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Excess Volumes of Mixing for Some Primary Alcohols with Secondary Amines at 293.15 K and 323.15 K

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The excess volumes of mixing for methanol and ethanol with secondary amines (diethylamine, di-*n*-propylamine and di-*n*-butylamine) have been measured over the whole composition range at 293.15 and 323.15 K. The excess volumes have been fitted to an equation of the type

$$V^E/\mathrm{cm^3\,mol^{-1}} = x(1-x)\sum_{n=0}^{3} A_n(1-2x)^n$$

The different temperature dependences of the mixtures were explained by means of the association theory.

(Keywords: Association; Density measurements; Excess volume; Thermodynamics)

Excessvolumina der Mischungen einiger primärer Alkohole mit sekundären Aminen bei 293,15 und 323,15 K

Die Excessvolumina der Mischungen von Methanol und Ethanol mit sekundären Aminen (Diethylamin, Di-*n*-propylamin und Di-*n*-butylamin) wurden über den ganzen Mischungsbereich bei 293,15 und 323,15 K gemessen und über die Beziehung

$$V^E/\mathrm{cm^3\,mol^{-1}} = x(1-x)\sum_{n=0}^{3} A_n(1-2x)^n$$

angepaßt. Die Temperaturabhängigkeit wurde auf Basis von Assoziationsphänomenen interpretiert.

Introduction

The secondary amine + alcohol mixtures contain components forming associated complexes in their pure form too, on mixing the two components may also associate with each other as well[1,2]. The excess

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volume of mixing is presumably influenced by two opposing effects: the associated species of pure components break down on mixing (generally resulting in a positive contribution to V^E), and as it can be expected at the same time also new, mixed complexes are formed what should have a negative influence on V^E. The sign of V^E therefore will depend on the relative importance of these two effects. Naturally, the temperature also influences the degree of association.

In the present paper we report on the excess volume of systems containing methanol and ethanol mixed with diethyl- di-*n*-propyl and di-*n*-butyl amines and its variation with temperature.

Table 1. *Characteristics of the materials used*

Material	Density at 293.15 K related to density of water at 277.15 K ρ_4^{20}/g cm^{-3}	Refr. index related to line "D" of Na at 293.15 K. n_D^{20}	Origin
methanol	0.79212	1.3250	REANAL (Hungary)
ethanol	0,78904	1.3578	REANAL (Hungary)
diethylamine	0.70341	1.3851	Carlo-Erba (Italy)
di-*n*-propylamine	0.73890	1.4046	BHD-Chemicals Ltd. (England)
di-*n*-butylamine	0.75824	1.4183	LOBA-Chemie, Wien (Austria)

Experimental

Purification of the amines was achieved as follows: the liquids were dried for some days over solid sodium-hydroxide, and distilled.

The alcohols used were water-free, high purity chemicals produced by REANAL (Hungary), and since good agreement was found between their physical properties and the corresponding data in the literature, no further purification was effected.

Table 1 shows the origin, density, and refractive index of the purified materials used. The density of pure materials and their refractive indices were determined by pycnometry and an Abbé type refractometer, respectively.

The density measurement of the liquid mixtures was carried out by a vibrating tube densimeter DMA O2C. The constant required for calculations was determined on the basis of the densities of distilled water and air. The density of the air was determined two times every day. The reference substance was air for all measurements which were carried out at two temperatures: 293.15 and 323.15 K. The accuracy of temperature setting was ± 0.02 K.

All mixtures were prepared by weight and the density of mixtures was measured at approximately tenths of molar fractions.

Table 2. *Excess volume of mixing of the system diethylamine—methanol*

$T = 293.15$ K		$T = 323.15$ K	
x_{amine}	$V^E/cm^3\,mol^{-1}$	x_{amine}	$V^E/cm^3\,mol^{-1}$
0.0000	0.0000	0.0000	0.0000
0.0992	−0.728	0.0990	−0.866
0.1942	−1.318	0.3015	−2.207
0.4386	−2.173	0.4550	−2.643
0.5051	−2.188	0.5043	−2.674
0.5941	−2.146	0.5940	−2.622
0.6666	−1.905	0.6933	−2.375
0.7126	−1.694	0.8393	−1.5398
0.8913	−0.868	0.8992	−1.0442
1.0000	0.000	1.0000	0.000

Table 3. *Excess volume of mixing of the system di-n-propylamine—methanol*

$T = 293.15$ K		$T = 323.15$ K	
x_{amine}	$V^E/cm^3\,mol^{-1}$	x_{amine}	$V^E/cm^3\,mol^{-1}$
0.0000	0.000	0.0000	0.000
0.1042	−0.707	0.1124	−0.712
0.2105	−1.314	0.2283	−1.412
0.3065	−1.733	0.3087	−1.710
0.3988	−1.943	0.4094	−1.896
0.4994	−1.936	0.5252	−1.874
0.5811	−1.831	0.5857	−1.792
0.6662	−1.626	0.6863	−1.538
0.8115	−1.060	0.7855	−1.172
0.9010	−0.722	0.8949	−0.666
1.000	0.000	1.0000	0.000

Results

The density data obtained were used for calculating the excess volumes of mixing on the basis of the following equation:

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho_{12}} - \left(x_1 \frac{M_1}{\rho_1^0} + x_2 \frac{M_2}{\rho_2^0} \right) \tag{1}$$

where x is the molar fraction, M is the relative molar mass, ρ^0 the density of the pure liquid, 1, 2 are the index of the amine and alcohol respectively.

The data obtained are shown in Tab. 2-7, and Figs. 1 and 2. The obtained excess volume of mixing was fitted to the following equation:

$$V^E = x_1 (1 - x_1) [A_0 + A_1 (1 - 2x_1) + A_2 (1 - 2x_1)^2 + A_3 (1 - 2x_1)^3] \tag{2}$$

Table 4. *Excess volume of mixing of the system di-n-butylamine –methanol*

$T = 293.15$ K		$T = 323.15$ K	
x_{amine}	$V^E/cm^3\ mol^{-1}$	x_{amine}	$V^E/cm^3\ mol^{-1}$
0.0000	0.000	0.0000	0.000
0.1128	−0.629	0.1047	−0.610
0.2092	−1.104	0.1944	−1.071
0.2967	−1.484	0.2914	−1.440
0.3940	−1.705	0.3976	−1.637
0.4901	−1.715	0.5063	−1.658
0.5756	−1.594	0.5930	−1.548
0.7015	−1.317	0.6848	−1.346
0.8034	−1.012	0.7503	−1.169
0.8952	−0.530	0.8509	−0.793
1.0000	0.000	1.0000	0.000

Table 5. *Excess volume of mixing of the system diethylamine –ethanol*

$T = 293.15$ K		$T = 323.15$ K	
x_{amine}	$V^E/cm^3\ mol^{-1}$	x_{amine}	$V^E/cm^3\ mol^{-1}$
0.0000	0.000	0.0000	0.000
0.1069	−0.752	0.1185	−0.871
0.2091	−1.290	0.2166	−1.431
0.3082	−1.674	0.3145	−1.812
0.3554	−1.814	0.3937	−1.999
0.5096	−1.988	0.4973	−2.038
0.5996	−1.817	0.5995	−1.917
0.7020	−1.547	0.7019	−1.681
0.7920	−1.189	0.8008	−1.276
0.8740	−0.738	0.9018	−0.718
1.0000	0.000	1.0000	0.000

Table 6. *Excess volume of mixing of the system di-n-propylamine –ethanol*

$T = 293.15$ K		$T = 323.15$ K	
x_{amine}	$V^E/cm^3\ mol^{-1}$	x_{amine}	$V^E/cm^3\ mol^{-1}$
0.0000	0.000	0.0000	0.000
0.1101	−0.706	0.1476	−0.838
0.2144	−1.144	0.2048	−1.111
0.3054	−1.364	0.3072	−1.356
0.3372	−1.469	0.4037	−1.527
0.4293	−1.603	0.5121	−1.508
0.5058	−1.599	0.6014	−1.395
0.6007	−1.480	0.6972	−1.255
0.6969	−1.261	0.7949	−0.947
0.7933	−0.956	0.8563	−0.747
0.8899	−0.551	1.0000	0.000
1.0000	0.000		

Table 7. *Excess volume of mixing of the system di-n-butylamine -ethanol*

$T = 293.15$ K		$T = 323.15$ K	
x_{amine}	V^E/cm³ mol⁻¹	x_{amine}	V^E/cm³ mol⁻¹
0.0000	0.000	0.0000	0.000
0.0632	-0.367	0.0628	-0.340
0.1287	-0.737	0.1302	-0.607
0.2118	-1.034	0.3350	-1.148
0.2705	-1.170	0.4216	-1.301
0.3624	-1.347	0.5069	-1.287
0.4619	-1.344	0.5880	-1.208
0.5634	-1.245	0.6881	-1.035
0.6273	-1.154	0.7853	-0.837
0.7682	-0.790	0.8665	-0.597
0.8098	-0.658	1.0000	0.000
0.8895	-0.348		
1.0000	0.000		

Table 8. *The constants of equation (2), calculated on the basis of experimental data of the investigated systems*

System	Temp. K	A_0/cm³ mol⁻¹	A_1/cm³ mol⁻¹	A_2/cm³ mol⁻¹	A_3/cm³ mol⁻¹	Mean diff./cm³ mol⁻¹
diethylamine -	293.15	—8.776	—0.508	0.711	1.546	0.017
methanol	323.15	-10.748	0.764	0.018	0.542	0.008
diethylamine -	293.15	-7.883	-0.532	1.023	-0.279	0.011
ethanol	323.15	—8.174	—0.735	—0.112	1.014	0.005
di-*n*-propylamine -	293.15	-7.798	-1.483	0.935	1.801	0.007
methanol	323.15	-7.641	-1.558	0.709	2.389	0.008
di-*n*-propylamine -	293.15	-6.345	-0.637	0.097	-0.570	0.011
ethanol	323.15	-6.061	-0.980	-0.659	0.921	0.013
di-*n*-butylamine -	293.15	-6.858	-1.255	1.169	1.938	0.017
methanol	323.15	-6.639	-1.176	0.289	1.761	0.003
di-*n*-butylamine -	293.15	-5.332	-1.535	0.329	-0.329	0.013
ethanol	323.15	-5.099	-6.642	-0.268	0.726	0.014

The constants of the equation were obtained by the method of the least squares. Table 8 shows the resulting values of the constants and the mean difference between data calculated using the equation and the experimental data.

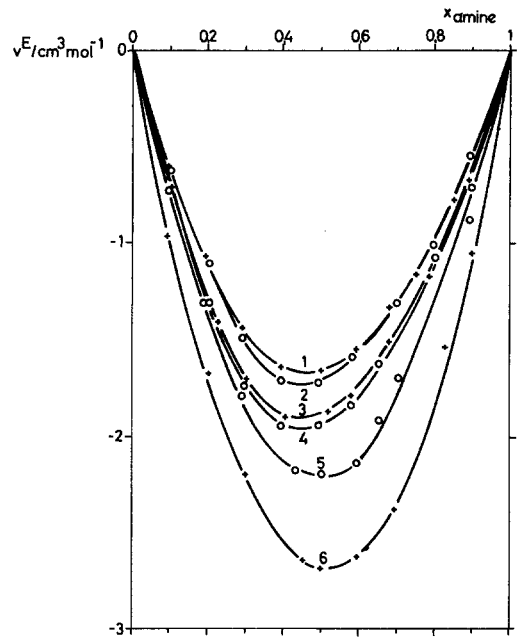

Fig. 1. The excess volume of mixing for methanol with: *1* di-*n*-butylamine at 323.15 K; *2* di-*n*-butylamine at 293.15 K; *3* di-*n*-propylamine at 323.15 K; *4* di-*n*-propylamine at 293.15 K; *5* diethylamine at 293.15 K; *6* diethylamine at 323.15 K

Discussion

It may be seen from the Figures that the excess volume of mixing increases (the absolute value decreases) with the number of CH groups in the components of the mixture.

It may also be seen from the data that while in the case of diethylamine—methanol and diethylamine—ethanol mixtures the excess volume values observed at 323.15 K are smaller (more negative) than those observed at 293.15 K, in the case of the other four systems the values observed at 323.15 K are the larger ones.

It is known from the literature that pure alcohols can form either ring or chain like complexes, and while the fraction of ring complexes increases with the number of the CH groups in the alcohol, the degree of the association decreases[3,4]. The associated rings break down to chains with increasing temperature which is then followed by a total breakdown of the associated species.

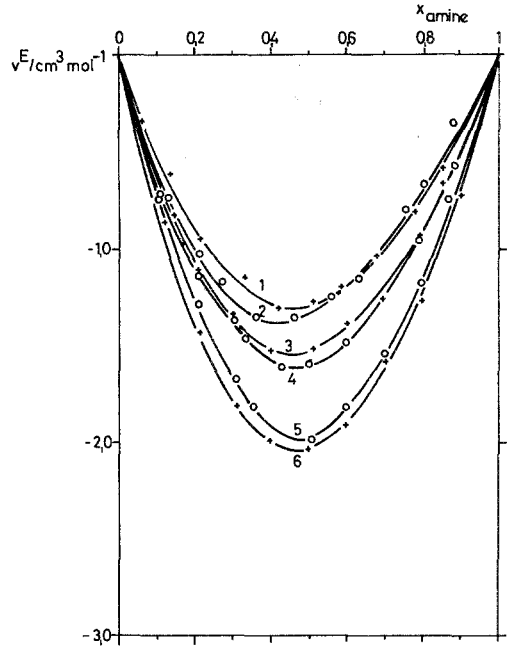

Fig. 2. The excess volume of mixing for ethanol with: *1* di-*n*-butylamine at 323.15 K; *2* di-*n*-butylamine at 293.15 K; *3* di-*n*-propylamine at 323.15 K; *4* di-*n*-propylamine at 293.15 K; *5* diethylamine at 293.15 K; *6* diethylamine at 323.15 K

The degree of association of secondary amines also decreases with increasing temperature[5].

The formation of mixed complexes is an exothermic reaction, and also this equilibrium constant decreases with increasing temperature[6]. It must be taken also into account that associated ring-like complexes are not able to form mixed species with the amine molecules.

On the basis of these considerations our experimental data may be explained as follows.

The number of the mixed associated species is influenced by two opposing effects with increasing temperature:

1. The number of species which are able to form mixed complexes (alcohol—amine) is increasing with temperature: the self associated alcohole rings and amine complexes break down.

2. The equilibrium constant of the association resulting mixed complexes is decreasing with increasing temperature.

In the case of diethylamine—methanol and —ethanol the first effect is dominant, the number of hydrogen bonds increases with temperature so the contraction of mixing increases.

The second effect seems to be dominant in the case of the other four systems: the concentration of mixing decreases with increasing temperature.

The variation of the excess volume of mixing with the number of CH groups is in agreement with the excess enthalpy data[6].

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