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Surface Tensions and Surface Heats of Mixing of Mixtures containing Bromobenzene at 293.15 and 303.15 K

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Surface tensions of mixtures of bromobenzene with cyclohexane, benzene, *o*-, *m*-, and *p*-xylene have been determined by the capillary rise method at 293.15 and 303.15 K. The data have been used to check the various theories of surface tension of liquid mixtures. The surface heats of mixing have been computed at 293.15 K as a function of composition.

(Keywords: Mixing, surface heats of; Surface tension, calculation of)

Oberflächenspannungen und Oberflächen-Mischungswärmen von Mischungen mit Brombenzol als eine Komponente, bei 293,15 und 303,15 K

Die Oberflächenspannungen von Mischungen von Brombenzol mit Cyclohexan, Benzol und *o*-, *m*- und *p*-Xylol wurden mit der Kapillarmethode bei 293,15 und 303,15 K bestimmt. Die Daten wurden zur Überprüfung verschiedener Theorien der Oberflächenspannung herangezogen. Die Oberflächen-Mischungswärmen wurden für 293,15 K berechnet.

Introduction

Excess volumes of the above mentioned mixtures have been reported earlier[1,2]. In this paper, the surface tensions of the same mixtures are reported. Surface tensions of the liquid mixtures have been treated theoretically by *Butler*[3], *Schuchowitsky*[4], *Belton* and *Evans*[5], *Guggenheim*[6], *Kirkwood*[7], *Defay* and *Prigogine*[8,9]. *Prigogine* and *Englert-Chwoles*[10] used a combined average potential model for interactions in the cell theory. *Bellemans* and *Stecki*'s approach[11] dispensed with the specification of layers in which the composition differed from the bulk phase. *James et al.*[12] have used surface entropy

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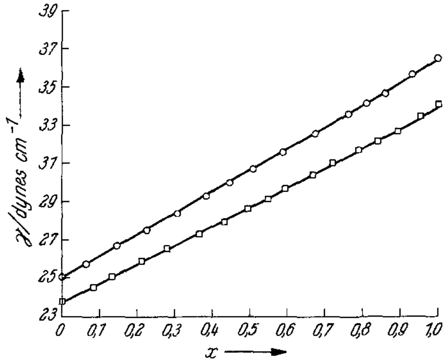

Fig. 1. Surface tension vs. x Bromobenzene, $1-x$ cyclohexane;
○ ○ ○ 293.15 K; □ □ □ 303.15 K

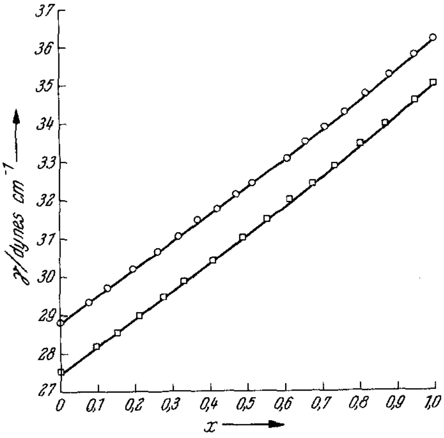

Fig. 2. Surface tension vs. x Bromobenzene, $1-x$ benzene;
○ ○ ○ 293.15 K; □ □ □ 303.15 K

and surface heats of mixing to study the formation of complexes in binary mixtures. We analysed the surface tension data in the light of above approaches including *Hildebrand*'s model[13].

Experimental

Cyclohexane, benzene, *o*-, *m*-, and *p*-xylene (all B.D.H.) and bromobenzene (Reidel) were purified as described earlier[14, 15]. The purities of the samples were checked by measuring their densities, which agreed to within 0.00002 g cm^{-3} with the corresponding literature[16, 17] values.

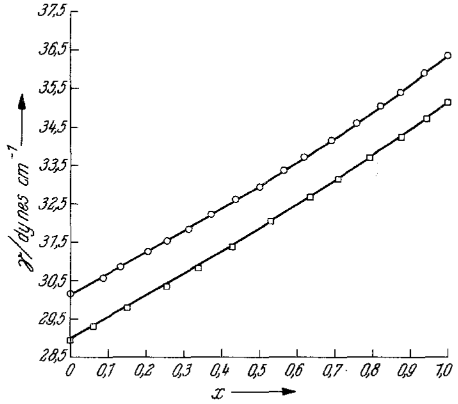

Fig. 3. Surface tension vs. x Bromobenzene, $1-x$ *o*-xylene;
○ ○ ○ 293.15 K; □ □ □ 303.15 K

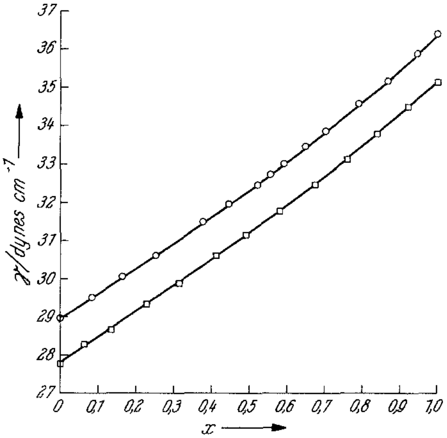

Fig. 4. Surface tension vs. x Bromobenzene, $1-x$ *m*-xylene;
○ ○ ○ 293.15 K; □ □ □ 303.15 K

The surface tensions were measured by capillary rise method. Uniform bore pyrex glass capillaries were fixed in a glass cell (specially designed for this purpose). The uniformity of the bore of the capillary was checked by measuring the length and weight of mercury thread in its different parts. The diameter of the capillary was found to be reproducible to 0.0001 cm. The glass cell containing the mixture and capillaries was placed in a water-filled thermostat controlled to within 0.01 K. The angle of contact of the glass and liquid was taken to be zero. Densities of the mixtures were taken from excess volume measurements[1,2]. Furthermore two capillaries of different diameters were always employed so as to reduce errors in the measurement of lower meniscus of the liquid in the capillary. The difference Δh in the heights of the liquid in two capillaries was noted and surface tension ν was determined from the relation:

$$\nu = 0.5 \cdot \Delta h \cdot d \cdot g \cdot r_1 \cdot r_2/(r_1 - r_2) \quad (1)$$

where r_1 and r_2 are the radii of the capillaries.

The measured surface tension values of the pure components agreed to within 0.1 dyn cm^{-1} with their corresponding literature values[16,17].

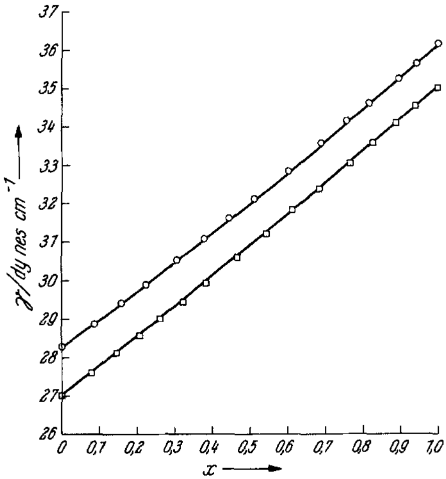

Fig. 5. Surface tension vs. x Bromobenzene, $1-x$ *p*-xylene;
○ ○ ○ 293.15 K; □ □ □ 303.15 K

Results

Surface tensions of mixtures of bromobenzene + cyclohexane, + benzene, + *o*-, + *m*-, and + *p*-xylenes were determined from relation (1) at 293.15 and 303.15 K as a function of composition. The surface tension values are plotted in Figs. 1 to 5.

Discussion

The average potential model assumes that the exact interactions between the molecules can be replaced in the configurational partition function of the solution by average interactions which depend in the case of random mixing on the individual interactions and on composition. Assuming the validity of mean interactions in the surface phase and surface phase to monomolecular, *Prigogine* and *Englert-Chwoles*[10] deduced the expression for the surface tension.

Table 1. *The calculated*[10,11,13] *and experimental* ν_{mix} *values at round mole fractions of mixtures containing bromobenzene*

x	$\nu_{\mathrm{mix}}/\mathrm{dyn\ cm^{-1}}$			
	Experimental	*Englert-Chwoles et al.*[10]	*Bellemans et al.*[11]	*Hildebrand et al.*[13]
	x bromobenzene + $(1-x)$ cyclohexane at 293.15 K			
0.1	26.32	26.33	26.34	26.36
0.2	27.40	27.41	27.42	27.43
0.3	28.48	28.49	28.50	28.52
0.4	29.61	29.62	29.63	29.64
0.5	30.66	30.68	30.70	30.71
0.6	31.81	31.83	31.84	31.85
0.7	32.96	32.97	32.99	33.00
0.8	34.06	34.07	34.08	34.09
0.9	35.28	35.29	35.30	35.31
	x bromobenzene + $(1-x)$ cyclohexane at 303.15 K			
0.1	24.83	24.84	24.85	24.86
0.2	25.82	25.83	25.84	25.84
0.3	26.80	26.81	26.82	26.83
0.4	27.80	27.81	27.83	27.83
0.5	28.75	28.77	28.78	28.79
0.6	29.77	29.79	29.80	29.81
0.7	30.81	30.81	30.83	30.83
0.8	31.82	31.83	31.83	31.84
0.9	32.94	32.95	32.96	32.96
	x bromobenzene + $(1-x)$ benzene at 293.15 K			
0.1	29.55	29.56	29.57	29.58
0.2	30.28	30.29	30.30	30.31
0.3	30.96	30.97	30.98	30.99
0.4	31.68	31.70	31.71	31.72
0.5	32.40	32.42	32.43	32.44
0.6	33.12	33.15	33.16	33.16
0.7	33.86	33.88	33.89	33.90
0.8	34.61	34.62	34.62	34.63
0.9	35.41	35.43	35.43	35.44
	x bromobenzene + $(1-x)$ benzene at 303.15 K			
0.1	28.24	28.25	28.26	28.27
0.2	28.98	28.99	29.00	29.01
0.3	29.69	29.70	29.71	29.72
0.4	30.42	30.44	30.45	30.46
0.5	31.14	31.16	31.17	31.18
0.6	31.90	31.92	31.94	31.95
0.7	32.63	32.67	32.68	32.68
0.8	33.40	33.42	33.43	33.44
0.9	34.18	34.20	34.21	34.22

Table 1 (continued)

x	ν_{mix}/dyn cm^{-1}			
	Experimental	*Englert-Chwoles et al.*[10]	*Bellemans et al.*[11]	*Hildebrand et al.*[13]
	x bromobenzene + $(1-x)$ *o*-xylene at 293.15 K			
0.1	30.62	30.63	30.64	30.65
0.2	31.15	31.16	31.17	31.18
0.3	31.72	31.74	31.75	31.77
0.4	32.31	32.33	32.34	32.35
0.5	32.92	32.95	32.96	32.97
0.6	33.53	33.56	33.57	33.59
0.7	34.16	34.18	34.20	34.21
0.8	34.82	34.83	34.85	34.86
0.9	35.50	35.51	35.52	35.53
	x bromobenzene + $(1-x)$ *o*-oxylene at 303.15 K			
0.1	29.42	29.43	29.44	29.45
0.2	30.00	30.01	30.02	30.03
0.3	30.57	30.59	30.61	30.62
0.4	31.12	31.15	31.16	31.17
0.5	31.72	31.76	31.76	31.77
0.6	32.35	32.38	32.40	32.42
0.7	32.93	32.96	32.97	32.97
0.8	33.61	33.63	33.64	33.66
0.9	34.30	34.32	34.33	34.34
	x bromobenzene + $(1-x)$ *m*-xylene at 293.15 K			
0.1	29.61	29.62	29.63	29.64
0.2	30.27	30.28	30.29	30.30
0.3	30.92	30.94	30.95	30.97
0.4	31.58	31.61	31.62	31.63
0.5	32.30	32.34	32.36	32.37
0.6	33.02	33.04	33.05	33.06
0.7	33.79	33.82	33.83	33.85
0.8	34.58	34.60	34.61	34.62
0.9	35.40	35.42	35.43	35.44
	x bromobenzene + $(1-x)$ *m*-xylene at 303.15 K			
0.1	28.46	28.47	28.48	28.49
0.2	29.13	29.15	29.16	29.17
0.3	29.82	29.84	29.85	29.86
0.4	30.43	30.51	30.52	30.53
0.5	31.16	31.20	31.21	31.23
0.6	31.87	31.89	31.91	31.92
0.7	32.62	32.64	32.66	32.67
0.8	33.40	33.41	33.42	33.43
0.9	34.20	34.22	34.23	34.24

Table 1 (continued)

x	ν_{mix}/dyn cm^{-1}			
	Experimental	*Englert-Chwoles et al.*[10]	*Bellemans et al.*[11]	*Hildebrand et al.*[13]
	x bromobenzene + (—x) p-xylene at 293.15 K			
0.1	29.02	29.03	29.04	29.05
0.2	29.79	29.80	29.81	29.82
0.3	30.54	30.56	30.58	30.58
0.4	31.33	31.35	31.36	31.38
0.5	32.10	32.13	32.15	32.16
0.6	32.92	32.95	32.97	32.98
0.7	33.71	33.74	33.75	33.77
0.8	34.55	34.57	34.58	34.59
0.9	35.36	35.37	35.38	35.40
	x bromobenzene + (1—x) p-xylene at 303.15 K			
0.1	27.73	27.74	27.75	27.76
0.2	28.52	28.54	28.55	28.56
0.3	29.30	29.32	29.33	29.34
0.4	30.06	30.09	30.10	30.11
0.5	30.86	30.89	30.90	30.91
0.6	31.64	31.68	31.68	31.69
0.7	32.51	32.53	32.54	32.56
0.8	33.32	33.33	33.34	33.35
0.9	34.15	34.16	34.17	34.18

In our calculations according to this theory[10], a slight simplification was made concerning dispersion forces, i.e., $\theta = —\delta^2/8$. The value of ν^E were calculated by taking the second component as reference in each case. The values of ν_{mix} in place of ν^E are recorded in Table 1.

Bellemans and *Stecki*[11] have suggested that there is no need to specify any layer in which the composition differs from that of the bulk phase and surface tension was calculated by applying the expansion method od *Kirkwood*. The calculated values according to [11] are summarized in Table 1.

Hildebrand's ideal solution model[13] assumes both the liquid and surface layer form ideal solutions. The values of ν_{mix} computed from this approach are recorded in Table 1 as well.

It should be interesting to examine the conclusions obtained from the computation of surface heats of mixing from surface tension data. The surface heat of mixing per unit area can be written by:

$$\Delta H^s/A = H^s/A — [x_1(H^s/A)_1 + x_2(H^s/A)_2] \qquad (2)$$

Table 2. *Surface heats of mixing of mixtures containing bromobenzene at 293.15 K*

x	$\Delta H^s/A$	x	$\Delta H^s/A$	x	$\Delta H^s/A$
x Bromobenzene + $(1-x)$ cyclohexane					
0.0624	16.34	0.1428	18.40	0.2103	21.30
0.2965	23.92	0.3710	24.90	0.4388	25.36
0.5004	25.58	0.5765	25.50	0.6621	24.86
0.7503	23.65	0.8002	21.40	0.8507	19.32
0.9228	17.56				
x bromobenzene + $(1-x)$ benzene					
0.0735	−10.48	0.1247	−12.39	0.1928	−14.88
0.2541	−17.26	0.3107	−19.41	0.3664	−21.02
0.4147	−22.86	0.4663	−23.00	0.5004	−23.24
0.6017	−22.69	0.6512	−22.04	0.7001	−21.80
0.7556	−20.01	0.8121	−18.41	0.8748	−16.36
0.9430	−12.88				
x bromobenzene + $(1-x)$ *o*-xylene					
0.0796	−12.39	0.1287	−14.44	0.2004	−16.36
0.2431	−17.08	0.3008	−19.36	0.3642	−21.88
0.4287	−23.46	0.4931	−24.00	0.5584	−23.94
0.6107	−23.68	0.6796	−22.07	0.7487	−19.46
0.8188	−17.38	0.8671	−15.12	0.9327	−13.33
x bromobenzene + $(1-x)$ *m*-xylene					
0.0826	−11.86	0.1612	−13.41	0.2430	−16.26
0.3764	−19.41	0.4438	−21.37	0.5146	−22.00
0.5538	−21.89	0.5902	−21.26	0.6490	−20.06
0.6998	−18.36	0.7865	−16.41	0.8617	−13.85
0.9388	−11.29				
x bromobenzene + $(1-x)$ *p*-xylene					
0.0806	−12.36	0.1502	−15.55	0.2101	−18.31
0.2998	−21.44	0.3711	−23.96	0.4386	−24.44
0.5009	−24.59	0.5948	−24.40	0.6819	−23.88
0.7502	−21.76	0.8127	−19.21	0.8908	−17.75
0.9411	−13.86				

where $(H^s/A)_1$ is the surface heat content of the pure component A and H^s/A is the surface heat content of the mixture.

The values of $\Delta H^s/A$ were computed for these mixtures over the entire composition range at 293.15 K and are recorded in Table 2.

From Table 2, it is evident that $\Delta H^s/A$ values are positive for bromobenzene + cyclohexane mixtures indicating the presence of dispersion forces in these mixtures. The $\Delta H^s/A$ values are negative for bromobenzene + benzene, + *o*-, + *m*-, and + *p*-xylenes indicating the presence of attractive interactions between the components of these mixtures. The magnitude of $\Delta H^s/A$ are more negative in bromobenzene+xylene mixtures than in comparison to bromobenzene+benzene mixtures.

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