Gas–Liquid Chromatography on Polymers. II. Temperature Coefficients for Polyisobutylene–Hydrocarbons

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ABSTRACT: Gas–liquid chromatography results obtained with polyisobutylene stationary phase and the solvents *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, benzene, and cyclohexane at 25, 45, and 65° are reported. The normal alkanes mix as ideal polymer solutions, whereas benzene, and to a lesser extent cyclohexane, exhibit departures from the Flory–Huggins entropy. The results are suggestive of specific entropic effects which profoundly influence the mixing of geometrically dissimilar molecules.

Gas–liquid chromatography has been shown to be an effective means to obtain activity coefficients for solvents at high dilutions in polymers.[1-6] Not only is it possible to make these measurements rapidly (which is unusual in polymer physical chemistry), but more importantly, glc is the only method presently available to explore thermodynamics in the concentration region near pure polymer, static vapor sorption methods notwithstanding.

We report here further measurements, over a range of temperatures, on polyisobutylene with the solvents *n*-pentane (*n*-C_5), *n*-C_6, *n*-C_7, *n*-C_8, benzene, and cyclohexane. The enthalpy and entropy of dilution are obtained for each of the solvents and are compared with vapor sorption data and/or other glc data where possible.

Experimental Section

The apparatus, procedure, and chromatographic materials used for the determination of net retention volumes have been described in detail in an earlier publication.[6] Two columns were prepared for the present work. The columns, I and II, contained 0.245 g (9.45% by weight) and 0.652 g (13.92% by weight) of polyisobutylene, respectively. Measurements were performed at 25.00, 45.00, and 65.00° with C_5–C_8 *n*-alkanes, benzene, and cyclohexane. Data presented here at 25 and 45° are averages of values obtained with both columns, whereas data at 65° were obtained from column II alone. No differences in retention volumes were observed outside of experimental error for the above columns with different coverage.

Results

The retention volume data were analyzed in the manner described previously.[6,7] In this work, as in the previous,[6] about 0.05 μmol of solvent was injected for each run. We have previously demonstrated that extrapolation of retention volumes to zero pressure gradient gives results in agreement with extrapolations to zero-flow rate. Measured gas-phase mixed second virial coefficients B_{13} are not reported here, but were in general 10–20% higher than those calculated from the principle of corresponding states using the Hudson and McCoubrey combining rule.[8] This theory invariably underestimates the second virial coefficients by about the amount observed. The agreement between measured and calculated values of B_{13} supports the method of data analysis. The net retention volumes (at zero column pressure) are 1–2% higher than those observed at a mean column pressure of 1.5 atm.

The Flory–Huggins solution parameter χ_v is obtained from[6]

$$\chi_v = \ln (RTV^L/V_1^0 p_1^0 V_N^0) - (B_{11} - V_1^0)p_1^0/RT - 1 + 1/r \qquad (1)$$

where V^L is the volume of the polymer, V_1^0, p_1^0, and B_{11} are respectively the molar volume, the vapor pressure, and the gas-phase second virial coefficient of pure solvent at the column temperature T°K, r is the ratio of molar volumes of polymer and solvent. With this χ_v the solvent activity is to be calculated from the Flory–Huggins equation using volume fractions for the composition variables. On the other hand, if segment fractions are used for calculation of activities as required in applications of the Flory, Orwoll, and Vrij (FOV) theory,[9] the mixing parameter χ_s is appropriate and is obtained from

$$\chi_s = \chi_v + \ln (\tilde{v}_1/\tilde{v}_2) \qquad (2)$$

Here $\tilde{v}_1$ and $\tilde{v}_2$ are the reduced volumes of solvent and polymer, respectively.

The reduced partial molar residual enthalpy κ_s is obtained from the temperature coefficient of χ_s by use of the relation

$$\kappa_s \equiv \bar{H}_1^R/RT\phi_2^2 = -(\partial\chi_s/\partial \ln T) \qquad (3)$$

and consequently the reduced partial molar residual entropy is

$$\bar{S}_1^R/R\phi_2^2 = \kappa_s - \chi_s \qquad (4)$$

The sources of values for the various parameters required for calculation of χ_v and χ_s from glc data have been reported earlier.[6] Values of χ_s thus obtained are listed in the first three columns of Table I, while the values of κ_s, calculated as the average of two values obtained for the two pairs of temperatures (25–45° and 45–65°), are entered in the fourth column. (We have set $d\kappa_s/dT = 0$ by this procedure.) The temperature coefficient of the correction term for gas-phase nonideality makes a significant contribution in the calculation of the reduced partial molar residual enthalpy.[10] We have taken care to evaluate the correction term containing the B_{11} coefficient in eq 1 at each temperature. The differences between this term at 45 and 65° vary from 0.029, 0.018, 0.011 to 0.007 for *n*-C_5, *n*-C_6, *n*-C_7 to *n*-C_8 respectively, which amounts to 58, 36, 28, and 23% of the decrease in χ_s. Large inaccuracies in κ_s as indicated are a consequence of the fact that there is but a small change in χ_s with temperature. All methods for obtaining enthalpy data by measurement of temperature coefficients of activities are similarly afflicted by large errors encountered on taking small differences between large numbers.

Discussion

Reduced partial molar residual enthalpies have in some cases also been obtained by static vapor sorption. However, this method is subject to large uncertainties at low concen-

Table I
Flory-Huggins Mixing Parameters, Reduced Partial Molar Residual Enthalpies and Entropies for Polyisobutylene-Hydrocarbon Systems

	χ_s			κ_s						$\bar{S}_1^R/R$	
	This work[a]				Other glc work						
Solvent	25°	45°	65°	This work[a]	Newman[b] and Prausnitz	Newman[c] and Prausnitz	Hammers[d] and DeLigny	Vapor sorption	Theory[i]	This work[j]	Theory[i]
n-Pentane	0.89	0.83	0.79	0.7_9	0.91		−0.39	0.06[e]	0.20	-0.0_4	−0.69
n-Hexane	0.77	0.72	0.68	0.7_0		−0.25	−0.69		0.11	-0.0_2	−0.66
n-Heptane	0.69	0.65	0.62	0.5_6			−0.33		0.07	-0.0_9	−0.62
n-Octane	0.63	0.58	0.56	0.5_5			−0.66		0.06	-0.0_3	−0.57
Benzene	0.98	0.89	0.75	1.8_5	1.37	0.28	0.54	1.4 ± 0.7[f]; 1.0[g]	0.62	$+0.9_6$	−0.36
Cyclohexane	0.66	0.61	0.56	0.7_9	0.25	−0.22	−0.42	0.6[h]	0.15	$+0.1_8$	−0.51

[a] Calculated as described in the text. The estimated precision of χ_s and κ_s is ±0.015 and ±0.3, respectively. [b] Reference 16. [c] Reference 17. [d] Reference 15. [e] Reference 14, extrapolated from $\phi_2 < 0.4$. [f] Reference 11. [g] Reference 12. [h] Reference 13. [i] Calculated in terms of Flory, Orwoll, and Vrij theory as described in the text. [j] Estimated uncertainty is ±0.3.

trations of solvent. Data for benzene[11,12] and cyclohexane[13] with PIB have been reported and are recorded in column 8. Fair agreement between extrapolated κ_s values and glc results are observed. Analysis[11] of the mixing parameters reported by Baker, *et al.*,[14] *for PIB–n*-pentane solutions gives $\kappa_s \simeq -0.04 + 0.1\phi_2$ for $\phi_2 < 0.4$. On the assumption that the foregoing expression is valid beyond the stated range, the extrapolated values of κ_s at very high concentrations will be *ca.* +0.06. This value can only be viewed qualitatively.

Gas–liquid chromatographic measurements for polyisobutylene have been reported by Hammers and DeLigny[15] and Newman and Prausnitz.[16,17] We have recalculated enthalpy parameters from these data by means of

$$\kappa_s = \kappa_v + (\alpha_2 - \alpha_1)T \tag{5}$$

where α_i is the thermal expansivity of component *i*, and have listed these values in columns 5, 6, and 7 of Table I. Our results are in reasonably close agreement with the earlier work of Newman and Prausnitz[16] but are at variance with those obtained from the other two publications mentioned. Much smaller, even negative, values of κ_s are computed from those results.

Experimental values for the reduced partial molar residual entropy, which refers to the difference between the observed entropy of mixing and the combinatory entropy of mixing, are near zero for PIB–*n*-alkane systems. If partial ordering prevails in amorphous polymers as is often postulated, it would affect the apparent residual entropy to an extent depending upon the order (the entropy change on dissolving such ordered regions is larger than the entropy change on dissolving randomly disposed segments). Our observations give no indication that the bulk amorphous polymer contains regions of extraordinary order. We have remarked earlier[6] that benzene and cyclohexane behave peculiarly at high dilutions in PIB, and similar conclusions may be drawn from the data presented here for the residual enthalpies and entropies. As suggested earlier,[6] benzene is "absorbed" on the PIB chain and cyclohexane clusters in cavities, according to arguments derived from those of Zimm and Lundberg.[18] The experimental value of $\bar{S}_1^R/R$ for benzene is certainly larger than that for the *n*-paraffins, while $\bar{S}_1^R/R$ for cyclohexane is within experimental error of the value zero. The fact that the benzene solution is very endothermic suggests that the "absorption" is entropically driven. It seems, therefore, that the entropy of solution is in some cases subject to subtle influences which defy explanation.

According to the FOV theory,[9] the enthalpy parameter κ_s at $\phi_2 = 1$ is expressed as

$$\kappa_s = [(\tilde{v}_1^{-1} - \tilde{v}_2^{-1}) + (T_2^*/T_1^* - 1)\alpha_2 T\tilde{v}_2^{-1}] \times P_1^*V_1^*/RT + (1 + \alpha_2 T)V_1^*X_{12}/\tilde{v}_2 RT \tag{6}$$

where T_1^*, P_1^*, and V_1^* are respectively the characteristic temperature, pressure, and molar volume of the solvent, T_2^* is the characteristic temperature of the polymer, and X_{12} is the contact interaction parameter. The theory also gives

$$\bar{S}_1^R/R = -\{3(T_1^*)^{-1} \ln [(\tilde{v}_1^{1/3} - 1)/(\tilde{v}_2^{1/3} - 1)] - \alpha_2\tilde{v}_2^{-1}(T_2^*/T_1^* - 1)\}P_1^*V_1^*/R + \alpha_2 V_1^*X_{12}/R\tilde{v}_2 \tag{7}$$

Values for the reduced partial molar residual enthalpy and entropy were calculated from eq 7 and 8 by using the corresponding X_{12} values from glc data at 25° and the characteristic parameters specified earlier.[6] They are recorded in columns 9 and 10. The theory appears to give accurate descriptions of *integral* enthalpies of mixing and chemical potentials but gives poorer results for *partial molar* enthalpies and entropies of dilution. The observed residual enthalpies are much larger than the predicted values; the discrepancy is a factor of about 5. It will be noted, however, that the theory predicts the correct sign for the enthalpy parameter.

Inspection of eq 8 reveals that the equation-of-state term contributes overwhelmingly to the value of $\bar{S}_I^R$. Equation 8 yields the observed value of the residual entropy only by use of an unrealistically large value for X_{12}. Introduction of a second parameter Q_{12}, denoted as the "interaction entropy" between unlike segments,[19] would lead to improved agreement with experiment, but we prefer to avoid this approach. Quantitative comparisons also suffer from the large uncertainties inherent in present experimental methods. An estimated error of +0.3 applies to the glc results, and an even larger error is inherent in the sorption results for the reduced partial molar residual enthalpy.

Conclusion

Studies of the thermodynamics of polymer solutions by conventional static methods at very high concentrations of polymer are relatively few. Therefore, comparisons between enthalpy parameters obtained by the methods of glc and vapor sorption are limited to only a few cases. One other system for which comparable data are available is natural rubber and benzene. In this case, the glc value[4] of κ_S is +0.18, while $\kappa_S = 0.01 \pm 0.1$ has been obtained by vapor sorption.[11] It appears from the somewhat sparse data collected to date that estimates of the residual enthalpy obtained by glc methods are as reliable as those obtained by static methods. Corrections for gas phase imperfection must be very carefully applied.

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Sorption of Solutes by Poly(ethylene oxide) Using Gas–Liquid Chromatography

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ABSTRACT: We have used gas–liquid chromatography (glc) to study equilibrium sorption by poly(ethylene oxide) (PEO) of small amounts of 12 organic solutes between 50 and 150° at essentially atmospheric pressure. Solute specific retention volumes and infinite-dilution volatilities are presented and discussed. Comparison of glc and static results for benzene sorption shows fair agreement between the data obtained using the two methods.

Poly(ethylene oxide) (PEO) is a commercially important, water-soluble polymer which is used in formulation of adhesives, pharmaceuticals, cosmetics, water-soluble packaging films, paper coatings, textile warp sizes, and friction-reducing additives. In some of these applications, the PEO is applied to a surface as a thin layer of concentrated solution and then dried to form a thin, water-soluble film. In order to understand the drying process more fully, we have studied sorption of small amounts of several organic solvents and water in PEO from 50 to 150°.

The experimental technique we have used is gas–liquid chromatography (glc). Its use in determining the activities of solvents in polymers was originally proposed by Smidsrød and Guillet[1] and described in detail by Newman and Prausnitz.[2,3]

Experimental Section

Apparatus and Procedure. The gas chromatograph used is an F & M 500 equipped with a thermal conductivity detector. The column oven was rebuilt, and oven temperature was controlled to ±0.1° by a Hallikainen Thermotrol. The carrier gas was helium, and its flow rate was controlled by a Negretti and Zambra precision regulator. Carrier gas flow rate was measured with a soap-bubble flowmeter. Carrier gas flow rate was measured to ±0.2 ml/min (at STP). Inlet and outlet column pressures were read to ±0.1 mm with two mercury manometers. Liquid samples were injected into the flowing helium stream through a silicone rubber septum with a 1 μl Hamilton syringe. The reliability of the apparatus was tested by reproducing, within experimental error, the data of Newman and Prausnitz[4] for poly(vinyl acetate) with various solutes.

Preparation of Columns. Two column packing materials were tested for use as PEO substrates: Chromosorb P (AW-DMCS) and Fluoropak-80, both 60–80 mesh. Columns were prepared by mixing a dilute solution of PEO in chloroform with substrate and evaporating to constant weight by heating. The coated support was packed into 5 ft of 0.25-in. stainless-steel tubing which was subsequently coiled to conform to the shape of the chromatograph oven. Unless care was taken to remove all but traces of water from the chloroform and air in the drying oven, some PEO was lost by depolymerization.

Column Support Materials. Chromosorb P (AW-DMCS) and Fluoropak 80 were tested as support materials. Our data indicate that specific retention volume Vg (defined later) was highly flow-rate dependent using Chromosorb P but much less so using Fluoropak 80. In addition, the solute chromatogram peaks were highly asymmetric using Chromosorb P but nearly symmetric using Fluoropak 80. For these reasons, we selected Fluoropak 80 as the support material to be used for this study.

Stationary Phase and Solutes. The PEO was WSR-301 "Polyox" supplied by the Union Carbide Corp., having a viscosity-average molecular weight of 4×10^6 g/g-mol, a melting range of 65 ± 2°, and a density of 1.21 g/cm^3 (determined by Union Carbide) at 25°.

The solutes were reagent grade materials supplied by various chemical suppliers.

Data Reduction. The state of aggregation of polymer coated material in a glc column is quite different from that of bulk polymer. According to Conder, *et al.*,[5] the observed retention volume is given by

$$V_N = V_L K_L + K_I A_I + K_S A_S \qquad (1)$$

where V_N = retention volume, V_L = volume of the liquid phase, K_L = distribution coefficient for the bulk solution, K_S = distribution coefficient for the surface adsorption, A_S = surface area of the