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Studies of partial molar volumes of alkylamine in non-electrolyte solvents III: Alkyl amines in butanols at 303.15 K

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ABSTRACT

Apparent molar volumes $V_{\phi,B}$ of *n*-propylamine, *n*-butylamine, di-*n*-propylamine, di-*n*-butylamine, triethylamine, tri-*n*-propylamine, and tri-*n*-butylamine in 1-butanol and 2-butanol at 303.15 K have been determined with high precision vibrating tube Anton Paar densimeter (model DMA 60/602). From these data limiting partial molar volumes V_B^{∞} and limiting excess partial molar volumes $\bar{V}_B^{E,\infty}$ were estimated. The results are analysed and interpreted in terms of solute–solvent interactions and structural effects of the molecules. An attempt to find a measure of the contribution of the specific interactions to the partial molar volumes of primary, secondary and tertiary amines in 1-butanol and 2-butanol was made using Terasawa model, hard-sphere theory (HST) and scaled particle theory (SPT). The ERAS model has also been applied to estimate apparent molar volumes, and excess apparent molar volumes of alkylamine solutions in 1-butanol and 2-butanol. The results agree well in the different approaches used.

1. Introduction

Partial molar properties of dilute solutions provide information about the molecular interactions between solute–solute and solute–solvent interactions, and can be used for the development of molecular models for describing the thermodynamic behaviour of solutions. This laboratory is engaged in systematic investigations of thermodynamic and transport properties of solutions involving important organic bases: primary, secondary and tertiary alkylamines in polar and non-polar solvents [1–10]. It is well known, that mixtures containing associating components like alkanols and amines are highly non-ideal systems [11–16]. Due to the formation of hydrogen bonds between the different species large negative heat as well as volumetric effects is observed upon mixing. As the partial molar volumes depend upon molecular size, shape, and interaction of different components, it is of interest and significance, to study the partial molar volumes of alkylamines in different types of solvents to extract information on specific interactions, conformational effects, and packing efficiencies [17–22].

In previous papers [23,24] apparent molar volumes of dilute solutions of *n*-propylamine ($C_3H_7NH_2$), *n*-butylamine ($C_4H_9NH_2$), di-*n*-propylamine ($(C_3H_7)_2NH$), di-*n*-butylamine ($(C_4H_9)_2NH$), tri-*n*-propylamine ($(C_3H_7)_3N$), and tri-*n*-butylamine ($(C_4H_9)_3N$) in cyclohexane, benzene, tetrachloromethane, and trichloromethane, and of triethylamine $(C_2H_5)_3N$ in cyclohexane and benzene at 303.15 and 313.15 K have been reported. In this work we extend our studies to volumetric properties of dilute solutions of same alkylamines in 1-butanol and 2-butanol.

The contribution to partial molar volumes of the methyl, methylene, and primary, secondary, and tertiary amine groups in 1-butanol and 2-butanol solutions has been calculated using simple additive schemes at 303.15 K [25,26]. The contributions of the specific interactions to the limiting partial molar volumes of presently investigated amines in 1- and 2-butanols were then calculated using Terasawa model [17], scaled particle theory [27], and hard-sphere theory [28]. The ERAS model [29–31] has also been applied to estimate apparent molar volumes, excess apparent molar volumes and limiting values of partial molar volumes and excess partial molar volumes of mono-, di- and tri-*n*-alkylamines in 1-butanol and 2-butanol solutions.

2. Experimental

2.1. Method

Densities at 303.15 K were measured with Anton Paar densimeter (model DMA 60/602) with thermostatted bath controlled to ±0.01 K. The details of the method and technique used to determine densities have been described previously [1,23].

All the solutions were prepared by mixing known masses of pure liquids in air tight, narrow-mouth ground stoppered bottles taking due precautions to minimize the evaporation losses. Dilute solutions up to 0.1 mole fraction of each alkylamine in both the solvents were prepared.

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Table 1
Comparison of experimental densities ρ with the literature, values of molar volumes V^o, isothermal compressibilities k_T, and hard sphere diameters σ of pure components at 303.15 K

Solvents	Density (g cm^{-3})		V^o	k_T	σ[a]
	Expt.	lit.	cm^3 mol^{-1}	TPa^{-1}	Å
$C_3H_7NH_2$	0.70610	0.70615[b]	83.71	1275[c]	4.76
$C_4H_9NH_2$	0.72865	0.7282[d]	100.37	1189[c]	5.17
		0.72848[e]			
		0.72849[f]			
$(C_3H_7)_2NH$	0.73121	0.73019[g]	138.39	1237[c]	5.88
$(C_4H_9)_2NH$	0.75228	0.75248[g]	171.80	1078[c]	6.48
		0.75228[e]			
$(C_2H_5)_3N$	0.71844	0.71845[h]	140.85	1493[c]	5.91
		0.7185[i]			
		0.71875[b]			
$(C_3H_7)_3N$	0.74915	0.7484[b]	191.24	1193[c]	6.72
$(C_4H_9)_3N$	0.77021	0.7709[b]	240.65	1012[c]	7.44
		0.7701[i]			
		0.77018[e]			
1-C_4H_9OH	0.80192	0.80191[j]	92.43	976[k]	5.08
		0.80193[k]			
		0.80220[h]			
2-C_4H_9OH	0.79840	0.79841[h]	92.84	1041[l]	5.06
		0.79825[j]			

[a] Derived from Mayer's method using isothermal compressibility and molar volume [33].
[b] [34].
[c] [35].
[d] [36].
[e] [37].
[f] [38].
[g] [39].
[h] [32].
[i] [40].
[j] [41].
[k] [42].
[l] [43].

The values of molality m and density ρ are accurate to $\pm 1\times10^{-4}$ mol kg^{-1} and $\pm 2\times10^{-5}$ g cm^{-3}, respectively.

2.2. Materials

n-Propylamine (Merck, Schuchardt), *n*-butylamine (Fluka AG), di-*n*-propylamine (Fluka AG), di-*n*-butylamine (Fluka AG), triethylamine (Sisco, extra pure), tri-*n*-propylamine (Fluka AG), and tri-*n*-butylamine (SRL, Bombay), of purity better than 99.0 mol% were refluxed over Na metal and fractionally distilled twice before use. 1-butanol (BDH AR) and 2-butanol (BDH AR) of purity better then 99.5 mol % were used after further purification and drying by standard procedures [32]. The measured values of densities were compared with literature values in Table 1.

3. Results and discussion

The experimentally determined values of densities ρ for dilute solutions of seven alkylamines in 1-butanol and 2-butanol at different concentrations and at 303.15 K were fitted to polynomial equations of type

$$\rho = A + B + Cm^2 + Dm^3. \quad (1)$$

The values of A, B, and C coefficients along with standard deviations values (σ) are given in Table 2. The apparent molar volumes $V_{\phi,B}$ of all solutes were calculated in the usual way

$$V_{\phi,B} = \frac{M_B}{\rho} - \left(\frac{\rho-\rho_A}{\rho\rho_A}\right)\frac{1000}{m} \quad (2)$$

where M_B is molar mass of solute (amine) and m is concentration of amine in molality. ρ and ρ_A are densities of solution and pure solvent, respectively. The values of ρ and $V_{\phi,B}$ are presented in Tables 3 and 4.

The limiting partial molar volume of amines $\bar{V}_B^{\infty}$ was obtained by the least-square method through the fitting of the following equation

$$V_{\phi,B} = \bar{V}_B^{\infty} + S_v m. \quad (3)$$

The values of coefficients of Eq. (3) are given in Table 5, which includes the excess partial molar volumes at infinite dilution $\bar{V}_B^{E,\infty}(\bar{V}_B^{E,\infty}=\bar{V}_B^{\infty}-\bar{V}_B^{0})$ and the partial molar volumes at infinite dilution of transference of solute from cyclohexane to alkanols, $\Delta\bar{V}_B^{\infty}\mathrm{tr}(C_6H_{12}\rightarrow C_4H_9OH)$ calculated as $\{\bar{V}_B^{\infty}(C_4H_9OH)-\bar{V}_B^{\infty}(C_6H_{12})\}$.

The dependence of $V_{\phi,B}$ on m is shown in Figs. 1 and 2. The values of $V_{\phi,B}$, $\bar{V}_B^{\infty}$ or $\bar{V}_B^{E,\infty}$ of amines depend to a great extent on the type of solute and solvent used.

3.1. Solutions in 1-butanol

In 1-butanol, the values of excess apparent molar volumes $V_{\phi,B}^E$ and limiting excess partial molar volumes $\bar{V}_B^{E,\infty}$ of alkyl amines are negative. The sequence of $\bar{V}_B^{E,\infty}$(Table 5) is $C_3H_7NH_2\approx(C_3H_7)_2NH\approx(C_2H_5)_3N>C_4H_9NH_2\approx(C_3H_7)_3N>(C_4H_9)_2NH>(C_4H_9)_3N$. The large reduction in the volume indicates strong solute–solvent interaction leading to structure formation. Similar were conclusions drawn from the earlier volumetric studies of alkylamine solutions in alkanols [5–8,44–46].

Primary amine and secondary amines in methanol have been studied by French and Criss [46] and Lampreia and Barbosa [47]. Their results suggested stronger complex formation in case of primary amines than in the case of secondary amines. Present results also corroborate that the strength of complex formation decreases from primary to secondary to tertiary. Transference functions have often been used to clarify the influence of solvent characteristics in thermodynamic quantities [47]. As can be seen, from Table 5, the negative transference volumes from cyclohexane to butanol decrease in the same order primary to secondary to tertiary. This is also in agreement with the conclusions drawn by Spencer et al. [48], based on spectroscopic and enthalpic data for the formation of complexes between 1-butanol and diethyl- and butylamines.

The measured excess molar enthalpies H_m^E [49–53] for propylamine, butylamine, di-*n*-propylamine, di-*n*-butylamine, triethylamine and tri-*n*-butylamine+butanol are −2669, −2682, −2432, −2268, −1500 and −389 J mol^{-1}, respectively. Further, their excess molar volumes are also large and negative [5–8,44,45]. This suggests strong interaction leading to cross association, through hydrogen bond formation between amine and alcohol: $NH_2\cdots OH$ and $OH\cdots NH_2$ for primary amine, $NH\cdots OH$ and $OH\cdots NH$ for secondary amine, and $OH\cdots N$ for tertiary amine.

Table 2
Empirical parameters[a] in the Eq. (1) for alkylamine in 1-butanol and 2-butanol at 303.15 K

Solute	A	$B\times10^2$	$C\times10^3$	$D\times10^4$	$\sigma\times10^5$
In 1-butanol					
$C_3H_7NH_2$	0.80194	−0.22519	−0.18012		1.29
$C_4H_9NH_2$	0.80193	−0.21110	−0.40777	1.2410	0.67
$(C_3H_7)_2NH$	0.80193	−0.36413	−0.14155	0.9648	0.76
$(C_4H_9)_2NH$	0.80193	−0.43139	0.32138		0.69
$(C_2H_5)_3N$	0.80193	−0.52932	0.23389		0.74
$(C_3H_7)_3N$	0.80193	−0.46942	0.24659		0.72
$(C_4H_9)_3N$	0.80193	−0.42858	0.49390		0.62
In 2-butanol					
$C_3H_7NH_2$	0.79841	−0.41570	0.15788		0.52
$C_4H_9NH_2$	0.79840	−0.42325	0.23347		0.46
$(C_3H_7)_2NH$	0.79840	−0.44551	0.17199		0.46
$(C_4H_9)_2NH$	0.79841	−0.34476	0.08409		0.50
$(C_2H_5)_3N$	0.79840	−0.53890	0.26758		0.34
$(C_3H_7)_3N$	0.79840	−0.53894	0.50926		0.58
$(C_4H_9)_3N$	0.79843	−0.48306	1.08314	−3.4456	2.18

[a] Unit of A=(g cm^{-3}); unit of B=(g cm^{-3} mol^{-1} kg); unit of C=(g cm^{-3} mol^{-2} kg^2); unit of D=(g cm^{-3} mol^{-3} kg^3), unit of σ=(g cm^{-3}).