Thermodynamic Studies on Poly(*n*-butyl methacrylate)–Solute Systems Using Gas Chromatography¹

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ABSTRACT: Using gas chromatographic technique, various thermodynamic parameters were determined at infinite dilution of some alkane, aromatic and chlorinated-aliphatic solutes in poly(*n*-butyl methacrylate) in the temperature range of 70–150°C. The values of $-\Delta H_s$ vary from 22 to 42 kJ·mol⁻¹ depending on the solute. Flory–Huggins interaction parameter was affected considerably by both the nature of solute and temperature. The surface contact interaction parameter depended mainly on the chemical nature of solute.

KEY WORDS Polymer–Solute Interaction / Thermodynamics / Gas Chromatography / Poly(*n*-butyl methacrylate) /

Since Patterson and coworkers^{2,3} successfully developed thermodynamic equations for polymer stationary phases, attention continues to be drawn to the need for derivation of reliable data from inverse gas chromatography (IGC) to assist in establishing solution theories. (*e.g.*, ref 2–9). This technique can provide experimental data to effectively study solution properties of small molecules (solutes) isolated in a pure macromolecular matrix. Secondly, unlike in many conventional methods, the data may be obtained with reasonable accuracy for a number of solutes widely differing in their solubilities in the polymer, and over a wide range of temperature, provided certain explicit and implicit assumptions are met—the most important being the sorption equilibrium in the GC column. In a majority of cases, the results have been reported for a narrow temperature-range. Tait and Abushihada⁸ have demonstrated that IGC may also be helpful in testing Prigogine–

Flory–Patterson theory of corresponding states in concentrated polymer solutions if the temperature-coefficient of polymer–solute interaction parameter (χ) can be studied over a sufficiently wide temperature-range. This aspect deserves a systematic investigation, and various thermodynamic parameters should be analyzed using both classical and modern theories.

DiPaola-Baranyi¹⁰ has reported the activity coefficients and χ values of some solutes in poly(*n*-butyl methacrylate) (PnBMA) from 120 to 150°C. This temperature is too high, and the range too narrow, to predict the solution behavior of the mixtures at lower temperatures (as may be seen later) in some cases. Newman and Prausnitz¹¹ have also determined the activity coefficients of a number of solutes in PnBMA from 50 to 150°C. They have reported that they found no difficulty in obtaining a linear retention diagram (at the carrier gas-flow rate of about 20 ml·min⁻¹). It

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should assure the bulk-sorption equilibrium in the column in the above temperature-range, that is a fulfilment of the precondition for thermodynamic measurements. In gas chromatographic studies on the glass transition of PnBMA, the present authors,^{12a} on the other hand, have observed (i) that the nonequilibrium sorption conditions in the column have persisted even when the temperature was raised above 50°C, (ii) that the specific retention volume (V_g^0) of every solute used, except dichloromethane, has depended appreciably on the flow rate employed resulting into nonlinear retention diagrams up to as high a temperature as 100°C, and (iii) that the extrapolation of V_g^0 to zero flow rate could also not yield linear retention diagrams at temperatures just below 70°C. The retention data given in ref 11 are, however, not corrected for this effect. It may be noted that the flow rate-effect should become more strong at a higher polymer-to-support mass ratio employed in ref 11 as compared to ref 12a. The comparison of thermodynamic results between ref 10 and 11 is difficult because there are only two common solutes, and because the former lists V_g^0 values at one temperature alone—also not common with ref 11. Incidentally, in the case of poly(vinyl acetate) also a similar disagreement is reported, that is the data in ref 11 does not agree with other studies,^{12b,c} including the same laboratory.

In this work, therefore, we have undertaken an independent reevaluation of various solution properties for a number of solutes in PnBMA, that are mostly unreported. The solutes were selected from among the diluents differing in their solubilities in PnBMA, and included a few solutes common with both ref 10 and 11 for comparison of V_g^0 values. The knowledge gained in our earlier study^{12a} has been utilized to select proper experimental conditions for thermodynamic measurements. The results have been used to establish the dependence of thermodynamic interactions on

the solute-nature and temperature using various theories, old and new.

EXPERIMENTAL

The polymer ($\bar{M}_v=372,000$, $\bar{M}_n=91,300$, $T_g=18\pm 2^\circ\text{C}$), and the two columns (150 cm $\times$ 6.25 mm) used were the same as described earlier.^{12a} The mass ratios of the polymer to the support (Chromosorb W, AW, DMCS, 80/100) in the columns I and II were 0.0741 and 0.1033, respectively. The density of the polymer was determined by dilatometric measurements in the temperature range of 50–150°C, and was found to vary linearly with temperature according to eq 1.

$$\rho \text{ (g} \cdot \text{cm}^{-3}\text{)} = 1.049647 - 7.390643 \times 10^{-4} \times t \text{ (}^\circ\text{C)} \quad (1)$$

The solutes were analytical or chromatography grade chemicals (Table I).

The gas chromatograph apparatus and the methodology to determine the specific retention volume (V_g^0) of the solutes at infinite dilution in polymer stationary phase have been described earlier.^{12c} The column-temperature was regulated to the accuracy of $\pm 0.2^\circ\text{C}$ at the set temperature. Hydrogen was used as the carrier gas. The experimental error in V_g^0 was found to be less than 1.5%.

At temperatures below 110°C, V_g^0 decreased linearly with an increase in the flow-rate of the carrier gas (F). Therefore, the experimental data were extrapolated to zero flow rate, and the measurements were repeated on two column loadings in order to assure the reproducibility of the data. The values of V_g^0 ($F=0$) for these columns were found to be in agreement with each other within $\pm 0.7\%$, and produced the linear retention diagrams ($\log V_g^0$ vs. $1/T$) at $T \geq 70^\circ\text{C}$. Therefore, the retention data have been considered suitable to derive the solution properties only at $T \geq 70^\circ\text{C}$. However, the data at zero flow rate obtained by using

Table I. Equation of state parameters of solutes and polymer at 20°C

Compound	Abbreviation	$\alpha \times 10^3$	$\tilde{v}$	$\tilde{T} \times 10^2$	v^*	P^*	Reference
		K^{-1}			$cm^3 \cdot mol^{-1}$	$cal \cdot cm^{-3}$	
<i>n</i> -Pentane	nC ₅	1.565	1.351	7.063	85.42	101.9	22
<i>n</i> -Hexane	nC ₆	1.367	1.314	6.6214	99.43	101.8	21
<i>n</i> -Heptane	nC ₇	1.243	1.290	6.3084	114.64	102.9	21
<i>n</i> -Octane	nC ₈	1.146	1.273	6.0759	127.74	104.6	21
<i>n</i> -Nonane	nC ₉	1.065	1.2675	5.8927	141.76	104	20
<i>n</i> -Decane	nC ₁₀	1.038	1.250	5.7346	155.6	105.1	13 ^a
Isooctane	iC ₈	1.197	1.283	6.2128	128.7	93.2	21
Cyclohexane	cC ₆	1.206	1.2885	6.2949	84.39	126	20
Dichloromethane	CH ₂ Cl ₂	1.3412	1.3096	6.5657	48.87		13 ^a
Chloroform	CHCl ₃	0.418	1.113	3.153	72.269		13 ^a
Carbon tetrachloride	CCl ₄	1.219	1.2869	6.2633	74.97	134	23
1,1,2-Trichloroethane	C ₂ HCl ₃	1.1880	1.2812	6.1877	70.022		13 ^a
Benzene	C ₆ H ₆	1.204	1.2881	6.2823	69.41	148	24 ^c
		1.1942	1.2828	6.2041	69.27		13 ^a
Toluene	Tol	1.077	1.2633	5.933	84.58	134	20
<i>para</i> -Xylene	<i>p</i> -Xyl	1.013	1.2501	5.735	99.10	127	20
					$v^*/cm^3 \cdot g^{-1}$		
Polymer	PnBMA	0.7147	1.1833	4.610	0.81662		^b

^a Calculated from molecular parameters.^b Determined from experimental data (eq 1).^c At 25°C.**Table II.** Constants of the linear plots of $\log V_g^0$ vs. $1/T$, and heats of solution $-\Delta H_s$ for PnBMA + solute systems^a

Solute	Intercept	Slope	Correlation factor r	$-\Delta H_s$	No. of points	Temp range
				$kJ \cdot mol^{-1}$		$^{\circ}C$
nC ₅	-2.3275	1157.168	0.9986	22.17	5	70—100
nC ₆	-2.5183	1342.543	0.9995	25.72	9	70—150
nC ₇	-2.8019	1562.430	0.9996	29.93	9	80—150
nC ₈	-3.0243	1756.120	0.9998	33.65	10	70—150
nC ₉	-3.2515	1951.242	0.9999	37.39	8	80—150
nC ₁₀	-3.5185	2160.743	0.9997	41.38	5	110—150
iC ₈	-2.3824	1389.998	0.9993	26.63	7	90—150
cC ₆	-2.3919	1411.423	0.9998	27.04	9	70—150
CH ₂ Cl ₂	-2.7666	1529.621	0.9998	29.30	5	70—110.3
CHCl ₃	-2.8735	1685.512	0.9996	32.29	10	70—150
CCl ₄	-2.5078	1506.395	0.9998	28.86	10	70—150
C ₂ HCl ₃	-2.8561	1717.921	0.9999	32.92	11	50—150
C ₆ H ₆	-2.6116	1584.702	0.9999	30.36	11	50—150
Tol	-2.9017	1806.172	0.9999	34.61	9	70—150
<i>p</i> -Xyl	-3.1342	2000.462	0.9998	38.33	10	70—150

^a Maximum error in $-\Delta H_s$ is 2%.

Column II alone have been utilized for this purpose. The slope, intercept and the linearity coefficient (r) of the corresponding retention diagrams are given in Table II.

The V_g^0 results, however, are comparatively close to those in ref 10 than in ref 11.

Data Treatment

Flory-Huggins interaction energy parameters, χ and χ^* based on the volume and segment fractions, respectively, were calculated from V_g^0 using the following equations²:

$$\chi = \ln \frac{273.16 R v_2}{P_1^0 V_1 V_g^0} - 1 + \frac{V_1}{\bar{M}_2 v_2} - \frac{P_1^0}{RT} (B_{11} - V_1) \quad (2)$$

$$\chi^* = \ln \frac{273.16 R v_2^*}{P_1^0 V_1^* V_g^0} - 1 + \frac{V_1^*}{\bar{M}_2 v_2^*} - \frac{P_1^0}{RT} (B_{11} - V_1) \quad (3)$$

where subscripts 1 and 2 refer to the solute and polymer, respectively; R is the universal gas constant; v_i is the specific volume; V_i is the molar volume; P_1^0 and B_{11} are, respectively, the vapor pressure and second virial coefficient of the pure solute in the vapor state; $\bar{M}_2$ is the number average molecular weight of the polymer; the reduction parameters are marked by an asterisk (*). B_{11} , V_1 , and P_1^0 were calculated from the standard data on the physical properties of pure solutes¹³. The other quantities are given in Table I.

The surface "contact" or "exchange" interaction parameter defined in the new Flory theory¹⁴ was derived from χ^* using the relation¹⁵:

$$\chi^* = \frac{P_1^* V_1^*}{RT} \left[\left\{ 3 \tilde{T}_1 \ln \left(\frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}_2^{1/3} - 1} \right) + \tilde{v}_1^{-1} - \tilde{v}_2^{-1} \right\} + \tilde{v}_2^{-1} \left(\frac{X_{12}}{P_1^*} \right) \right] \quad (4)$$

where tilde ($\sim$) denotes the reduced quantities. The various equation-of-state parameters required in these calculations are listed in Table I. The following well-known relations were

employed to derive the partial molar enthalpy of solution ($-\Delta H_s$),¹⁶ partial molar excess enthalpy ($\bar{h}_1^\infty$),² and the entropic and enthalpic components¹⁷ of χ :

$$-\Delta H_s = -R[d \ln V_g^0 / d(1/T)] \quad (5)$$

$$\bar{h}_1^\infty = R[d \chi^* / d(1/T)] \quad (6)$$

$$\chi = (z \Delta w_H / kT) - (z \Delta w_S / k) \quad (7)$$

$$= \beta' / T - \alpha' \quad (7a)$$

$$= \chi_H + \chi_S \quad (7b)$$

where z is the lattice coordination number; Δw is the change in free energy on the formation of unlike pair (1-2); the subscripts H and S identify the enthalpy and entropy contributions to the quantity being described; k is Boltzmann's constant; α' and β' are, respectively, the intercept and slope of the linear plots of χ against $1/T$.

RESULTS AND DISCUSSION

Partial Molar Enthalpy of Solution

n-Pentane have yielded the lowest value of $-\Delta H_s$ and *n*-decane the highest (Table II). The data exhibit many characteristics of the free energy. For example, the addition of the similar structural units to an alkane or an aromatic solute molecule produces a constant increment of about $4 \text{ kJ} \cdot \text{mol}^{-1}$ in $-\Delta H_s$. The increment in $-\Delta H_s$ between normal and cyclic hexane is almost the same as that between cyclohexane and benzene. The branching, on the other hand, has caused a reduction in the magnitude of this parameter.

Flory-Huggins Interaction Parameter

Both χ and χ^* have shown similar trends (Tables III and IV). Therefore, only one of them (χ) is described here. The results predict weak interactions and poor miscibility of the solutes in PnBMA. They also indicate that PnBMA being a moderately polar polymer should have H-bonding type interactions with

Table III. Interaction parameter χ for PnBMA + solute systems

Solute	Temperature/°C									
	70	80	85	90	100	110.3	120	130	140	150
nC ₅	0.903	0.930	0.846	0.786	0.749					
nC ₆	0.975	0.854	0.812	0.794	0.743	0.739	0.748	0.772	0.659	
nC ₇	0.969	0.860	0.840	0.792	0.753	0.770	0.743	0.727	0.686	0.680
nC ₈	0.898	0.893	0.860	0.817	0.771	0.782	0.749	0.730	0.688	0.689
nC ₉	0.961	0.892	0.871	0.850	0.793	0.790	0.756	0.721	0.698	0.693
nC ₁₀	0.954	0.939	0.917	0.882	0.818	0.786	0.787	0.744	0.709	0.679
iC ₈	1.292	1.107	0.991	0.852	0.779	0.732	0.730	0.676	0.633	0.651
cC ₆	0.871	0.712	0.600	0.606	0.550	0.519	0.488	0.475	0.457	0.442
CH ₂ Cl ₂	0.029	0.013	0.068	0.030	0.046	0.037				
CHCl ₃	−0.317	−0.255	−0.196	−0.206	−0.175	−0.113	−0.048	−0.014	0.009	0.037
CCl ₄	0.289	0.284	0.281	0.246	0.247	0.241	0.258	0.244	0.235	0.252
C ₂ HCl ₃	0.061	0.088	0.099	0.081	0.091	0.126	0.126	0.133	0.133	0.148
C ₆ H ₆	0.194	0.190	0.198	0.181	0.162	0.180	0.191	0.180	0.176	0.184
Tol	0.187	0.193	0.180	0.181	0.179	0.183	0.199	0.188	0.191	0.189
<i>p</i> -Xyl	0.202	0.201	0.220	0.209	0.181	0.205	0.209	0.201	0.193	0.192
Uncertainty $\pm$	0.005 ^a	0.005	0.010	0.005	0.005	0.011	0.008	0.012	0.014	0.010

^a Uncertainties in the cases of nC₅ (0.02), nC₆ (0.05), nC₇ (0.04), and cC₆ (0.04) are not accounted.

Table IV. Interaction parameter χ^* for PnBMA + solute systems

Solute	Temperature/°C									
	70	80	85	90	100	110.3	120	130	140	150
nC ₅	1.069	1.100	1.025	0.996	0.940					
nC ₆	1.112	0.999	0.960	0.945	0.902	0.905	0.922	0.892	0.849	
nC ₇	1.073	0.970	0.952	0.908	0.875	0.897	0.877	0.867	0.833	0.833
nC ₈	0.993	0.993	0.962	0.922	0.881	0.886	0.869	0.856	0.818	0.825
nC ₉	1.043	0.977	0.960	0.940	0.886	0.888	0.857	0.827	0.807	0.807
nC ₁₀	1.028	1.017	0.996	0.963	0.903	0.875	0.879	0.840	0.809	0.784
iC ₈	1.411	1.217	1.104	0.967	0.900	0.858	0.862	0.814	0.777	0.800
cC ₆	0.994	0.844	0.710	0.748	0.702	0.682	0.664	0.659	0.652	0.648
CH ₂ Cl ₂	0.104	0.151	0.165	0.178	0.202	0.201				
CHCl ₃	−0.393	−0.334	−0.277	−0.289	−0.261	−0.202	−0.141	−0.110	−0.090	−0.065
CCl ₄	0.399	0.398	0.397	0.365	0.372	0.372	0.394	0.386	0.384	0.406
C ₂ HCl ₃	0.166	0.198	0.211	0.196	0.212	0.252	0.252	0.271	0.277	0.297
C ₆ H ₆	0.297	0.302	0.310	0.295	0.282	0.306	0.323	0.318	0.319	0.334
Tol	0.257	0.275	0.264	0.267	0.260	0.278	0.298	0.291	0.298	0.300
<i>p</i> -Xyl	0.267	0.270	0.294	0.281	0.256	0.284	0.291	0.287	0.282	0.285

chloroform and strong or specific interactions with the aromatic and chlorinated aliphatic solutes. The more polar the solute, the lower is the χ -value. The increase in the chain length of *n*-alkanes has caused a marginal increase in χ . Alkylbenzenes too have displayed a similar

trend with respect to methyl group. Cyclohexane gives smaller values of χ than its normal analogues.

The dependence of χ on temperature has shown different trends for different families of the solutes (Figure 1). In the case of alkane

Table V. Constants of the linear plots of χ vs. $1/T$ for PnBMA + solute systems

Solute	Intercept, α'	Slope, β'	Correlation factor, r	No. of points	Temp range
					$^{\circ}\text{C}$
nC ₅	-0.35550	440.359	0.45470	4	70—100
nC ₇	0.01509	282.733	0.91709	5	100—150
nC ₈	-0.37911	446.282	0.93810	9	70—150
nC ₉	-0.18066	366.67	0.97461	6	100—150
nC ₁₀	-0.5506	519.98	0.98814	9	70—150
iC ₈	-5.01667	2163.488	0.98624	4	70—90
cC ₆	-0.27541	302.695	0.98968	5	110—150
CH ₂ Cl ₂	0.7534	-12.0538	0.8815	5	70—110.3
CHCl ₃	1.5688	-643.02	0.9913	10	70—150
CCl ₄	0.05411	76.211	0.62728	10	70—150
C ₂ HCl ₃	0.4888	-144.104	0.94556	10	70—150
C ₆ H ₆	0.1259	21.96	0.7431	7	70—150
Tol	0.1833	2.305	0.2272	6	70—150
<i>p</i> -Xyl	0.1271	21.4139	0.3831	10	70—150

Table VI. Constants of the linear plots of χ^* vs. $1/T$, and partial molar heats of mixing $\bar{h}_1^{\infty}$ for PnBMA + solute systems^a

Solute	Intercept	Slope	Correlation factor, r	$\bar{h}_1^{\infty}$	No. of points	Temp range
				$\text{kJ} \cdot \text{mol}^{-1}$		$^{\circ}\text{C}$
nC ₅	-0.584	569.055	0.9678	4.73	4	70—100
nC ₆	0.0208	348.031	0.7875	2.89	9	70—140
nC ₇	0.1631	281.236	0.9699	2.34	5	110—150
nC ₈	0.0180	334.46	0.9628	2.78	10	70—150
nC ₉	-0.2070	419.207	0.9770	3.49	9	70—150
nC ₁₀	-0.3159	464.364	0.9860	3.86	10	70—150
iC ₈	-6.3268	2656.6	0.9936	22.09	3	70—90
cC ₆	-0.0713	360.288	0.9283	2.995	6	100—150
	-5.5523	2249.4	0.9859	18.70	3	70—85
CH ₂ Cl ₂	0.2407	170.43	0.9819	1.42	5	100—150
	0.5581	-135.83	0.9474	-1.13	4	70—110
CHCl ₃	1.3539	-595.019	0.9902	-4.95	10	70—150
CCl ₄	0.4005	-5.9308	0.0598	-0.05	10	70—150
C ₂ HCl ₃	0.8286	-225.44	0.9784	-1.87	10	70—150
C ₆ H ₆	0.4699	-61.130	0.7379	-0.51	10	70—150
Tol	0.4889	-78.9833	0.9526	-0.66	8	70—150
<i>p</i> -Xyl	0.3865	-40.7455	0.8060	-0.34	8	70—150

^a Maximum uncertainty in $\bar{h}_1^{\infty}$ is 3.7%.

solutes, χ is a decreasing function of temperature as expected from its original definition, but it varies linearly with $1/T$ over a narrow range only, and tends to a minimum value that also becomes independent of the chain length of the solute as the temperature is increased. In

comparison with *n*-octane, isooctane has a higher value of χ at lower temperatures but smaller value at higher temperatures. On the other hand, the aromatic and chlorinated aliphatic solutes have produced the linear plots of χ against $1/T$, with a negative slope, through-

hout the temperature range studied, probably because the polar-polar type interactions normally become weak with an increase in the thermal energy. The temperature-dependence is strongest in the case of chloroform and weakest in the case of aromatic solutes; the other polar solutes fall in between.

The linear-plots in Figure 1 could be easily analyzed by least squares method by using Guggenheim's approach (eq 7) which treats $\chi(\chi^*)$ as a free energy divided into the entropic and enthalpic parts (Tables V and VI). In some cases, the deviation of the linearity correlation coefficient (r) from its ideal value of unity has resulted due to the small magnitude of χ and χ^* despite the truly linear plots in Figure 1. Therefore, the values of r are not considered as an indication of a large error in the derived values of $\chi_H (= \beta'/T)$, $\chi_S (= \alpha')$, or $\bar{h}_1^\infty$, except in the case of *n*-pentane and *n*-hexane where the major part of the curve is nonlinear. Moreover, the data have been used to indicate only the order of magnitude and the relative trends of these parameters. The small positive and negative values of χ_H and $\bar{h}_1^\infty$ support the view that there are specific interactions between PnBMA and the polar solutes. The large magnitude of χ_S suggests the possibility of some kind of short-range orientation or ordering between the segments of PnBMA and these solutes (Table V). Similarly, one may predict random mixing of carbon tetrachloride and the alkane solutes in PnBMA. The values of $\bar{h}_1^\infty$ increases by about 0.4 to 0.7 kJ·mol⁻¹ for each CH₂ unit added into the *n*-alkane chain (Table VI). Cyclohexane and isooctane have yielded appreciably large values of $\bar{h}_1^\infty$ at $T < 90^\circ\text{C}$. Hence, one may predict an extreme variation in their miscibility in PnBMA with temperature.

A complete and general explanation about the observed changes in the polymer-solute interaction energy over the whole range of temperature, and for each solute, is provided by the modern theories of Flory¹⁸ and

Figure 1. Dependence of χ on temperature. Solutes are *n*-pentane (1), *n*-hexane (2), *n*-heptane (3), *n*-octane (4), *n*-nonane (5), *n*-decane (6), isooctane (7), cyclohexane (8), dichloromethane (9), chloroform (10), carbon tetrachloride (11), 1,2-trichloroethylene (12), benzene (13), toluene (14), and *p*-xylene (15).

Patterson¹⁹ based on the corresponding state theory of Prigogine. Tait and Abushihada⁸ have successfully applied Patterson's theory to the results of IGC. The similar approach is being utilized in the present study without going into the details of theory. It divides χ into two terms to account for the "contact energy" and "free volume" dissimilarities between a solute-molecule and the segments of a polymer. The former is a decreasing function of temperature and the latter an increasing function without limit. Their cumulative effect results into a minima in the plots of χ against T . The present trends in χ suggest that the "contact energy" dissimilarity term is dominating in the case of alkane solutes, while the "free volume" dissimilarity is mainly responsible for the increase in χ in the case of aromatic and chlorinated-aliphatic solutes. These effects are more pronounced for the solutes which have shown a larger slope and a higher position of the χ vs. T (or $1/T$) plot.

In addition to the "contact energy" and

Table VII. Contact interaction parameter X_{12} ($\text{J} \cdot \text{cm}^{-3}$) for PnBMA + solute systems

Solute	Temperature/ $^{\circ}\text{C}$									
	70	80	85	90	100	110.3	120	130	140	150
nC ₅	27.78	30.50	27.36	25.25	24.23					
nC ₆	28.12	25.19	24.06	23.77	22.55	23.05	24.10	25.82	21.47	
nC ₇	24.73	22.59	22.30	21.17	20.50	21.72	21.42	21.38	20.42	20.63
nC ₈	21.01	22.01	21.38	20.50	19.75	20.38	20.25	20.21	19.21	19.75
nC ₉	20.96	20.25		19.83	18.87	19.42	18.95	18.45	18.20	18.49
nC ₁₀	19.41	20.08	19.87	19.33	18.41	18.16	18.70	18.08	17.53	17.11
iC ₈	31.84	27.74	24.99	23.72	19.75	18.87	19.37	18.12	17.11	18.16
cC ₆	32.72	27.74	22.26	24.18	22.64	22.23		21.55	21.34	21.21
CCl ₄	8.62	9.08	9.04	7.49	6.49	7.66	8.74	8.16	7.78	8.91
C ₆ H ₆	5.06	5.73	6.11	5.27	4.39	5.52	6.32	5.77	5.52	6.15
Tol	5.02	6.15	6.11	5.86	5.31	6.36	7.28	6.90	7.20	7.20
p-Xyl	5.52	6.03	6.95	6.53	5.61	6.78	7.11	6.99	6.74	6.86

“free volume” dissimilarities, there are differences in the thermal expansivities among the solutes themselves. Moreover, this difference also changes with temperature. Thus, the relative value of the temperature-coefficient of χ changes from solute to solute within a family. In the case of alkanes, this difference is reduced with an increase in temperature; hence, χ tends to become independent of their chain-length. The upper critical solution temperature of cyclohexane may be predicted at about 110°C where χ is found to decrease below 0.5 (Figure 1).

X_{12} Parameter

In the modified Flory theory,¹⁴ the parameter X_{12} defines the polymer–solute interaction energy resulting from the difference in the chemical potentials of their interacting surfaces. The positive values of X_{12} obtained in this study are characteristic of nonpolar and weakly polar systems (Table VII). It may be noted that the values of X_{12} have decreased with an increase in the chain length of *n*-alkanes, but have increased as the alkane character of the aromatic solutes was enhanced. However, unlike χ and χ^* , X_{12} remains almost constant throughout the temperature range studied, except in the cases of cyclohexane and isooctane where it increases with a decrease in temperature

below 100°C . A plot of X_{12} against the reciprocal of the carbon number of solutes would reveal that the contribution of the terminal groups of *n*-alkanes to the neighbouring interaction with PnBMA is much greater than that of the mid-chain groups. IGC technique has offered an advantage in the derivation of X_{12} in the sense that it has not required any specification of the contact site which is a necessary condition in the heat of dilution route.

CONCLUSIONS

In general, the miscibility of the alkane solutes with PnBMA has improved with an increase in the temperature, especially in the case of cyclohexane and isooctane. The solubility of all other solutes in PnBMA is very good throughout the temperature range studied, but the polymer–solute interaction energy is a decreasing function of temperature. The insignificant variation in the “contact” interaction with temperature indicates that the configurational heat capacity may probably be the key factor in the temperature dependence of polymer–solute interactions in the present systems. Modified Flory theory, however, does not explain the temperature-dependence of PnBMA–various solutes inter-

actions. Flory-Patterson-Prigogine theory has provided a satisfactory, yet qualitative, understanding about this aspect since the present data are insufficient for a more quantitative analysis. Nevertheless, the older approach of Guggenheim based on the Flory-Huggins interaction parameter theory seems to provide a satisfactory explanation of various trends in polymer-solute interactions with respect to the temperature and the solute-nature.

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