Surface tension and surface excess heats of mixing of n-butyric acid with various solvents

Satindar Kaur*, Bhajan S Lark, Suresh K Aggarwal & Surjit Singh

Department of Chemistry, Guru Nanak Dev University, Amritsar 143 005, India

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Surface tension (σ) of binary mixtures of n-butyric acid (BA) + cyclohexane, + n-octane, + benzene, + toluene, + carbon tetrachloride, + chloroform, + methanol, + acetone, has been measured at 298.15 and 308.15 K over the entire composition range using a differential capillary rise method. The surface tension data have been used to evaluate the excess surface tension (σ^E). It is found that σ^E values, in accordance with the prediction of Gibbs adsorption equation, for the first five of the eight systems negative at both the temperatures while for the remaining three systems are positive. This may be ascribed to the heteromolecular hydrogen bonding.

Excess properties of mixing of carboxylic acids with various polar and non-polar solvents show interesting dependence on concentration and their magnitude and sign depend on difference in the sizes, shapes and nature of heteromolecules[1-18]. Surface studies of such mixtures are scarce. Singh et al. have reported acetic acid—methanol system at 308.15 K (ref. 10) In continuation with our work on the study of excess functions of acids with various solvents[7-16], excess surface tension of n-butyric acid with cyclohexane, n-octane, benzene, toluene, carbontetrachloride, chloroform, methanol and acetone at 298.15 and 308.15 K is reported and compared with the corresponding and already reported V^E values.

Materials and Methods

Most of the chemicals used were of AR grade except BA (LR), cyclohexane (LR) and n-octane (GR) and were purified by the methods reported in literature[20]. The purities of the samples were checked by measuring their densities and refractive indices, which were found to agree very well with those in the literature[19,20]. All the solvents were thoroughly degassed before use.

Surface tensions were determined using a differential capillary rise method[10]. The uncertainty in the measurement is found to be of the order of 0.06×10^{-3} Nm^{-1}. The temperature of the thermostat was controlled to ± 0.01 K with the help of a 0.01 K Beckmann thermometer, calibrated by determining the transition temperature of Glauber salt as 305.534 K.

Results and Discussion

σ^E values of various systems as a function of mole fraction of the acid (x) at both the temperatures, and as calculated from Eq. (1) are summarised in Table 1.

$$\sigma^E = \sigma - (x\sigma_1 + (1-x)\sigma_2) \qquad \ldots (1)$$

where σ is the measured surface tension of the mixture and σ_i (i = 1, 2) is the surface tension of the pure component (i). σ^E values have been fitted by least squares regression analysis to Eq. (2),

$$\sigma^E/(N\ m^{-1}) = x(1-x) \Sigma C_j (2x-1)^{j-1} \qquad \ldots (2)$$

where x is the mole fraction of the acid.

The values of the C_j coefficients along with the standard deviations (s) for the various systems and at the two temperatures have been summarised in Table 2. The plots of σ^E versus x at 298.15 K only, for the various stystems have been illustrated in Fig. 1. The plots at 308.15 K show similar disposition except for enhanced overall negative trend.

It is apparent from the plots (Fig. 1), that σ^E increases in the order n-octane < benzene < toluene < cyclohexane < carbon tetrachloride < chloroform < acetone < methanol. All the systems except chloroform, methanol and acetone exhibit negative σ^E values in accordance with the Gibbs adsorption equation.

In order to compare the surface phase behaviour with that of the bulk phase, σ^E values have been compared with the corresponding V^E values reported earlier[13]. It is found that systems exhi-

Table 1—Surface tension of acid + solvent systems

xBA + $(1-x)$ cyclohexane

298.15 K			308.15 K		
x	σ	σ^E	x	σ	σ^E
	10^{-3}N. m^{-1}			10^{-3}N.m^{-1}	
0.0000	24.42	0.00	0.0000	23.22	0.00
0.0498	24.48	-0.03	0.0539	23.26	-0.16
0.1539	24.60	-0.09	0.1177	23.29	-0.14
0.2372	24.71	-0.12	0.2187	23.37	-0.24
0.2950	24.79	-0.14	0.2672	23.41	-0.28
0.3445	24.85	-0.17	0.3111	23.46	-0.31
0.3792	24.91	-0.17	0.3948	23.57	-0.35
0.4395	25.00	-0.19	0.5186	23.77	-0.37
0.4916	25.09	-0.19	0.5720	23.86	-0.37
0.5432	25.18	-0.19	0.6035	23.93	-0.36
0.5941	25.28	-0.17	0.6939	24.13	-0.32
0.6591	25.41	-0.16	0.7632	24.31	-0.26
0.6885	25.47	-0.15	0.8391	24.53	-0.18
0.7710	25.65	-0.11	0.8937	24.67	-0.13
0.8213	25.75	-0.10	0.9486	24.84	-0.06
0.8547	25.83	-0.08	1.0000	24.99	0.00
0.9682	26.09	-0.02			
1.0000	26.16	0.00			

xBA + $(1-x)n$-C$_8$H$_{18}$

298.15 K			308.15 K		
0.0000	21.27	0.00	0.0000	20.31	0.00
0.0850	21.55	-0.14	0.0693	20.39	-0.24
0.1792	21.90	-0.25	0.1992	20.69	-0.55
0.2136	22.04	-0.27	0.2529	20.86	-0.63
0.2927	22.37	-0.33	0.3442	21.18	-0.74
0.3747	22.74	-0.36	0.4056	21.44	-0.77
0.4144	22.93	-0.37	0.4883	21.80	-0.80
0.5429	23.58	-0.34	0.5224	21.97	-0.78
0.6197	23.98	-0.32	0.5741	22.23	-0.77
0.6863	24.34	-0.29	0.5843	22.40	-0.74
0.7348	24.61	-0.25	0.6899	22.87	-0.69
0.7729	24.83	-0.22	0.7500	23.24	-0.58
0.8598	25.33	-0.14	0.7982	23.53	-0.52
0.9377	25.79	-0.07	0.8756	24.05	-0.36
1.0000	26.16	0.00	0.9565	24.65	-0.14
			1.0000	24.99	0.00

xBA + $(1-x)$C$_6$H$_6$

298.15 K			308.15 K		
0.0000	28.14	0.0	0.0000	26.85	0.00
0.0687	27.88	-0.12	0.0550	26.62	-0.13
0.1329	27.67	-0.21	0.1492	26.31	-0.26
0.2057	27.48	-0.25	0.2099	26.15	-0.31
0.2773	27.31	-0.28	0.3223	25.87	-0.38
0.3115	27.24	-0.28	0.3843	25.73	-0.40
0.3862	27.08	-0.30	0.4692	25.56	-0.42
0.4434	26.97	-0.29	0.5320	25.45	-0.41
0.4933	26.89	-0.27	0.5488	25.41	-0.42
0.5125	26.85	-0.28	0.5827	25.36	-0.41
0.5543	26.77	-0.27	0.6286	25.30	-0.38
0.6755	26.55	-0.25	0.7062	25.17	-0.37
0.7145	26.50	-0.23	0.7433	25.13	-0.34
0.7831	26.38	-0.21	0.8074	25.07	-0.28
0.8789	26.25	-0.15	0.8762	25.02	-0.20
0.9342	26.19	-0.10	0.9135	25.01	-0.14
1.0000	26.16	0.00	0.9542	25.00	-0.08
			1.0000	24.99	0.00

xBA + $(1-x)$C$_6$H$_5$CH$_3$

298.15 K			308.15 K		
x	σ	σ^E	x	σ	σ^E
	10^{-3}N m^{-1}			10^{-3}N m^{-1}	
0.0000	27.93	0.00	0.0000	26.75	0.00
0.0581	27.78	-0.05	0.0832	26.48	-0.12
0.1130	27.64	-0.09	0.1633	26.24	-0.22
0.1771	27.50	-0.12	0.2213	26.07	-0.29
0.2198	27.41	-0.13	0.2844	25.90	-0.35
0.2975	27.22	-0.18	0.3201	25.82	-0.36
0.3645	27.02	-0.21	0.3943	25.67	-0.39
0.4287	26.94	-0.23	0.4849	25.52	-0.38
0.4894	26.83	-0.23	0.5462	25.43	-0.36
0.5566	26.70	-0.24	0.6066	25.36	-0.32
0.6279	26.58	-0.24	0.6885	25.27	-0.28
0.7153	26.45	-0.21	0.7400	25.23	-0.22
0.7843	26.35	-0.19	0.8213	25.13	-0.17
0.8529	26.27	-0.15	0.8811	25.07	-0.12
0.9643	26.17	-0.05	0.9442	25.01	-0.06
1.0000	26.16	0.00	1.0000	24.99	0.00

xBA + $(1-x)$CCl$_4$

298.15 K			308.15 K		
0.0000	26.15	0.00	0.0000	24.95	0.00
0.0778	26.13	-0.02	0.0629	24.88	-0.07
0.1538	26.11	-0.04	0.1459	24.84	-0.12
0.2065	26.10	-0.05	0.2012	24.82	-0.14
0.2662	26.10	-0.05	0.2917	24.79	-0.17
0.3043	26.09	-0.06	0.3593	24.79	-0.17
0.4250	26.09	-0.06	0.4205	24.78	-0.19
0.4800	26.09	-0.06	0.4924	24.79	-0.19
0.5414	26.09	-0.08	0.5529	24.80	-0.18
0.5805	26.09	-0.07	0.6327	24.81	-0.17
0.6694	26.09	-0.07	0.7048	24.82	-0.16
0.7349	26.10	-0.06	0.7849	24.85	-0.13
0.8097	26.11	-0.05	0.8459	24.88	-0.10
0.8586	26.12	-0.04	0.9319	24.93	-0.06
0.9630	26.15	-0.01	1.0000	24.99	0.00
1.0000	26.16	0.00			

xBA + $(1-x)$CHCl$_3$

298.15 K			308.15 K		
0.0000	26.53	0.00	0.0000	25.25	0.00
0.0931	26.51	0.01	0.0581	25.24	0.01
0.1874	26.48	0.02	0.1129	25.23	0.01
0.2433	26.45	0.01	0.1860	25.21	0.01
0.3517	26.44	0.02	0.2450	25.20	0.01
0.3663	26.42	0.03	0.3179	25.19	0.02
0.4314	26.40	0.03	0.3710	25.18	0.03
0.4505	26.39	0.03	0.4507	25.17	0.04
0.5085	26.37	0.03	0.5030	25.16	0.04
0.5512	26.33	0.04	0.5678	25.14	0.03
0.5954	26.32	0.01	0.6678	25.11	0.02
0.6621	26.30	0.01	0.7035	25.08	0.01
0.7035	26.28	0.01	0.8661	25.02	0.01
0.7749	26.25	0.01	0.9442	25.01	0.01
0.8289	26.23	0.01	1.0000	24.99	0.00
0.8887	26.20	0.00			
0.9312	26.19	0.00			
1.0000	26.16	0.00			

Table 1—Surface tension of acid + solvent systems—*Contd*

	298.15 K			308.15 K	
x	σ	σ^E	x	σ	σ^E
	10^{-3}N. m^{-1}			10^{-3}N.m^{-1}	

x BA + $(1-x)$ CH$_3$OH

0.0000	22.10	0.00	0.0000	21.26	0.00
0.0497	22.36	0.05	0.0572	21.58	0.11
0.1025	22.64	0.12	0.1642	22.11	0.24
0.1887	23.11	0.24	0.2396	22.44	0.29
0.2607	23.46	0.30	0.2882	22.67	0.33
0.3159	23.73	0.35	0.3514	22.94	0.37
0.4043	24.16	0.42	0.3996	23.15	0.40
0.4677	24.44	0.44	0.4579	23.39	0.42
0.5052	24.61	0.46	0.5062	23.59	0.44
0.5547	24.82	0.48	0.5662	23.83	0.46
0.6692	25.28	0.46	0.6389	24.10	0.46
0.7224	25.47	0.44	0.6843	24.24	0.43
0.8043	25.73	0.36	0.7236	24.37	0.41
0.8772	25.92	0.26	0.8042	24.59	0.33
0.9448	25.07	0.13	0.9053	24.82	0.18
1.0000	26.16	0.00	0.9444	24.92	0.14
			1.0000	24.99	0.00

x BA + $(1-x)$ (CH$_3$)$_2$CO

0.0000	22.72	0.00	0.0000	21.78	0.00
0.0386	22.90	0.05	0.0657	22.08	0.09
0.1052	23.20	0.11	0.1381	22.40	0.18
0.1490	23.41	0.17	0.2057	22.68	0.24
0.2243	23.75	0.26	0.2963	23.03	0.30
0.2742	24.95	0.29	0.3519	23.23	0.32
0.3227	24.16	0.33	0.4281	23.51	0.36
0.3643	24.32	0.35	0.4853	23,70	0.36
0.4508	24.68	0.41	0.5123	23.78	0.36
0.4912	24.84	0.43	0.5774	23.98	0.35
0.5422	25.03	0.44	0.6383	24.14	0.32
0.5932	25.21	0.45	0.7111	24.35	0.29
0.6272	25.32	0.44	0.8084	24.58	0.21
0.7059	25.55	0.40	0.8937	24.78	0.13
0.7485	25.67	0.38	0.9570	24.91	0.07
0.8235	25.87	0.32	1.0000	24.99	0.00
0.9217	26.06	0.17			
1.0000	26.16	0.00			

Fig. 1—Plot of σ^E versus x(BA) at 298.15 K; 1 : cyclohexane; 2: *n*-octane; 3: benzene; 4: toluene; 5: carbontetrachloride; 6: chloroform; 7: methanol; 8: acetone

Table 2—Values of C_i constants in Eq. (1), standard deviation (s)

T/K	C_1	C_2	C_3	s
	BA + Cyclohexane			
298.15	-0.718	0.028	—	0.01
308.15	-1.502	-0.027	0.281	0.00
	BA + n–C$_8$H$_{18}$			
298.15	-1.439	0.354	-0.035	0.01
308.15	-3.147	0.198	-0.497	0.01
	BA + C$_6$H$_6$			
298.15	-1.115	0.260	-0.843	0.01
308.15	-1.669	0.102	-0.516	0.01
	BA + C$_6$H$_5$CH$_3$			
298.15	-0.942	-0.248	-0.123	0.01
308.15	-1.502	0.455	0.224	0.01
	BA + CCl$_4$			
298.15	-0.276	-0.040	-0.080	0.01
308.15	-0.737	0.089	-0.29	0.01
	BA + CHCl$_3$			
298.15	0.107	-0.054	-0.1008	0.01
308.15	0.127	-0.012	-0.122	0.01
	BA + CH$_3$OH			
298.15	1.850	0.666	0.104	0.01
308.15	1.760	0.440	0.383	0.01
	BA + (CH$_3$)$_2$CO			
298.15	1.716	0.610	0.104	0.01
308.15	1.430	-0.060	0.00	0.01

biting positive V^E values show negative σ^E values and vice versa with similar disposition and order except in the case of cyclohexane which shows maximum V^E of all the systems. This may be due to various reasons.

Carboxylic acids are associated solvents with trimers in equilibrium with dimers and monomers. V^E behaviour of BA in various solvents has been explained on the basis of the following equilibria[13].
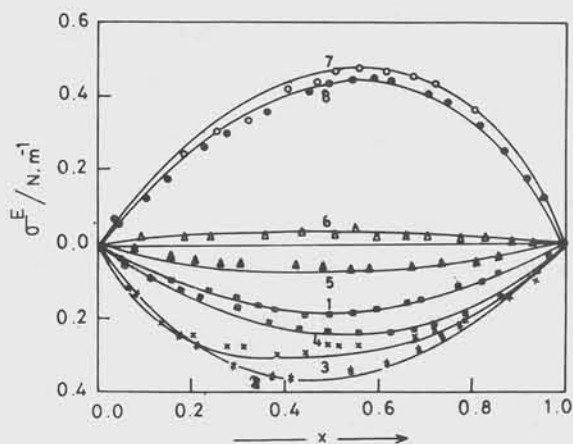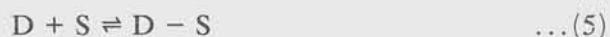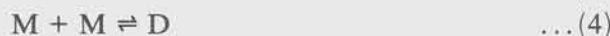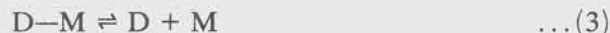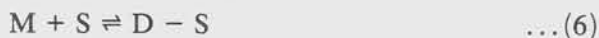
$$D-M \rightleftharpoons D + M \qquad \ldots(3)$$
$$M + M \rightleftharpoons D \qquad \ldots(4)$$
$$D + S \rightleftharpoons D - S \qquad \ldots(5)$$

$$M + S \rightleftharpoons D - S \qquad \ldots(6)$$

Similar equilibria (with minor differences) may be invoked to explain the surface phase behaviour. Non-polar solvents like cyclohexane and *n*-octane depolymerize the acid to dimers giving positive V^E and negative σ^E values stemming mainly from the first two equilibria (Eqs 4, 5).

The dimers being relatively flat molecules find it easy to be in the surface. In fact better depolymerization is seen with *n*-octane being a long chain molecule, resulting in much lower values of σ^E. Concomitantly, cyclohexane being a spherical molecule does not seem to be properly accommodated in the surface resulting in lower negative σ^E value. The planer benzene molecules is preferred to be in the surface resulting again in higher negative σ^E value further supplemented by the interaction of the acid dimer with a π-electron cloud of the benzene ring through hydrogen bonding. Toluene possessing some planar part in its molecule shows σ^E to be more positive as compared to that of benzene. Carbon tetrachloride also being a spherical bulky molecule is not preferred to show interaction with acid dimers in the surface phase. Chloroform, though a bulky molecule, undergoes antiparallel dipolar association with acid dimers, thus resulting in slight positive σ^E values[21-23]. The depolymerization of methanol and acetone solvents is overshadowed by the stronger hydrogen bond hetero molecular $M-S$ and $D-S$ interaction[17,18] resulting in high positive σ^E values.

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