Thermodynamics of Solutions of Hydrocarbons in Low Molecular Weight Poly(isobutylene): A Gas Chromatographic Study

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ABSTRACT: The reduced chemical potentials (χ^*) of 20 normal and branched alkanes, cyclohexane, and three aromatic hydrocarbons at infinite dilution in poly(isobutylene) (PIB) were measured by gas liquid chromatography at five temperatures between 35 and 65 °C. Reduced partial molar residual enthalpies (κ^*) were calculated from the temperature dependence of χ^*; they are positive for PIB + alkane systems but smaller than those obtained in former chromatographic studies. Although uncertainties on κ^* are at least 1 order of magnitude larger than those on χ^*, binary X_{12} Flory parameters obtained from κ^* display a good correlation with the structural parameter θ_{e1}, defined as the ratio of the number of hydrogen atoms on methyl groups to the total number of hydrogen atoms in the alkane molecule. Very poor or nil correlation exists between X_{12} values obtained from χ^* and θ_{e1}. The evidence is by no means conclusive, but in principle the χ^* results obtained for PIB + alkane systems could be explained in terms of free volume contributions and the antipathy between methyl groups on the alkane molecules and the polymer side groups. Positive partial molar residual entropies were detected for the three aromatic hydrocarbons; their partial molar residual enthalpies are however highly positive, resulting in their poor solvent properties toward PIB.

Introduction

Notwithstanding that many years have passed since its conception, Flory theory[1,2] is probably still the most useful interpretative framework for the discussion of the thermodynamic properties of nonelectrolyte mixtures. The theory recognizes three contributions to the mixing functions: combinatorial, free volume, and interactional; they were reviewed in a recent paper.[3]

The theory has been most usually checked against calorimetric results; the interactional contribution is obtained by deducting the free volume contribution (calculated from equation of state data of the pure components by means of Flory's equations) from the excess enthalpy, H^E. The interactional contribution is characterized by the X_{12} parameter that denotes the energy change for formation of contacts between species 1 and 2 in exchange for contacts between like species; according to the theory, X_{12} is temperature and concentration independent. Another way of approach has been the measurement of excess free energies, G^E, by osmometric methods, vapor sorption, or gas liquid chromatography (GLC). After correction for the free volume and combinatorial contributions (the latter usually calculated in terms of segment fractions using the Flory−Huggins equations[4,5]), the interactional contribution and the X_{12} parameter are obtained. Both experimental approaches, but more frequently the calorimetric one, have been profusely employed to study hydrocarbon mixtures.[3,6]

It is not surprising that the behavior of real systems deviates from the predictions of Flory's semiempirical approach. Flory himself discovered that X_{12} parameters obtained by fitting to experimental H^E were larger than those obtained when fitting was made to G^E.[2,7] Patterson and collaborators advanced the idea that the discrepancies stem from the theory's neglect of liquid structure; their arguments were supported on Rayleigh scattering measurements of Bothorel *et al.*[8,9] and latter reinforced with numerous calorimetric results on carefully selected systems.[10−12] Short range orientational order, which can be thought as a partial alignment of neighboring segments or even whole molecules, would be present in liquids formed from long nonbranched molecules; this order is destroyed or replaced by weaker correlations on mixing with molecules of more globular shape, giving rise to positive contributions to both H^E and S^E. Since H^E and TS^E are almost equal, an enthalpy−entropy compensation occurs during the process, which is characterized by small contributions to G^E. Furthermore, order would be expected to decrease as the temperature raises, and its contributions to all the excess properties should become smaller.

A new contribution related with liquid structure was detected when the number of available experimental results increased. Important differences were found among the mixing enthalpies of a given normal alkane with a group of isomeric branched alkanes for which Rayleigh scattering indicated the same decrease in order during mixing; differences in H^E correlated with differences in the branched alkane molar volumes.[13,14] The same type of correlation was later found between mixing entropies (corrected for combinatorial and free volume contributions) and molar volumes.[15] A lower molar volume is associated with a higher crowding of groups within the molecule, *i.e.*, with steric hindrance to the free rotation of groups; negative enthalpy and entropy contributions occur on mixing rigid molecules with molecules freer in rotation, such as normal alkanes, through mechanisms not yet known but that could be related to a coupling of the modes of both types of molecules that results in an increase of order in the solution.

Delmas *et al.*,[16] using calorimetry, found that the enthalpy of mixing poly(isobutylene) (PIB) with alkanes at low polymer concentration is negative. Flory and collaborators[17,18] suggested that this behavior could be accounted for by a combination of a negative free volume contribution and a small positive term that the authors attributed to interchange of neighbor species in contact; their prediction for the PIB + *n*-pentane system was a

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strong concentration dependence of the κ^* parameter (*i.e.*, the reduced excess enthalpy calculated on a segment fraction basis), which was negative through most of the range but reached 0.2 at the GLC condition of polymer segment fraction $\varphi_2 = 1$.

In contradiction with these predictions, GLC measurements by Hammers and de Ligny[19] resulted in negative κ^*'s for a group of PIB + alkane systems that included *n*-pentane. Negative values of κ^* at several concentrations were also obtained by Gaecklé *et al.*[20] for the system PIB + *n*-pentane using calorimetry; concentration dependence was negligible so that it would be negative at $\varphi_2 = 1$.

Leung and Eichinger[21,22] employed the GLC method to study the mixing of PIB with hydrocarbons; their residual chemical potentials at 25 °C, χ^*, were very near to those obtained by extrapolating vapor sorption results to infinite dilution of the hydrocarbon, and the X_{12} parameters calculated from χ^* differed by less than 1.2 J cm^{-3} from those calculated by Flory from integral heats of mixing. The values of χ^* for normal alkanes fell markedly with increase of temperature; hence the κ^* parameters were large, between 0.6 and 0.8.

Hammers and de Ligny injected the solutes in the liquid form, and their sample sizes were large, about 1 μmol, obtaining skewed peaks whose retention volumes decreased with mean flow rate; both deleterious effects disappeared above 100 °C. Smaller sample sizes were used by Leung and Eichinger, about 0.05 μmol in the vapor form, and no dependence of the fully corrected retention volumes from flow rate was detected; however their peaks were skewed, a fact that the authors attributed to instrumental causes. The polymers employed in both chromatographic studies had a viscosity average molecular weight of 4×10^4; results could be affected by poor equilibration in the column due to slow diffusion of the vapors in PIB. This by no means explains the reasons why κ^* parameters with opposite sign were obtained by both groups of workers.

The study of PIB + hydrocarbon mixtures by the GLC method is taken up again in the present paper with the aim of settling some of the aforementioned discrepancies. A PIB specimen with a molecular weight markedly lower from those employed in former studies was used in order to minimize eventual diffusional effects; sample sizes were the smallest compatible with instrumental noise, and dead volumes between column and detector were minimized. Results for 24 hydrocarbons, most of them normal and branched alkanes, were obtained at five temperatures within the interval 35−65 °C. The choice of the solutes was dictated by our interest in studying the effects of branching on the excess properties; measurements were performed at several temperatures in the hope that, in spite of known restrictions of the GLC method for the measurement of excess enthalpies, the most important tendencies could be detected.

Experimental Section

Materials and Columns. PIB was a gift from Polibutenos Argentinos SA; GPC analysis resulted in $\bar{M}_n = 2300$, $\bar{M}_w/\bar{M}_n = 1.45$, and less than 1% by weight of molecules with $M_n < 500$. The polymer was coated on Chromosorb P AW DMCS 60/80 from a solution in *n*-hexane (Mallinckrodt pa) in a rotary evaporator, under a slow nitrogen flow. Coated support contained 9.95$_4$% by weight of PIB and was packed into 0.43 cm i.d. and 1−2 m in length stainless steel tubes; columns were kept overnight at 90 °C with 5−10 mL/min nitrogen flow rate before using. Hydrocarbons of several origins, more than 99% pure, were used without further purification.

Apparatus and Procedure. Measurements were performed with a home-assembled apparatus, in which column temperature was controlled to better than ±0.05 °C by immersion in a water bath. Nitrogen, successively passed through a molecular sieves trap (Davidson 5A), a Brooks 8606 pressure regulator, a Brooks 8743 flow controller, and a 2 m × 1/8 in. o.d. copper tube immersed in the column bath, was used as the carrier gas. Inlet pressures were measured by means of a mercury manometer at a point between the copper coil and a Swagelok 1/4 in. s.s. "T"; one branch of the latter was connected to the column, and the remaining branch was provided with a septum through which solute vapors were injected by means of Hamilton microsyringes, applying the headspace sampling technique. Eluates were detected with a Hewlett-Packard 5750 FID instrument and electrometer; signals were fed to a Hewlett-Packard 3396A integrator. Flow rates ranging between 20 and 50 mL/min were measured by means of a water-jacketted soap film flow meter.

Sample sizes were always smaller than 0.05 μmol; highly symmetrical peaks were obtained, indicating that Henry's law conditions had been attained. Solute vapors and a small methane sample were simultaneously injected; net retention times (in no instance smaller than 2 min) were measured to ±0.001 min between the times for the solute (t_R) and the methane (t_o) peaks maxima. Retention times for groups of three to six solutes were measured at five temperatures equally spaced between 35 and 65 °C; measurements at each temperature were made at least in quadruplicate. Measurements for a given solute, repeated after an interval of several days, differed from the original ones by less than 0.5%.

Density of the PIB sample was measured at 10 temperatures between 23 and 65 °C, by means of a 25 mL pycnometer that had been carefully calibrated through the same temperature interval, and least-squares-fitted to the equation

$$\rho_2 = 0.9166 - 5.470 \times 10^{-4} t \qquad (1)$$

where t is the temperature in °C. Equation 1 is accurate to $\pm 1.7 \times 10^{-4}$ in the temperature range of the measurements; the fit does not improve by using a second-degree polynomial. The thermal expansion coefficient derived from eq 1 is (in deg^{-1})

$$\alpha_2 = 5.96 \times 10^{-4} + 3.74 \times 10^{-7} t \qquad (2)$$

Results

Specific retention volumes, V_g°, were calculated from the relation[23]

$$V_g^\circ = j(F_f/w)(273.15/T_f)(t_R - t_o)(P_o - p_w)/P_o \qquad (3)$$

where j is the James−Martin carrier gas compressibility correction factor, w is the mass of PIB within the column, F_f is the carrier flow rate measured at the temperature T_f and pressure P_o of the flowmeter, and p_w is the water vapor pressure at T_f. Measurements at 50 °C for a selected group of solutes were performed at several flow rates between 17 and 55 mL/min; V_g° results, as calculated by eq 3, were coincident within experimental error.

Equation 4 was used to calculate the χ^* parameters[24]

$$\chi^* = \ln(273.15Rv_2^*/p_1^\circ V_g^\circ V_1^*) - 1 + V_1^*/\bar{M}_n v_2^* - p_1^\circ(B_{11} - V_1)/RT + (2B_{13} - \bar{V}_1^\infty)P_o J_3^4/RT \qquad (4)$$

where p_1°, V_1, and $\bar{V}_1^\infty$ are the solute vapor pressure, liquid-state molar volume, and partial molar volume at infinite dilution in the polymeric solvent (approximated by V_1 in the present paper), respectively, B_{11} and B_{13} are the second-virial coefficients for the solute−solute

Table 1. Equation of State Data and Characteristic Parameters for Two PIB Specimens of Different Molecular Weight

	$\bar{M}_v = 4 \times 10^4$ [a]		$\bar{M}_n = 2300$ [b]	
	25 °C	50 °C	25 °C	50 °C
ρ_2 (g cm^{-3})	0.9169	0.9042	0.9029	0.8893
α_2 (deg^{-1})	5.55	5.60	6.06	6.15
$\tilde{v}_2$	1.1488	1.1610	1.1609	1.1752
v_2^* (cm^3 g^{-1})	0.9493	0.9525	0.9540	0.9562
T_2^* (K)	7577	7726	7134	7250

[a] Viscosity-average molecular weight, ref 30. [b] Number-average molecular weight, this work.

and solute−nitrogen interactions in the vapor phase, and J_3^4 is a function of the column inlet and outlet pressures.[23]

The polymer characteristic specific volume, v_2^*, and the solute characteristic molar volume, V_1^*, are obtained from pure component volumetric data, as detailed by Flory and collaborators.[1,2] Vapor pressures were calculated by using the equation of Antoine with the coefficients compiled by Dreisbach;[25] for the molar volumes the density data of Orwoll and Flory[7] or those given by Timmermans[26] were used. Second-virial coefficients were computed by means of the corresponding states equation of McGlashan and Potter,[27] using critical constants given by Kudchadker *et al.*[28] and Reid *et al.*[29] The solute characteristic parameters in terms of the Flory state equation theory (V_1^*, T_1^*, and p_1^*), calculated from density, thermal expansion coefficient, and thermal pressure coefficient at 25 °C, have been tabulated in former publications.[30,31] The polymer characteristic parameters v_2^* and T_2^* were calculated by using eqs 1 and 2; our results at two temperatures are compared in Table 1 with those obtained by Eichinger and Flory[32] for a higher molecular weight specimen. Differences in the properties of both polymers are in the sense that could be qualitatively predicted from their molecular weights; values of v_2^*, however, differ by less than 0.5%.

Values of χ^* at each of the five experimental temperatures were calculated using mean values for not less than two independent measurements of V_g°. Our estimation of the uncertainty on χ^* is about ± 0.01, resulting from the quoted dispersion in V_g° plus contributions of the remaining terms in eq 4. Partial molar residual enthalpies were calculated by means of the equation

$$\bar{H}_1^R = R\{\partial\chi^*/\partial(1/T)\} \quad (5)$$

assuming $\bar{H}_1^R$ constant within the 35−65 °C interval. No trend could be detected for the residuals, this indicating that the error of the model (*i.e.*, assuming a temperature independent excess enthalpy) is overcome by the experimental error. The uncertainties on $\bar{H}_1^R$, as estimated from the least-squares fit, range between ±100 and ±250 J mol. Therefore, only a semiquantitative significance can be assigned to the values of the reduced partial molar residual enthalpy and entropy, calculated by means of the relations $\kappa^* = \bar{H}_1^R/RT$ and $\bar{S}_1^R/R = \kappa^* - \chi^*$, respectively. Results for χ^*, κ^*, and $\bar{S}_1^R/R$ at 50 °C have been gathered in Table 2. All the alkanes' κ^* values are positive, in coincidence with the findings of Leug and Eichinger; our results, however, are considerably smaller than theirs.

Table 2. Reduced Residual Chemical Potentials (χ^*), Reduced Partial Molar Residual Enthalpies (κ^*), and Reduced Partial Molar Residual Entropies ($\bar{S}_1^R/R$) for Hydrocarbons at Infinite Dilution in PIB at 50 °C

solute	χ^*	κ^*	$\bar{S}_1^R/R$
n-pentane	0.70_7	0.2_8	-0.4_3
n-hexane	0.62_3	0.1_7	-0.5_0
2-methylpentane	0.64_8	0.3_2	-0.3_3
3-methylpentane	0.60_5	0.3_2	-0.2_9
2,2-dimethylbutane	0.67_8	0.5_6	-0.1_2
2,3-dimethylbutane	0.60_6	0.4_9	-0.1_2
n-heptane	0.57_0	0.1_3	-0.4_4
2-methylhexane	0.58_9	0.2_8	-0.3_1
3-methylhexane	0.55_8	0.3_0	-0.2_6
2,2-dimethylpentane	0.62_5	0.5_7	-0.0_5
2,3-dimethylpentane	0.50_4	0.4_5	-0.0_6
2,4-dimethylpentane	0.62_9	0.3_8	-0.2_5
n-octane	0.51_8	0.1_1	-0.4_1
2-methylheptane	0.53_5	0.2_5	-0.2_9
4-methylheptane	0.51_0	0.2_6	-0.2_5
2,2-dimethylhexane	0.57_0	0.40	-0.1_7
2,5-dimethylhexane	0.57_2	0.3_5	-0.2_2
2,2,4-trimethylpentane	0.56_3	0.5_2	-0.0_4
2,3,4-trimethylpentane	0.45_1	0.4_9	-0.0_4
n-nonane	0.48_7	0.1_3	-0.3_6
cyclohexane	0.47_8	0.5_5	0.08
benzene	0.81_8	0.9_5	0.1_4
toluene	0.66_5	0.9_2	0.2_5
ethylbenzene	0.64_1	0.8_7	0.2_3

Discussion

According to the Flory state equation theory, the solute residual chemical potential and partial molar enthalpy at infinite dilution in the polymer are given by the following equations:

$$\chi^* RT = p_1^* V_1^* \{3\tilde{T}_1 \ln[(\tilde{v}_1^{1/3} - 1)/(\tilde{v}_2^{1/3} - 1)] + \tilde{v}_1^{-1} - \tilde{v}_2^{-1}\} + X_{12} V_1^*/\tilde{v}_2 \quad (6)$$

$$\kappa^* RT = p_1^* V_1^* [(\alpha_2 T/\tilde{v}_2)(T_2^*/T_1^* - 1) + \tilde{v}_1^{-1} - \tilde{v}_2^{-1}] + X_{12} V_1^* (1 + \alpha_2 T)/\tilde{v}_2 \quad (7)$$

where reduced volumes and temperatures are defined by $\tilde{v}_i = v_i/v_i^*$ and $\tilde{T}_i = T/T_i^*$, respectively. The first term in eqs 6 and 7 represents the contribution from free volume effects. In Flory's original model, the second term in each of these equations was identified with contact interaction contributions only, but in Patterson's scheme they could equally well represent contributions from order, steric hindrance, or eventually a combination of the three effects. Furthermore, Patterson and collaborators have denied any importance to interactional contributions in alkane mixtures; as a matter of fact, much of the work done in this area during the last 20 years was devoted to the identification of the origins of these contributions. Such an assignment is not a direct or simple matter in the present circumstances, as we pass to discuss.

In order to validate our results, it is necessary to mention that our χ^* results are smaller than those obtained by Leung and Eichinger;[21,22] differences drop from 0.08−0.15 at 25 °C (extrapolation of our data) to 0.04−0.10 at 65 °C. These discrepancies have their origin in the different volumetric behavior displayed by the polymer employed by Leung and Eichinger and that used in the present paper; when the free volume contributions are deducted from the experimental χ^* by using eq 6 and the data in Table 1, coincident residual contributions are obtained from both sets of results.

Values of X_{12} calculated from χ^* (eq 6) decrease linearly with temperature (0.01−0.05 J cm^{-3} K^{-1} for alkanes and 0.02−0.08 J cm^{-3} K^{-1} for aromatics and cyclohexane). On the other side, X_{12} parameters obtained from κ^* by means of eq 7 are between 2 and 4

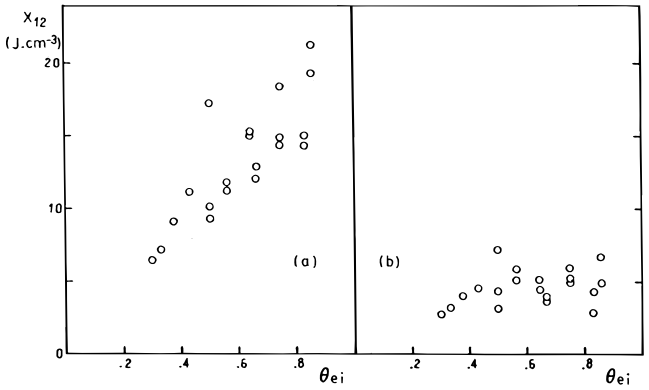

Figure 1. Binary Flory interaction parameters (X_{12}, J cm^{-3}) for PIB + alkane mixtures against the fraction of hydrogen atoms on methyl groups (θ_{e1}): (a) X_{12} calculated from κ^* and (b) X_{12} calculated from χ^*.

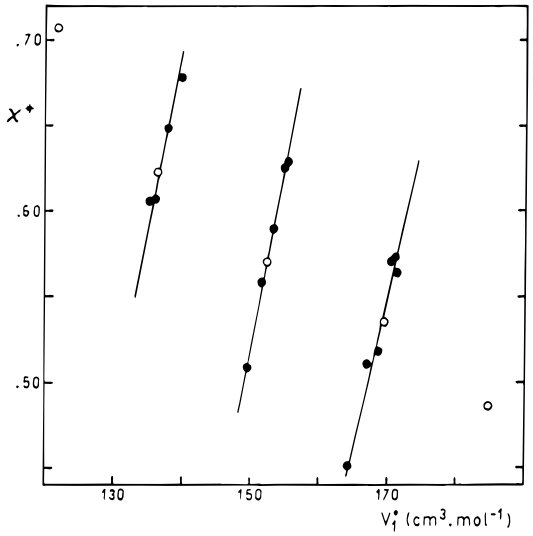

Figure 2. Infinite dilution residual chemical potentials of alkanes at 50 °C (χ^*) against their molar volumes (V_1): (○) normal alkanes and (●) branched alkanes.

times larger than those obtained from χ^*. These are very large differences and are displayed by all the systems studied in the present work; therefore they cannot be attributed to the uncertainties inherent in the calculation of the excess enthalpies from experimental activity coefficients. This is the type of behavior that could be expected in case orientational order exists in PIB, a hypothesis difficult to sustain on account of the numerous methyl side groups in the polymer molecule. However similar behavior was detected in chromatographic studies involving hydrocarbons and stationary phases for which it would be rather bold to assume order, such as tetra-*n*-amyltin.[31] It may be presumed that some degree of ordering could exist in almost any liquid suitable to be employed as stationary phase in GLC and that the effects of this order should be especially noticeable under the conditions of extremely low concentration prevailing in chromatographic measurements; the first molecules to get into solution will find the stationary phase in its more ordered state, promoting the largest order perturbations. The solid support surface, on the other side, may well induce some type of ordering of the stationary phase molecules.

Flory *et al.*[18] found that a smooth curve was obtained when X_{12} values for PIB + normal alkane systems (calculated from enthalpies of mixing) were plotted against the reciprocal of the number of carbon atoms in the alkane chain. This was attributed by the authors to contact interactions, and since X_{12} increase with the proportion of methyl groups in the alkane molecule, important chemical differences have to be admitted between this last type of group and the highly crowded methyl groups that constitute, almost completely, the surface of the polymer molecule. Delmas[33] suggested that this effect could have its origin in an overestimation of the free volume term by the Flory theory for systems with large differences in expansion coefficient. The value of α_2 for our low molecular weight PIB is about 10% higher than those of polymers used by former authors, and it was seemingly interesting to check whether the effect persisted or not.

Following this line of argument, X_{12} values calculated from κ^* have been plotted in Figure 1a against the fraction of methyl type surface in the alkane molecules θ_{e1}, calculated as the ratio of the number of hydrogen atoms on methyl groups to the total number of hydrogens in the molecule. There is a strong correlation between both variables; a least-squares analysis performed under the assumption of a first-order linear relationship results in a correlation coefficient of 0.83 and an ordinate that does not differ significantly from zero. The mean of the residuals is 2.3 J cm^{-3}, in coincidence with our estimation of the uncertainty on X_{12} parameters calculated from κ^*. On the other side, no correlation can be detected between values of X_{12} calculated from χ^* at 50 °C and θ_{e1}, as shown in Figure 1b; individual points are scattered about a mean of 4.6 J cm^{-3}, with a mean deviation smaller than 1 J cm^{-3}. Flory[2,7] suggested that contact interaction contributions to the excess properties were not only of enthalpic nature; it may be expected that entropy will also be affected. To account for this effect, he substituted X_{12} in eq 6 for $X_{12}^H - Q_{12}T\tilde{v}_2$, where X_{12}^H and Q_{12} are temperature and volume independent terms, associated with enthalpic and entropic effects of contact interactions; differentiation of the so-modified eq 6 results in eq 7 but with X_{12} replaced by X_{12}^H. The results displayed in Figure 1 suggest the existence of positive contributions from contact interaction, of similar importance in both H^E and TS^E, that compensate so as to leave only a small contribution to G^E. In our opinion ordering of the stationary phase by the solid support, although not totally rejectable, cannot be responsible for such notorious effects; a silanized solid support was employed, and according with its specific surface area (about 4 m^2 g^{-1}) and the stationary phase concentration, the mean thickness of the PIB film was about 300 Å.

χ^* values for alkanes at 50 °C are plotted against molar volumes in Figure 2. First to be noted is the smooth downfall of the normal alkane points; second, straight lines can be drawn through points corresponding to isomeric solutes. The slopes of those drawn in the figure for hexanes, heptanes, and octanes are coincident, and the correlation coefficients are higher than 0.98 in the three cases. These trends could be associated with steric hindrance effects; however there are several reasons to disregard that possibility. First, κ^* values do not change regularly with molar volumes within a given isomer group. Second, since PIB segments are highly sterically hindered, the larger effects (negative contributions to H^E, S^E, and G^E) should be observed on mixing with isomers of larger molar volume. Finally a plot of free volume contributions to χ^* against V_1 reproduces the principal characteristics of Figure 2, although a larger scatter of the points is observed; the quality of thermal pressure coefficient values of the

Table 3. Interactional Contributions to the Reduced Chemical Potential (χ^*_{int}), Reduced Partial Molar Residual Enthalpy (κ^*_{int}), and Reduced Partial Molar Residual Entropy ($\bar{S}_1^R/R_{int}$)

solute	χ^*_{int}	κ^*_{int}	$\bar{S}_1^R/R_{int}$
n-hexane	0.1_4	0.4	0.3
cyclohexane	0.1_3	0.7	0.6
benzene	0.4_7	1.1	0.7

branched alkanes, taken from different sources, can be the cause of this poorer correlation.

Solutions of aromatic hydrocarbons are markedly more endothermic than those of the alkanes; partial molar residual entropies, however, are positive for aromatics and negative for the alkanes. Since free volume contributions do not justify these differences, they must be attributed to their chemical dissimilarity. Interactional contributions to the reduced chemical potential and reduced partial molar enthalpy and entropy for *n*-hexane, cyclohexane, and benzene have been gathered in Table 3; they were calculated using X_{12} parameters obtained from residual enthalpies in eqs 6 and 7. These results, which must be considered cautiously on account of their very indirect origin, indicate important differences between the three solutes. According with these numbers, cyclohexane molecules are more strongly repelled by the PIB segments and are freer in their motions than those of *n*-hexane. PIB repulsion for benzene is yet stronger than that for cyclohexane, but no difference exists between the interactional partial molar entropy of both solutes.

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