Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 93, No. 2, March 1984, pp. 83–86.

Excess volumes and isentropic compressibilities of binary mixtures of di-*n*-butylamine with iso-alkanols at 303·15 K

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MS received 17 February 1983; revised 7 May 1983

Abstract. Volumes of mixing and deviations in isentropic compressibility for binary mixtures of di-*n*-butylamine with iso-propanol, iso-butanol and iso-pentanol were measured at 303·15 K. The excess volumes and deviations in isentropic compressibility are negative over the entire range of mole fractions in all the systems. The results point out that there is a strong H-bond interaction between unlike molecules.

Keywords. Mole fraction; dilatometer; isentropic compressibility; interferometer; volume fraction; sound velocity.

1. Introduction

New experimental data for excess volume and isentropic compressibility for mixtures of di-*n*-butylamine with iso-propanol, iso-butanol and iso-pentanol, determined at 303·15 K, are reported in this paper.

2. Experimental

Di-*n*-butylamine was dried over potassium hydroxide for three days, refluxed for 2 hr and fractionally distilled. Iso-propanol, iso-butanol and iso-pentanol were purified by the methods described in the literature (Riddick and Bunger 1970). The purity of the samples was checked by comparing the experimental densities with those reported in the literature (Timmermans 1950). The values were accurate to $\pm 5 \times 10^{-5}$ g cm^3.

Excess volumes were measured directly using a single composition per loading type dilatometer described earlier (Rao and Naidu 1974) at 303·15 K. Excess volumes were reproducible to $\pm 0{\cdot}003$ cm^{3}mol^{-1}.

Isentropic compressibilities were computed from densities and sound velocities determined at 303·15 K. Densities of the mixture were obtained from experimental excess volumes using the relation

$$\rho = (x_1 M_1 + x_2 M_2)/(V + V^E), \tag{1}$$

where x_1, x_2 and M_1, M_2 stand for the mole fractions and molecular weights of amine and alcohols respectively. V and V^E denote molar volume and excess volume respectively. Sound speed was measured as discussed earlier (Ramamurthy *et al* 1983).

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The experimental densities of pure components at 303·15 K were compared with those reported below.

di-*n*-butylamine 0·75519 (−), iso-propanol 0·77692 (0·77690), iso-butanol 0·79439 (0·79437), iso-pentanol 0·80177 (0·80179)

Isentropic compressibilities were calculated from the relation

$$K_s = u^{-2}\rho^{-1} \tag{2}$$

where u and ρ denote sound velocity and density respectively. The deviation in isentropic compressibility (ΔK_s) was computed employing the equation

$$\Delta K_s = K_s - \phi_1 K_{s,1} - \phi_2 K_{s,2} \tag{3}$$

where K_s, $K_{s,1}$, $K_{s,2}$ are the isentropic compressibilities of the mixture and the pure components. ϕ_1 and ϕ_2 are the volume fractions of amine and alcohols. The deviation in isentropic compressibility (ΔK_s) for an ideal mixture is assumed to be additive with respect to volume fraction.

3. Results and discussion

Experimental V^E data for the three binary mixtures are included in table 1. The values of V^E may be expressed by an empirical equation of the form

$$V^E/\text{cm}^3\text{mol}^{-1} = x_1 x_2[a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2], \tag{4}$$

where a_0, a_1 and a_2 are adjustable parameters, x_1 and x_2 are the molefractions of amines and alcohols respectively.

The values of the parameters obtained by least squares procedure are shown in table 1 along with the standard deviation (V^E).

Experimental ΔK_s values for the three binary mixtures are included in Table 2. The ΔK_s values for the binary mixtures at 303·15 K fit an empirical equation of the form

$$\Delta K_s/Tpa^{-1} = \phi_1\phi_2[b_0 + b_1(\phi_1 - \phi_2) + b_2(\phi_1 - \phi_2)^2], \tag{5}$$

Table 1. Experimental excess volumes for three binary mixtures at 303·15 K.

di-*n*-butylamine + iso-propanol		di-*n*-butylamine + iso-butanol		di-*n*-butylamine + iso-pentanol	
x	V^E (cm^{3}mol^{-1})	x	V^E (cm^{3}mol^{-1})	x	V^E (cm^{3}mol^{-1})
0·0651	−0·184	0·0578	−0·357	0·0809	−0·419
0·1912	−0·508	0·1841	−0·875	0·1552	−0·735
0·3100	−0·718	0·1923	−0·892	0·2360	−0·989
0·4012	−0·817	0·2704	−1·055	0·3850	−1·241
0·4920	−0·853	0·3345	−1·128	0·5464	−1·227
0·5992	−0·815	0·4411	−1·154	0·6212	−1·131
0·6558	−0·748	0·5502	−1·084	0·6864	−1·006
0·7959	−0·522	0·6357	−0·981	0·7662	−0·807
0·8812	−0·323	0·7096	−0·857	0·8356	−0·598
		0·8227	−0·592	0·9062	−0·361
$V^E = -3·415 + 0·042(\ ) + 0·528(\ )$		$V^E = -4·512 + 0·359(\ ) - 1·073(\ )$		$V^E = -5·037 + 0·889(\ ) + 0·152(\ )$	
$\sigma(V^E) = 0·005$ cm^3 mol^{-1}		$\sigma(V^E) = 0·004$ cm^3 mol^{-1}		$\sigma(V^E) = 0·003$ cm^3 mol^{-1}	

Table 2. Experimental isentropic compressibility values for three binary mixtures at 303·15 K.

ϕ	ρ (g cm^{-3})	u (msec^{-1})	K_s (Tpa^{-1})	ΔK_s (Tpa^{-1})
di-n-butylamine + iso-propanol				
0·00000	0·77692	1132	1004	0
0·12662	0·77589	1146	981	−7
0·34341	0·77358	1172	941	−19
0·49850	0·77129	1190	915	−26
0·59716	0·76941	1194	911	−29
0·68181	0·76740	1210	890	−28
0·76786	0·76490	1218	881	−26
0·80826	0·76347	1222	877	−25
0·89613	0·76005	1226	875	−16
0·94256	0·75796	1228	874	−11
1·00000	0·75519	1228	878	0
di-n-butylamine + iso-pentanol				
0·00000	0·80177	1218	840	0
0·12096	0·80018	1228	828	−16
0·22236	0·79631	1236	822	26
0·32472	0·79294	1240	820	−32
0·49355	0·78608	1242	824	−34
0·65219	0·77805	1242	833	−31
0·71853	0·77422	1238	842	−25
0·79186	0·78969	1228	839	−21
0·83611	0·76677	1234	856	−15
0·88780	0·76324	1234	860	−13
0·93765	0·75974	1232	860	−8
1·00000	0·75519	1228	878	0
di-n-butylamine + iso-butanol				
0·00000	0·79439	1176	910	0
0·10115	0·79332	1184	899	−7
0·29273	0·78933	1196	885	−15
0·30397	0·78897	1198	883	−17
0·40470	0·78577	1204	877	−20
0·47970	0·78298	1210	872	−22
0·59155	0·76948	1222	870	−21
0·69171	0·76683	1226	867	−20
0·75945	0·76239	1228	869	−16
0·81760	0·76287	1228	869	−14
0·89486	0·75993	1228	872	−9
1·00000	0·75519	1228	878	0

Table 3. Values of constants b_0, b_1, b_2 and $\sigma(K_s)$ in (Tpa^{-1}).

	di-*n*-butylamine plus		
	iso-propanol	iso-butanol	iso-pentanol
T(K)	303·15	303·15	303·15
b_0	−101·6302	−84·8580	−135·1384
b_1	−73·6595	−13·2037	3·3824
b_2	−33·5939	−0·5151	−0·4427
$\sigma(K_s)$	1	1	2

where b_0, b_1 and b_2 are adjustable parameters obtained by the method of least-squares and are given in table 3.

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