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Surface Tension Behavior and Micellization of Cadmium(II) Soap-Benzene and Methanol at 40°C

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ABSTRACT

The surface tension of cadmium caprate and laurate in benzene-methanol mixtures of varying composition has been measured at $40 \pm 0.1^\circ\text{C}$. The critical micelle concentration (CMC) values depend upon the composition of the solvent mixture and are found to decrease with increasing chain length of cadmium soaps. Previous findings about the CMC of the soaps are in general confirmed. The data have been discussed on the basis of Szyskowski's empirical equation,

$$\nu = \nu_0(1 + X \ln Y) - X\nu_0 \ln C$$

The parameters X , Y , and $(-X \ln Y)$ are found to decrease up to $\sim 50\%$ methanol concentration. Above that, the trend vanishes. This confirms that the nature of the micelles formed below and above 50% methanol concentration is quite different. The area covered by 1 g-mole of the soap also shows that the change in the nature of micellization takes place at $\sim 50\%$ methanol concentration.

INTRODUCTION

Thermogravimetry of cadmium(II) soaps in the solid state has recently been reported from a kinetic standpoint [1]. The characteristics of cadmium(II) soaps in benzene and methanol mixtures have been studied from viscometric data [2]. This communication is part of our ongoing program concerned with the investigation of cadmium-(II) soaps in the solid state, in nonaqueous solvents, and in mixed solvents of varying compositions. Surface tension, one of the obvious methods to study the behavior of surface-active substances [3-6], has been employed as a tool to find the CMC of the system cadmium soap (caprate and laurate)-benzene and methanol of varying percent concentrations. The aim of the present work is to enumerate qualitatively the effect of the nature of the solvent on the micellar aggregate and to gain insight into the size of the soap micelles in the presence of these mixed solvents.

EXPERIMENTAL

Material and Measurements

All chemicals used were of reagent grade. Fatty acids were purified by distillation under reduced pressure. Cadmium soaps were prepared by the method described earlier [1]. The soaps prepared in the laboratory were purified by washing with distilled water and ethanol, recrystallized from a hot benzene-methanol mixture (1:1), and dried in vacuum. The purity of the monohydrated soaps was confirmed by their elementary analysis [1].

A calculated amount of the soap was weighed in a volumetric flask and the solution made up to the mark by adding the required amount of benzene and methanol. In this way a number of solutions containing 20, 30, 40, 50, 60, 70, 80, and 90% methanol and different concentrations of soaps were prepared.

The surface tensions of the soap solutions were measured by means of a stalagmometer in a thermostatically controlled bath ($40 \pm 0.1^\circ\text{C}$). The accuracy of the results was checked by measuring the surface tension of pure and dried benzene of analytical grade. The difference in the results was below 0.5%. The surface tension results are in dyn/cm. The densities were measured with an accuracy of ± 0.001 using a pycnometer.

RESULTS AND DISCUSSION

The surface tension ν of soap solutions decreases with an increase in the soap concentration for all compositions of benzene and methanol.

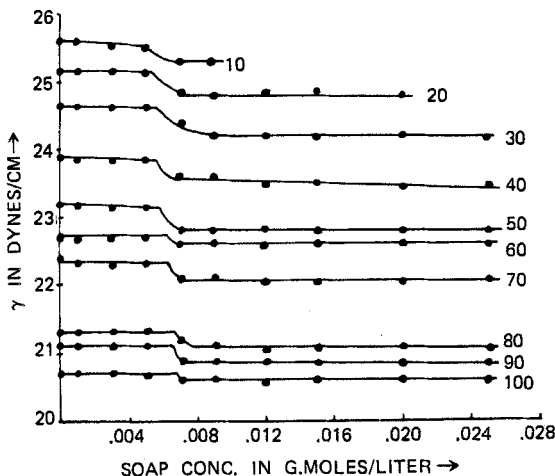


FIG. 1. Surface tension of the system cadmium caprate in benzene and methanol.

This may be due to the increasing tendency of soap molecules to form aggregates as micelles and the decreasing effects of the surface energy of the solvent mixture [7]. Plots of ν against the soap concentration C are linear but assume a concave shape and show a sharp change in surface deficiency of the soap at a definite soap concentration corresponding to the CMC (Fig. 1) of the soap. At the CMC, the hydrocarbon chain structure of soap molecules allows extensive contact between adjacent chains, possibly accompanied by changes in the vibrational and rotational degrees of freedom of the methylene group [8]. The values of CMC (Table 1) in the solutions containing methanol up to 50% are lower than those in solutions containing a higher volume percent of methanol. This may be ascribed to the predominance of a nonhydrogen-bonded solvent (benzene) below 50% methanol and the predominance of a hydrogen-bonded solvent above 50% methanol. It is suggested that methanol takes different positions in the micellar packing and that the soap exhibits different degrees of aggregation in mixed solvents of varying compositions.

It is easily seen from Table 1 that the CMC of cadmium soaps are in the order caprate > laurate. This is in agreement with the fact that there is a decrease in CMC values with an increase in the number of carbon atoms in the hydrophobic chain [9]. It is also known that the CMC decreases by about 1/3 per methylene group in aqueous solutions. This change is smaller in nonaqueous solutions [1] because the energy required to transfer a methylene group from micelle to bulk is small.

TABLE 1. Values of $\text{CMC} \times 10^3$ (in g-mol/L) for Cadmium Soap Solutions in Benzene-Methanol Mixtures

Soap	Volume percent of methanol									
	10	20	30	40	50	60	70	80	90	100
Cadmium caprate	5.5	5.6	5.6	5.8	5.9	6.2	6.4	6.6	6.9	7.1
Cadmium laurate	2.2	2.2	2.3	2.4	2.5	2.8	2.9	2.9	3.1	3.2

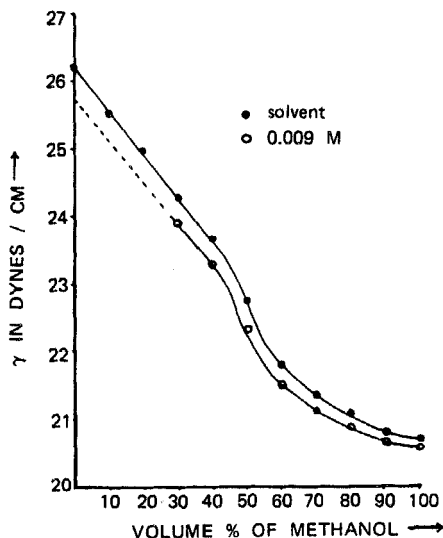


FIG. 2. Surface tension of the system cadmium caprate in benzene and methanol.

The surface tension of soap solutions shows a decrease with an increase in the volume percent of methanol in the system cadmium soap-benzene and methanol (Fig. 2). There is a rapid decrease in the surface tension up to 50% methanol; above it, there is a slow decrease. The change around 50% methanol may be due to the change in the nature of the solvent as the composition of the mixed solvent is varied. An earlier communication supports this viewpoint [2]. Again referring to Fig. 3, which is a plot of the mole fraction of the soap vs CMC, it is clear that there is a break at 50% methanol

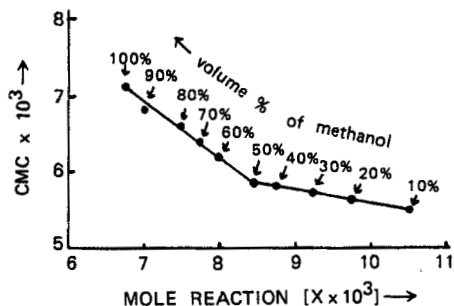


FIG. 3. Plots of CMC vs mole fraction X for cadmium caprate in benzene and methanol.

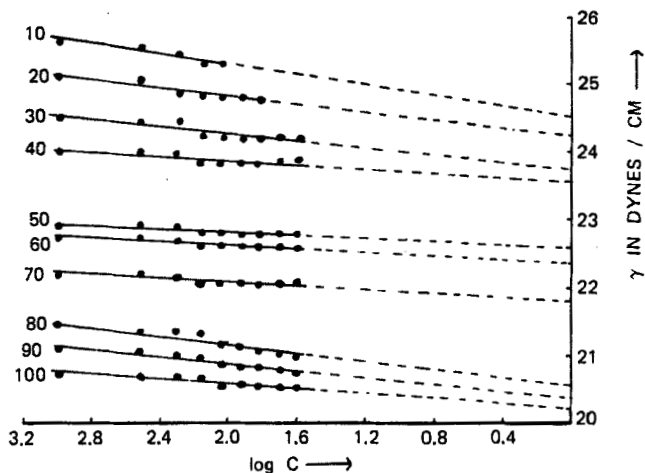


FIG. 4. Surface tension of the system cadmium caprate in benzene and methanol.

concentration, showing that the composition of the solvent plays a significant role in the micellization of the soaps.

The plots (Fig. 4) of ν vs $\log C$ are linear. The results are in agreement with Szyszkowski's empirical equation [11] for solutions of fatty acids:

$$\frac{\nu}{\nu_0} = 1 - X \ln \frac{C}{Y} \tag{1}$$

TABLE 2. Values of X, Y, and $-X \ln Y$ for Cadmium Soaps

Volume percent of methanol	Values of $X \times 10^3$		Values of $Y \times 10^4$		Values of $(-X \ln Y) \times 10^3$	
	Name of soap		Name of soap		Name of soap	
	Caprate	Laurate	Caprate	Laurate	Caprate	Laurate
10	6.35	5.59	9.68	6.30	44.09	41.17
20	4.86	5.71	7.42	8.34	35.02	40.46
30	4.15	3.08	6.30	2.16	30.61	26.00
40	2.54	2.55	6.29	14.27	18.75	16.74
50	1.78	2.41	16.86	7.58	11.37	17.34
60	2.39	4.38	9.10	2.02	16.72	32.78
70	2.76	4.75	44.96	6.30	14.91	35.00
80	5.69	5.12	5.80	3.97	42.40	40.09
90	5.17	4.56	25.10	7.78	30.95	32.60
100	3.61	4.58	21.02	4.59	22.26	35.20

where ν and ν_0 are the surface tensions of a solution of concentration C (mol/L) and of a pure solvent, respectively, and X and Y are constants.

The equation may be expressed as

$$\nu = \nu_0 (1 + X \ln Y) - \nu_0 X \ln C \quad (2)$$

On differentiating Eq. (2),

$$\frac{d\nu}{d(\ln C)} = -X\nu_0 \quad (3)$$

and by substitution into Gibb's adsorption equation, the adsorption excess (τ) is found to be

$$\tau = -\frac{C}{RT} \frac{d\nu}{d \ln C} = \frac{X\nu_0}{RT} \quad (4)$$

TABLE 3. Area Covered by the Soap Micelle Formed from 1 g-mole of the Cadmium Soap in Benzene and Methanol ($A \times 10^{-10} \text{ cm}^{-1}$)

Soap	Volume percent of methanol									
	10	20	30	40	50	60	70	80	90	100
Cadmium caprate	15.99	21.32	25.61	42.65	63.97	47.98	42.64	21.32	23.99	34.91
Cadmium laurate	18.28	18.28	34.89	42.65	47.98	27.41	25.59	23.99	27.41	27.49

Hence the surface area A covered by the soap micelles formed by 1 g-mole of the soap is

$$A = RT/X\nu_0 \quad (5)$$

The values of X are evaluated from the slopes ($-2.303 \nu_0 X$), and the values of Y and $-X \ln Y$ are calculated from the intercepts [$= \nu_0(1 + X \ln Y)$] of their plots vs $\log C$ have been recorded in Table 2. A perusal of Table 2 shows that the parameters X , Y , and $-X \ln Y$ are not independent of the composition of the solvent mixture. It is interesting to point out that the values of X , Y , and $-X \ln Y$ decreases up to 50% methanol concentration whereas this consistency disappears above 50% methanol. This reveals that the process of agglomeration of soap molecules into micelles above and below 50% methanol is not the same. Further, it is suggested that the ordering of micellar structure is less pronounced above 50% methanol because methanol, being a polar solvent having a resultant dipole moment, exhibits a perturbing effect on the micelles due to its electric field [12].

The approximate values of the surface areas occupied by the micelles formed by 1 g-mole of the soap in the mixed solvents are recorded in Table 3. It is noteworthy that the area covered by 1 g-mole of the soap (caprate and laurate) increases up to 50% methanol. This may be attributed to the fact that entrapping of solvent molecules in the palisade layers of the micelles results in the enhancement of the surface area. Here it is pertinent to suggest that scattering of micelles is more sensitive to the amount of methanol up to ~50% methanol. Beyond 50% methanol the increasing trend of the surface area vanishes, indicating the disarray in the clustering of methanol molecules in the peripheral region of the micelles and their incorporation in the micelles. From the above considerations it may be concluded that the nature and size of the micelles below and above 50% methanol are quite different.

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