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Excess Volumes of a Homologous Series of Aliphatic Alcohols with Benzonitrile

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Excess volumes of binary mixtures of 1-propanol, 1-butanol, 1-pentanol, isopropyl alcohol, isobutyl alcohol, and isopentyl alcohol with benzonitrile have been measured at 308.15 K by using a dilatometer and are reported in this paper.

Introduction

In continuation of earlier work on excess volumes of binary mixtures of alcohols in a common solvent (*1-4*), V^E values of binary mixtures of 1-propanol, 1-butanol, 1-pentanol, isopropyl alcohol, isobutyl alcohol, and isopentyl alcohol with benzonitrile at 308.15 K are reported here. A literature survey showed that no one has reported V^E data for the mixtures of the six alcohols with benzonitrile at 308.15 K.

Experimental Section

Mixing Cell. The cell used for measuring excess volumes was similar to that used by Brown and Smith (*5*) except for the detachable capillary arrangement. The cell was basically a U-tube with mercury at the bottom to separate the two components. One arm of the U-tube was closed with a ground-glass stopper, and the other arm was fitted with a capillary (1-mm i.d.) having a Teflon cap with a small orifice at the top, which was detachable. Composition was determined directly by weighing. The cell was immersed in a thermostatic bath maintained at 308.15 ± 0.01 K. The change in liquid level after mixing in the capillary with reference to a fixed mark was read by a traveling microscope which had an accuracy of ±0.01 mm. Excess volumes were accurate to ±0.003 cm^3 mol^{-1}. Four cells with different capacities were used to cover the mole fraction range from 0.1 to 0.9.

Purification of Materials

Benzonitrile (Riedel) was dried over freshly fused calcium chloride for 2 days and distilled at atmospheric pressure. 1-Propanol (E. Merck) was refluxed over lime for 5 h and then distilled through a 1-m fractionating column.

1-Butanol (BDH) was refluxed over freshly ignited calcium oxide for 4 h. The alcohol was decanted from the lime, refluxed with magnesium turnings, and then fractionally distilled. The middle fraction which boiled at 390.75 K was collected.

1-Pentanol (E. Merck) was dried over Drierite and fractionally distilled.

Isopropyl alcohol (BDH) was dried first with calcium chloride and then with barium oxide and fractionally distilled.

Isobutyl alcohol (BDH) was purified by repeated fractional distillation through a 1-in.-90-plate column.

Isopentyl alcohol (BDH) was dried with calcium chloride and then purified by careful fractional distillation.

The purity of the above samples has been verified from densities at 303.15 K and boiling points reported in the literature (*6*) and presented in Table I. The densities are accurate to 5 parts in 10^6 parts.

Table I. Boiling Points and Densities of Pure Components

component	bp, K		density, g cm^{-3}	
	present work	lit. (*6*)	present work	lit. (*6*)
1-propanol	370.15	370.15	0.795 60	0.795 67
1-butanol	390.15	390.22	0.802 05	0.802 06
1-pentanol	411.00	411.10	0.807 54	0.807 64
isopropyl alcohol	354.85	355.35	0.776 85	0.776 90
isobutyl alcohol	380.94	381.04	0.794 31	0.794 37
isopentyl alcohol	404.35	405.05	0.801 67	0.801 79
benzonitrile	463.93	464.04	0.996 19	0.996 28

Results and Discussion

The excess volume data at 308.15 K of the six binary mixtures are presented in Table II and represented in Figures 1 and 2. The values of V^E are negative over the entire range of composition in all of the mixtures. The negative excess volumes of the six binary mixtures fall in order. The normal alcohols fall in the order 1-propanol > 1-butanol > 1-pentanol, and the isoalcohols also fall in the same order, i.e., isopropyl alcohol > isobutyl alcohol > isopentyl alcohol.

The excess volume–composition curves of the systems are given by

$$V^E/(x_A x_B) = a_0 + a_1(x_A - x_B) + a_2(x_A - x_B)^2 \quad (1)$$

where x_A and x_B are the mole fractions of components A and B, respectively, and a_0, a_1, and a_2 are arbitrary constants which have been evaluated by the principle of least squares.

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Table II. Excess Volumes of Aliphatic Alcohols with Benzonitrile at 308.15 K

x_A[a]	V^E, cm³ mol⁻¹	ΔV^E,[b] cm³ mol⁻¹	x_A[a]	V^E, cm³ mol⁻¹	ΔV^E,[b] cm³ mol⁻¹
		Benzonitrile + 1-Propanol			
0.1032	−0.163	+0.002	0.4602	−0.249	−0.001
0.1424	−0.210	−0.005	0.5169	−0.225	+0.002
0.2850	−0.268	+0.005	0.6398	−0.160	+0.000
0.3120	−0.277	+0.002	0.7586	−0.113	+0.000
0.3225	−0.277	−0.002	0.8219	−0.084	−0.001
0.4270	−0.258	+0.001			
		Benzonitrile + 1-Butanol			
0.1198	−0.115	+0.000	0.5856	−0.147	+0.000
0.2158	−0.164	+0.002	0.6749	−0.111	+0.004
0.3162	−0.196	−0.007	0.7778	−0.079	−0.004
0.4028	−0.187	+0.002	0.8536	−0.044	+0.001
0.4784	−0.175	+0.002			
		Benzonitrile + 1-Pentanol			
0.1394	−0.091	−0.004	0.5885	−0.123	+0.003
0.1857	−0.106	+0.001	0.6411	−0.111	+0.005
0.2870	−0.127	+0.008	0.7295	−0.082	−0.003
0.3919	−0.143	+0.002	0.7388	−0.076	+0.000
0.4389	−0.136	+0.008	0.8732	−0.029	+0.003
0.5404	−0.137	−0.006			
		Benzonitrile + Isopropyl Alcohol			
0.1008	−0.135	−0.003	0.5464	−0.134	+0.002
0.1814	−0.187	+0.003	0.6516	−0.079	+0.003
0.2384	−0.207	+0.003	0.7483	−0.049	−0.001
0.3550	−0.208	+0.002	0.8379	−0.003	+0.005
0.4358	−0.190	−0.004			
		Benzonitrile + Isobutyl Alcohol			
0.1203	−0.103	−0.002	0.6050	−0.095	+0.000
0.2123	−0.134	+0.006	0.6737	−0.071	+0.001
0.3237	−0.157	−0.003	0.7882	−0.043	−0.006
0.3772	−0.150	+0.001	0.8543	−0.017	+0.003
0.4799	−0.132	+0.000			
		Benzonitrile + Isopentyl Alcohol			
0.1337	−0.066	−0.001	0.5830	−0.073	−0.003
0.2394	−0.090	+0.002	0.6099	−0.067	−0.003
0.3468	−0.103	+0.002	0.7283	−0.033	+0.002
0.4469	−0.089	+0.006	0.8124	−0.019	−0.003
0.5402	−0.079	+0.000	0.8756	−0.003	+0.002

[a] Mole fraction of benzonitrile. [b] $\Delta V^E = V^E_{obsd} - V^E_{calcd}$ (eq 1).

Table III. Values of the Arbitrary Constants[a] in Eq 1 and Standard Deviation[a] (σ) at 308.15 K for All Six Binary Liquid Mixtures

system	a_0	a_1	a_2	τ
benzonitrile + 1-propanol	−0.9339	0.7932	−0.3536	0.003
benzonitrile + 1-butanol	−0.6883	0.4923	−0.0475	0.003
benzonitrile + 1-pentanol	−0.5500	0.2944	−0.0755	0.005
benzonitrile + isopropyl alcohol	−0.6334	0.9352	−0.1278	0.005
benzonitrile + isobutyl alcohol	−0.5066	0.5341	−0.0692	0.003
benzonitrile + isopentyl alcohol	−0.3471	0.3446	−0.0721	0.003

[a] Units: cm³ mol⁻¹.

The values of these constants are included in Table III along with the standard deviation, σ, which is calculated from the equation

$$\sigma = \left[\frac{\sum (V^E_{expt} - V^E_{calcd})^2}{n - p} \right]^{1/2} \quad (2)$$

where n is the number of results and p is the number of parameters in eq 1.

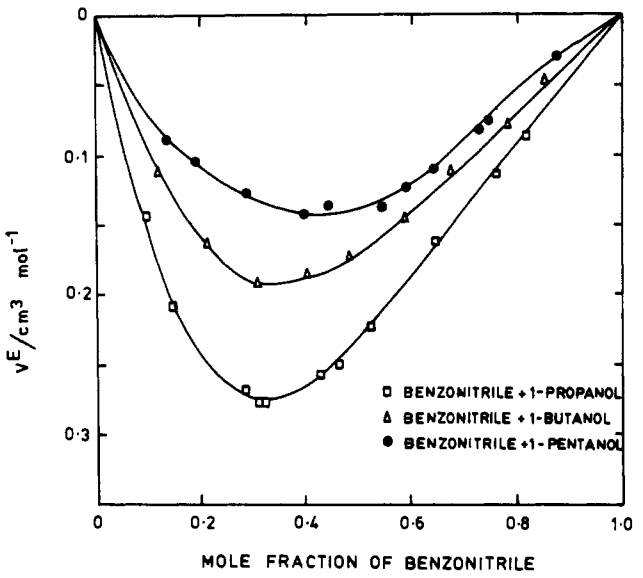

Figure 1. Excess volume–composition curves for normal alcohols with benzonitrile at 308.15 K.

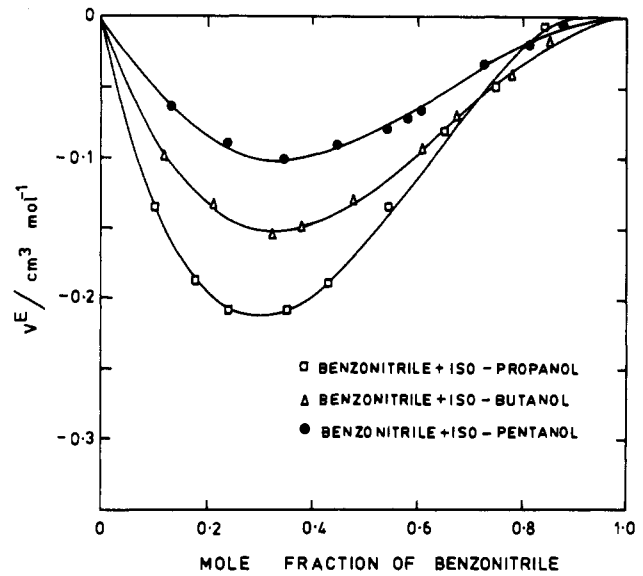

Figure 2. Excess volume–composition curves for isoalcohols with benzonitrile at 308.15 K.

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