Studies on Surface Tension of the System: Barium Soap-Water and Propanol-1

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Abstract

The surface tension results of the barium soap solutions in water-propanol-1 mixtures have been explained on the basis of Szyszkowski's empirical equation: $\gamma = \gamma_0 (1 + X \ln Y) - X \gamma_0 \ln C$. The values of the constants X and Y of the equation have been calculated for various soap systems. The constant X is found to be almost independent of the composition of the solvent mixture but it depends to some extent on the chain length of the soap. The values of Y show a marked increase at 50% propanol-1 concentration which confirms that the transition in the nature of the micelles takes place at about 50% propanol-1 concentration. The values of X and Y are suggestive of the size and nature of the micelles, respectively.

Introduction

In the previous communications (1,2), the conductivity and viscosity of the barium soap-water and propanol-1 system have been investigated. In the present work, the surface tension of barium soap solutions in water-propanol-1 mixtures of varying composition has been studied. Szyszkowski's (3) empirical equation has been applied with a view to find out the size and nature of the micelles formed in mixed solvents.

Experimental Procedures

The chemicals have been purified and the soap solutions prepared by the methods described in the previous communication (1). The surface tension and density of the soap solutions have been determined by means of stalagmometer and pyknometer, respectively at 40 ± 0.05 C. The surface tension results are in dynes/cm.

Results and Discussion

The surface tension, γ, of barium soap solutions in water-propanol-1 mixtures of varying composition decreases with the increase in volume per cent of propanol-1 in the system. The decrease may be due to the increasing size of the micelles as the alcohol is also incorporated in the micelles. The surface tension at first decreases rapidly, then slowly and finally linearly with the increase in propanol-1 concentration. The plots of the surface tension, γ, against volume per cent of propanol-1 show a marked change at 50% propanol-1 concentration (Fig. 1) which may be due to the change in the nature of the micelles formed in soap solutions. A change at 50% propanol-1 concentration is also observed in conductivity and viscosity results (1,2). It has been suggested that hydrophilic oleomicelles are formed below 50% propanol-1 concentration and the change in the nature of the micelles from hydrophilic oleomicelles to lipophilic hydromicelles [according to the classifica-

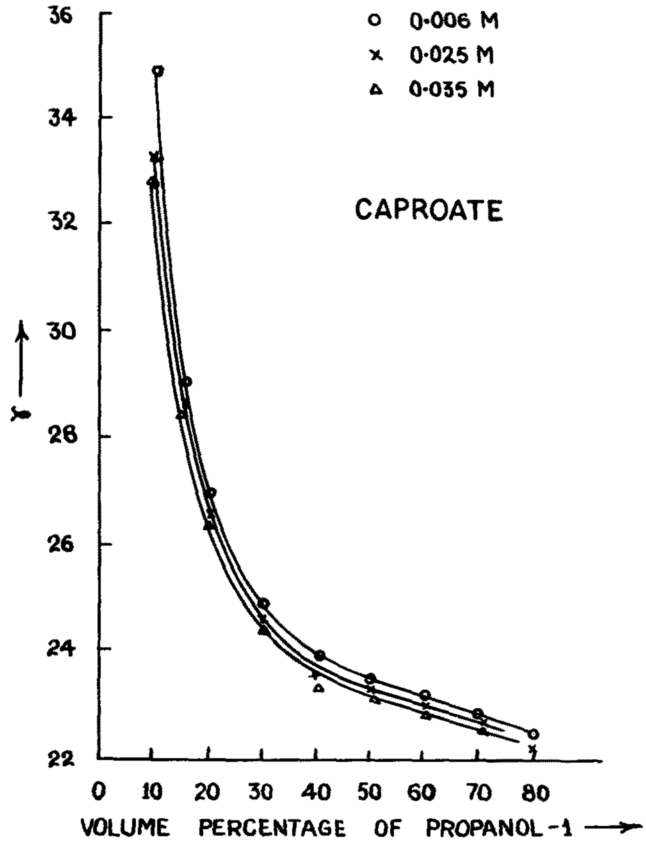

FIG. 1. Surface tension, γ, against volume per cent of propanol-1.

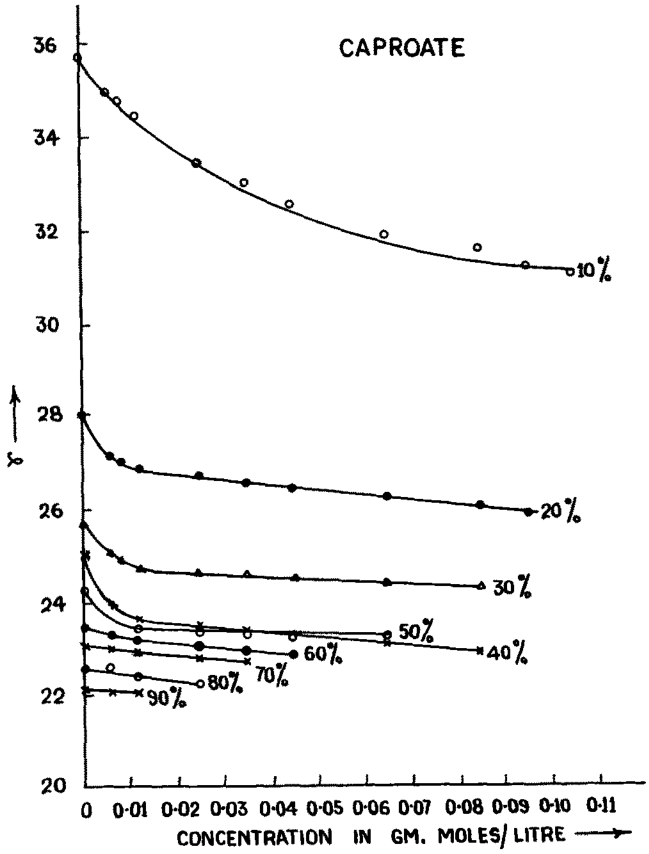

FIG. 2. Surface tension, γ, against concentration of soap.

TABLE I
Values of X

Volume % of Propanol-1	Soap name			
	Laurate	Caprate	Caprylate	Caproate
10	....	....	....	0.019
20	....	....	0.010	0.011
30	0.006	0.005	0.011	0.010
40	0.005	0.006	0.011	0.011
50	0.006	0.008	0.010	0.009
60	0.005	0.006	0.010	0.009
70	0.005	0.007	0.010	0.007
80	0.006	0.004	0.010	0.011

TABLE II
Values of Y

Volume % of Propanol-1	Soap name			
	Laurate	Caprate	Caprylate	Caproate
10	....	....	....	6.4×10^{-6}
20	....	....	1.7×10^{-4}	1.2×10^{-4}
30	8.0×10^{-6}	5.4×10^{-6}	5.8×10^{-4}	4.9×10^{-4}
40	9.2×10^{-7}	2.9×10^{-5}	7.3×10^{-4}	8.2×10^{-5}
50	4.2×10^{-3}	4.2×10^{-2}	2.4×10^{-2}	8.0×10^{-3}
60	1.0×10^{-3}	2.6×10^{-3}	1.3×10^{-2}	3.2×10^{-3}
70	1.5×10^{-3}	7.1×10^{-3}	1.3×10^{-2}	7.1×10^{-3}
80	2.7×10^{-3}	1.2×10^{-2}	2.6×10^{-2}	8.9×10^{-3}

tion of the micelles by Schulman and Riley (4)] takes place at about 50% propanol-1 concentration.

It has also been observed that the surface tension of barium soap solutions decreases as the concentration of the soap increases. The decrease in the surface tension may be due to the increase in the size of the micelles due to the increasing tendency to form aggregates with the increase in the soap concentration. The plots of surface tension, γ, against the soap concentration (g mole/liter) show that at first the surface tension decreases rapidly and then linearly with the increase in the soap concentration (Fig. 2). The plots show a sharp change in the surface deficiency of the soap at a definite concentration, 0.0125 M, which is independent of the chain length of the soap and of the composition of water-propanol-1 mixture used as a solvent. However, it may be pointed out that no sharp change in the behavior is observed in soap solutions containing 10% propanol-1.

It may also be pointed out that the plots of surface tension, γ, against logarithm of soap concentration, log C, are linear for soap solutions containing 30% to 80% propanol-1 (Fig. 3). The results are in agreement with Szyszkowski's (3) empirical equation for solutions of fatty acids:

$$\frac{\gamma}{\gamma_0} = 1 - X \ln \frac{C}{Y} \quad [1]$$

where γ and γ_0 are the surface tensions of solution of concentration C and of pure solvent, respectively and X and Y are constants. The equation [1] can be written in the form:

$$\gamma = \gamma_0 \left[1 + X \ln Y\right] - X \gamma_0 \ln C \quad [2]$$

Hence,

$$\frac{d\gamma}{d \ln C} = -X \gamma_0 \quad [3]$$

and by substitution in Gibbs adsorption equation, the adsorption excess, (τ), i.e., the excess concentration of solute per unit area of the surface is found to be:

$$\tau = -\frac{C}{RT} \frac{d\gamma}{dC} = \frac{X\gamma_0}{RT} \quad [4]$$

Therefore, the surface area covered by the soap micelles formed by 1 g mole of the soap:

$$\text{Area} = \frac{RT}{X\gamma_0}$$

The values of X have been calculated from the slopes ($-2.303\ \gamma_0 X$) of the plots of the surface tension against logarithm of soap concentration and the results are given in Table I.

It has been observed that the values of X are independent of the volume per cent (between 30% to 80%) of propanol-1 in the system but depend to some extent on the chain length of the soap. Therefore, the surface area covered by the soap micelles formed by 1 g mole of the soap depends only on the surface tension of water-propanol-1 mixture used as a solvent. The surface tension of the water-propanol-1 mixture decreases with the increase in the volume per cent of propanol-1 and so results in the increase in the surface area covered by the soap micelles. The increase in surface area may be due to the increase in the size of the micelles as the alcohol is also incorporated in the micelles. The approximate values of the surface area covered by the micelles formed by 1 g mole of different soaps are as follows: Laurate (18–21) 10^{10}, Caprate (17–19) 10^{10}, Caprylate (9–11) 10^{10} and Caproate (9–11) 10^{10} cm^2. It is observed that the area occupied by laurate and caprate micelles is much greater than that of caprylate and caproate. This difference may be due to the increase in the size of the micelles with the increase in the chain length of the soap. It is interesting to note that the surface area covered by the micelles of caproate and caprylate is almost half that of caprate and laurate.

However, it may be pointed out that the plots of γ against log C in presence of 10% and 20% propanol-1 are linear for dilute soap solutions but show deviations at higher soap concentrations (above 0.090 and 0.045 M for 10% and 20% propanol-1, respectively). The values of X calculated from the slope of the linear portion of the graph for 10% and 20% propanol-1 are higher than that for 30% to 80% propanol-1 systems and so the soap micelles formed in 10% and 20% propanol-1 cover less surface area. This is in agreement with the view that the size of the micelles increases as the volume per cent of propanol-1 in the system increases.

The values of Y have been calculated from the intercepts [$= \gamma_0 (1 + X \ln Y)$] of the plots of γ against log C and the results are summarized in Table II. It is observed that the values of Y for soap solutions containing 50% to 80% propanol-1 are much higher than the corresponding values for solutions containing propanol-1 below 50%. This may be due to the fact that Y depends on the nature of the micelles formed in soap solutions in mixed solvents. The large difference in the values of Y (below and above 50% propanol-1) suggests that the change in the nature of the micelles takes place at about 50% propanol-1 concentration.

TABLE III
Values of $-X \ln Y$

Volume % of Propanol-1	Soap name			
	Laurate	Caprate	Caprylate	Caproate
10	......	......		0.23
20	......	......	0.09	0.10
30	0.07	0.06	0.08	0.08
40	0.07	0.06	0.08	0.10
50	0.03	0.03	0.04	0.04
60	0.03	0.04	0.04	0.05
70	0.03	0.03	0.04	0.03
80	0.03	0.02	0.04	0.05

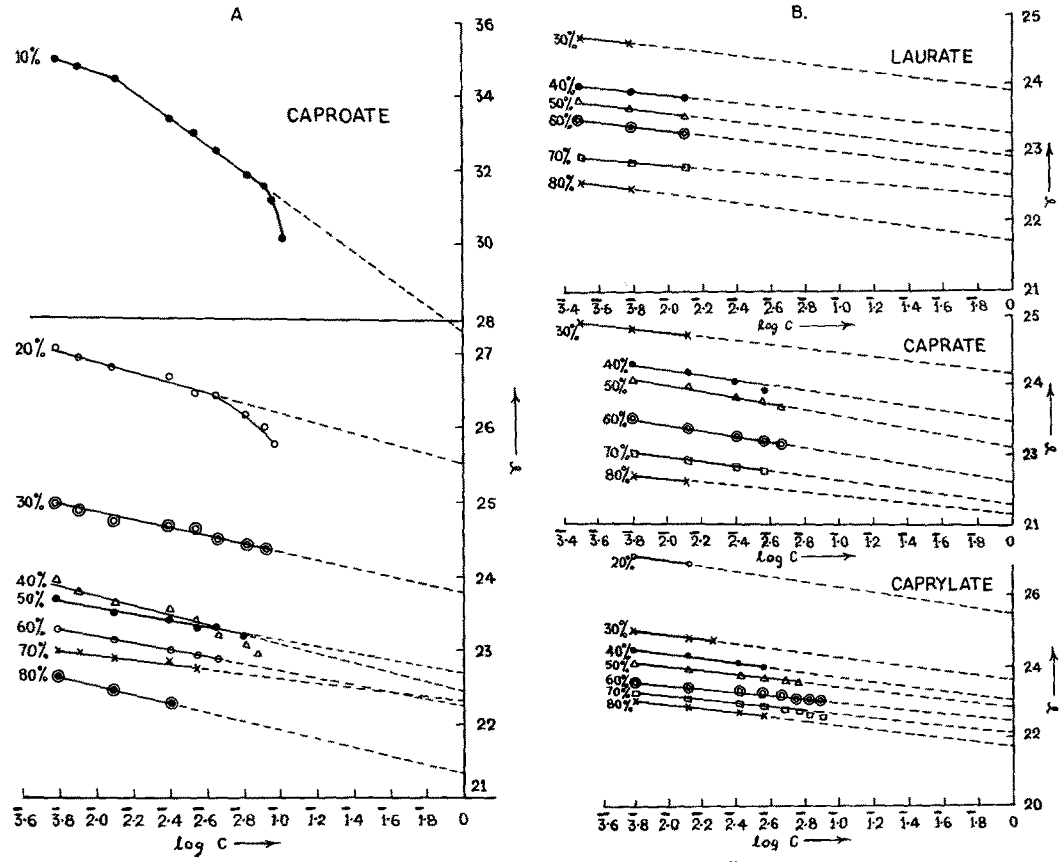

FIG. 3. Surface tension, γ, against log C.

It is also observed that the values of Y also vary with the chain length of the soap. This variation may be partly due to the difference in the values of X for different soaps, which have been used in the calculation of Y from the values of the intercepts $[=\gamma_0(1+X\ln Y)]$ of the plots of γ against log C (Fig. 3) but it is not entirely due to it.

The results show that the values of X and Y depend to some extent on the chain length of the soap. The constant X is almost independent of the composition of the solvent mixture whereas the values of Y show a marked change at 50% propanol-1 concentration. However, it may be pointed out that X and Y seem to be interdependent on each other in such a way that the values of $-X \ln Y$ become almost independent of the chain length of the soap (Table III). It is further interesting to note that the values of $-X \ln Y$ for systems containing propanol-1 above 50% are almost half of the values obtained for the systems containing propanol-1 below 50%. This again confirms that the change in the nature of the micelles occurs at about 50% propanol-1 concentration.

Therefore, there is justification in applying the Szyszkowski's equation to find the size and nature of the micelles formed in soap solutions in water-propanol-1 mixtures of varying composition. The constant X suggests the size of the micelles and is independent of the composition of the solvent mixture (between 30% to 80% propanol-1) but depends to some extent on the chain length of the soap. The constant Y depends on the nature of the micelles formed in mixed solvents and has different values below and above 50% propanol-1 concentration.

ACKNOWLEDGMENTS

R. C. Kapoor, Head of the Chemistry Department, Jodhpur University, Jodhpur gave valuable criticism. The work was supported in part by a grant from C.S.I.R., New-Delhi.

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