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ARTICLE *in* JOURNAL OF CHEMICAL & ENGINEERING DATA · JANUARY 1995

Impact Factor: 2.04 · DOI: 10.1021/je00017a044

Excess Molar Volumes of Binary Mixtures of Amino Alcohols with 1,4-Dioxane

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Excess molar volumes, V_m^E, for binary mixtures of eight aliphatic amino alcohols (2-aminoethanol, 3-amino-1-propanol, 4-amino-1-butanol, 5-amino-1-pentanol, 2-amino-1-propanol, 1-amino-2-propanol, 2-amino-2-methyl-1-propanol, and 2-amino-1-butanol) with 1,4-dioxane have been determined from the density measurements at 293.15 K by means of a vibrating tube densimeter.

Introduction

In a previous paper (*1*) we reported the excess molar volumes, V_m^E, measured in binary mixtures of diols with water. Strong interactions between diols and water molecules via hydrogen bonds O−H···O lead to a negative value of the excess molar volumes ($V_m^E < 0$) in the whole range of diol concentration.

Here we report the results of measurements of V_m^E carried out for binary mixtures of amino alcohols with dioxane. The amino alcohol molecules offer several hydrogen bonding possibilities. One may expect the intramolecular hydrogen bonds as for 2-aminoethanol, where the O−H···N bonds exist in isolated molecules (*2*) and in dilute solutions (*3*). In the pure amino alcohols a variety of intra- and intermolecular H-bonds is possible: O−H···N, O−H···O, and N−H···O (*4*, *5*).

Experimental Section

The amino alcohols 2-aminoethanol, 3-amino-1-propanol, 2-amino-1-propanol, 1-amino-2-propanol, and 2-amino-1-butanol were supplied by Aldrich and 4-amino-1-butanol, 5-amino-1-pentanol, and 2-amino-2-methyl-1-propanol by Fluka. All were stored with activated 4A molecular sieves. 1,4-Dioxane was double-distilled and degassed before use. Table 1 contains the measured density of pure amino alcohols and dioxane.

Density measurements were carried out with an A. Paar DMA 60/602 vibration tube densimeter. The measuring cell was thermostated (±0.05 K) by using a Heto Birkeroad ultrathermostat. The density measurements were reproducible to $\pm 1 \times 10^{-5}$ g·cm^{-3}. The solutions were prepared by weight; the accuracy in the molar fraction determination was $\pm 1 \times 10^{-4}$.

Results and Discussion

The excess molar volumes V_m^E for eight mixtures {x amino alcohol + (1 − x)dioxane}, where x denotes the molar fraction, measured at 293.15 K are collected in Table 2.

Functions of the form

$$V_m^E/\text{cm}^3\cdot\text{mol}^{-1} = x(1-x)\sum_i A_i(2x-1)^i \qquad (1)$$

have been fitted to the experimental data by the least-squares method for each mixture. The values of the coefficients A_i and the standard deviation σ of the fits are listed in Table 2. An estimated accuracy of the values of the excess volumes is $\pm 2 \times 10^{-4}$ cm^3·mol^{-1}.

Table 1. Densities, ρ, of Pure Components at 293.15 K

component	ρ/(g·cm^{-3})	lit. (*6*)[b]
2-aminoethanol	1.01458	1.022
3-amino-1-propanol	0.98650	0.98
4-amino-1-butanol	0.96003	
5-amino-1-pentanol	1.03179	
2-amino-1-propanol	0.92829	0.962
1-amino-2-propanol	0.95946	0.9611
2-amino-2-methyl-1-propanol[a]	0.96233	
2-amino-1-butanol	0.94288	0.944
1,4-dioxane	1.03171	
	1.02269[a]	

[a] At 298.15 K. [b] Temperature not specified.

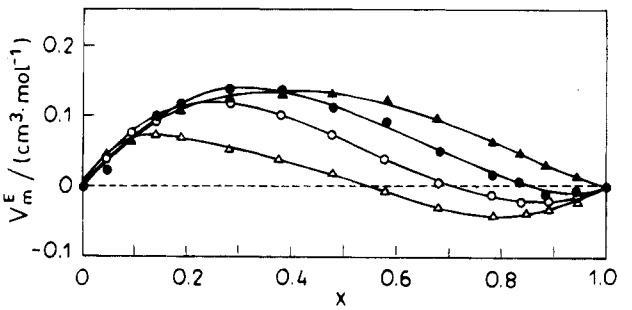

Figure 1. Excess molar volumes of {x amino alcohol + (1 − x)-dioxane} at 293.15 K: △, 2-aminoethanol; ○, 3-amino-1-propanol; ●, 4-amino-1-butanol; ▲, 5-amino-1-pentanol.

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0021-9568/95/1740-0214$09.00/0

Table 2. Excess Molar Volumes, V_m^E, Coefficients A_i of Equation 1, and Standard Deviations, σ, for Amino Alcohol + Dioxane Mixtures at 293.15 K

x	V_m^E/ (cm^3·mol^{-1})	x	V_m^E/ (cm^3·mol^{-1})	x	V_m^E/ (cm^3·mol^{-1})
		x 2-Aminoethanol + $(1-x)$Dioxane			
0.0459	0.0458	0.2796	0.0538	0.6801	−0.0316
0.0924	0.0658	0.3780	0.0397	0.7859	−0.0414
0.1391	0.0740	0.4783	0.0182	0.8471	−0.0385
0.1863	0.0708	0.5793	−0.0078	0.8892	−0.0325
				0.9432	−0.0195
		$A_0 = 0.0490, A_1 = -0.4571, A_2 = -0.1219,$ $A_3 = -0.3517, A_4 = 0.5944$			
		$\sigma(V_m^E)$/(cm^3·mol^{-1}) = 0.0019			
		x 3-Amino-1-propanol + $(1-x)$Dioxane			
0.0456	0.0371	0.2821	0.1184	0.6819	0.0047
0.0921	0.0776	0.3782	0.1026	0.7811	−0.0099
0.1379	0.0940	0.4765	0.0726	0.8362	−0.0227
0.1861	0.1169	0.5776	0.0408	0.8906	−0.0227
				0.9444	0.0149
		$A_0 = 0.2589, A_1 = -0.6832, A_2 = 0.2244,$ $A_3 = -0.0184, A_4 = -0.2111$			
		$\sigma(V_m^E)$/(cm^3·mol^{-1}) = 0.0020			
		x 4-Amino-1-butanol + $(1-x)$Dioxane			
0.0458	0.0235	0.2815	0.1376	0.6830	0.0502
0.0915	0.0673	0.3794	0.1366	0.7830	0.0179
0.1394	0.0999	0.4783	0.1127	0.8364	0.0075
0.1860	0.1183	0.5792	0.0930	0.8868	−0.0112
				0.9425	−0.0073
		$A_0 = 0.4398, A_1 = -0.5642, A_2 = 0.1334,$ $A_3 = 0.0127, A_4 = -0.4447$			
		$\sigma(V_m^E)$/(cm^3·mol^{-1}) = 0.0032			
		x 5-Amino-1-pentanol + $(1-x)$Dioxane			
0.0459	0.0362	0.2799	0.1247	0.6807	0.0975
0.0924	0.0706	0.3782	0.1343	0.7845	0.0648
0.1383	0.0963	0.4770	0.1330	0.8366	0.0476
0.1847	0.1111	0.5810	0.1229	0.8875	−0.0311
				0.9435	−0.0144
		$A_0 = 0.5247, A_1 = -0.1828, A_2 = 0.0292,$ $A_3 = -0.2449, A_4 = 0.0541$			
		$\sigma(V_m^E)$/(cm^3·mol^{-1}) = 0.0029			
		x 2-Amino-1-propanol + $(1-x)$Dioxane			
0.0456	0.0521	0.2806	0.1929	0.6789	0.1367
0.0924	0.1037	0.3785	0.2110	0.7844	0.0993
0.1381	0.1426	0.4778	0.1942	0.8362	0.0713
0.1864	0.1623	0.5786	0.1844	0.8821	0.0507
				0.9422	0.0259
		$A_0 = 0.7847, A_1 = -0.3746, A_2 = 0.0402,$ $A_3 = -0.1303, A_4 = 0.0924$			
		$\sigma(V_m^E)$/(cm^3·mol^{-1}) = 0.0058			
		x 1-Amino-2-propanol + $(1-x)$Dioxane			
0.0455	0.0947	0.2810	0.2732	0.6808	0.2067
0.0921	0.1741	0.3776	0.2795	0.7848	0.1581
0.1388	0.2108	0.4670	0.2715	0.8370	0.1235
0.1902	0.2309	0.5779	0.2474	0.8912	0.0774
				0.9409	0.0463
		$A_0 = 1.0682, A_1 = -0.3363, A_2 = 0.3024,$ $A_3 = -0.5393, A_4 = 0.3231$			
		$\sigma(V_m^E)$/(cm^3·mol^{-1}) = 0.0035			
		x 2-Amino-2-methyl-1-propanol + $(1-x)$Dioxane at 298.15 K			
0.0459	0.0595	0.2811	0.3517	0.6791	0.3174
0.0924	0.1574	0.3792	0.3875	0.7849	0.2341
0.1334	0.2252	0.4788	0.3997	0.8374	0.1882
0.1864	0.2651	0.5766	0.3651	0.8901	0.1367
				0.9381	0.0734
		$A_0 = 1.5587, A_1 = -0.3857, A_2 = 0.2296,$ $A_3 = 0.1468, A_4 = -0.3175$			
		$\sigma(V_m^E)$/(cm^3·mol^{-1}) = 0.0056			
		x 2-Amino-1-butanol + $(1-x)$Dioxane			
0.0459	0.1063	0.2818	0.2973	0.6740	0.1575
0.0923	0.1884	0.3759	0.3020	0.7867	0.0914
0.1364	0.2118	0.4771	0.2505	0.8351	0.0494
0.1863	0.2516	0.5813	0.2118	0.8919	0.0242
				0.9461	0.0095
		$A_0 = 1.0112, A_1 = -0.8497, A_2 = 0.0902,$ $A_3 = -0.4275, A_4 = 0.2187$			
		$\sigma(V_m^E)$/(cm^3·mol^{-1}) = 0.0044			

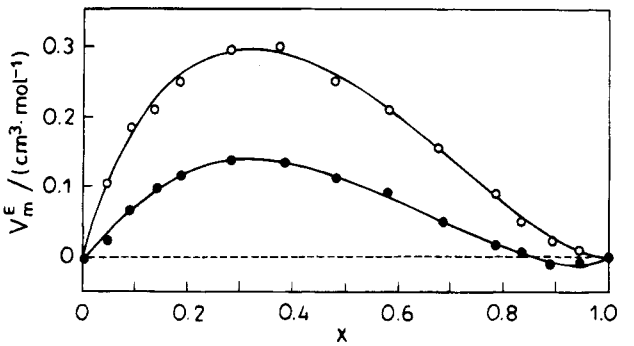

Figure 2. Excess molar volumes of {x aminobutanol + $(1-x)$-dioxane} at 293.15 K: ●, 4-amino-1-butanol; ○, 2-amino-1-butanol.

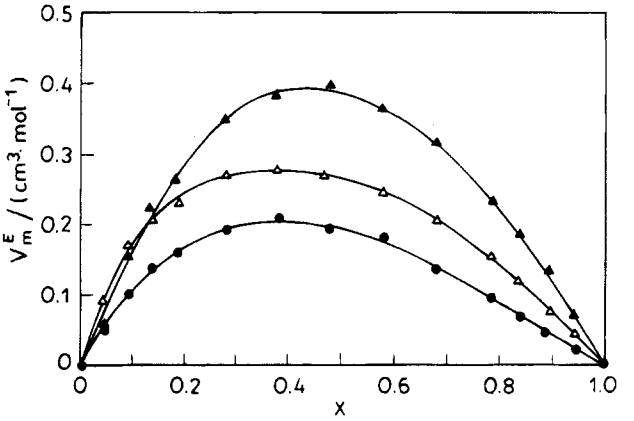

Figure 3. Excess molar volumes of {x aminopropanol + $(1-x)$-dioxane} at 293.15 K: ●, 2-amino-1-propanol; △, 1-amino-2-propanol; ▲, 2-amino-2-methyl-1-propanol (at 298.15 K).

Figure 1 shows the concentration dependence of V_m^E for the mixtures of $NH_2(CH_2)_nOH$, n = 2, 3, 4, and 5, with dioxane. Strong self-association leads to a negative value of V_m^E in concentrated solutions of 2-aminoethanol, 3-amino-1-propanol, and 4-amino-1-butanol. In diluted and moderately concentrated solutions V_m^E is positive due to the heteroassociation of amino alcohols with dioxane molecules: the energy value of O−H···O hydrogen bonds formed between alcohol−dioxane molecules is much less than that between alcohol−alcohol or alcohol−water molecules.

Figure 2 shows V_m^E for mixtures of 4- and 2-aminobutanols and dioxane, respectively. In Figure 3 we compare V_m^E in solutions of three aminopropanols in dioxane.

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Received for review June 1, 1994. Accepted August 11, 1994.[⊗]
JE940099N

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1994.