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Surface Tension of Aqueous Lithium Bromide + 2-Ethyl-1-hexanol

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The surface tension of an aqueous lithium bromide solution containing an active surfactant (2-ethyl-1-hexanol) was measured over the lithium bromide concentration range $40 \le C_{LiBr} \le 60$ wt % and surfactant concentration range $0 \le C_{sur} \le 200$ ppm. The Du Nouy ring method was employed to determine the surface tension.

Introduction

When surfactants exist in aqueous lithium bromide, the surface tension of the solution is a function of the concentration of lithium bromide, the concentration of surfactants, and the temperature. In the literature, there is a limited number of studies related to the surface tension of lithium bromide with surfactants such as alcohols with 6–10 carbon atoms. Surface tension in the 50 mass % LiBr + octan-1-ol system has been measured by Kashiwagi et al. (*1*) and Hozawa et al. (*2*). Considerable differences in surface tension in these studies were found. Studies of 60 mass % LiBr with 2-ethyl-1-hexanol have been done by Grosman and Naumov (*3*) and Ziukanov et al. (*4*) using the maximum bubble pressure method. Again, there are large differences in the surface tension results. Yao et al. (*5*) recently measured the surface tension of lithium bromide with octan-1-ol or 2-ethyl-1-hexanol for lithium bromide concentrations 10–50 mass % and surfactant concentrations 1–4000 ppm using a drop volume method. The effect of temperature was also studied by Yao et al. (*5*).

In the present study, the surface tension of an aqueous lithium bromide solution containing an active surfactant was measured over the lithium bromide concentration range $40 \le C_{LiBr} \le 60$ mass % and surfactant concentration range $0 \le C_{sur} \le 200$ ppm by mass. Studies on absorption of water vapor into aqueous lithium bromide with a single surfactant (typically 2-ethyl-1-hexanol) requires information about the surface tension, because surface tension gradients at the liquid–vapor interface can influence the film flow characteristic as well as the interfacial mass transfer.

Experimental Section

The Du Nouy ring method was employed to determine the surface tension. A tensiometer (CSC Scientific Co., model CSC 70535) was used. Measurement values were obtained by a direct scale reading within ±0.1 mN·m^{-1}. Avoiding disturbances and keeping the ring horizontal were essential to precise measurements. The scale readings of a tensiometer may not have true values of surface tension since the pull of the liquid on the ring is not perfectly vertical, and there is a pressure difference between the top and bottom of the ring.

Table 1. Surface Tension for Aqueous Lithium Bromide + 2-Ethyl-1-hexanol

	σ/(mN·m^{-1})				
C_{sur}/ppm	60 mass % LiBr $t = 24$ °C	60 mass % LiBr $t = 48$ °C	50 mass % LiBr $t = 24$ °C	50 mass % LiBr $t = 48$ °C	40 mass % LiBr $t = 24$ °C
0	81.3 ± 0.1	78.7 ± 0.1	77.6 ± 0.4	75.9 ± 0.2	75.8 ± 0.4
10	71.0 ± 0.4	73.9 ± 0.1	74.6 ± 0.9	75.7 ± 0.2	75.5 ± 0.7
20	67.6 ± 0.4	73.7 ± 0.7	69.8 ± 0.2	74.3 ± 0.7	74.1 ± 0.8
30	47.7 ± 0.3	69.9 ± 0.7	65.4 ± 0.9	72.1 ± 0.9	73.3 ± 0.2
50	36.5 ± 0.4	65.7 ± 0.4	59.8 ± 1.3	67.2 ± 0.8	65.4 ± 1.6
100	35.4 ± 0.3	56.0 ± 0.3	51.1 ± 1.1	57.9 ± 0.7	59.1 ± 1.6
200	34.9 ± 0.8	44.1 ± 0.7	38.2 ± 1.0	47.2 ± 0.4	53.4 ± 0.6

The direct readings from the surface tension measurements were corrected by the method suggested by Harkins and Jordan (*6*). All the measurements of surface tension were made at 24 ± 0.5 and 48 ± 0.5 °C. Solution temperatures were controlled by a constant-temperature bath and were monitored during the experiments. All preparations and measurements were at normal atmospheric pressure with surfaces exposed to air.

Solutions were prepared by using 99.9 mass % anhydrous lithium bromide purchased from Sigma. Deionized water was added to make up the required solution concentration. The solution concentration was checked by a pycnometer. A micropipet was used to add 2-ethyl-1-hexanol obtained from Aldrich Chemical to the solution. Then, solutions were mixed by a magnetic stirrer and left at room temperature for at least 48 h. For pure water the surface tension, σ, at 24 °C was measured as 71.5 ± 0.1 mN·m^{-1}, and for pure 2-ethyl-hexanol the measured value was 26.1 ± 0.1 mN·m^{-1}.

Results and Discussion

The surface tensions for the aqueous lithium bromide + 2-ethyl-1-hexanol are given in Table 1. The table describes the surface tensions with the experimental standard deviation at the given lithium bromide concentration, surfactant concentration, and temperature. The surface tension of the lithium bromide with an additive will approach the surface tension of the additive + water phase when a second phase is present on the surface.

The experimental results are compared with the results of Yao et al. (*5*) in Figure 1 for 50 mass % lithium bromide with 10–200 ppm by mass 2-ethyl-1-hexanol. As expected, surface

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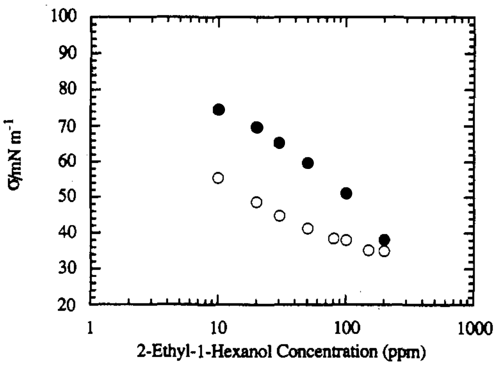

Figure 1. Surface tension of 50 mass % lithium bromide with 2-ethyl-1-hexanol concentrations of 10–200 ppm by mass. Key: (●) present study at 24 °C; (○) from Yao et al. (*5*) at 25 °C.

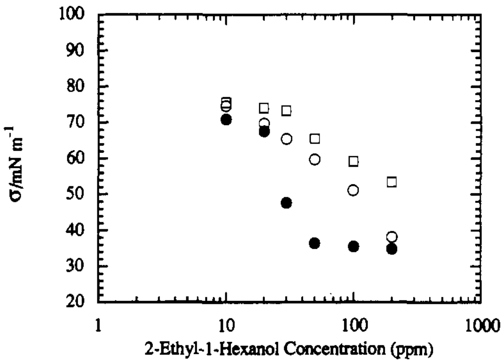

Figure 2. Effect of 2-ethyl-1-hexanol concentration on the surface tension of aqueous lithium bromide at 24 °C. Key: (●) 60 mass % LiBr; (○) 50 mass % LiBr; (□) 40 mass % LiBr.

tensions are decreased with increasing surfactant concentrations, but the results from the Du Nouy ring method are higher than those from the drop volume method. This may be due to stretching the surface at the moment of measurement when detachment takes place. The pulling of the ring from the surface may destroy the surface equilibrium; then there may be a surface deficient portion created by the ring movement (*7*).

Figure 2 shows the effect of 2-ethyl-1-hexanol concentration on the surface tension of different lithium bromide concentrations. The results show that higher lithium bromide concentrations lead to lower surface tensions for the same concentration of additive. This is due to the lower solubility of 2-ethyl-1-hexanol in the higher lithium bromide concentration. Consequently, there is more surface excess and lower surface tension as the lithium bromide concentration increases.

The measured values of the surface tensions of aqueous lithium bromide with surfactants shown in Figures 1–4 show complex behavior. It is of interest to briefly review the subject of the surface tension of binary systems given by Adamson (*8*). The surface tension of a one-component system is only a function of temperature, and the surface tension of most liquids decreases linearly with temperature. In Figure 3, the measured surface tension of aqueous lithium bromide at constant concentration without surfactants decreases as the temperature increases. For a binary system, the Gibbs equation (*8*) describes the surface tension, σ, as

$$d\sigma = -\Gamma_1^{\sigma}\, d\mu_1 - \Gamma_2^{\sigma}\, d\mu_2 \tag{1}$$

where Γ_1^{σ} and Γ_2^{σ} are the arbitrary chosen dividing surface excesses per unit area for phases 1 and 2, respectively. μ_1 and μ_2 are the surface chemical potentials of each phase defined as

$$\mu = RT \ln a \tag{2}$$

where a is the activity of the solute, R is the gas constant, and T is the absolute temperature. If the dividing surface is appropriately chosen so that Γ_1^{σ} becomes zero, then Γ_2^{σ} can be written as Γ_2^1 and

$$\Gamma_2^1 = -\left(\frac{a}{RT}\right)\left(\frac{d\sigma}{da}\right) \tag{3}$$

If there is surface deficiency of the solute ($\Gamma_2^1 < 0$), the value of $d\sigma/da$ becomes positive. Figure 4 shows an increase in the surface tension of lithium bromide with increasing solute activity (top curve). If there is a surface excess of solute ($\Gamma_2^1 > 0$), $d\sigma/da$ is negative. Thus, if there are surfactants in the lithium bromide solution (considering the aqueous lithium bromide as one component and the surfactant as the second component), the surface tension of the solution drops with increasing surfactant concentration at constant lithium bromide concentration. This effect is also shown in Figure 4. In a lithium bromide + surfactant system, the solubility of the surfactant in aqueous lithium bromide appears to increase as temperature increases (*5*). In turn, the decreased surface excess results in a higher surface tension. Figure 3 illustrates this effect and shows that the temperature effect for the surfactant-containing cases is different from that of the usual binary system.

If surfactants are added to aqueous lithium bromide, the equilibrium surface is not established as fast as in pure liquids due to the required time for the solution to reach its equilibrium condition. Diffusivities in the high salt concen-

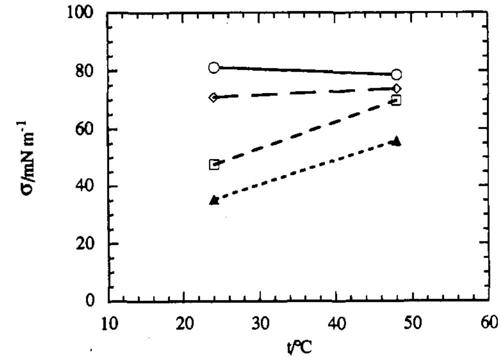

Figure 3. Effect of temperature on the surface tension of 60 mass % LiBr with 2-ethyl-1-hexanol (a linear relationship is assumed between the two temperatures). Key: (○) no surfactant; (◇) 10 ppm 2-ethyl-1-hexanol; (□) 20 ppm 2-ethyl-1-hexanol; (▲) 30 ppm 2-ethyl-1-hexanol.

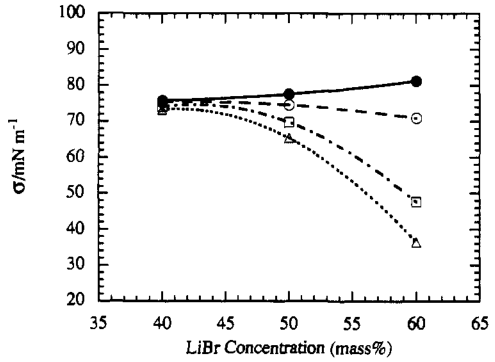

Figure 4. Effect of LiBr concentration on surface tension with 2-ethyl-1-hexanol at 24 °C. Key: (●) no surfactant; (○) 20 ppm 2-ethyl-1-hexanol; (□) 20 ppm 2-ethyl-1-hexanol; (△) 30 ppm 2-ethyl-1-hexanol.

tration case may be much longer than the diffusivities in pure water (*9*). This occurs because the water exists in the coordination shell around the Li ion, and little or no free water would exist at the higher salt concentration. Therefore, the time to reach equlibrium with 2-ethyl-1-hexanol and aqueous lithium bromide could be very long. Consequently, the surface tensions of aqueous lithium bromide containing surfactants would show different values if the method resulted in a short surface age. This may be why surface tension measurements in the literature differ widely. The measurements in this work are consistent for the Du Nouy ring procedure, but the actual surface tension in the aqueous lithium bromide with 2-ethyl-1-hexanol system depends on the surface age.

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