene) was assumed as equal to that of polystyrene. (The $\tilde{v}_2$ value of polystyrene at 160°C is 1.217 from ref. 23 by extrapolation of existing data.)

The thermal pressure coefficients, γ, of the solutes were calculated from the following empirical relation:

$$\gamma = 1.1\delta_1^2/T \qquad (15)$$

where δ_1 represents the cohesive energy density of the solute. Equation (15) was obtained by using the argument given in refs 6 and 27. Calculated γ values of cyclohexane, benzene, ethylbenzene and n-hexane deviate only about 5% from literature values[23–26] for the temperature range 20–70°C. The highest deviation ($\sim$15%) is observed for methyl ethyl ketone. Equation (15) was used because γ values were not available at 160°C for all solutes used in this work.

The calculated values of the thermal expansion and thermal pressure coefficients and equation of state parameters of the solutes and polymer at 160°C are collected in *Table 1*.

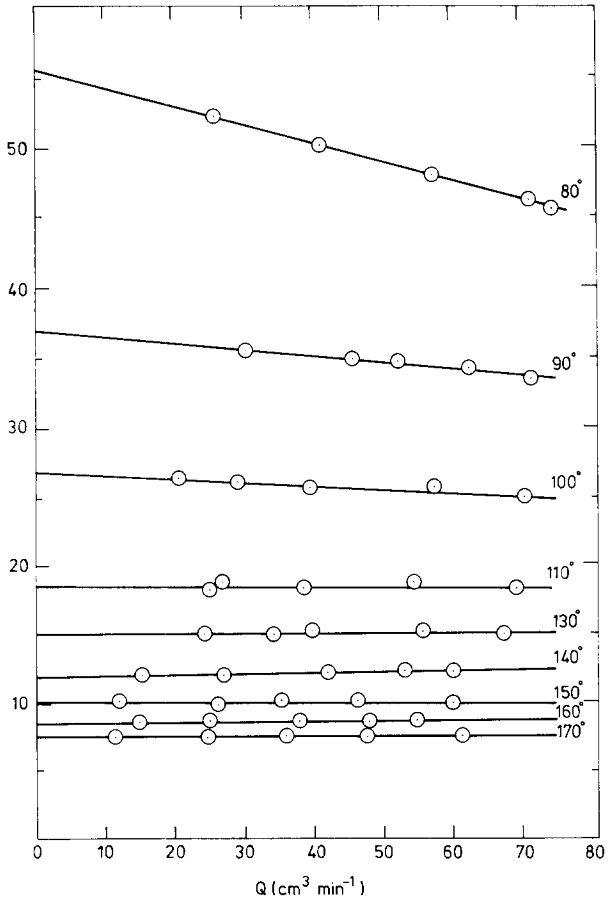

Figure 1 Dependence of the specific retention volume (V_g^0) for the poly(*p*-chlorostyrene)/benzene system on the flow rates of the carrier gas at different temperatures (°C)

RESULTS AND DISCUSSION

Figure 2 shows the variation of the specific retention volumes of benzene with temperature between 80 and 170°C. *Figure 3* exhibits plots of logarithm of the specific retention volumes of all solutes, given in *Table 2*, *versus* reciprocal of the absolute temperature. χ_{12}^∞ and Ω_1^∞ values, obtained using equations (1) and (6), respectively, are also collected in *Table 2*. Interaction parameters, χ_{12}^*, based on hard-core volumes obtained from equation (7), and the effective exchange interaction parameters, X_{12}, in the equation of state theory calculated from equation (13), are given in *Table 3*.

The molar enthalpies of sorption of the solutes, $\Delta\bar{H}^s$ calculated from equation (4) and partial molar heats of mixing at infinite dilution of solutes, $\Delta\bar{H}_1^\infty$, calculated from equation (5) are collected in *Table 4*. Values of the molar heat of vaporization for the solutes, $\Delta\bar{H}_v$, at this temperature range were obtained from values of the molar enthalpy of sorption and partial molar heat of mixing at infinite dilution, given in *Table 4*, according to the relation[1]:

$$\Delta\bar{H}_v = \Delta\bar{H}_1^\infty - \Delta\bar{H}^s \qquad (16)$$

The values of the heat of vaporization for the solutes at 160°C, $\Delta\bar{H}_v^{160}$, given in *Table 4*, were calculated using the Watson relation[18].

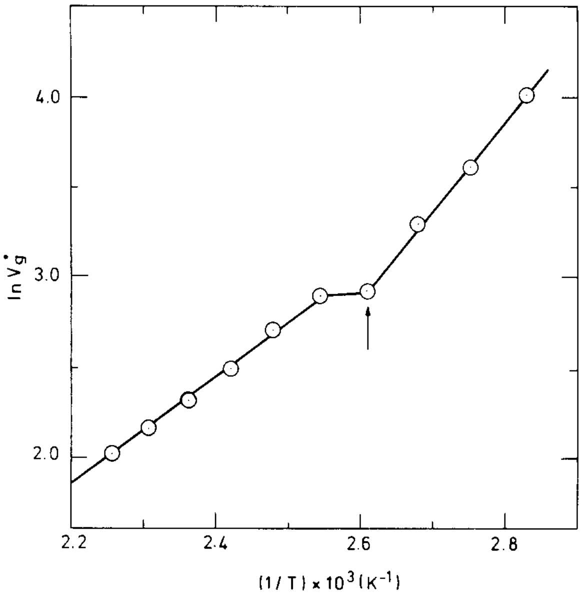

Figure 2 Variation of the specific retention volumes for benzene with reciprocal absolute temperature. The arrow indicates the glass transition temperature of poly(*p*-chlorostyrene)

Table 1 Thermal expansion (α) and thermal pressure (γ) coefficients and equation of state parameters of solutes and polymer at 160°C

Substance	$\alpha \times 10^3$ (°C^{-1})	γ (J cm^{-3} °C^{-1})	$\tilde{v}$	$\tilde{T}$	V^* (cm^3 mol^{-1})	p^* (J cm^{-3})
n-Pentane	5.360	0.176	1.874	0.101	85.0	268
n-Hexane	3.187	0.266	1.699	0.095	99.2	333
n-Heptane	2.390	0.318	1.600	0.091	115.1	353
Benzene	2.035	0.513	1.546	0.087	70.2	531
Toluene	1.740	0.536	1.494	0.084	83.5	518
Isopropylbenzene	1.445	0.531	1.436	0.079	111.3	474
n-Propylbenzene	1.402	0.531	1.427	0.078	115.9	468
Poly(*p*-chlorostyrene)	0.582	–	1.217	–	–	–

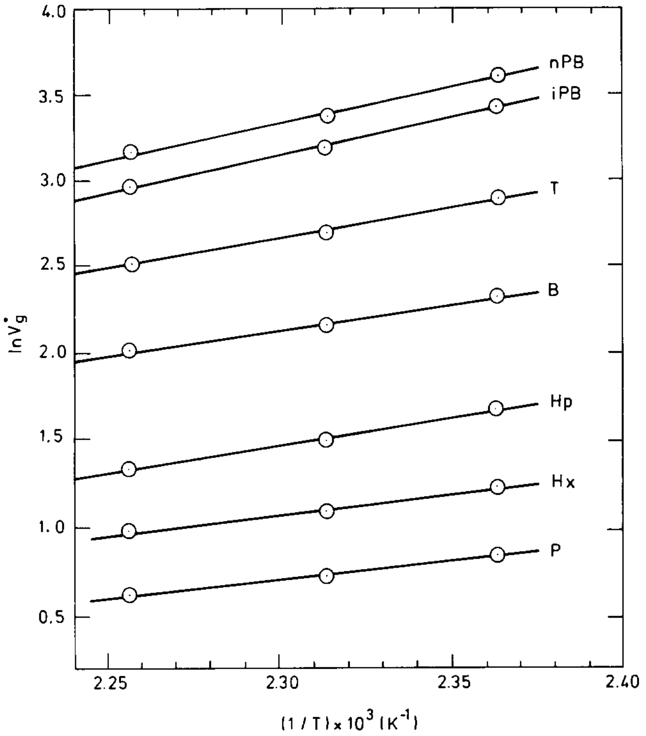

Figure 3 Specific retention diagrams for all solute probes on poly(*p*-chlorostyrene) as a function of reciprocal absolute temperature. Abbreviations: P, pentane; Hx, hexane; Hp, heptane; B, benzene; T, toluene; iPB, isopropylbenzene; nPB, no-propylbenzene

The glass transition temperature of poly(*p*-chlorostyrene) was estimated as 110°C from *Figure 2*; a temperature 40°C above this was therefore chosen for meaningful thermodynamic data in this work. *Figure 3* shows that a linear dependence is observed for the logarithm of the retention volumes, V_g^0, of all solute probes, in *Table 2*, as a function of reciprocal of absolute temperature.

In *Table 2*, Ω_1^∞ values of poly(*p*-chlorostyrene)/solute systems are compared with those of polystyrene (given in parentheses), because there is not a similar study for this polymer. Our Ω_1^∞ values for toluene and n-hexane at 150°C, are quite consistent with the values given by Olabisi[28] at 150°C, but our Ω_1^∞ for the same solute probes at 170°C are lower than the values given by Gündüz and Dinçer[8] at 171.84°C. Our Ω_1^∞ values for benzene and toluene at 170°C are also in good agreement with the values given by Newman and Prausnitz[29] at 175°C. As mentioned above, for poly(*p*-chlorostyrene), n-alkanes are non-solvents, benzene and toluene are good solvents while isopropylbenzene and n-propylbenzene are θ solvents with upper critical solution temperature ($UCST$)[11–15]. It has been proposed that Ω_1^∞ values greater than 5 are indicative of poor polymer–solute systems while lower values characterize good solubility for such a system. The results of Ω_1^∞ tabulated in *Table 2* are consistent with this proposal.

Values of χ_{12}^∞ greater than 0.5 represent unfavourable polymer–solvent interactions while values lower than 0.5

Table 2 Specific retention volumes (V_g^0), weight fraction infinite dilution activity coefficients (Ω_1^∞) and Flory–Huggins interaction parameters (χ_{12}^∞) of poly(*p*-chlorostyrene)/solute systems

	V_g^0			$\Omega_1^{\infty\,a}$			χ_{12}^∞		
Solute	150°C	160°C	170°C	150°C	160°C	170°C	150°C	160°C	170°C
n-Pentane	2.34	2.08	1.86	11.5	11.4	11.3	0.600	0.540	0.470
n-Hexane	3.45	3.02	2.65	12.1 (11.5)^b	11.8	11.5 (17.93)^c	0.755	0.694	0.641
n-Heptane	5.39	4.53	3.78	12.5	12.3	12.2	0.843	0.798	0.771
Benzene	10.20	8.62	7.50	5.6	5.5	5.3 (5.67)^a	0.305	0.271	0.225
Toluene	18.11	14.89	12.41	5.4 (5.3)^b	5.3	5.2 (7.28)^c (5.29)^d	0.294	0.270	0.233
Isopropylbenzene	30.83	24.18	19.40	6.4	6.4	6.4	0.491	0.473	0.455
n-Propylbenzene	36.85	29.08	23.54	6.7	6.6	6.4	0.497	0.472	0.429

[a] Values in parentheses are for polystyrene
[b] From ref. 28
[c] From ref. 8
[d] From ref. 29

Table 3 Interaction parameters based on hard-core volumes (χ_{12}^*) and effective exchange interaction parameters ($\bar{X}_{12}$) of poly(*p*-chlorostyrene)/solute systems

	χ_{12}^*			$\bar{X}_{12}$		
Solute	150°C	160°C	170°C	150°C	160°C	170°C
n-Pentane	0.965	0.951	0.941	19.3	20.8	24.5
n-Hexane	1.047	1.016	0.996	17.6	18.1	18.1
n-Heptane	1.085	1.064	1.061	17.8	17.2	18.6
Benzene	0.517	0.503	0.479	2.8	3.2	1.2
Toluene	0.478	0.466	0.451	2.7	1.4	0.5
Isopropylbenzene	0.640	0.635	0.632	9.5	9.9	9.3
n-Propylbenzene	0.641	0.629	0.608	9.8	10.0	8.7

Table 4 Molar enthalpy of sorption ($\Delta\bar{H}_s$), partial molar heat of mixing at infinite dilution ($\Delta\bar{H}_1^\infty$), molar heat of vaporization ($\Delta\bar{H}_v$) obtained from equation (16) and molar heat of vaporization ($\Delta\bar{H}_v^{160}$) obtained from Watson's relation[18] at 160°C

Solute	$\Delta\bar{H}^s$ (kcal mol^{-1})	$\Delta\bar{H}_1$ (kcal mol^{-1})	$\Delta\bar{H}_v$ (kcal mol^{-1})	$\Delta\bar{H}_v^{160}$ (kcal mol^{-1})	T_b^a (°C)
n-Pentane	4.28	0.33	4.61	3.51	36.0
n-Hexane	4.91	0.95	5.86	5.08	68.7
n-Heptane	6.61	0.45	7.06	6.37	98.4
Benzene	5.73	0.86	6.59	6.12	80.1
Toluene	7.04	0.70	7.74	7.15	110.6
Isopropylbenzene	8.64	0.17	8.81	8.84	152.4
n-Propylbenzene	8.36	0.74	9.10	9.12	159.2

^{a}Boiling points of solutes

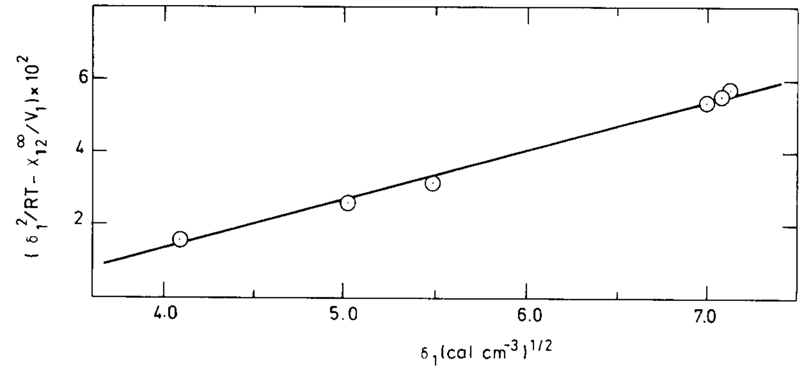

Figure 4 Estimation of solubility parameter (δ_2) of poly(*p*-chlorostyrene) from solubility parameter of the solute probes (δ_1) and Flory–Huggins interaction parameters (χ_{12}^∞) at 160°C (see equation (18))

indicate favourable interactions in dilute polymer solutions. For poly(*p*-chlorostyrene), χ_{12}^∞ values at infinite dilution of solutes are also given in *Table 2*. It will be seen that these values for isopropylbenzene and n-propylbenzene are lower than the corresponding values for non-solvents, but higher than χ_{12}^∞ values of good solvents.

Values of $\bar{X}_{12}$ given in *Table 3* were calculated using equation (13) and χ_{12}^* values, given in the same table, and the equation of state parameters in *Table 1*. For this purpose we assumed that the equation of state parameters were independent of temperature between 150 and 170°C. It is seen from *Table 3* that for benzene and toluene, the values of the effective exchange interaction parameters, $\bar{X}_{12}$, of equation of state theory are small compared to the other polymer–solute pairs. Such small values may denote that there are specific interactions between these solutes and poly(*p*-chlorostyrene). These interactions may arise from π-electrons of aromatic rings of solutes and polymer. Effective exchange interaction parameter, $\bar{X}_{12}$, obtained in the IGC technique depends on exchange energy, X_{12} and entropy, Q_{12} parameters in the following way[2,6]:

$$\bar{X}_{12} = X_{12} - T\tilde{v}_2 Q_{12} \qquad (17)$$

A negative Q_{12} value has been reported for the polystyrene–ethylbenzene pair[24]. Similarly, we may expect a negative Q_{12} value for poly(*p*-chlorostyrene)–aromatic solute systems. Therefore, an explanation exists for the small positive $\bar{X}_{12}$ values reported in *Table 3*. It seems that the presence of the n-propyl and isopropyl groups hinders the above-mentioned specific interactions, therefore $\bar{X}_{12}$ values are higher for these solutes. For non-solvents, all $\bar{X}_{12}$ values exceed 17 (*Table 3*).

There is a very good agreement between $\Delta\bar{H}_v$ and $\Delta\bar{H}_v^{160}$ values for isopropyl- and n-propylbenzene, as reported in *Table 4*. The boiling points of these two compounds are very close to 160°C. However, for other solutes, the calculated values of molar heat of vaporization deviate somewhat at 160°C.

The solubility parameter of a polymer, δ_2, can be estimated by using the following relation[30]:

$$[(\delta_1^2/RT) - (\chi_{12}^\infty/V_1)] = (2\delta_2/RT)\delta_1 - \delta_2^2/RT \qquad (18)$$

where δ_1 is the solubility parameter of the solute. δ_2 is estimated from either slope or intercept of a straight line obtained by plotting the left-hand-side of equation (18) *versus* δ_1. The solubility parameter of poly(*p*-chlorostyrene) was evaluated from either the slope or intercept of *Figure 4* as 6.0 ± 0.1 (cal cm^{-3})$^{1/2}$ at 160°C. This value was calculated as 9.8 (cal cm^{-3})$^{1/2}$ using the group contribution method[27] at 25°C. The reported experimental values were 9.7 and 9.3 (cal cm^{-3})$^{1/2}$ at 25°C[11]. We have calculated the solubility parameter of *p*-chlorotoluene as a low molecular weight analogue of poly(*p*-chlorostyrene) as 7.9 (cal cm^{-3})$^{1/2}$ at 162°C. In this calculation we have used the following values: $\Delta\bar{H}_v^b = 10\,151.7$ cal mol^{-1} (at 162°C), $\rho = 1.0697$ g cm^{-3} (at 20°C) for *p*-chlorotoluene[31] and $d\rho/dT = -15 \times 10^{-4}$ for *o*-chlorotoluene[32].

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