other group contribution methods.

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Glossary

a, *b*	first- and second-order coefficient of a polynomial least-squares fit
A, *B*, *C*	coefficients of the Antoine vapor pressure equation
B_{ii}, B_{ij}	second virial coefficients
f	evaporation factor
f_i^V, f_i^L	fugacity of the liquid and vapor phases for component *i*
K_i	volatility of component *i*
N_V	total amount of moles of vapor holdup
N_L^{VLE}, N_V^{VLE}	total moles in liquid and vapor equilibrium phases
P	absolute pressure
P_i^{sat}	saturation vapor pressure of component *i*
R	gas constant
T	absolute temperature
ΔT	temperature difference
VLE	vapor–liquid equilibrium
v_i^L	liquid molar volume of component *i*
x	independent variable in least-squares fit
x_i	equilibrium liquid-phase mole fraction of component *i*
y	dependent variable in least-squares fit
y_i	equilibrium vapor-phase mole fraction of component *i*
z_i	feed mole fraction component *i*

Greek Letters

β	$=1 + P_2^{sat}((B_{22} - v_2^L)/RT)$
δ_{12}	$=2B_{12} - B_{11} - B_{22}$
γ_i^∞	activity coefficient at infinite dilution of component *i*
ϵ_i^∞	vapor-phase correction

Registry No. Tetrahydrofuran, 109-99-9; cyclohexane, 110-82-7; *n*-pentane, 109-66-0; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5; ethyl acetate, 141-78-6; 1,4-dioxane, 123-91-1; 2-furaldehyde, 98-01-1; butyl ether, 142-96-1.

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Activity Coefficients in Benzene–Alcohol Systems near the Freezing Point of Benzene

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Activity coefficients of seven light alcohols and benzene were determined by measuring freezing point depressions of benzene with each alcohol as a solute. Fits to van Laar, Wilson, and some continuous association models showed that the latter models work much better in all cases, considering alcohols as monomeric solutes. This behavior is similar to that observed at much lower temperatures when thiophene is the solvent of butanols. The magnitudes of the association equilibrium constants in the low-concentration range are also much lower than those calculated on the basis of properties of pure alcohols with athermal models of continuous association.

Introduction

Activity coefficients of both components in benzene–alcohol systems were calculated from smoothed freezing point depressions of benzene in a similar manner to that used when either cyclohexane (*1*) or thiophene (*2*) was the solvent. As expected, monomers appeared to be the smallest species at high dilution, the same behavior that was observed when thiophene was the solvent.

A fit to six different solution models showed analogous trends. However, in this study there were indications of difficulties in fitting some particular models, the ones that showed large standard deviations in past reports (*1*, *2*).

Experimental details have been given elsewhere (*1*).

Calculation of Activity Coefficients from Experimental Data

The sequence of calculations is the same as given in a previous paper (*2*). Smoothing of freezing point depressions, θ, is done through

$$\theta = \frac{z[A_0 + (A_1 - 1)z + A_2z^2]}{A[A_0 + A_1z + A_2z^2]} \qquad (1)$$

in which $z = x_2/x_1$, the mole fraction ratio

$$A = \lambda_1/RT_0^2 = 0.015418 \qquad (2)$$

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Table I. Parameters and Standard Deviations When Smoothing θ Data with Eq 1

solute	A_0	A_1	A_2	σ
methanol	0.036 109 5	1.099 311	−0.166 189	0.024
ethanol	0.066 995 0	0.139 070	9.218 150	0.005
1-propanol	0.095 854 5	−1.348 745	32.192 850	0.007
2-propanol	0.113 764 0	−2.233 080	45.503 750	0.007
2-butanol	0.114 186 0	−0.360 065	12.509 800	0.017
isobutyl alcohol	0.096 091 5	−0.119 330	9.766 450	0.010
tert-butyl alcohol	0.250 046 0	−4.774 735	49.251 400	0.017

where λ_1 is the heat of fusion (*3*) of benzene (9951.2 J/mol), T_0 is the melting point of benzene (278.61 K), and R is the gas constant. A_0, A_1, A_2 are the optimum parameters from the minimization of the objective function

$$\psi_\theta = \sum_k^N (\theta - \hat{\theta})_k^2 \tag{3}$$

in which N is the number of experimental data points, $\hat{\theta}$ is the experimental freezing point lowering, and θ is the value calculated by means of eq 1.

The quality of the smoothing of the experimental data can be appreciated from Table I. Standard deviations are low enough as to support the application of the empirical eq 1.

The activity coefficients were calculated with the following equation:

$$\hat{\gamma}_1 = \frac{\exp[A\theta z]}{x_1} \tag{4}$$

$$\hat{\gamma}_2 = \frac{\eta}{x} \exp\left[-\frac{z}{A_0 + A_1 z + A_2 z} \right] \tag{5}$$

in which z is the mole fraction ratio x_2/x_1, and

$$\eta = [\{1 + 2A_2 z/(A_1 + \epsilon)\}/\{1 + 2A_2 z/(A - \epsilon)\}]^\epsilon \tag{6}$$

$$\epsilon = \{A_1^2 - 4A_0 A_2\}^{1/2} \tag{7}$$

when $A_1^2 > 4A_0A_2$, and

$$\eta = \exp\left[\frac{2}{\epsilon} \left\{ \tan^{-1}(A_1/\epsilon) - \tan^{-1}\left(\frac{A_1 + A_2 z}{\epsilon} \right) \right\} \right] \tag{8}$$

$$\epsilon = \{4A_0A_2 - A_1^2\}^{1/2} \tag{9}$$

when $A_1^2 < 4A_0A_2$.

Table II gives mole fractions, experimental and calculated freezing point lowerings, and activity coefficients calculated in the described manner.

Correlation of Activity Coefficients with Models

In order to appraise the interpretative ability of several simple models with regard to the activity coefficients calculated in the section above, a fit of these activity coefficients was made. The objective function minimized was the following

$$\psi_\gamma = \sum_j^2 \sum_k^N \{1 - (\gamma_j/\hat{\gamma}_j)\}_k^2 \tag{10}$$

and percentagewise standard deviations were determined according to

$$\sigma = 100\{\psi_\gamma/(N - 1)\}^{1/2} \tag{11}$$

γ_j and $\hat{\gamma}_j$ are respectively calculated from the model and from the experimental data.

Table II. Mole Fractions, Experimental and Calculated Freezing Point Lowerings, and Activity Coefficients from Experimental Data

x_2	$\hat{\theta}$, °C	θ	$\hat{\gamma}_1$	$\hat{\gamma}_2$
		Benzene (1)–Methanol (2)		
0.0211	0.927	0.893	1.0076	0.4502
0.0313	1.160	1.148	1.0142	0.3521
0.0413	1.352	1.346	1.0216	0.2897
0.0511	1.485	1.509	1.0296	0.2467
0.0607	1.614	1.647	1.0379	0.2153
0.0701	1.734	1.767	1.0465	0.1914
0.0701	1.800	1.767	1.0465	0.1914
0.0884	1.961	1.968	1.0641	0.1575
0.1059	2.141	2.133	1.0823	0.1346
0.1228	2.273	2.273	1.1007	0.1180
0.1391	2.387	2.393	1.1194	0.1055
		Benzene (1)–Ethanol (2)		
0.0074	0.440	0.431	1.0008	0.8092
0.0147	0.768	0.765	1.0030	0.6619
0.0219	1.017	1.017	1.0065	0.5502
0.0290	1.203	1.208	1.0109	0.4658
0.0360	1.358	1.359	1.0158	0.4023
0.0429	1.493	1.487	1.0211	0.3544
0.0497	1.608	1.608	1.0265	0.3181
0.0497	1.606	1.608	1.0265	0.3181
		Benzene (1)–1-Propanol (2)		
0.0058	0.353	0.353	1.0004	0.8845
0.0115	0.659	0.652	1.0015	0.7735
0.0115	0.658	0.652	1.0015	0.7735
0.0172	0.901	0.892	1.0036	0.6729
0.0172	0.880	0.892	1.0036	0.6729
0.0228	1.077	1.082	1.0064	0.5866
0.0228	1.079	1.082	1.0064	0.5866
0.0283	1.235	1.233	1.0097	0.5164
0.0338	1.372	1.367	1.0134	0.4617
0.0392	1.500	1.502	1.0170	0.4205
		Benzene (1)–2-Propanol (2)		
0.0057	0.359	0.353	1.0003	0.9010
0.0057	0.358	0.353	1.0003	0.9010
0.0114	0.665	0.657	1.0014	0.7993
0.0114	0.667	0.657	1.0014	0.7993
0.0170	0.899	0.904	1.0032	0.7018
0.0226	1.088	1.098	1.0059	0.6149
0.0281	1.254	1.253	1.0092	0.5427
0.0335	1.399	1.392	1.0127	0.4866
0.0389	1.535	1.539	1.0160	0.4455
		Benzene (1)–2-Butanol (2)		
0.0187	1.045	1.023	1.0031	0.7259
0.0277	1.390	1.387	1.0067	0.6217
0.0366	1.648	1.675	1.0115	0.5387
0.0454	1.920	1.913	1.0171	0.4742
0.0540	2.143	2.129	1.0229	0.4248
0.0624	2.336	2.343	1.0287	0.3877
		Benzene (1)–Isobutyl Alcohol (2)		
0.0094	0.561	0.555	1.0009	0.8279
0.0094	0.568	0.555	1.0009	0.8279
0.0187	1.001	0.992	1.0035	0.6879
0.0277	1.329	1.325	1.0077	0.5775
0.0366	1.569	1.578	1.0131	0.4923
0.0454	1.770	1.780	1.0192	0.4276
0.0540	1.959	1.956	1.0256	0.3788
0.0624	2.146	2.130	1.0321	0.3422
0.0707	2.309	2.318	1.0383	0.3146
		Benzene (1)–*tert*-Butyl Alcohol (2)		
0.0092	0.585	0.576	1.0004	0.9271
0.0181	1.090	1.071	1.0017	0.8415
0.0224	1.298	1.281	1.0029	0.7955
0.0308	1.615	1.618	1.0063	0.7021
0.0389	1.827	1.851	1.0112	0.6151
0.0505	2.112	2.094	1.0197	0.5136
0.0615	2.371	2.376	1.0272	0.4534

The equations for calculating activity coefficients are those of the six models already detailed elsewhere (*1*): model I, either van Laar (*4*) or its symmetrical Margules form; model II, Wilson (*5*); model III, ideal associated solution with two chemical equilibrium constants (*6*); model IV, ideal associated

Table III. Parameters and Percentagewise Standard Deviations for the Six Different Models

model		methanol	ethanol	1-propanol	2-propanol	2-butanol	isobutyl alcohol	*tert*-butyl alcohol	av dev
I	A_3	11.59	12.41	11.58	10.73	8.22	9.13	6.41	
	σ	33.2	5.03	1.21	1.64	2.89	4.68	4.26	3.18 ± 1.50[a]
II	$\lambda_{12} - \lambda_{22}$[b]	2262	1860	1607	1547	1335	1424	1148	
	$\lambda_{12} - \lambda_{11}$[b]	-362.2	∞	∞	∞	∞	∞	∞	
	σ	0.56	2.32	3.32	3.99	2.03	2.59	6.53	3.05 ± 1.87
III	K_1	19.27	11.66	8.60	7.43	7.25	8.47	2.80	
	K_2	54.73	42.04	38.39	36.73	25.70	30.34	26.05	
	σ	0.67	0.63	0.33	0.39	0.26	0.56	0.70	0.51 ± 0.18
IV ($\beta \to \infty$)	K	30.40	20.74	16.01	14.61	12.23	14.80	8.51	
	σ	1.20	4.13	4.42	5.04	3.44	4.42	7.66	4.33 ± 1.98
V	K_1	247.4	86.8	48.9	40.8	33.6	38.7	13.6	
	K_2	291.6	165.1	119.3	111.8	65.0	75.8	62.2	
	σ	0.04	0.25	0.33	0.49	0.41	0.49	0.72	0.39 ± 0.21
VI ($\beta = 0$)	K	274	89.0	24.9	0	0	0	0	
	χ[b]	42	381	560	~800	?	?	?	
	σ	0.48	1.07	1.17	1.51	?	?	?	

[a] $\sigma = 2.58$ for $A_{21} = 2.716$ and $A_{12} = 0.332$ is considered for methyl alcohol in this average (van Laar model). [b] Values given in cal/mol.

solution with chemical equilibrium constant dependent on the degree of association (*7*); model V, athermal associated solution with two chemical equilibrium constants (*1*, *2*); model VI, athermal associated solution with one chemical equilibrium constant and physical interaction contributions (*8*).

Results and Discussion

Table III gives the respective optimum parameters and percentagewise standard deviations for the six models. At first, the classical van Laar model for solutions was tried with no success in most of the systems, except in benzene-methyl alcohol solutions. The minimization procedure showed an objective function too flat with a minimum in a region of large values for both the two parameters. That being the case, it was chosen to look for the best parameters of the Margules symmetrical form, in which

$$\hat{\gamma}_1 = \exp[A_3 x_2^2]; \quad \hat{\gamma}_2 = \exp[A_3 x_1^2] \tag{12}$$

In general, the van Laar model in its two forms gives relatively high deviations, apart from the difficulties indicated. Practically the same type of results and problems arise from the attempt to fit the data to the Wilson model. Except for the benzene-methanol system, one of the parameters tends to infinity and the percentagewise deviations are too high to consider Wilson model a good one for these systems under these conditions.

The lowest standard deviations of models III and IV confirm that simple ideal or athermal associated solutions with two chemical equilibrium constants give the best fit of the activity coefficients near the freezing point of the solvent. K_2 being much greater than twice the K_1 value, the good fit with model V makes the poor fit with model IV understandable. The ideal associated solutions model of gradually varying chemical equilibrium constant (model IV) has a ratio $K_\infty/K_1 = 2$ when β tends to infinity.

The athermal associated solution (model VI, UMAS with $\beta = 0$) with physical interaction contributions of the Scatchard-Hildebrand type gave results indicative of its inadequacy for interpreting the behavior of the systems discussed herein. Model VI shows a trend where the heavier the alcohol the lower the value of the chemical equilibrium constant and the higher the Scatchard-Hildebrand parameter, χ, arising from the fit. Percentagewise standard deviations are not low and increase gradually with the molecular weight of the solute. Chemical equilibrium constants would be nonexistent for the heavier alcohols, thus showing that there would be no association in these alcohols under this treatment.

Table IV. Comparison of K_2 from Model V with K_A Values Calculated according to Nath and Bender (*9*)

solute	K_A	K_2
methanol	958.1	291.6
ethanol	469.6	165.1
1-propanol	299.6	119.3
2-propanol	152.7	111.8
2-butanol	88.1	65.0
isobutyl alcohol	138.1	75.8
tert-butyl alcohol	39.9	62.2

It should be remarked that again, as in two similar papers (*1*, *2*), chemical equilibrium constants arising from the fit to the athermal model V are lower than those calculated from pure alcohol properties, now with the exception of *tert*-butyl alcohol. Table IV gives a comparison of K_2 against K_A given by Nath and Bender (*9*).

Table III summarizes also the average percentagewise standard deviations for five out of six models tried with the seven systems. It is quite clear that models III and V, respectively ideal and athermal associated solutions models, give the best fits. It is practically the same result observed when thiophene was the solvent (*2*).

Thiophene and benzene are so similar to one another that a very crude estimation of the heat of association can be obtained through the van't Hoff equation by assuming that both of them would be the same solvent. There are three butanols which allow this calculation to be made. For the ideal associated solution model III that heat of association would be about -7.2 ± 1.9 kcal/mol from K_1 and -3.9 ± 0.3 kcal/mol from K_2. From the athermal solution model V the values estimated are -4.2 ± 1.9 kcal/mol from K_1 and -1.4 ± 0.3 kcal/mol from K_2. The figures obtained from K_1 are not to far from the hydrogen bond energy. Figures arising from K_2 are more difficult to explain, except if a solvation effect, not considered in both models, is taken into account additionally.

Glossary

A, A_0, A_1, A_2	constants (see eq 1)
A_3	Margules symmetrical parameter
A_{12}, A_{21}	van Laar parameters
K, K_A, K_1, K_2	chemical equilibrium constants
N	number of experimental data points
R	gas constant

z	mole fraction ratio x_2/x_1
β	parameter in ideal associated solution model
γ_1, γ_2	activity coefficients of solvent and solute
ϵ	see eq 6 and 8
η	see eq 5 and 7
θ	calculated freezing point depression
$\hat{\theta}$	corrected experimental freezing point depression
λ_{ij}	Wilson equation parameters
λ_1	heat of fusion of solvent
σ	standard deviation
χ	Scatchard–Hildebrand type parameters
ψ_θ, ψ_γ	objective functions

Registry No. Benzene, 71-43-2; methanol, 67-56-1; ethanol, 64-17-5; 1-propanol, 71-23-8; 2-propanol, 67-63-0; 2-butanol, 78-92-2; isobutyl alcohol, 78-83-1; *tert*-butyl alcohol, 75-65-0.

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Molar Excess Volumes and Molar Excess Enthalpies of Some Ternary Mixtures of Nonelectrolytes

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Molar excess volumes, V^E_{ijk}, and molar excess enthalpies, H^E_{ijk}, have been measured at 298.15 K for benzene (i) + toluene (j) or *o*-xylene (j) or *p*-xylene (j) + *o*-chlorotoluene (k), and toluene (i) + *o*-xylene (j) + *o*-chlorotoluene (OCTE) (k) mixtures. While the V^E_{ijk} and H^E_{ijk} data are positive for benzene (i) + toluene (j) or *o*-xylene (j) or *p*-xylene (j) + OCTE (k) mixtures, the V^E_{ijk} and H^E_{ijk} data for toluene (i) + *o*-xylene (j) + OCTE (k) mixtures change sign with composition.

Introduction

Thermodynamic studies (*1–3*) on the binary mixtures of aromatic hydrocarbons with chlorobenzene or *m*-dichlorobenzene or *o*-chlorotoluene (OCTE) mixtures have indicated that attractive interactions (*1*, *2*) take place between the components of these binary mixtures. It would, therefore, be instructive to study the influence of the addition of another aromatic hydrocarbon (c) entity to the binary mixtures of aromatic hydrocarbon + *o*-chlorotoluene mixtures. In this paper we present molar excess volumes, V^E_{ijk}, and molar excess enthalpies, H^E_{ijk}, for benzene (i) + toluene (j) or *o*-xylene (j) or *p*-xylene (j) + OCTE (k), and toluene (i) + *o*-xylene (j) + OCTE (k) mixtures at 298.15 K.

Experimental Section

Materials and Their Purification. Analytical grade benzene (E. Merck), toluene (E. Merck), *o*-xylene (E. Merck), *p*-xylene (Thomas Baker & Co., London), *m*-xylene (Fluka AG), and *o*-chlorotoluene (J. T. Baker Chemical Co.) were purified in the following manner (*4*).

Benzene was shaken repeatedly with about 15% of its volume of concentrated sulfuric acid in a stoppered separatory funnel until the acid layer was colorless on standing. After each shaking lasting a few minutes, the mixture was allowed to settle and the lower layer was drawn off. The benzene layer was shaken twice with water (in order to remove most of the acid), once with 10% sodium carbonate solution, again with water, and finally dried over anhydrous calcium chloride for a fortnight. It was then distilled and then stored over sodium wire.

Table I. Comparison of the Measured Density at 298.15 ± 0.01 K of the Various Compounds with Their Corresponding Literature Values

compound	density, g mL^{-1} this work	density, g mL^{-1} lit.	reference
benzene	0.873 63	0.873 63	Nyvlt et al. (*6*)
toluene	0.862 26	0.862 32	Kyle et al. (*7*)
o-xylene	0.876 00	0.875 96	Forziati et al. (*8*)
m-xylene	0.859 85	0.859 90	Forziati et al. (*8*)
p-xylene	0.856 73	0.856 69	Forziati et al. (*8*)
o-chlorotoluene	1.076 44	1.076 40	Timmermans (*9*)

Toluene and *o*-, *m*-, and *p*-xylene were purified by shaking with concentrated sulfuric acid in a manner similar to that of benzene but keeping the temperaure below 30 °C. They were then distilled and finally dried over sodium wire.

o-Chlorotoluene "Baker" grade was distilled as such and stored.

The purity of the final compounds was checked by measuring their densities at 298.15 ± 0.01 K using the apparatus shown in Figure 1.

Procedure for Density Measurement. The apparatus consists of a small bulb A (capacity ≈ 30 mL) having a B-7 joint at its neck C, and a capillary tube B with a B-7 joint at one end and a B-10 joint at its other end was fixed in the neck C of the bottle A. The capillary tube B carried a reference mark D on its surface and was calibrated from the weight of an average length *l* of a column of mercury. The length *l* of the mercury column in the capillary B was read by a travelling microscope that could read to ±0.001 cm. The entire apparatus was first dried and weighed. The bulb A was first filled with double-distilled water and then the capillary B was inserted into the neck C. The apparatus was then suspended in a water bath maintained at 298.15 ± 0.001 K and the position of water level in the capillary B relative to the reference mark D was noted after thermal equilibrium by means of a cathetometer (OSQW, India) that could read to ±0.001 cm. The apparatus was taken out of the thermostat, dried, and weighed again on an analytical