Densities and Excess Molar Volumes of Binary and Ternary Mixtures of Ethanol, 2, Haloethanols and Triethylamine in Carbontetrachloride and Cyclohexane

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Sumary: Densities were determined for the binary and ternary mixture of the alcohols and triethylamine in CCl_4 and cyclo-C_6H_{12} at 298 K. From the experimental results, the excess molar volume (V_M^E) were calculated. V_M^E are positive for binary mixtures of the alcohols in both, CCl_4 and cyclo-C_6H_{12}. But for ternary mixture (in CCl_4), the excess molar volumes are negative in the low concentration range of the alcohols. The difference has been explained in terms of interstitial accomodation of the solvent and possible H-bond interaction of the type OH...Cl between the components of the system. Besides, positive excess molar volumes are higher for 2-haloethanols than those for ethanol. These high values have been attributed to the substitution of hydrogen atom by halogen atoms.

Introduction

Density and viscosity data are of increasing interest as they are the basis of structural studies of liquid mixture. Measurement of volumes and viscosities of various systems have suggested that geometrical effects and intermolecular interactions such as H- bonding affect the properties of the mixture [1]. Excess volumes for the binary mixtures of 1,2-dichloroethane with alkanes [2], alcohols [3], Ketones [4] and 1,2-dibromoethane with acids [5], and alcohols have been reported earlier. Quite recently R. Palepu and his co-workers [7] have determined the excess molar volumes and viscosities of binary mixtures of anilines and substituted anilines with phenols, substituted phenols and 2,2,2- trichloroethanol. On the basis of composition at maxima of the curve for excess volume, F. Kohler and his associates [8] suggested the formation of strongly polar 3:1 complexes between carboxylic acids (acetic, proponic and trimethyl acetic) and trimethylamine. Besides, they also have discussed the formation of 1:1 complexes. In this paper we report the measurement of densities and excess molar volumes of the binary and ternary mixtures of ethanol, 2-haloethanols and triethylamine in carbonatetrachloride and cyclohexane at 298 K.

Discussion

Binary system

It was difficult to obtain density of Br-ethanol in cyclohexane and that of I-ethanol in CCl_4 due to solubility problem of these compounds in the respective solvents. The curves in Fig. 1 show that V_M^E is positive over the entire range of composition in all the five binary mixtures. The values show gradual increase from F-ethanol to I-ethanol with the increase in concentration of the alcohol in cyclohexane. But in case of ethanol, excess molar volumes are smaller and decrease towards the region rich in alcohol. The difference in the V_M^E data for solutions having ethanol and 2, haloethanols may be attributed to the substitution of hydrogen atom by the halogen atoms.

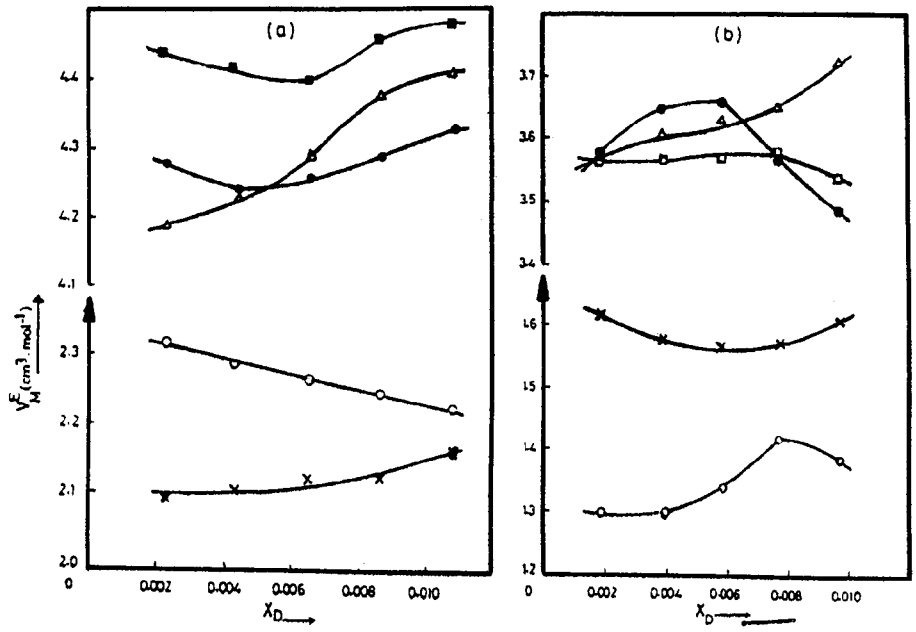

Fig. 1: Variation of excess molar volume, V_M^E for binary mixture of ethanol (o), F-ethanol (●), Cl-ethanol (Δ) Br- ethanol (□) I-ethanol (■) and TEA (x) at 298 K (a) cyclohexane (b) CCl_4

However, there is an inversion of the trend of V_M^E values for all the mixtures in CCl_4 Fig. 1b. Here V_M^E vary in the order F- ethanol <Cl-ethanol < Br-ethanol < TEA < ethanol, in the region of 0.006 mole fraction.

It is apparent from data that TEA behaves differently as compared to the other compounds. In CCl_4, V_M^E for TEA are higher than those of ethanol. These high values are indicative of the TEA- CCl_4 interactions [10-12].

In the literature positive excess volumes have been attributed to a loose liquid structure which may be due to the breaking of the H-bond in the pure components [3,13]. According to Naidu [3] and Venkateswarlu [6] the values of V_M^E may be explained in terms of different factors; (i) dissociation of self associated alcohols, (ii) decrease in dipolar association of the components (iii) difference in size and shape of the components (iv) interstitial accommodation of the solvent in H-bonded aggregatges of alcohols and (v) possible H-bond interaction of the type -N--OH in the mixture having TEA as a base. The first two factors contribute to expansion in volume, while the remaining two factors may lead to contraction in volume. The actual values of V_M^E would depend upon the balance between the two apposing contributions. The experimental values indicate that the factors responsible for expansion in volume are dominent in all the mixtures.

Ternary system

Examination of Fig. 2b shows that the values of V_M^E for ternary systems are negative in the low concentration range ($X_{Alcohol}$ = 0.06) and become positive at higher mole fraction of the alcohol in CCl_4. But for mixture of alcohol and TEA in cyclohexane (Fig. 2a) excess molar volumes remain positive in the entire range of the composition. The negative values of VM^E may be attributed to the strong effects, these components have on each other's structure [13]. Negative excess volumes for binary mixtures of 1- chlorobutane with 1-pentanol, 1-bexanol, 1-heptanol and 1-octanol at 303.15 K have been reported by Krishnaiah and Naidu [2]. They attributed this to the factors responsible for the contraction of the volume; while Palepu and his co-workers [7] explained the minimum values of V_M^E in terms of acid-base interactions between m-cresol and anilines.

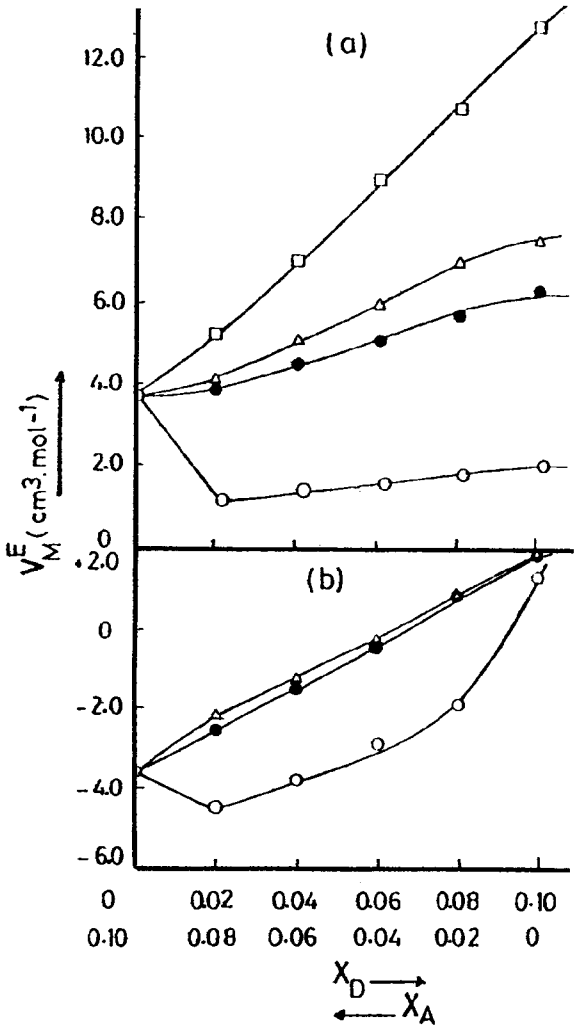

Fig. 2: Excess molar volumes, V_M^E for ternary mixture of TEA and Ethanol (O), F-ethanol (●), Cl-ethanol (Δ), Br-ethanol (▲) in (a) cyclohexane, (b) CCl_4.

In the present study positive values of V_M^E for mixture of 2, haloethenols with TEA suggests that interactions between alcohols and TEA in cyclohexane are responsible for expansion in the volume, while for the mixture in CCl_4 the factors contributing to contraction in volume are dominent at low concentrations of alcohols.

Experimental

Carbon tetrachloride and cyclohexane were purified by standard method [9]. Alcohols and triethylamine were dried over activated molecular sieves (4A). Densities of the solutions were determined with glass pycnometer of 5.0 ml capacity. Pycnometer was calibrated with distilled water. It was filled with solution by suspending it in a water bath. The temperature of the bath was maintained at 298 ± 0.1 K. Once the pyconomter was filled up to the mark, the capillary tips of the pycnometer were closed with stopper to avoid evaporation loss. Weighings were made to ± 0.1 mg.

Each density (Tables 1,2) is the average of three values. Density data which are close to ± 0.0003 g cm^{-1} were converted into molar volumes using the relationship:

$$V_M = (X_1M_1 + X_2M_2)/\rho$$

where X_1 and X_2 are the mole fractions of solvent and solute respectively M_1 and M_2 are the corresponding molecular weight and p is the density of the solution.

Excess molar volume (V^E_M) was calculated by using the euqation

Table 1: Denisities, ρ (g cm^{-3}) and excess molar volumes, V_M^E (cm^3 mol^{-1}) for binary solution of alcohols in (a) cyclohexane (b) CCl_4 at 298 K.

Alcohol	Ethanol		F-ethanol		Cl-ethanol		Br-ethanol		I-ethanol	
	ρ	V_M^E	ρ	V_M^E	ρ	V_M^E	ρ	V_M^E	ρ	V_M^E
			(a) Cyclohexane							
0.0022	0.7636	2.3200	0.7506	4.2775	0.7514	4.1862	0.7505	4.4418	0.7504	4.3298
0.0043	0.7638	2.2939	0.7512	4.2364	0.7516	4.2306	0.7519	4.4227	0.7509	4.3460
0.0065	0.7639	2.2679	0.7514	4.2615	0.7518	4.2850	0.7534	4.4044	0.7516	4.3106
0.0086	0.7641	2.2505	0.7515	4.2890	0.7516	4.3840	0.7543	4.4552	0.7524	4.2865
0.0108	0.7642	2.2304	0.7516	4.3300	0.7520	4.4087	0.7555	4.4819	0.7529	4.2810
				(b) CCl_4						
0.0019	1.5681	1.2968	1.5327	3.5837	1.5329	3.5699	1.5336	3.5714	1.5340	3.5912
0.0039	1.5670	1.3042	1.5311	3.6491	1.5319	3.6057	1.5340	3.6554	1.5345	3.6270
0.0058	1.5659	1.3157	1.5309	3.6576	1.5310	3.6266	1.5340	3.5749	1.5351	3.6431
0.0077	1.5632	1.4248	1.5304	3.5678	1.5300	3.6540	1.5341	3.5778	1.5367	3.5931
0.0097	1.5629	1.3855	1.5305	3.4892	1.5286	3.7151	1.5355	3.5391	1.5387	3.5320

Table 2: Denisities, ρ (g cm^{-3}) and excess molar volumes V_M^E (cm^3mol^{-1}) for tenary mixtures of alcohols (D) and triethylamine (A) in (a) cyclohexane (b) CCl_4 at 298 K

(a)	X_o	X_A	Ethanol ρ	Ethanol V_M^E	F-ethanol ρ	F-ethanol V_M^E	Cl-ethanol ρ	Cl-ethanol V_M^E	Br-ethanol ρ	Br-ethanol V_M^E
						(a) cyclohexane				
	0.00	0.10	0.7503	3.3772	0.7503	3.3772	0.7504	3.3770	0.7504	3.3770
	0.02	0.08	0.7640	1.5289	0.7502	4.0492	0.7503	4.2904	0.7506	5.3429
	0.04	0.06	0.7640	1.7088	0.7506	4.6307	0.7499	5.2487	0.7523	7.0878
	0.06	0.04	0.7642	1.8637	0.7514	5.1539	0.7506	6.0410	0.7530	0.9795
	0.08	0.02	0.7644	2.0156	0.7515	5.7821	0.7497	7.0738	0.7539	10.8239
	0.10	0.00	0.7642	2.2266	0.7516	6.4109	0.7525	7.5554	0.7532	12.9465
(b)	X_o	X_A	Ethanol ρ	Ethanol V_M^E	F-ethanol ρ	F-ethanol V_M^E	Cl-ethanol ρ	Cl-ethanol V_M^E	Br-ethanol ρ	Br-ethanol V_M^E
						(b) CCl_4				
	0.00	0.10	1.5233	-3.4783	1.5233	-3.4783	1.5233	-3.4783	1.5233	-3.4783
	0.02	0.08	1.5538	-4.4761	1.5258	-2.4937	1.5203	-2.1086	1.5270	-1.5495
	0.04	0.06	1.5554	-3.6569	1.5262	-1.3744	1.5245	-1.1996	1.5300	+0.4212
	0.06	0.04	1.5560	-2.7796	1.5275	-0.3114	1.5270	-0.1801	1.5314	+2.4934
	0.08	0.02	1.5564	-1.8843	1.5285	+0.7713	1.5273	+0.6710	1.5347	+4.4394
	0.10	0.00	1.5629	-1.3503	15305	+1.7124	1.5286	+1.8505	1.5387	+6.3362

$$(V_M^E) = V_M(\text{exp}) - V_M(\text{calc}) \quad (2)$$

where $V_M(\text{exp}) = (X_1M_1 + X_2M_2)/\pi$

and $V_M(\text{calc}) = X_{11}/\pi_1 + X_2M_2/\rho_2$

Where ρ_1 and π_2 are the densities of the pure components. V_M^E obtained for binary and ternary mixture were plotted against mole fraction of the solute (Fig. 2).

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