Surface Tension of Lithium Bromide Solutions with Heat-Transfer Additives

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The surface tensions of concentrated aqueous solutions of lithium bromide and of lithium chloride are measured by using a drop-volume method. The effect of 1-octanol and 2-ethylhexanol on surface tension is determined for a 50% by weight lithium bromide solution.

1. Introduction

Surfactants are routinely used in large absorption refrigerating or heat pumping equipment to enhance heat and mass transfer in the absorber (*1*, *2*). Although the general consensus is that these additives promote interfacial or Marangoni convection (*3-5*), one is still unable to assign details in the mechanism whereby they trigger convection. A recent progress is the demonstration by Kashiwagi that the presence of excess surfactant as globules on the liquid surface yields optimal enhancement of the absorption rate (*5*).

The standard compound for lithium bromide aqueous solutions is 2-ethylhexanol (*1*). Other branched-chain compounds, as well as straight-chain (e.g. 1-octanol (*5*)) or fluorinated compounds (*6*), have been put forward. In order to pick a best surface-active additive for a particular pair of working medium and absorbent, a better understanding of the interfacial convection is needed. To interpret results from absorption experiments, reliable data are required on the behavior of the surface tension of these systems of working pair and so-called heat-transfer additive.

Some surface tension data are available in the literature, although they are few and incomplete. Furthermore, results from different authors do not agree. The system 1-octanol and LiBr(aq) (50 wt %) has been studied by Iyoki and Uemura (*7*), Kashiwagi et al. (*5*), and Hozawa et al. (*8*), but these three sets present differences on surface tension and solubility for octanol. Both Grosman and Naumov (*9*) and Ziukanov et al. (*10*) give data for 2-ethylhexanol in LiBr(aq) (60 wt %) and also disagree on solubility of the additive. An attempt to resolve the conflicts by comparing surface tension data for lithium bromide solutions without any additive revealed another conflict in data. There are rather large discrepancies between the three existing sets: that of Hasaba et al. (*11*, *12*), that of Bogatykh et al. (*13*), and that of Gruzdev and Kiselev (*14*). However, there is acceptable agreement between the three existing sets, those of Hasaba et al. (*15*, *16*), Bogatykh et al., and Gruzdev and Kiselev, for lithium chloride solutions. The data of Bogatykh et al. cover only the high concentrations. Except for Hozawa et al., who do not mention the method utilized, all Japanese measurements have been carried out by using the capillary method. In all Soviet measurements, the maximum bubble pressure method has been utilized, although Gruzdev and Kiselev used both methods for lithium bromide solutions.

In this report, we present new, independent measurements of the surface tension for these systems. In the case of aqueous lithium bromide solutions, we hope to resolve the existing conflict in data. In the case of lithium bromide solutions with alcoholic additives, complementary information is provided as necessary data in the analysis of interfacial convection. Hopefully, these data also settle the question of the solubility of the alcohols.

2. Experimental Section

Solutions were prepared by using anhydrous LiBr or LiCl of 99.9% purity, supplied by Merck, and doubly distilled water. The concentrations of the LiCl solutions were checked by atomic absorption spectrometry. The alcohols, 1-octanol (99.9% purity) and 2-ethylhexanol (99% purity), were also obtained from Merck and used without further purification. After the alcohols were added to the solutions with use of a micropipet, the samples were homogenized in an ultrasonic bath and allowed to cool.

The drop-volume apparatus developed by Tornberg (*17*) was used to determine the surface tension of the samples. Here, the displaced length of the piston in a precision-bore syringe is utilized to calculate the volume of the drop just detached from the tip. The instrument, manufactured by Tornberg, is connected to a personal computer for control and data acquisition. Syringe and glass receiver were thermostated within 0.5 °C. At elevated temperatures, the receiver was filled to a third of its volume with the sample liquid in order to minimize evaporation from the drop. Each value of surface tension reported here for the salt solutions is the average of four to six series of measurements, twenty drops in each series. The results for the ternary systems are the average of two series of measurements. Most samples were prepared twice.

The liquid density values used for calculating the surface tension from the volume of the drop were taken from the International Critical Tables (ICT) (*18*) and, when these were not sufficient, from Hasaba et al. (*11*, *15*). The discrepancies between the ICT set of data and more recent complete (*11*) or partial (*19*, *20*) experimental data are at most of the order of 0.3%. The small concentrations of alcohols, less than 1000 ppm, were assumed to have a negligible influence on solution density.

3. Results

Results obtained for the salt solutions are presented in Table I and Figure 1 for lithium chloride solutions and in Table II and Figures 2 and 3 for lithium bromide solutions. The experimental standard deviation is reported for each value in the tables. A comparison with previous workers' data for lithium chloride is done in Figure 1. The results in the present investigation are in good agreement with those of previous authors, if a little low, within 2% of literature data. In the case of lithium bromide, see Figure 2, there is generally good agreement at low concentrations, but differences increase at higher concentrations and temperatures. A comparison between all four sets of data is shown in Figure 3 for the 60 wt % solution. For the sake of completeness, the values that Loewer (*21*) calculated by extrapolating data for dilute solutions are also shown.

The results obtained for LiBr(aq) (50 wt %) solutions with additives are reported in Table III, together with standard de-

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Table I. Surface Tension Data for LiCl Aqueous Solutions (mN/m)

	surface tension at various T							
C, %	20 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C
10	76.81 ± 0.07	75.92 ± 0.08	74.30 ± 0.02	72.70 ± 0.04	71.10 ± 0.03	69.17 ± 0.07	67.39 ± 0.12	
20	82.58 ± 0.02	81.42 ± 0.02	80.03 ± 0.05	78.73 ± 0.04	77.17 ± 0.06	75.50 ± 0.08	73.81 ± 0.08	
30	90.17 ± 0.25	89.11 ± 0.03	87.94 ± 0.10	86.79 ± 0.05	85.27 ± 0.06	84.05 ± 0.15	82.46 ± 0.13	80.76 ± 0.42
40	96.81 ± 0.08	95.89 ± 0.03	94.73 ± 0.05	93.57 ± 0.10	92.47 ± 0.02	91.06 ± 0.05	89.55 ± 0.20	88.09 ± 0.17

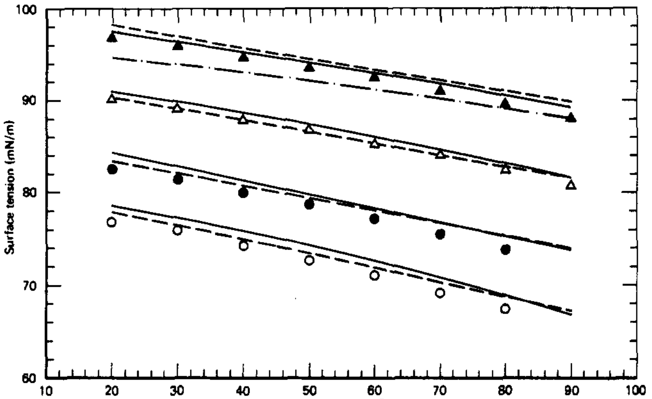

Figure 1. Surface tension of aqueous lithium chloride solutions. Key: (○, ●, △, and ▲) 10, 20, 30, and 40 wt %, respectively; (full line) Gruzdev and Kiselev (*14*); (dashed line) Hasaba et al. (*15*, *16*); (dashed-dotted line) Bogatykh et al. (*13*).

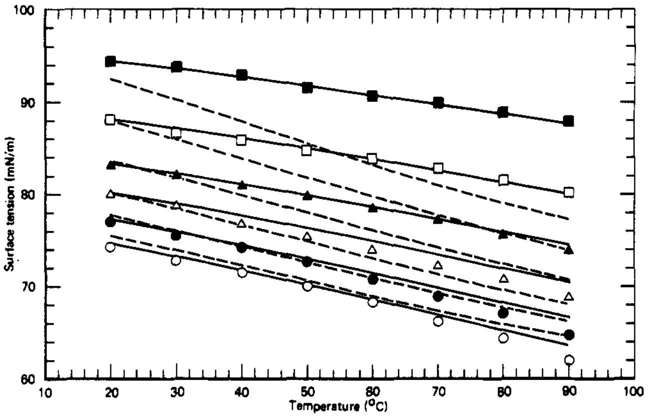

Figure 2. Surface tension of aqueous lithium bromide solutions. Key: (○) 10 wt %; (●) 20 wt %; (△) 30 wt %; (▲) 40 wt %; (□) 50 wt %; (■) 60 wt %; (full-drawn line) Gruzdev and Kiselev (*14*); (dashed line) Hasaba et al. (*11*, *12*).

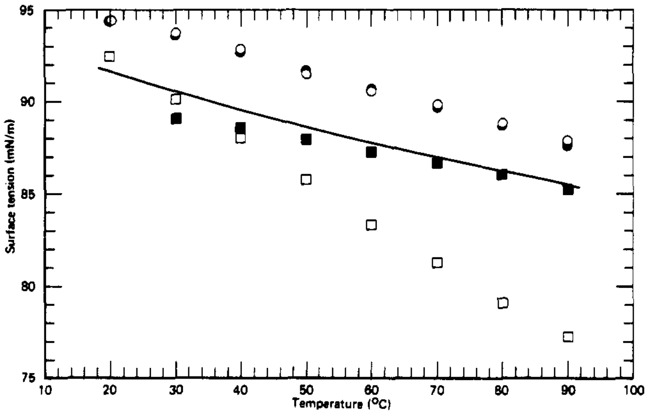

Figure 3. Surface tension of LiBr(aq) (60 wt %) solutions. Key: (○) the present investigation; (●) Gruzdev and Kiselev (*14*); (□) Hasaba et al. (*11*, *12*); (■) Bogatykh et al. (*13*); (line) Loewer (*21*).

viations for each value. Error bars corresponding to a 95% confidence interval are drawn in Figure 4 (1-octanol) and Figure 5 (2-ethylhexanol). The deviations from the data of previous investigators are larger than for additive-free solutions.

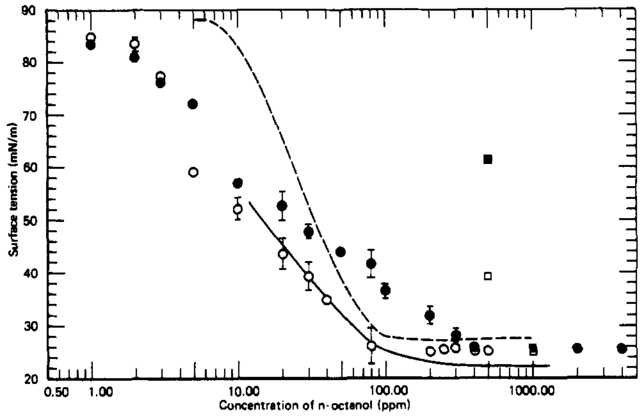

Figure 4. Surface tension for the system LiBr(aq) (50 wt %) and 1-octanol. Key: for the present investigation, (○) 25 °C and (●) 50 °C; for Iyoki and Uemura (*7*), (□) 25 °C and (■) 50 °C; (dashed line) Kashiwagi et al. (*5*), 25 °C; (full line) Hozawa et al. (*8*), 20 °C.

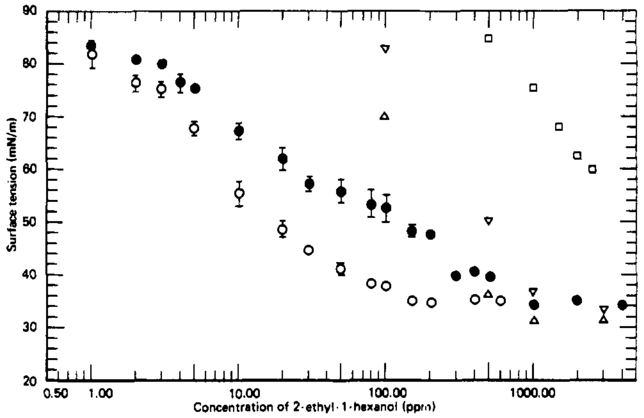

Figure 5. Surface tension for the system LiBr(aq) (50 wt %) and 2-ethylhexanol. Key: for the present investigation, (○) 25 °C and (●) 50 °C; for the sake of comparison, literature data for the systems with LiBr(aq) (60 wt %) are also shown: for Grosman and Naumov (*6*), (□) 25 °C; for Ziukanov et al. (*9*), (▽) 25 °C and (△) 50 °C.

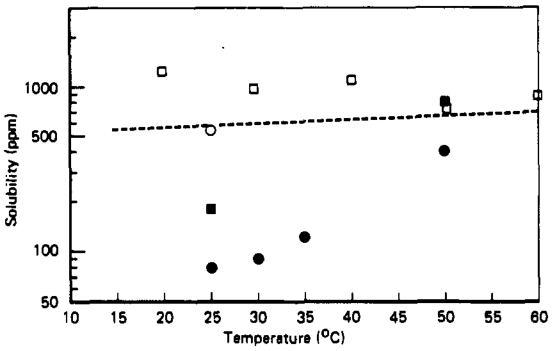

Figure 6. Solubility of 1-octanol and of 2-ethylhexanol. Key: in LiBr(aq) (50 wt %), the present investigation, (●) octanol and (■) ethylhexanol; in water, (○) octanol (value recommended in ref 22) and (□) ethylhexanol (*23*); (dashed line) the general trend of literature data for 1-octanol (*22*, *23*).

Solubilities for the alcohols may be estimated from the data in Figures 4 and 5. These are shown in Figure 6, together with solubilities in pure water (*22*, *23*). The solubility of 1-octanol at 30 and 35 °C has been determined from surface tension

Table II. Surface Tension Data for LiBr Aqueous Solutions (mN/m)

	surface tension at various *T*							
C, %	20 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C
10	74.28 ± 0.06	72.84 ± 0.07	71.54 ± 0.11	70.01 ± 0.17	68.28 ± 0.25	66.20 ± 0.11	64.37 ± 0.12	61.97 ± 0.41
20	77.03 ± 0.01	75.53 ± 0.24	74.27 ± 0.10	72.66 ± 0.03	70.76 ± 0.09	68.95 ± 0.10	67.08 ± 0.03	64.65 ± 0.42
30	80.18 ± 0.08	78.85 ± 0.05	76.93 ± 0.07	75.51 ± 0.10	74.09 ± 0.07	72.37 ± 0.09	70.97 ± 0.27	69.03 ± 0.50
40	83.27 ± 0.05	82.21 ± 0.17	81.05 ± 0.02	79.88 ± 0.04	78.54 ± 0.02	77.30 ± 0.05	75.68 ± 0.29	73.98 ± 0.16
50	88.10 ± 0.15	86.60 ± 0.20	85.85 ± 0.09	84.76 ± 0.10	83.79 ± 0.07	82.75 ± 0.18	81.49 ± 0.16	80.20 ± 0.03
60	94.40 ± 0.11	93.71 ± 0.06	92.88 ± 0.10	91.51 ± 0.07	90.59 ± 0.09	89.86 ± 0.08	88.84 ± 0.01	87.88 ± 0.17

Table III. Surface Tension Data for LiBr (50 %) with 1-Octanol or with 2-Ethyl-1-hexanol

	1-octanol		2-ethyl-1-hexanol	
C, ppm	25 °C	50 °C	25 °C	50 °C
1	84.90 ± 0.16	83.37 ± 0.23	81.92 ± 1.31	83.46 ± 0.21
2	83.36 ± 0.65	80.97 ± 0.52	76.27 ± 0.77	80.65 ± 0.40
3	77.19 ± 0.29	76.24 ± 0.30	75.23 ± 0.72	80.16 ± 0.31
4				76.40 ± 0.88
5	59.09 ± 0.53	72.18 ± 0.52	67.86 ± 0.66	75.44 ± 0.47
10	52.12 ± 1.04	56.86 ± 0.22	55.51 ± 1.17	67.94 ± 0.77
20	43.59 ± 1.46	53.54 ± 1.38	48.73 ± 0.76	59.93 ± 1.05
30	39.62 ± 1.33	47.93 ± 0.65	44.81 ± 0.54	57.34 ± 0.70
40	34.74 ± 0.27	43.94 ± 0.35		
50			41.23 ± 0.56	55.97 ± 1.11
80	26.08 ± 1.69	41.66 ± 1.30	38.52 ± 0.34	53.54 ± 1.29
100		36.45 ± 0.71	38.06 ± 0.42	52.60 ± 1.29
150			35.23 ± 0.06	48.45 ± 0.61
200	25.07 ± 0.06	31.99 ± 0.84	34.96 ± 0.04	47.75 ± 0.53
250	25.36 ± 0.05			
300	25.68 ± 0.02	28.14 ± 0.71		40.08 ± 0.53
400	25.16 ± 0.58	25.92 ± 0.78	35.52 ± 0.12	40.79 ± 0.05
500	25.17 ± 0.19			39.72 ± 0.36
600			35.24 ± 0.06	
1000		25.53 ± 0.33		34.48 ± 0.39
2000		25.41 ± 0.19		35.28 ± 0.06
4000		25.38 ± 0.02		34.53 ± 0.10

measurements, which are not reported here for the sake of brevity.

4. Discussion

The good agreement between our surface tension data and those of Hasaba et al. and of Gruzdev and Kiselev for the lithium chloride solutions shows that the experimental technique adopted is well-suited. The deviation from literature data for both LiCl and LiBr solutions is largest, 1.5 mN/m or 2%, for the lower concentrations and high temperatures, where our surface tension values show a tendency to drop off from those of previous authors. One of the reasons could be the formation of bubbles in the sample liquids at 80 and 90 °C, in spite of their having been degassed previously. The two missing values in Table I have been excluded because they were obviously in error. Bubbles do not appear for the more concentrated solutions, e.g. LiCl(aq) (30 wt %).

The differences between the now four sets of data for lithium bromide solutions are much larger. Our results confirm those of Gruzdev and Kiselev (*14*). We suggest that the surface tension data reported by Hasaba et al. (*11*, *12*) should be disregarded. The extrapolation by Loewer comes quite close to the experimentally determined surface tensions but is superseded by these experimental data. The data of Bogatykh et al. (*13*) for both lithium chloride and lithium bromide solutions fall 2-6 mN/m below other sets and should also be disregarded.

For solutions with additives, the present results do not confirm any set of data in total. In the case of 1-octanol, there is partial agreement in some concentration range with any of the three previous results. However, our data confirm the solubility of ca. 100 ppm at 25 °C obtained by Kashiwagi et al. and by Hozawa et al. For ethylhexanol, the comparison is complicated by the different concentrations of lithium bromide: 50 wt % here, 60 wt % in the Soviet reports (*9*, *10*). Surface tension measurements of the system octanol and LiBr(aq) (60 wt %) could not be performed because LiBr precipitated. This does not occur for ethylhexanol. The data of Ziukanov et al. show a decrease of surface tension with temperature, which neither should be expected for these systems, nor is found in the present results.

The solubility of both alcohols at 25 °C in LiBr(aq) (50 wt %) is an order of magnitude lower than in pure water; see Figure 6. The increase in solubility of 2-ethylhexanol from a 50 wt % to a 60 wt % solution of LiBr shown by the data of Ziukanov et al. is not consistent with this salting out effect. The solubilities obtained here for the alcohols in concentrated salt solutions show a much stronger dependence on temperature than those in the case of salt-free systems. It would be interesting to investigate the behavior of these systems at temperatures above 50 °C.

Acknowledgment

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