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Molar Excess Volumes of Ternary Mixtures of Nonelectrolytes at 308.15 K

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Molar excess volumes, V_m^E, for methylene bromide (i) + pyridine (j) + β-picoline (k), pyridine (i) + β-picoline (j) + cyclohexane (k), benzene (i) + toluene (j) + 1,2-dichloroethane (k), benzene (i) + *o*-xylene (j) + 1,2-dichloroethane (k), and benzene (i) + *p*-xylene (j) + 1,2-dichloroethane (k) have been measured dilatometrically at 308.15 K. The experimental results are positive over the whole range of composition for all the ternary mixtures.

Introduction

A binary (i + j) mixture is characterized by the replacement of the i–i and j–j contacts in the pure i and j components by the i–j contacts in the mixture. Since the interactions in a ternary (i + j + k) mixture are closely dependent on the interaction in the (i + j), (j + k), and (i + k) mixture, it would be interesting to study molar excess volumes of ternary (i + j + k) mixtures of nonelectrolytes. In this paper we report molar excess volumes for methylene bromide (i) + pyridine (j) + β-picoline (k), pyridine (i) + β-picoline (j) + cyclohexane (k), benzene (i) + toluene (j) + 1,2-dichloroethane (k), benzene (i) + *o*-xylene (j) + 1,2-dichloroethane (k), and benzene (i) + *p*-xylene (j) + 1,2-dichloroethane.

Experimental Section

Purification of Materials. Analytical grade benzene, toluene, pyridine, β-picoline, and methylene bromide were purified by standard procedures (*1a–e*). Cyclohexane was purified as suggested by Wood and Austin (*2*). *o*-Xylene, *p*-xylene, and 1,2-dichloroethane were purified by the method suggested by Nigam et al. (*3*). The purities of the final samples were checked by measuring their densities at 298.15 ± 0.01 K. These agreed to within ± 0.000 05 g cm^{-3} with the values reported in the literature (*4–9*) as is apparent from Table I.

Experimental Apparatus. Molar excess volumes for the various ternary mixtures were measured in a three-limbed specially designed dilatometer shown in Figure 1. The dilatometer consisted of two limbs having a vacuum tested B-7 standard joint at one end and two bulds B and C of different capacities (approximately 8 mL) at the other end. The two limbs were interconnected by a small bent tubing. A thin uniform bored capillary having a reference mark R on it was fused to the side of compartment A.

Experimental Procedure. A column of mercury (3–5 mL) was placed in the dilatometer and the dilatometer weighed. One of the degassed liquids, say i, was added to the bulb B with the help of a hypodermic syringe (having a 9 in. long needle at its end) in such a way that no air bubbles were entrapped in this bulb. The dilatometer was weighed again. The second degassed liquid (j) was similarly added to the bulb C with the help of another hypodermic syringe and the dilatometer weighed again. The third degassed liquid (k) was next added to side A and the stopper replaced in such a way that the liquid in the capillary was at a suitable position. The dilatometer was then placed in a water thermostat controlled to ±0.01 K by a mercury-in-toluene regulator. After thermal equilibrium, the reference mark and the position of the liquid in the capillary were noted with a cathetometer (OSAW, Ambala) that could read to ±0.001 cm. The contents of the dilatometer were then mixed by tilting it gently sideways several times. In order to ensure that the liquid in the capillary stem had the same composition as that of the bulk solution on mixing, the dilatometer (after mixing the components) was placed in a cold bath so that there was minimum liquid in the capillary and then again placed in the experimental water bath. This process was repeated three or four times. The position of the reference mark and that of the level of the liquid in the capillary was again noted after thermal equilibrium. The dilatometer was then taken out of the thermostat, dried completely, and weighed to determine the weight of the third liquid (k). The molar excess volumes of mixing, V_m^E, for the various ternary (i + j + k) mixtures were then calculated as explained elsewhere (*10*). By varying the amount of mercury in the dilatometer and also by adjusting its position in the bulbs, V_m^E values over the entire mole fraction range were obtained by a set of three dilatometers having different capacities of the three bulbs.

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

compd	density, g cm^{-3} present work	density, g cm^{-3} lit.	ref
methylene bromide	2.458 44	2.458 49	Timmerman (1950)
pyridine	0.977 8	0.978 2	Rochdestwensky et al. (1935)
β-picoline	0.952 31		
cyclohexane	0.773 89	0.773 89	Forziati et al. (1946)
toluene	0.862 24	0.862 20	Forziati et al. (1946)
o-xylene	0.875 88	0.875 83	Forziati et al. (1946)
benzene	0.873 66	0.873 70	Singh et al. (1968)
p-xylene	0.856 65	0.856 7	Williams and Krechma (1927)
1,2-dichloroethane	1.245 35	1.245 30	Coulson et al. (1948)

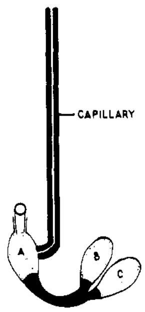

Figure 1. Dilatometer for molar excess volumes.

The radius of the capillary tube was determined from the weight of a length of mercury column in the capillary. The length of the mercury column at various positions in the capillary was read by a travelling microscope that could read to ±0.001 cm. The density of mercury was taken from the literature (*11*). From the average length, *l*, of the mercury column in the ca-

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Table II. Molar Excess Volumes for Ternary Systems (i + j + k) at 308.15 K

x_i	x_j	V_m^E, cm^3 mol^{-1}
Methylene bromide (i) + Pyridine (j) + β-Picoline (k)		
0.0658	0.4737	0.092
0.0679	0.8778	0.072
0.0696	0.7826	0.078
0.1222	0.1333	0.126
0.1725	0.5765	0.146
0.2391	0.0590	0.203
0.3111	0.3143	0.245
0.5560	0.2320	0.297
0.8021	0.0451	0.228
0.8782	0.0641	0.150
Pyridine (i) + β-Picoline (j) + Cyclohexane (k)		
0.0196	0.4216	0.655
0.0617	0.4026	0.654
0.0772	0.0695	0.470
0.1089	0.8119	0.153
0.1761	0.0998	0.626
0.2718	0.3240	0.570
0.2752	0.6744	0.108
0.3379	0.0685	0.611
0.5248	0.2562	0.358
0.6101	0.0688	0.433
0.7202	0.1842	0.172
0.8365	0.0881	0.131
Benzene (i) + Toluene (j) + 1,2-Dichloroethane (k)		
0.0895	0.1689	0.156
0.1805	0.5499	0.159
0.1814	0.1887	0.192
0.1834	0.2005	0.194
0.1933	0.6547	0.115
0.2007	0.5482	0.157
0.3506	0.4058	0.105
0.4541	0.3278	0.180
0.4917	0.0967	0.213
0.5025	0.1622	0.206
0.5098	0.3467	0.153
0.6108	0.1871	0.171
0.6141	0.1366	0.183
0.7186	0.1580	0.129
Benzene (i) + *o*-Xylene (j) + 1,2-Dichloroethane (k)		
0.1069	0.5618	0.292
0.1335	0.0868	0.198
0.1613	0.6392	0.257
0.1658	0.6808	0.229
0.2007	0.6420	0.252
0.2012	0.2204	0.310
0.2600	0.4421	0.333
0.3555	0.3781	0.343
0.3778	0.2982	0.338
0.4069	0.0507	0.249
0.4841	0.1814	0.309
0.6296	0.0848	0.248
0.7053	0.1474	0.229
0.7529	0.0852	0.194
Benzene (i) + *p*-xylene (j) + 1,2-Dichloroethane		
0.1150	0.4440	0.299
0.1261	0.1165	0.215
0.1606	0.6833	0.191
0.1811	0.1252	0.242
0.1940	0.5847	0.242
0.1964	0.6568	0.202
0.2018	0.1097	0.237
0.2812	0.5273	0.254
0.3684	0.1554	0.289
0.4142	0.2767	0.315
0.6648	0.1099	0.231
0.7117	0.1621	0.209

pillary and the volume of this mercury column, the cross-sectional area of the capillary was found to be (for a typical dilatometer) 21 × 10^{-4} mL cm^{-1}.

Results

Molar excess volumes, $V_m^E(T,x_i,x_j)$, for the various (i + j + k) mixtures as a function of composition at 308.15 K are recorded in Table II.

Discussion

The $V_m^E(T,x_i,x_j)$ data were fitted to the expression

$$V_m^E(T,x_i,x_j)/(\text{cm}^3\ \text{mol}^{-1}) = x_ix_j\Big[\sum_{n=0}^{2} A_{ij}^n(x_i - x_j)^n\Big] + x_jx_k\Big[\sum_{n=0}^{2} A_{jk}^n(x_j - x_k)^n\Big] + x_ix_k\Big[\sum_{n=0}^{2} A_{ik}^n(x_i - x_k)^n\Big] + x_ix_jx_k\Big[\sum_{n=0}^{2} A_{ijk}^n(x_j - x_k)^n x_i^n\Big] \quad (1)$$

and the parameters A_{ijk}^n (n = 0–2) of eq 1 were evaluated by fitting

$$\Big[V_m^E(T,x_i,x_j) - x_ix_j\Big(\sum_{n=0}^{2}(x_i - x_j)^n A_{ij}^n\Big) - x_jx_k\Big(\sum_{n=0}^{2}(x_j - x_k)^n A_{jk}^n\Big) - x_ix_k\Big(\sum_{n=0}^{2}(x_i - x_k)^n A_{ik}^n\Big)\Big]/(x_ix_jx_k)$$

to

$$[A_{ijk}^0 + A_{ijk}^1\,(x_j - x_k)x_i + A_{ijk}^2\,(x_j - x_k)^2x_i^2] \quad (2)$$

by the method of least squares. These parameters along with the standard deviations, $\sigma(V_m^E)$, of $V_m^E(T,x_i,x_j)$ defined by

$$\sigma(V_m^E) = [\textstyle\sum(V_m^E(T,x_i,x_j)_{\text{exptl}} - V_m^E(T,x_i,x_j)_{\text{calcd,eq1}})^2/(P - Q)]^{0.5}$$

where P is the number of data points and Q is the number of adjustable parameters in eq 1, are recorded in Table III. (All the data points were equally weighted in least-squares fit).

The A_{ijk}^n and A_{ij}^n (n = 0, 2) parameters along with their standard deviations for the various mixtures are recorded in Table II. The A_{ij}^n (n = 0–2), etc., parameters of various binary mixtures were taken from the literature (*3*, *12*). The uncertainties in V_m^E values due to uncertainties in the A_{ij}^n, etc., parameters of the (i + j), etc., mixtures is about ±0.0003 cm^3 mol^{-1} at the worst. It is thus apparent that the present $V_m^E(T,x_i,x_j)$ data could not be expressed (*13*) by the expression

$$V_m^E(T,x_i,x_j) = \sum_{i<j} V_m^E(T,x_i) \quad (3)$$

where $V_m^E(T,x_i)$ are expressed by

$$V_m^E(T,x_i) = x_ix_j\Big[\sum_{n=0}^{2} A_{ij}^n\,(x_i - x_j)^n\Big] \quad (4)$$

Expression 3 is based on the assumption that the $V_m^E(T,x_i,x_j)$ data for a ternary mixture may be expressed (*13*) by

$$V_m^E(T,x_i,x_j) = \sum_{i<j}(x_ix_j/x_i^1x_j^1)V_m^E(T,x_i^1) \quad (5)$$

where x_i, x_j, etc., are the mole fractions of i and j components in the (i + j + k) mixture, x_i^1, x_j^1 are such that $x_i^1 + x_j^1 = 1$ and $V_{ij}^E\,(x_i^1)$ is the molar excess volume for the binary (i + j) mixture at (x_i^1). (In this scheme although the mole fractions x_i^1 and x_j^1 for a ternary mixture may be obtained from a triangular diagram by projecting points representing the ternary mixture on to the corresponding binary axis by various kinds of projections, we have used the normal projections where x_i^1 and x_j^1 are defined by $x_i^1 = {}^1/_2(1 + x_i - x_j)$ and $x_j^1 = {}^1/_2(1 + x_j - x_i)$).

From Table III, it is evident that whereas the introduction of the k moieties to the (i + j) binary mixture decreases the molar

Table III. Values of Constants A_{ijk}^0, A_{ijk}^1, and A_{ijk}^2 and $\sigma(V_m^E)$ at 308.15 K

system	A_{ijk}^0, cm^3 mol^{-1}	A_{ijk}^1, cm^3 mol^{-1}	A_{ijk}^2, cm^3 mol^{-1}	$\sigma(V_m^E)$, cm^3 mol^{-1}
methylene bromide (i) + pyridine (j) + β-picoline (k)	−1.388 (±0.1870)	−7.038 (±0.3639)	−82.541 (±13.3)	0.001
pyridine (i) + β-picoline (j) + cyclohexane (k)	−1.405 (±0.0848)	6.0 (±0.29)	−69.327 (±7.56)	0.001
benzene (i) + toluene (j) + 1,2-dichloroethane (k)	−0.344 (±0.04)	0.562 (±0.04)	−5.991 (±0.5)	0.001
benzene (i) + o-xylene (j) + 1,2-dichloroethane (k)	0.008 (±0.0002)	2.83 (±0.1)	18.137 (±6.2)	0.002
benzene (i) + p-xylene (j) + 1,2-dichloroethane (k)	0.364 (±0.02)	−1.77 (±0.1)	−40.892 (±5.0)	0.002
methylene bromide (i) + pyridine (j)	1.22 (±0.0023)	0.09 (±0.0088)	0.038 (±0.0125)	0.002
methylene bromide (i) + β-picoline (j)	1.3 (±0.0052)	2.69 (±0.0004)	0.138 (±0.0432)	0.002
pyridine (i) + β-picoline (j)	0.017 (±0.0009)	−0.018 (±0.0042)	−0.076 (±0.0129)	0.001
pyridine (i) + cyclohexane (k)	2.36 (±0.0003)	−0.92 (±0.0004)	0.281 (±0.016)	0.002
β-picoline (j) + cyclohexane (k)	2.44 (±0.002)	−1.518 (±0.0112)	1.342 (±0.0084)	0.003

[a] For (i + j), etc.; mixtures A_{ijk}^0 denotes A_{ij}, $A_{ijk}^1 = A_{ij}^1$ and $A_{ijk}^2 = A_{ij}^2$, etc. [b] A_{ij}^n, etc., constants of the (i + j), etc., binary mixtures along with their standard deviations are recorded.

excess volumes for methylene bromide (i) + pyridine (j) + β-picoline (k) and pyridine (i) + β-picoline (j) + cyclohexane (k) ternary mixtures, it increases the molar excess volumes for benzene (i) + toluene (j) + 1,2-dichloroethane (k), benzene (i) + o-xylene (j) + 1,2-dichloroethane (k) and benzene (i) + p-xylene (j) + 1,2-dichloroethane (k) mixtures.

Glossary

x_i, etc.	mole fraction of i, etc.
$V_m^E(T, x_i, x_j)$	molar excess volumes for ternary (i + j + k) mixture
A_{ijk}^n (n = 0–2)	constants in eq 1
A_{ij}^n (n = 0–2)	constants in eq 1 for (i + j) etc. mixtures.

Registry No. Pyridine, 110-86-1; β-picoline, 108-99-6; cyclohexane, 110-82-7; benzene, 71-43-2; toluene, 108-88-3; 1,2-dichloromethane, 107-06-2; o-xylene, 95-47-6; p-xylene, 106-42-3.

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Viscosity Studies of Water–Acetamide–Potassium Nitrate Ternary System at Different Temperatures

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Viscosities of KNO_3 solutions in water–acetamide mixed solvents were measured within the temperature range 25–85 °C. The values of relative viscosity and coefficient *B* of the viscosity equation of investigated systems were calculated. The effect of KNO_3 and temperature on the structure of the investigated systems has been discussed.

While ion–solvent interactions have been studied in detail in aqueous solutions, less consideration has been given to such effects in nonaqueous solvents but investigations in mixed solvents are scanty. The variation of viscosity with temperature and solvent composition has been employed to study the ion–solvent interaction by many workers (*1*) both in aqueous and nonaqueous solutions. Although it is difficult to obtain information concerning the structural effects from the absolute magnitude of the viscosity, it is possible to obtain more information from the temperature dependence because the structural effects involving hydrogen bonding are relatively weak.

The relative viscosity η_r of a solution can be expressed by the Jones–Dole (*2*) equation

$$\eta_r = \eta/\eta_0 = 1 + Ac^{1/2} + Bc \qquad (1)$$

where η and η_0 are the viscosity of the solution and solvent, respectively, and *A* and *B* are constants depending on solute, solvent, temperature, and pressure.

The coefficient *A* is determined by ion-atmosphere interaction and ionic mobilities. The second parameter *B* in eq 1 has been related to the solute–solvent interaction and it shows strong temperature dependence in water. In a previous paper