

Inverse Gas Chromatography of Poly(vinylisobutyl ethers) and Polymer-Solute Thermodynamic Interactions¹

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Synopsis

Gas chromatography (GC) retention behavior of atactic and isotactic poly(vinylisobutyl ether) stationary phases has been studied in the temperature range 30–90°C using 16 solutes which include various alkanes, alkylbenzenes, and chlorinated aliphatic hydrocarbons. The bulk sorption equilibrium retention data have been employed to derive various thermodynamic quantities at infinite dilution of solutes in the polymers, *viz.*, χ , χ^* , χ_H , χ_S , X_{12} , ΔH_S , h_1^∞ . Their dependence on temperature, polymer structure, and chemical nature of solutes has been discussed.

INTRODUCTION

Inverse gas chromatography (IGC)^{2,3} has been widely employed for accurate determination of various thermodynamic parameters for a large number of binary solutions at very high polymer concentrations, at temperatures well above the glass transition of polymer.^{1,3-13} However, some industrially important polymers like poly(vinylisobutyl ethers) (PVIBE)s have not been studied so far, and no thermodynamic data are available from other sources. In this work, we have studied the chromatographic characteristics and establishment of bulk sorption equilibrium of 16 probes (solutes) at infinite dilution in atactic and isotactic PVIBE stationary phases in the temperature range 30–90°C. Various thermodynamic quantities have been determined for binary PVIBE solutions, and their dependence on temperature, polymer structure, and chemical nature of solute has been discussed.

EXPERIMENTAL

Materials

Atactic and isotactic PVIBE were prepared by cationic polymerization of vinylisobutyl ether monomer in *n*-pentane, using borontrifluoride etherate as a catalyst, respectively, at 25° and –70°C.¹⁴ The polymer samples were

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purified by multiple precipitation. The number average molecular weight (\bar{M}_n) was determined by using Knauer vapor pressure osmometer and toluene as solvent at 37.0°C. The viscosity average molecular weight (\bar{M}_v) was determined from the intrinsic viscosity $[\eta]$ of polymer in benzene at 30.0°C using the relation¹⁵ $[\eta] = 7.55 \times 10^{-5} (\bar{M}_v)^{0.75}$ with polymer concentration expressed in g/dL. The value of $[\eta]$ was obtained with Ostwald's dilution viscometer. The density was determined by displacement of mercury by a known mass of polymer in a dilatometer. (The dilatometer will be described in a future communication.) The displaced volume was measured by recording the height of mercury meniscus in a calibrated capillary with a cathetometer (accuracy 0.01 mm), at various temperatures in the range of 25–90°C. The temperature was increased in steps and maintained for at least six hours to attain thermal equilibrium. The results were found to be reproducible when temperature cycle was reversed. The density (ρ) decreased linearly with increase in temperature (the linearity correlation (r) being better than 0.9998). The volumetric thermal expansion coefficient (α) and reduction parameters of the polymers were computed from density data in the usual manner. The basic properties thus obtained were: atactic PVIBE, $[\eta] = 0.06739$ dL/g, $\bar{M}_n = 2,340$, $\bar{M}_v = 8,600$, ρ (g/mL) = $0.916617 - 7.154621 \times 10^{-4} t(^{\circ}\text{C})$, ρ (25°C) = 0.89873 g/mL; isotactic PVIBE, $[\eta] = 0.08879$ dL/g, $\bar{M}_n = 2,500$, $\bar{M}_v = 12,400$, ρ (g/mL) = $0.918335 - 7.128803 \times 10^{-4} t(^{\circ}\text{C})$, ρ (25°C) = 0.900513 g/mL. Reference 16 gives density of PVIBE at 25°C in the range 0.91–0.92 g/mL. The solutes were analytical or chromatography grade chemicals, and were used as such. These are listed in Table I along with various equation of state parameters of both the solutes and polymers at 20°C.

Column Preparation

The polymers were deposited onto the surface of support from benzene solution by slow evaporation of solvent from the slurry (support + solution) under reduced pressure at 50°C in a rotavapor. The coated support was dried at 50°C in a vacuum oven until constant weight was achieved. The polymer/support ratio was adjusted empirically prior to coating. The exact amount of polymer coated (column loading) was estimated by calcination of the coated and uncoated supports at 600°C, in triplicate. Four columns were prepared by packing the coated support quantitatively in annealed copper tubings (o.d. 0.625 cm). The description of columns is given in Table II.

Chromatographic Measurements

The gas chromatograph apparatus and method of measurement of net retention times of solutes at infinite dilution were the same as described elsewhere.⁷ The amount of solutes used was of the order of nanograms unless specified otherwise. The measurements were carried out at various flow-rates (F) of carrier gas (dry hydrogen) in the range 20–150 mL/min, at 30°, 50°, 70°, and 90°C. The net retention time (t_R) was taken as an average of at least three runs for each solute at each flow rate.

TABLE I
Some Equation of State Parameters of Solutes and Polymers at 20° C

Compound	Abbreviation	$\alpha \times 10^3$ K ⁻¹	\bar{v}	$\bar{T} \times 10^2$	V* cm ³ /mol	P* Cal/cm ³	Remarks
Solutes							
<i>n</i> -Pentane	nC ₅	1.565	1.351	7.063	85.42	101.9	f
<i>n</i> -Hexane	nC ₆	1.367	1.314	6.6214	99.43	101.8	a
<i>n</i> -Heptane	nC ₇	1.243	1.290	6.3084	114.63	102.9	a
<i>n</i> -Octane	nC ₈	1.146	1.273	6.0759	127.74	104.6	a
<i>n</i> -Nonane	nC ₉	1.065	1.2675	5.8927	141.76	104.0	b
<i>n</i> -Decane	nC ₁₀	1.038	1.250	5.7346	155.6	105.1	c
Isooctane	iC ₈	1.197	1.283	6.2128	128.7	93.2	a
Cyclohexane	cC ₆	1.206	1.2885	6.2949	84.39	126	b
Dichloromethane	CH ₂ Cl ₂	1.341	1.3096	6.5657	48.87		c
Chloroform	CHCl ₃	0.418	1.113	3.153	72.269		c
Carbon tetrachloride	CCl ₄	1.219	1.2869	6.2633	74.97	134	g
1,1,2-Trichloroethane	C ₂ HCl ₃	1.188	1.2812	6.1877	70.022		c
Benzene	C ₆ H ₆	1.204	1.2881	6.2823	69.41	148	b,d
		1.194	1.2828	6.2041	69.27		c
Toluene	Tol	1.077	1.2633	5.933	84.58	134	b
<i>o</i> -Xylene	<i>o</i> -Xyl	0.963	1.2401	5.582	97.73	129	b
<i>p</i> -Xylene	<i>p</i> -Xyl	1.013	1.2501	5.735	99.10	127	b
Polymers							
Atactic PVIBE		0.7929	1.2007	4.926	0.92477		e,h
Isotactic-PVIBE		0.7885	1.1997	4.909	0.92194		e,h

^a Ref. 25 and Table 1 of Ref. 23; ^b ref. 24; ^c computed from molecular properties in ref. 20; ^d at 25° C; ^e calculated from experimental density data; ^f ref. 26; ^g ref. 27; ^h values in column 6 correspond to v* (cm³/g).

TABLE II
 Description of Columns

Polymer	Support	Column	Length cm	Coating wt%	Packing g	W_g g
Atactic PVIBE	Chromosorb W, AW, DMCS 80/100 mesh	A	182	10.4294	9.9997	1.04291
		B	150	12.5300	8.3800	1.05001
Isotactic PVIBE	Chromosorb G, AW, DMCS 60/80 mesh	C	87	7.3899	8.6014	0.63563
		D	92	9.5289	9.3356	0.88958

DATA REDUCTION

The specific retention volume (V_g^0) was determined using the well-known relation,¹⁷

$$V_g^0 = F \frac{P_o - P_w}{P_o} \frac{273.16}{T_a} \frac{3}{2} \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \frac{t_R}{W_g} \quad (1)$$

where P_i and P_o are, respectively, column inlet and outlet pressures, P_w is water vapor pressure in the flowmeter at ambient temperature T_a (K), and W_g is the weight of polymer in the column.

The following thermodynamic quantities were derived from V_g^0 at infinite dilution of solute (1) in polymer (2) using the relationships also given below. Flory-Huggins interaction parameter based on volume fraction³

$$\chi = \ln \left(\frac{273.16 R v_2}{P_1^0 V_1 V_g^0} \right) - \left(1 - \frac{V_1}{M_2 v_2} \right) - \frac{P_1^0}{RT} (B_{11} - V_1) \quad (2)$$

Flory-Huggins interaction parameter based on segment fraction³

$$\chi^* = \ln \left(\frac{273.16 R v_2^*}{P_1^0 V_1^* V_g^0} \right) - \left(1 - \frac{V_1^*}{M_2 v_2^*} \right) - \frac{P_1^0}{RT} (B_{11} - V_1) \quad (3)$$

Surface "contact" or "exchange" interaction energy parameter X_{12} based on modified Flory theory¹⁸

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

Heat of solution¹⁶

$$-\Delta H_S = R \frac{\partial \ln V_g^0}{\partial (1/T)} \tag{5}$$

Partial molar heat of mixing³

$$\bar{h}_1^\infty = R \frac{\partial \chi^*}{\partial (1/T)} \tag{6}$$

TABLE III
 Constants of Linear Plots of Log V_g^0 vs. T^{-1} , and $-\Delta H_S^{a,b,c}$

Solute	Intercept	Slope	Correlation factor r	$-\Delta H_S$ kJ/mol	No. of points	Temp. range °C
Atactic-PVIBE						
nC ₅	-2.3024	1216.795	0.9998	23.31	4	30-90
nC ₆	-2.7366	1491.042	0.9999	28.57	4	30-90
nC ₇	-3.0200	1711.162	0.9999	32.79	3	50-90
nC ₈	-3.4671	1983.569	0.9999	38.00	3	50-90
iC ₈	-2.8474	1638.008	0.9999	31.38	4	30-90
cC ₆	-2.7570	1603.949	0.9999	30.73	4	30-90
CH ₂ Cl ₂	-2.7968	1525.855	0.9999	28.63	4	30-90
CHCl ₃	-3.2968	1825.830	0.9999	34.97	3	50-90
CCl ₄	-2.8152	1645.536	0.9999	31.53	3	50-90
C ₂ HCl ₃	-3.2483	1863.256	0.9999	35.70	4	30-90
C ₆ H ₆	-2.9327	1703.845	0.9999	32.64	4	30-90
Toluene	-3.3738	1980.156	0.9999	37.94	3	50-90
Isotactic-PVIBE						
nC ₅	-2.5621	1301.847	0.9996	24.94	3	50-90
nC ₆	-2.7452	1488.077	0.9996	28.51	3	50-90
nC ₇	-2.9832	1696.569	0.9999	32.50	3	50-90
nC ₈	-3.4158	1969.751	0.9999	37.74	3	50-90
iC ₈	-2.3659	1462.350	0.9998	28.02	3	50-90
cC ₆	-2.7118	1584.366	0.9997	30.36	3	50-90
CH ₂ Cl ₂	-2.7746	1511.223	0.9998	28.95	3	50-90
CHCl ₃	-3.2510	1805.207	0.9999	34.58	3	50-90
CCl ₄	-2.9910	1705.184	0.9991	32.67	3	50-90
C ₂ HCl ₃	-3.1928	1841.362	0.9999	35.28	3	50-90
C ₆ H ₆	-2.8049	1656.208	0.9999	31.73	3	50-90
Toluene	-3.1937	1917.028	0.9998	36.73	3	50-90

^aMaximum standard error in slope is 1 × 10.

^bMaximum error in ΔH_S is 2%.

^cAdditional V_g^0 (mL/g) data at 90° C are:

	nC ₉	nC ₁₀	o-Xyl	p-Xyl
Atactic-PVIBE	205.03	425.89	301.93	241.08
Isotactic-PVIBE	211.26	433.63	304.59	243.56

TABLE IV
 Interaction Parameters χ (χ^*) for atactic PVIBE

Solute	χ				χ^*			
	30° ^a	50°	70°	90°	30° ^a	50°	70°	90° (°C)
nC ₅	0.694	0.594	0.551	0.531	0.813	0.726	0.697	0.692
nC ₆	0.654	0.591	0.526	0.531	0.748	0.696	0.643	0.660
nC ₇	0.677	0.598	0.536	0.524	0.743	0.673	0.620	0.618
nC ₈	0.684	0.602	0.586	0.555	0.744	0.670	0.661	0.638
nC ₉				0.572				0.639
nC ₁₀				0.579				0.638
iC ₈	0.654	0.570	0.523	0.497	0.723	0.646	0.607	0.591
cC ₆	0.454	0.404	0.358	0.362	0.523	0.490	0.461	0.481
CH ₂ Cl ₂	0.030	0.199	0.248	0.261	0.122	0.302	0.363	0.392
CHCl ₃	-0.351	-0.237	-0.101	0.025	-0.430	-0.324	-0.195	-0.077
CCl ₄	0.224	0.210	0.222	0.235	0.296	0.290	0.311	0.333
C ₂ HCl ₃	0.061	0.102	0.160	0.217	0.129	0.178	0.245	0.311
C ₆ H ₆	0.313	0.284	0.296	0.322	0.381	0.359	0.380	0.415
Toluene	0.299	0.233	0.282	0.307	0.276	0.286	0.341	0.372
<i>o</i> -Xylene				0.333				0.372
<i>p</i> -Xylene				0.334				0.385
Uncertainty ^b (±)		0.013	0.011	0.006		0.013	0.011	0.006

^aUsing extrapolated V_g^0 ($F = 0$) values at 30° C.

^bUncertainty for nC₅ and nC₆ is ±0.02.

Enthalpy and entropy contributions to χ ¹⁹

$$\chi = z \Delta\omega_H/kT - z \Delta\omega_S/k \quad (7)$$

$$= \beta'/T + \alpha' \quad (8)$$

$$= \chi_H + \chi_S \quad (9)$$

In the above equations v_2 is specific volume and \bar{M}_2 is molecular weight of the polymer; V_1 is molar volume, P_1^0 is vapor pressure, and B_{11} is second virial coefficient of solute in pure state; asterisk and tilde denote, respectively, the reduction parameters and reduced quantities; $z \Delta\omega$ is interchange energy per molecule acting against mixing, and kT is thermal energy acting in favor of mixing; and subscripts H and S denote enthalpy and entropy terms, respectively. B_{11} , P_1^0 , and V_1 were computed from standard data on physical properties of pure solutes.²⁰ The reduction parameters and reduced quantities of both solutes and polymers are given in Table I. Equations (5) to (7) were solved, wherever possible, by least-squares analysis of the linear regions of the plots of $\ln V_g^0$, χ , and χ^* against $1/T$, respectively. The computed results and errors are given in Tables III to VII. The present method of calculating $-\Delta H_S$ and \bar{h}_1^∞ diminishes the errors in the activity coefficient route such as in the measurement of flow rate and weight of polymer in the column.³ χ_H was obtained from χ , which has free energy characteristic, instead of \bar{h}_1^∞ based on χ^* .

TABLE V
 Interaction Parameters χ and χ^* for Isotactic PVIBE

Solute	χ			χ^*		
	50°	70°	90°	50°	70°	90° (°C)
nC ₅	0.573	0.594	0.565	0.706	0.742	0.727
nC ₆	0.610	0.594	0.544	0.716	0.712	0.675
nC ₇	0.488	0.552	0.520	0.564	0.638	0.615
nC ₈	0.529	0.548	0.520	0.598	0.624	0.605
nC ₉			0.534			0.603
nC ₁₀			0.552			0.613
iC ₈	0.538	0.595	0.489	0.616	0.681	0.584
cC ₆	0.417	0.407	0.362	0.504	0.511	0.483
CH ₂ Cl ₂	0.241	0.287	0.301	0.346	0.403	0.430
CHCl ₃	-0.206	-0.065	0.043	-0.291	-0.159	-0.059
CCl ₄	0.171	0.249	0.242	0.253	0.340	0.341
C ₂ HCl ₃	0.084	0.171	0.245	0.161	0.257	0.320
C ₆ H ₆	0.292	0.317	0.320	0.368	0.402	0.414
Toluene	0.231	0.289	0.285	0.285	0.349	0.351
<i>o</i> -Xylene		0.310	0.318		0.347	0.358
<i>p</i> -Xylene		0.299	0.317		0.346	0.370
Uncertainty \pm		0.006	0.006		0.006	0.006

 TABLE VI
 Constants of Linear Plots of χ vs. T^{-1} , and \bar{h}_1^∞ for Atactic PVIBE

Solute	Intercept α'	Slope β'	Correlation factor, r	\bar{h}_1^∞ kJ/mol	Temp. range, °C
nC ₅	0.01559	185.940	0.98488	0.840	50-90
nC ₆	0.02411	179.820	0.84771	0.911	50-90
nC ₇	-0.53539	367.158	0.99943	1.364	30-70
nC ₈	0.18119	136.887	0.97679	1.522	50-90
iC ₈	-0.09834	215.133	0.99143	1.351	50-90
cC ₆	0.38029	0.233	0.87804	1.341	30-70
CH ₂ Cl ₂	0.77270	-183.750	0.95829	-2.208	50-90
CHCl ₃	2.13990	-768.400	0.99993	-6.024	50-90
CCl ₄	0.43620	-73.209	0.99839	-1.047	50-90
C ₂ HCl ₃	1.14419	-337.080	0.99959	-3.241	50-90
C ₆ H ₆	0.62360	-110.568	0.97056	-1.358	50-90
Toluene	0.91140	-218.235	0.98855	-2.107	50-90

Maximum error in \bar{h}_1^∞ is 3.7%.

RESULTS AND DISCUSSION

Chromatographic Characteristics

The flow rate of carrier gas and the amount and chemical nature of solutes have influenced the retention behavior of both atactic and isotactic PVIBEs at temperatures below 50° and 70°C, respectively, almost in a similar manner. Figure 1 gives an example of flow rate dependence of V_g^0 . The V_g^0 versus F

TABLE VII
 Contact Interaction Parameter X_{12} (J/cm^3)

Solute	Atactic PVIBE				Isotactic PVIBE		
	30°	50°	70°	90°	50°	70°	90° (°C)
nC ₅	19.79	17.66	17.24	17.57	16.65	18.91	18.91
nC ₆	16.74	16.44	15.44		16.99	17.78	17.16
nC ₇	15.82	14.94	13.60	14.85	11.67	14.60	14.60
nC ₈	14.94	14.14	14.81	14.94	12.18	13.64	13.77
nC ₉				14.27			13.22
nC ₁₀				13.64			12.93
iC ₈	14.02	13.05	12.76	12.97	12.18	14.73	12.64
cC ₆	14.85	14.65	14.31	15.94	15.02	16.28	15.82
CCl ₄	7.15	7.24	8.45	9.75	5.44	9.66	9.96
C ₆ H ₆	12.05	11.76	13.43	15.90	12.01	14.39	15.65
Toluene	7.70	8.62	11.42	13.43	8.45	11.63	12.34
<i>o</i> -Xylene				13.26		11.46	12.64
<i>p</i> -Xylene				12.80		9.75	11.30

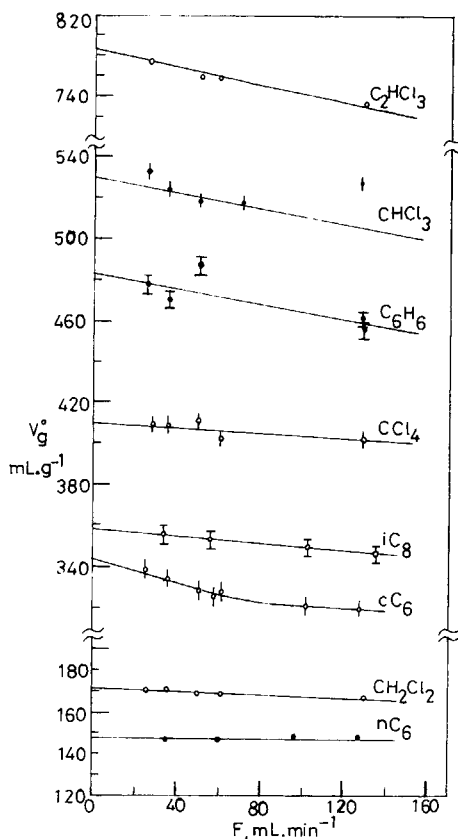


Fig. 1. Effect of flow rate on specific retention volumes of various solutes in atactic PVIBE at 30°C (column A).

plots (flow diagrams) for some solutes are nonlinear at 30 °C in case of atactic polymer, and at and below 50°C in case of isotactic polymer. A similar flow rate dependence was observed in our previous study on poly(vinyl acetate).⁷ We attribute the scatter observed in flow diagrams for some solutes to the peak asymmetry and tailing, and to the dependence of V_g^0 on the amount of solute. The latter did not alter V_g^0 value more than 1.5 to 2% for sample volumes smaller than 0.3 μL , which was within experimental error. The peak asymmetry has been observed on front profile for $n\text{C}_8$ and toluene, and on rear profile for all other solutes. However, $n\text{C}_5$, $n\text{C}_6$, and $i\text{C}_8$ have produced only a tailing effect in the peaks. The asymmetry has been found to increase with amount of solute, but the peak height has not increased proportionally in the case of $n\text{C}_8$ and toluene. The V_g^0 values for $n\text{C}_9$, $n\text{C}_{10}$, and xylenes could not be obtained under infinite dilution conditions at temperatures below 90°C because of strong influence of solute amount.

In the case of isotactic PVIBE, the peak broadening was comparatively small, and the peak width at half height was smaller than t_R for all solutes except $n\text{C}_5$. When fixed amounts of toluene were injected repeatedly immediately after appearance of the preceding peak at $T \leq 50^\circ\text{C}$, the column inlet pressure was found to have increased while the t_R and peak height were decreased. These observations suggest the swelling of PVIBE stationary phases and elution of peaks on concentration plateau or tailing of the preceding peaks. The bulk sorption equilibrium of solutes have been achieved comparatively faster and at lower temperatures in atactic than in isotactic polymer due to random structure and lower glass transition of the atactic PVIBE. We have used the minimum amount of solutes at highest detection sensitivity, and have allowed sufficient time to lapse after elution of peak before injecting next sample of solute in order to eliminate many sources of errors. We report, in this work, only those retention data which were obtained reliably at infinite dilution limit.

The extrapolation of V_g^0 to zero flow rate has yielded true bulk sorption data which have produced linear plots of $\ln V_g^0$ against reciprocal of absolute temperature (retention diagrams) for both the polymers above 50°C, and up to 30°C for some solutes in atactic PVIBE. However, the V_g^0 values for atactic polymer are consistently higher than those for isotactic polymer, although the difference is small, because of enhanced interactions of the solute with the random structure of the polymer. This stereoregularity effect is not significant above 70°C. Thus, the V_g^0 value of a solute in PVIBEs may be regarded as merely the weight average of the specific retention volume as a result of higher mobility of polymer chain in liquid state irrespective of its tacticity.

The above observations have been further confirmed by experiments on two different column loadings for each polymer. The extrapolated V_g^0 data at $F = 0$ have been found to be independent of column loading, and are within 0.7%. Hence, an average V_g^0 value on the two columns has been employed in thermodynamic calculations. The V_g^0 data thus obtained are given in Table III in terms of the slope and intercept of the linear region of the retention diagrams. The V_g^0 values for $n\text{C}_9$, $n\text{C}_{10}$, *o*- and *p*-xylenes are given only at 90°C because of the experimental difficulties already mentioned.

Thermodynamics of Polymer-Solute Interactions

The heat of solution ranges from about 23 to 38 kJ/mole (Table III). The smallest value is observed for nC_5 and largest for nC_8 . Heat of solution data exhibit many of the regularities usually observed with free energy data. For example, the addition of successive similar structural units to the solute molecule produces constant increments in ΔH_S value; cyclization, polarity and specific interactions of solutes with the polymer result in larger ΔH_S values. On the other hand, CCl_4 and iC_8 have given small and comparable heats of solution. The effect of stereoregularity on ΔH_S is not clear though some differences have been observed. The Flory-Huggins interaction parameters have been calculated in order to provide further understanding of solute-PVIBE interactions.

In general, PVIBE-solute interactions are strong, leading to small positive values of χ (χ^*) (Tables IV and V). It may be inferred from these tables that the trends in χ^* show better consistency than in case of χ . PVIBE is considered a moderately polar polymer. Therefore, a dipolar or specific interaction with solutes is likely to yield negative values of χ as in the case of $CHCl_3$. The χ values of alkanes are higher than those of other solutes because of their relatively low miscibility in PVIBEs. The addition of one CH_2 group in n -alkane chain length does not increase χ appreciably. A noticeable difference is observed only between solutes widely differing in chain length. On the other hand, the addition of one CH_3 group to benzene ring reduces the value of χ significantly. But further substitution of hydrogen in aromatic ring by CH_3 group does not have the same effect. Cyclohexane and iC_8 have smaller χ values than nC_6 and nC_8 , respectively.

The original definition of χ in Eq. (7) implies that it should decrease continuously with increase in temperature. Alkane solutes conform more or less to this trend in the temperature range studied. For other solutes, χ becomes less negative ($CHCl_3$) or more positive because specific and polar-polar interactions diminish with increase in temperature. However, χ (χ^*) versus $1/T$ plots are linear in most cases. Their slopes, intercepts and corresponding \bar{h}_1^∞ values are given in Table VI only for the atactic polymer so as to indicate the order of magnitudes of χ_H ($=\beta'/T$), χ_S ($=\alpha'$), and \bar{h}_1^∞ , which happen to be numerically very close for both polymers. Carbon tetrachloride and cC_6 show only an insignificant change in χ with temperature. The small positive and negative values of χ_H and \bar{h}_1^∞ in Table VI further confirm the observations in the previous paragraph regarding the aromatic and chlorinated solutes. The contribution by entropy term to χ is significant for these systems, the largest being for $CHCl_3$ followed by C_2HCl_3 . The reduced endothermicity of mixing also confirms the presence of enhanced specific interactions between PVIBEs and aromatic as well as chlorinated solutes. According to the advanced theories of Patterson²¹ and Flory,²² the free volume contribution becomes significant at higher temperatures, which is also responsible for increase in χ (χ^*) with temperature. Cyclohexane shows minimum χ value and, hence, maximum miscibility in atactic PVIBE at 70°C, while nC_6 shows scatter in data. The present measurements have been restricted to the 30–90°C range since the polymers were found to decompose

at higher temperatures in the absence of a stabilizer, and the retention diagrams were affected by kinetic factors at lower temperatures as described above. We attribute variation of χ (χ^*) between different solutes mainly to the free volume dissimilarity rather than to special steric effects or to differing force fields around the molecules.

The interaction parameters show similar trends for both polymers. However, the isotactic structure was found to give higher χ values at 70°C. The stereoregularity effect on χ (χ^*) is not substantial at 90°C because molecular mobility has increased considerably at this temperature, and the difference in specific volumes of the two polymers is also not sufficiently large.

In addition to χ , X_{12} parameter is also used to characterize the interactions, particularly the surface interactions, between solute and polymer. The positive values of X_{12} given in Table VII are characteristic of nonpolar and weakly polar systems. The trends in X_{12} are also the same as observed with χ (χ^*) except that X_{12} , unlike χ , decreases with increasing chainlength of *n*-alkane solutes.

CONCLUSION

The present investigations have established that reliable thermodynamic data could be obtained by gas chromatographic measurements on PVIBE stationary phases only between 50° and 90°C, and in a few atactic PVIBE-solute systems at 30°C also. Flory-Huggins approximation is found to explain the present results satisfactorily. The stereoregularity of PVIBE does not influence the polymer-solute interactions significantly under these experimental conditions. The differences in free volume dissimilarity between PVIBEs and various solutes are mainly responsible for the observed variation in χ values for the solutes.

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