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Topological studies of molecular interactions of 1,4-dioxane with formamides or anilines at 308.15 K

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ABSTRACT

Molar excess volumes have been measured for 1,4-dioxane (A) + formamide, or N,N-dimethylformamide, aniline, N,N-dimethylaniline (B) mixtures at 308.15 K. For an equimolar A + B mixture, molar excess volumes follow the sequence: aniline<formamide<N,N-dimethylformamide<N,N-dimethylaniline. The excess volume data have also been rationalized by graph-theoretical arguments. This analysis has further yielded information about the state of association in aniline, formamide and N,N-dimethylformamide that is consistent with the existing views on their nature of association. The existence of molecular entities in these mixtures has also been supported by their infrared spectral studies.

1. Introduction

Considerable controversy surrounds the state of pure aniline. Thus while Bellamy and Williams [1] maintain that aniline in the pure state exists as monomers, Wolf and Mathias [2] as also Kreglewski and Wilhoit [3] favor the associated structures in which one of the hydrogen atom of its NH_2 group is free to form H-bond and the other hydrogen atom is involved in weak interactions with the π-cloud of another aniline molecule. Further in view of the two well known resonance structures [4] of the amide group, the lower amides in pure state may exist like alkanols [5,6], as dimers and higher r-mers, though Davies [7] favor dimeric state for them in solution. The addition of 1,4-dioxane (A) to either aniline or formamide (B) thus provide an ideal situation of H-bonded interaction resulting in the formation of various molecular entities. Although such a situation can be handled by the Ideal association model approach [8,9] yet the result would be strongly dependent on the particular type of model assumed for A and/or B. This calls for an entirely different approach. Since A + B mixture is formed by the replacement of like contacts in the pure state by unlike contact in the mixture and as the formations of molecular entities in the present (A + B) mixtures may be visualized [10] to be due to the changes in the topology of A brought on by B, it appears that a recent Graph theoretical approach [11–13] should not only provide valuable information about the state of A and/or B in an (A + B) mixture but should also be in a position to explain as to why only certain characteristic infra-red absorptions in A and/or B are influenced in the process of mixture formation. This prompted us to perform molar excess volume studies at 308.15 K for 1,4-dioxane (A) + aniline or formamide or N,N-dimethylaniline (DMF) or N,N-dimethylformamide (B) mixtures.

2. Experimental section

Aniline, formamide, N,N-dimethylaniline (DMA), N,N-dimethylformamide (DMF), 1,4-dioxane (Merck or Sigma) were purified by standard procedures [14,15]. The purities of the purified samples were checked by measuring their densities and refractive indices at 298.15 K and 308.15 K. The densities were measured with a precision of $\pm 5 \times 10^{-5}$ g cm^{-3} by a specially designed densimeter, consisting of a bulb of approximate volume 35 cm^3 attached to a calibrated capillary through a B-10 standard joint in the manner described by Weissenberger [16]. Air buoyancy correction was also applied to achieve a greater accuracy. Refractive indices were measured with a thermostatically controlled Abbe refractometer (OSAW, India) using sodium D-line with an accuracy of ±0.0001. Our experimental values for the densities and refractive indices of the pure compounds compared well with the literature values as shown in Table 1. Molar

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Table 1
Measured densities (ρ) and refractive indices (n_D) of the pure components at 298.15 and 308.15 K.

Compound	Temperature K	ρ/(g cm^{-3})		n_D	
		Exptl.	Lit. [Ref.]	Exptl.	Lit. [Ref.]
1,4-Dioxane	298.15 K	1.02791	1.02797 [17]	1.4204	1.42025 [17]
			1.02787 [18]		1.419948 [18]
			1.0286 [19]		1.4203 [19]
	308.15	1.0173	1.0172 [19]	1.4146	1.4145 [19]
Formamide	298.15	1.12884	1.12878 [20]	1.4461	1.44597 [21]
			1.1291 [21]		
	308.15	1.11986	1.11984 [20]	1.4425	1.44258 [21]
			1.1202 [21]		
N,N-DMF	298.15	0.94385	0.94387 [17]	1.4282	1.42817 [17]
			0.9439 [22]		
			0.94385 [23]		1.4282 [22]
			0.94394 [20]		
	308.15	0.93466	0.93464 [20]	1.4305[a]	1.43047 [17]
Aniline	298.15	1.01755	1.01750 [17]	1.5836	1.58364 [17]
			1.0176 [24]		1.5836 [24]
	308.15	1.00860	1.00862 [17]	1.5784	1.57836 [17]
N,N-DMA	298.15	0.95235	0.95232 [25]	1.5565	1.55661 [25]
	308.15	0.94391	0.94393 [25]	1.5520	1.55157 [25]

[a] At 293.15 K

excess volumes, V^E, for the binary mixtures have been measured by V-shaped dilatometer at 308.15 K in the manner described elsewhere [26]. The temperature of water thermostat was controlled to ±0.01 K by a mercury-in-toluene regulator. The change in the position of the liquid level in the capillary was noted with a cathetometer (OSAW, Ambala) that could read to ±0.001 cm. The performance of dilatometer was checked by measuring the molar excess volume of the benzene + cyclohexane mixture at 298.15 K and these agreed to within the experimental limits with corresponding literature values [27]. The uncertainty in the measured V^E values was ±1%.

Table 2
Measured excess molar volume for binary mixtures of butyl chloride (BC)(A) + aromatics hydrocarbon (B) at 308.15 K.

x_A	V^E / cm^3 mol^{-1}	x_A	V^E / cm^3 mol^{-1}	x_A	V^E / cm^3 mol^{-1}	x_A	V^E / cm^3 mol^{-1}
1,4-Dioxane (A) + Aniline (B)							
0.0527	−0.108	0.2927	−0.491	0.5021	−0.578	0.7520	−0.396
0.0950	−0.193	0.3514	−0.548	0.5576	−0.550	0.8013	−0.332
0.1437	−0.285	0.3895	−0.567	0.6059	−0.530	0.8316	−0.295
0.1905	−0.360	0.4392	−0.574	0.6491	−0.495	0.9027	−0.186
0.2412	−0.434	0.4617	−0.574	0.6988	−0.45		
1,4-Dioxane (A) + N,N-Dimethylaniline (B)							
0.0509	0.015	0.3009	0.105	0.5605	0.163	0.7951	0.120
0.1121	0.035	0.3429	0.120	0.5902	0.163	0.8532	0.095
0.1551	0.050	0.3982	0.140	0.6421	0.160	0.8977	0.070
0.2082	0.070	0.4575	0.155	0.6954	0.150		
0.2603	0.090	0.4991	0.160	0.7526	0.135		
1,4-Dioxane (A) + Formamide (B)							
0.0491	−0.088	0.3124	−0.376	0.5422	−0.425	0.7929	−0.278
0.1123	−0.180	0.3533	−0.395	0.5891	−0.418	0.8603	−0.210
0.1611	−0.242	0.4015	−0.412	0.6235	−0.410	0.8931	−0.164
0.2151	−0.302	0.4597	−0.425	0.6709	−0.381		
0.2702	−0.350	0.5059	−0.427	0.7356	−0.338		
1,4-Dioxane (A) + N,N-Dimethylformamide (B)							
0.0412	−0.010	0.3149	0.010	0.5026	0.037	0.8119	0.029
0.1029	−0.018	0.3421	0.016	0.5569	0.042	0.8752	0.023
0.1592	−0.015	0.3701	0.021	0.6209	0.040	0.9389	0.010
0.2201	−0.007	0.4215	0.028	0.6751	0.042		
0.2715	0.003	0.4628	0.032	0.7595	0.036		

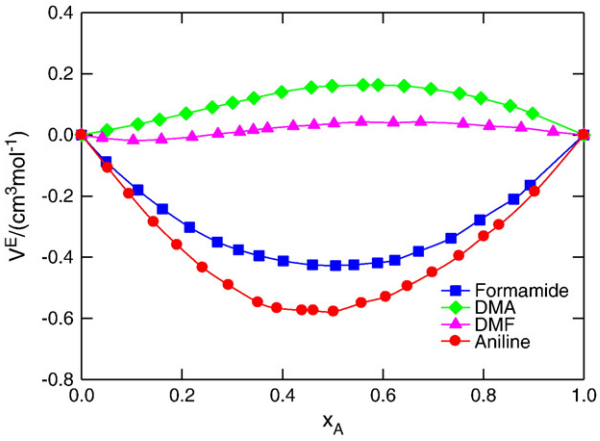

Fig. 1. Molar excess volume (V^E) of 1,4-dioxane(A) + B mixtures as a function of mole fraction (x_A) of 1,4-dioxane at 308.15 K; symbols represent experimental value and lines represent value calculated from Eq. (1).

3. Results

The measured V^E data for the present binary mixtures at 308.15 K were recorded in Table 2 and shown graphically in Fig. 1 and were fitted to the following Redlich and Kister equation

$$V^E / \mathrm{cm^3 mol^{-1}} = x_A(1-x_A)\left[\sum_{n=0}^{3} V_n(2x_A-1)^n\right] \quad (1)$$

where V_n are the adjustable parameters, and x_A is the mole fraction of 1,4-dioxane (A) in (A + B) mixture. These parameters were evaluated by fitting V^Edata to Eq. (1) by the least squares method and recorded in Table 3 with the standard deviations of V^E, ($\sigma(V^E)$), given as

$$\sigma\left(V^E\right) / \mathrm{cm^3 mol^{-1}} = \left\{\left[\sum\left(V^E_{\mathrm{expt.}} - V^E_{calcd\ \ Eq.(1)}\right)\right] / (m-n)\right\}^{1/2} \quad (2)$$

where m is the number of experimental values, and n is the number of adjustable parameters in Eq. (2). The choice of n to have 0–3 values was dictated by the consideration that the maximum deviation σ_m (V^E) of V^E (as calculated from Eq. (1) from the corresponding experimental V^E values) satisfied the relation $\sigma_m(V^E) \leq 2\sigma(V^E)$.

4. Discussion

We are unaware of any V^E data of the present mixtures with which to compare our results. It is, however, interesting to note that while V^E data for 1,4-dioxane (A) + aniline or formamide (B) are negative, large and almost symmetrical about $x_A = 0.5$, those of 1,4-dioxane (A) + DMA or DMF (B) are small and positive, V^E data for 1,4-dioxane + DMF mixtures also change sign with x_A; with $V^E_{\max} = 0.041 \mathrm{cm^3 mol^{-1}}$ at $x_A = 0.6$ and $V^E_{\min} = -0.017 \mathrm{cm^3 mol^{-1}}$ at $x_A = 0.11$. For an equimolar A + B mixture, V^E follow the sequence: aniline < formamide < DMF < DMA (Fig. 1).

The V^E data for 1,4-dioxane + aniline or DMA mixtures suggest that either one or both the hydrogen atoms of the NH_2 group of aniline

Table 3
Adjustable parameters of Eq. (1) and standard deviation (σ).

System	V_0	V_1	V_2	V_3	$\sigma \cdot 10^3$
1,4-Dioxane (A) + Aniline (B)	−2.2963	0.3979	0.1897	−0.495	3.3
1,4-Dioxane (A) + N,N-Dimethylaniline (B)	0.6327	0.2582	−0.1353	0.0121	1.7
1,4-Dioxane (A) + Formamide (B)	−1.7262	0.0052	−0.0872	0.0915	3.4
1,4-Dioxane (A) + N,N-Dimethylformamide (B)	0.1458	0.1693	−0.2153	0.118	1.2