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Volume change on mixing: Binary mixtures of isomeric butylamines with chloroform†

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Abstract. The excess volume of mixing for 1-aminobutane, 2-aminobutane, 1-amino-2-methylpropane and 2-amino-2-methylpropane with chloroform were determined at 30° by the density method. The V^E were negative for all the systems and showed the following order: 2-amino-2-methylpropane > 2-aminobutane > 1-amino-2-methylpropane > 1-aminobutane. The negative V^E were attributed to complex formation between the amine and chloroform molecules owing to H bonding, while the particular trend was attributed to the decreasing degree of self-association of amine isomers.

Keywords. Excess volume; butylamine; chloroform.

1. Introduction

The behaviour of non-electrolyte solutions of associated liquids is of constant interest. The present work is part of a programme to study the thermodynamic properties of associated liquids (Dutta Choudhary and Mathur 1976; Pradhan and Mathur 1979; Pradhan and Pathak 1983). The V^E for four isomeric butylamines with chloroform has been undertaken in order to obtain the information concerning the structural changes in solution due to hydrogen-bond breaking and making, the effect of branching of alkyl chain on V^E.

2. Experimental

The four isomeric butylamines (S.D. Chemicals, 98% GLC Pure) and chloroform (AR grade, S.D. Chemicals) were further purified by fractional distillation. All the compounds were dried by freshly activated molecular sieves.

The excess volumes of mixing were determined at 30° by the density method, the details of it are reported in an earlier communication (Pradhan 1981). The densities at any composition were reproducible within $\pm 2{\cdot}0 \times 10^{-5}$ g/ml.

3. Results and discussion

The results on 1-aminobutane (1), 1-amino-2-methylpropane (1), 2-aminobutane (1) and 2-amino-2-methylpropane (1)–chloroform (2) systems have been reported

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Table 1. Volume change on mixing of 1-aminobutane, 1-amino-2-methylpropane, 2-aminobutane and 2-amino-2-methylpropane with chloroform at 30°C.

x_1 mol fraction amine	d_{12} g/ml density of mixture	V^E (ml/mol)
1-Aminobutane (1) + $CHCl_3$ (2)		
0·0000	1·47143	—
0·0943	1·38771	− 0·075
0·2013	1·29729	− 0·116
0·2981	1·21891	− 0·264
0·4074	1·13400	− 0·348
0·4993	1·06534	− 0·399
0·5494	1·02895	− 0·423
0·6233	0·97432	− 0·429
0·6717	0·94265	− 0·426
0·7524	0·88782	− 0·400
0·8010	0·85544	− 0·359
0·8509	0·82276	− 0·307
0·8984	0·79209	− 0·233
0·9415	0·76472	− 0·156
1·0000	0·72801	—
1-Amino-2-methylpropane (1) + $CHCl_3$ (2)		
0·0000	1·47044	—
0·1035	1·37779	− 0·130
0·2057	1·29028	− 0·241
0·3147	1·20116	− 0·348
0·3932	1·13952	− 0·417
0·5031	1·05642	− 0·489
0·6069	0·98114	− 0·522
0·6930	0·92090	− 0·517
0·8027	0·84627	− 0·442
0·8497	0·81574	− 0·378
0·9074	0·77836	− 0·269
1·0000	0·71967	—
2-Aminobutane (1) + $CHCl_3$ (2)		
0·0000	1·46980	—
0·1050	1·37558	− 0·211
0·2041	1·29028	− 0·377
0·3000	1·21099	− 0·504
0·4059	1·12689	− 0·619
0·4971	1·05732	− 0·683
0·6019	0·98044	− 0·718
0·7035	0·90867	− 0·685
0·8047	0·83970	− 0·572
0·9015	0·77585	− 0·358
0·9502	0·74448	− 0·203
1·0000	0·71283	—

Table 1. (*contd.*)

x_1 mol fraction amine	d_{12} g/ml density of mixture	V^E (ml/mol)
2-Amino-2-methyl propane (1) + $CHCl_3$ (2)		
0·0000	1·47067	—
0·1035	1·36947	− 0·194
0·2099	1·27314	− 0·501
0·2972	1·19816	− 0·755
0·4044	1·11015	− 1·024
0·4548	1·07015	− 1·126
0·4998	1·03517	− 1·203
0·6060	0·95538	− 1·345
0·6591	0·91679	− 1·382
0·7257	0·86937	− 1·372
0·7831	0·82938	− 1·307
0·8255	0·80021	− 1·207
0·8822	0·76162	− 0·986
0·9492	0·71631	− 0·530
1·0000	0·68202	—

in table 1. The maximum uncertainty in V^E values due to the uncertainty of density values, is ± 0·004 ml/mole.

The V^E data have been fitted into the Redlich Kister equation of three parameters, viz.,

$$V^E = x_1x_2[B + C(x_1 - x_2) + D(x_1 - x_2)^2].$$

The Redlich-Kister parameters along with the standard deviations for these systems have been reported in table 2.

The V^E is negative for these systems and exhibits the following order:

2-amino-2-methylpropane > 2-amino-butane >

(V^E_{max} = − 1·385 ml/mole) (V^E_{max} = − 0·718 ml/mole)

1-amino-2-methylpropane > 1-aminobutane

(V^E_{max} = − 0·525 ml/mole) (V^E_{max} = − 0·430 ml/mole).

The negative V^E is attributed to hydrogen-bonded complex formation in liquid mixtures.

Butylamine isomers are self-associated liquids. So the observed volume change on mixing in these systems is the net effect of a positive volume change due to the breaking of self-associated amine species by chloroform and negative volume change due to hydrogen-bonded complex formation between amine and chloroform molecules. The self-association of butylamine isomers decrease according to the order:

1-aminobutane > 1-amino-2-methylpropane > 2-aminobutane > 2-amino-2-methylpropane.

Table 2. Redlich-Kister parameters for volume change on mixing of isomeric butylamines-chloroform systems at 30°C.

System	*B* ml/mole	*C* ml/mole	*D* ml/mole	Standard deviation
1-Aminobutane + $CHCl_3$	−1·5591	−1·1182	−0·2207	0·015
1-Amino-2-methyl-propane + $CHCl_3$	−1·9332	−1·0715	−0·5192	0·006
2-Aminobutane + $CHCl_3$	−2·7391	−1·1117	−0·6436	0·002
2-Amino-2-methyl-propane + $CHCl_3$	−4·7359	−4·4858	−2·1624	0·045

The contribution of the positive volume change due to the dissociation of polymeric amine species decreases accordingly, which explains the observed trend of V^E in the systems presently studied.

From the molar volumes of these butylamines, the negative V^E due to accommodation of chloroform molecules in the liquid structure of amines is also expected to increase in the same observed manner. However, its contribution is expected to be small.

References

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