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.

Literature Cited

(1) Aguirre-Ode, F. *J. Chem. Eng. Data* **1987**, *32*, 434.
(2) Aguirre-Ode, F., submitted for publication in *J. Chem. Eng. Data*.
(3) *Handbook of Chemistry and Physics*; The Chemical Rubber Co.: Cleveland, OH, 1973; p D-139.
(4) van Laar, J. J. *Z. Phys. Chem.* **1910**, *72*, 723.
(5) Wilson, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 127.
(6) Aguirre-Ode, F. *Scientia* **1977**, *42*(149), 25.
(7) Aguirre-Ode, F. *Scientia* **1979**, *44*(152), 19.
(8) Aguirre-Ode, F. *Fluid Phase Equilib.* **1988**, *30*, 315.
(9) Nath, A.; Bender, E. *Fluid Phase Equilib.* **1981**, *7*, 275.

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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

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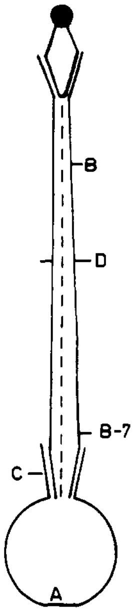

Figure 1. Apparatus for density measurement.

Table II. Measured Molar Excess Volumes, V^E_{ijk}, of the Various (i + j + k) Mixtures at 298.15 K

x_i	x_j	V^E_{ijk}, cm^3 mol^{-1}	x_i	x_j	V^E_{ijk}, cm^3 mol^{-1}
Benzene (i) + Toluene (j) + *o*-Chlorotoluene (k)					
0.0282	0.0776	0.005	0.3779	0.2348	0.161
0.0688	0.2838	0.024	0.5063	0.2935	0.086
0.0732	0.8647	0.011	0.6528	0.1727	0.144
0.1345	0.1365	0.057	0.7588	0.0666	0.122
0.1556	0.7329	0.018	0.9401	0.0494	0.018
0.3575	0.5321	−0.001			
Benzene (i) + *o*-Xylene (j) + *o*-Chlorotoluene (k)					
0.0691	0.1354	0.013	0.4108	0.2295	0.160
0.0789	0.0027	0.032	0.5314	0.1388	0.187
0.0955	0.8186	0.070	0.5742	0.2394	0.204
0.1655	0.2165	0.057	0.7831	0.1031	0.141
0.1791	0.1618	0.070	0.7973	0.0042	0.127
0.1924	0.7648	0.155	0.8133	0.0740	0.121
0.2039	0.6551	0.153	0.8333	0.0284	0.111
0.2563	0.6360	0.200	0.8937	0.0897	0.088
0.3065	0.3769	0.142			
Benzene (i) + *p*-Xylene (j) + *o*-Chlorotoluene (k)					
0.0504	0.0349	0.010	0.4786	0.714	0.166
0.0984	0.8605	0.040	0.5971	0.3669	0.188
0.1309	0.8890	0.043	0.6077	0.0048	0.179
0.2484	0.6099	0.107	0.6621	0.1172	0.158
0.3231	0.4934	0.117	0.8309	0.0353	0.108
0.3393	0.0714	0.134			
Toluene (i) + *o*-Xylene (j) + *o*-Chlorotoluene (k)					
0.0034	0.0469	−0.009	0.3222	0.0572	0.081
0.0045	0.0854	−0.011	0.3288	0.1456	0.079
0.0205	0.7995	−0.021	0.4755	0.1651	0.021
0.0296	0.6677	−0.040	0.5021	0.2446	−0.047
0.0329	0.9358	−0.001	0.5290	0.2743	−0.015
0.0609	0.0098	−0.010	0.6608	0.1304	−0.026
0.0765	0.1677	−0.031	0.6808	0.1733	−0.019
0.1247	0.2324	−0.042	0.6883	0.1787	−0.015
0.1452	0.1970	−0.028	0.9267	0.0711	0.010
0.1855	0.1671	−0.004			

Table III. Measured Molar Excess Enthalpies, H^E_{ijk}, of the Various (i + j + k) Mixtures at 298.15 K

x_i	x_j	H^E_{ijk}, J mol^{-1}	x_i	x_j	H^E_{ijk}, J mol^{-1}
Benzene (i) + Toluene (j) + *o*-Chlorotoluene (k)					
0.0369	0.8408	8.1	0.1894	0.1852	123.2
0.0397	0.9486	11.3	0.2195	0.0542	121.2
0.0663	0.7146	25.9	0.2743	0.6444	58.6
0.0756	0.6742	29.7	0.5303	0.3119	135.4
0.0770	0.9004	20.8	0.5615	0.2718	141.5
0.1143	0.5075	58.3	0.6363	0.1818	146.2
0.1514	0.3479	88.1	0.7083	0.0833	146.2
0.1636	0.2952	96.2	0.7582	0.0221	143.3
0.1642	0.7869	44.3			
Benzene (i) + *o*-Xylene (j) + *o*-Chlorotoluene (k)					
0.0499	0.9394	21.5	0.2108	0.0930	92.8
0.0941	0.8868	51.0	0.2210	0.0477	108.5
0.1225	0.4725	36.1	0.2905	0.6483	175.1
0.1568	0.3248	36.9	0.4727	0.4319	224.9
0.1586	0.3168	37.6	0.5970	0.2820	185.4
0.1702	0.7954	98.8	0.6353	0.2363	165.8
0.1891	0.1846	64.5	0.7124	0.1438	138.9
0.1942	0.1655	70.1	0.7985	0.0406	116.7
Benzene (i) + *p*-Xylene (j) + *o*-Chlorotoluene (k)					
0.0134	0.9463	4.8	0.2925	0.6447	114.1
0.0503	0.9388	8.0	0.3221	0.6086	131.1
0.0908	0.6447	18.2	0.4712	0.4274	166.6
0.0947	0.8848	14.8	0.5015	0.1466	208.9
0.1705	0.7928	62.7	0.6316	0.2328	167.2
0.1886	0.2618	92.1	0.7069	0.1411	151.1
0.2146	0.1616	111.3	0.7586	0.0784	107.9
0.2328	0.0907	121.5	0.7898	0.0402	126.0
0.2440	0.0464	124.3			
Toluene (i) + *o*-Xylene (j) + *o*-Chlorotoluene (k)					
0.0135	0.9502	−6.9	0.2194	0.1899	−18.8
0.0424	0.9475	2.5	0.2228	0.1777	−16.9
0.0471	0.8261	−18.9	0.2452	0.0957	−14.5
0.0574	0.7883	−22.1	0.2575	0.0491	−13.8
0.0805	0.9003	5.9	0.2659	0.0201	−13.9
0.0924	0.6570	−31.1	0.2925	0.6381	28.0
0.1324	0.5115	−32.0	0.4305	0.4675	435.7
0.1469	0.8181	12.9	0.5558	0.3125	31.0
0.1529	0.8108	13.4	0.5959	0.2628	26.8
0.1787	0.7789	17.4	0.6615	0.1816	7.0
0.1815	0.3322	−24.9	0.7708	0.0466	−2.8

balance (K. Roy, India) that could read to ±0.000 01 g. The apparatus was emptied, dried, and filled with the liquid under consideration. It was again placed in the thermostat and the position of the liquid level relative to the reference mark D on B was again noted. The density of the liquid was evaluated (*5*) from the weight of the liquid and of water (after applying buoyancy correction) occupying a volume V upto the reference mark D. The relevant density data are recorded in Table I.

Molar excess volumes V^E at 298.15 K for the ternary mixtures were determined in a specially designed three-limbed dilatometer in the manner described earlier (*10*). The temperature of the water bath was controlled to within ±0.01 K and the change of the liquid level in the dilatometer capillary was read with a cathetometer that could read to ±0.002 cm. The uncertainty in our measured V^E values is about 0.5%.

Molar excess enthalpies H^E for the present ternary mixtures were measured by an LKB flow microcalorimeter (LKB, Broma, Sweden) in the manner described by Monk and Wadso (*11*). For this purpose a binary mixture of known composition was fed into one end while the third pure component was introduced into the other end of the calorimeter. By use of 10-, 20-, and 50-cm^3 gas-tight Hamilton syringes and 10-speed gear boxes of two identical Braun Perfusor Pumps (B. Braun, Melsungen AG, W. Germany), different mixing ratios were achieved. The flow rates were determined by pumping distilled water through the calorimeter and weighing the amounts collected in a specific time interval. For each H^E_{ijk} measurement, different calibration constants were determined according to the flow rate, the amplification needed, and the composition of the mixture. The performance of the calorimeter was checked (*12*) by measuring H^E for benzene (i) + carbon tetrachloride (j) mixtures and these agreed (*12*) to within the experimental uncertainty with their corresponding literature values (*13*). The uncertainties in the present H^E_{ijk} data are about 1%.

Results

V^E_{ijk} and H^E_{ijk} data for the present ternary mixtures as a function of composition at 298.15 K are recorded in Tables II and III.

Discussion

A comparison of the V^E and H^E data at 298.15 K (*14*) for benzene + OCTE mixtures with the corresponding V^E_{ijk} and H^E_{ijk} data for benzene (i) + toluene or *o*-xylene or *p*-xylene (*j*) + OCTE mixtures, however, reveals that while the addition of toluene (j) to benzene + OCTE mixtures decreases both the V^E_{ijk} and H^E_{ijk} values for benzene (i) + toluene (j) + OCTE (k) mixtures, the addition of *o*-xylene (j) or *p*-xylene (j) to benzene + OCTE mixtures increases the V^E_{ijk} values but decreases the H^E_{ijk} values for the resulting (i + j + k) mixtures. On the other hand while the addition of *o*-xylene to toluene + OCTE mixtures increases the V^E_{ijk} values, it decreases the H^E_{ijk} values for the resulting (i + j + k) mixtures.

Registry No. Benzene, 71-43-2; toluene, 108-88-3; *o*-chlorotoluene, 95-49-8; *o*-xylene, 95-47-6; *p*-xylene, 106-42-3.

Literature Cited

(1) Mahl, B. S.; Bhardwaj, S. S.; Dhanda, S.; Kaur, S. *Thermochim. Acta* **1983**, *67*, 9.
(2) Singh, J.; Pflug, H. C.; Benson, G. C. *J. Phys. Chem.* **1968**, *72*, 1939.
(3) Otin, S.; Munoj, J.; Toledo, M. J.; Velasco, I.; Gutierrezosa, C. *J. Chem. Thermodyn.* **1985**, *17*, 419.
(4) Vogel, A. I. *A Text Book of Practical Organic Chemistry*; Longmans: London 1983; p 172.
(5) Weissberger, A. *Physical Methods of Organic Chemistry, Part I*; Interscience: 1965; p 148.
(6) Nyvlt, J.; Erdos, E. *Collect. Czech. Chem. Commun.* **1961**, *26*, 500.
(7) Kyle, B. G.; Reed, T. M. *J. Am. Chem. Soc.* **1958**, *80*, 6170.
(8) Forziati, A. F.; Rossini, F. D. *J. Res. Natl. Bur. Stand.* **1943**, *43*, 473.
(9) Timmermans, J. *Physico Chemical Constants of Pure Organic Compounds*; Elsevier: Amsterdam, 1950.
(10) Singh, P. P.; Sharma, S. P. *J. Chem. Eng. Data* **1985**, *30*, 477.
(11) Monk, P.; Wadso, I. *Acta Chem. Scand.* **1968**, *22*, 1842.
(12) Dahiya, H. P.; Singh, P. P.; Dagar, S. *Fluid Phase Equilib.* **1987**, *33*, 191.
(13) Stokes, R. H.; Marsh, K. N.; Tomlins, R. P. *J. Chem. Thermodyn.* **1969**, *1*, 211.
(14) Dahiya, H. P.; Dagar, S.; Singh, P. P. *J. Chem. Eng. Data* **1987**, *32*, 342.

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Mutual Diffusion Coefficients for Several Dilute Solutes in *n*-Octacosane and the Solvent Density at 371–534 K

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The Taylor dispersion technique was used to measure mutual diffusion coefficients at infinite dilution for six solutes (H_2, CO, CO_2, n-C_8H_{18}, n-$C_{12}H_{26}$, and n-$C_{16}H_{34}$) in liquid *n*-octacosane (n-$C_{28}H_{58}$) over the temperature range 371–534 K at 1.38 MPa pressure. The density of liquid *n*-octacosane was also measured at the same conditions. Using the rough hard-sphere theory, a correlation was developed which correctly represents the data.

Introduction

Mutual diffusion coefficients, density, and viscosity are the thermophysical properties needed to evaluate mass-transfer phenomena and to design equipment for mass-transfer operations. However, relatively few data are available for these properties at conditions far from ambient. At high temperatures, diffusion data are especially scarce for liquid solvents, and do not exist for high-boiling substances. Our objective has been to measure mutual diffusion, density, and viscosity in the homologous series of *n*-alkanes at conditions where data are not available. We have previously reported measurements in heptane, dodecane, hexadecane, and eicosane over a wide temperature range (*1–3*). This work extends our existing data base to include mutual diffusivity and density data for liquid *n*-octacosane.

Previous work (*1*, *2*) demonstrated that the diffusion coefficient was only weakly dependent on pressure over the modest pressure range of 0.10–3.40 MPa (15–500 psia). In most cases, the effect of pressure was within the error of the experiment. Since our equipment operated best near the middle of this pressure range, all data for this study were collected at 1.38 MPa (200 psia).

Experimental Techniques

Infinite dilution diffusion coefficients of three gaseous solutes (hydrogen, carbon monoxide, and carbon dioxide) and three *n*-alkane solutes (octane, dodecane, and hexadecane) in liquid *n*-octacosane were measured by using the Taylor dispersion technique (*4*, *5*). In this method, a narrow pulse of solute with mass *M*, diluted in the solvent, is injected into a tube in which the pure solvent is moving in slow laminar flow. The pulse quickly assumes a Gaussian distribution which is dependent on the average solvent velocity $\bar{u}$, residence time in the tube $\bar{t}$, tube radius *r*, and molecular diffusivity D_{12}. The concentration at the end of the diffusion tube, distance *L* from the injection point, is given by the following equations:

$$C = \frac{M}{\pi r^2 (4\pi K t)^{1/2}} \exp\left(\frac{-(L - \bar{u}t)^2}{4Kt}\right) \quad (1)$$

where

$$K = D_{12} + \frac{r^2 \bar{u}^2}{48 D_{12}} \quad (2)$$

Details of the Taylor dispersion apparatus used in our previous studies were given by Matthews and Akgerman (*6*). For this study, the original apparatus was modified extensively so that data could be collected in solvents which melt at temperatures well above ambient.

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