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Studies on Surface Tension of Titanium(III) Soaps in Mixed Organic Solvents

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Surface tension of titanium soaps solutions in mixed organic solvents has been measured at 313 K and the data have been discussed on the basis of Langmuir's approximate equation

$$\gamma = \gamma_0 (1 + x \ln \cdot \gamma) - \gamma_o x \ln c$$

The critical micelle concentration (CMC) values obtained from γ -log C plots, decrease with increasing chain length of soap. Constant χ depends on chain length of soap. Constant γ above CMC increase with increasing chain length, but do not show any definite trend above this concentration. Surface alloys covered by the soap micelles formed by male of soap have also been evaluated.

Key Words: Surface Tension, Titanium(III) soaps.

INTRODUCTION

The critical micelle concentration (CMC) of copper soaps in non-aqueous solvents has been determined by Mehrotra *et al.*[1]. Surface tension of mixed organic solvents solutions of surface active agents decreases rapidly until the CMC is reached and above this value, it remain almost constant. Number of studies have been made on surface tension of magnesium soap solutions of higher fatty acids measured in organic solvents[2] and in multicomponent system[3] at 40 °C. Many thermodynamic, transport and spectroscopic properties show a different change in the behaviour of surface active agents with concentration around well defined critical micelle concentration[4,5]. CMC values have been determined from inflection of γ *vs.* log C plots. The method is particularly useful because the surface tension value changes nearly the same magnitude and the accuracy of the determining the inflecting is also nearly the same for longer and shorter chain substances. Surface tension of magnesium soaps in alcohols[6,7] and copper soaps[8] in non-aqueous solvents have been studied recently.

Non-ionic surfactants derived from trehalose has been measured surface tension[9]. A dynamic and equilibrium surface tension of a soap/ builder system were determined as a function of soap concentration[10]. Equations for an adsorption isotherm and a surface tension isotherm are derived for the adsorption of one single surfactant or of a mixture of surfactants[11]. It is found that the CMC[12,13] and surface area[14] values of these soaps in aqueous methanol are independent of methanol concentration. Surface tension of magnesium soaps in alcohols in non-aqueous solvents have also been studied[15]. A study of this type surface tension properties of aqueous solution of lithium and magnesium chloride 303.15 K presence of surfactant[16,17] and chain molecules has been investigated previously[18,19].

Not much attention has been paid to wards the studies on this property of soaps in non-aqueous solvents. The present paper deals with the surface tension measurements of titanium(III) soaps (laurate, myristate, palmetate and stearate) solutions in mixed organic solvents (benzene + cyclohexane) at 313 K. The results have been discussed on the basis of Langmuir's approximate equation.

EXPERIMENTAL

Merck or BDH reagent grade alcohols, benezene, cyclohexane, titanium trichloride, lauric acid, myristric acid palmetic acid and stearic acid were used. The fatty acids were purified by distillation under reduced pressure and the purity of reagent was confirmed by boiling point measurements.

Theoretical

Surface tension, γ (Nm^{-1}) of soaps solutions decreases continuously with increasing soap concentration which is due to the effects in surface energy of the solvent A. The surface tension of the soap solutions was calculated by this formula

$$\frac{\gamma_1}{\gamma_1} = \frac{n_2 d_1}{n_1 d_2} \qquad (1)$$

where, γ_1 and γ_2 are the surface tension of the standard and known solutions η_1 and η_2 are the corresponding number of the drops and d_1 and d_2 are the densities of the solutions. The variation of the surface tension with the concentration of fatty acids in solutions can be represented by Szyszkoswki empirical equation[13]

$$\frac{\gamma}{\gamma_0} = 1 - x \ln \frac{C}{\gamma} \qquad (2)$$

where γ and γ_o are the surface tension of the solution of concentration C ($mol\ dm^{-3}$) and of the pure solvent, respectively and χ and γ are constants. The equation can be written in the form:

$$\gamma = \gamma_0 (1 + x \ln \gamma) - \gamma_o x \ln c \qquad (3)$$

Differentiating (2) with respect to ln c, it shows

$$\frac{d\gamma}{d\ln C} = -\chi\gamma_0 \quad (4)$$

On substituting the Gibb's adsorption equation, the absorption excess (*i.e.*, the excess concentration of the solute per unit area of the surface) is found to be:

$$\Gamma = -\frac{1}{RT},\frac{d\gamma}{d\ln C} = \frac{\chi\gamma_0}{RT} \quad (5)$$

If the condition for applicability of the equation is assumed to represent a complete layer, the area, A occupied by each mole in the surface is equal to 1/Γ:

$$i.e.,\ A = \frac{RT}{x\gamma_0} \quad (6)$$

surface tension of the solutions of active agents decreases rapidly.

RESULTS AND DISCUSSION

The surface tension γ, (Nm^{-1}) of titanium(III) soap solutions (Table-1) in mixed organic solvents decreases with increase in the soap concentration and temperature of the soap solutions. The decrease in surface tension with increasing soap concentration may be due to the increase in the tendency of soaps to form aggregates.

The plot of a surface tension *versus* soap concentration (mol dm^{-3}), C show a sharp change in the surface deficiency of the soaps at definite concentrations. These concentrations correspond to the critical micelle concentrations CMC of the soaps and are in complete agreement with viscosity measurements. The CMC is found to be independent of temperature and decreases as chain length of fatty acids in the soap increases.

The plot of γ *vs.* log C are found to be linear at 35-40 °C for all the soaps showing that the results are in good agreement with the szyszkoswki empirical equation for solution of fatty acids.

The constants χ and γ of szyszkoswki equation and the surface area A(m^2) have been calculated from the linear plots of γ *vs.* log C and are reported in Table-2. The value of χ calculated from the slopes (-2.303 $\chi\gamma_o$) of linear plots show a straight increase with increasing temperature and chain length of the soap. However, if may be pointed out that the value of χ are constant for series of fatty acids containing 2 to 6 carbon atoms studies in aqueous solutions.

The values of constants γ calculated from the intercepts [= γ_o (1+ ln γ)] of the linear plots of γ *vs.* log C are found to decrease with increasing temperature and chain length of fatty acids in the soap.

TABLE-1
SURFACE TENSION, γ OF TITANIUM (III) SOAPS IN MIXED ORGANIC SOLVENTS (BENZENE + CYCLOHEXANE) AT 35-50 ºC

Conc. of soap solutions in mol dm^{-3} $C \times 10^5$	$\gamma \times 10^3$ (nm^{-1}) Temperature (ºC)			
	35	40	45	50
	Laurate			
3	69.32	69.00	68.71	67.90
4	67.52	68.50	67.18	66.72
5	67.50	67.20	66.22	64.87
6	66.28	66.08	64.60	63.70
8	65.38	64.70	63.80	62.60
10	64.08	63.94	62.00	60.87
12	62.85	62.70	60.82	59.39
	Myristate			
3	69.28	68.50	67.81	67.20
4	68.92	67.18	66.20	66.12
5	66.78	66.06	65.50	63.18
6	65.85	64.68	63.50	62.04
8	64.10	63.92	62.18	61.06
10	63.08	62.92	60.40	60.00
12	62.28	61.80	59.24	58.88
	Palmitate			
3	68.88	68.29	67.33	67.00
4	68.92	67.00	66.10	64.62
5	66.45	65.08	63.50	62.00
6	66.42	65.02	64.82	63.17
8	64.56	63.70	62.20	61.04
10	62.57	61.90	60.80	59.25
12	61.08	60.49	59.24	58.86
	Stearate			
3	69.50	68.20	67.92	66.65
4	68.22	67.00	65.48	63.18
5	67.57	66.20	66.12	64.64
6	66.51	65.30	64.30	63.48
8	64.97	64.04	63.40	61.90
10	64.01	62.88	62.20	60.82
12	62.18	61.52	61.02	60.06

TABLE-2
VALUES OF CONSTANT x, y AND SURFACE AREA, A OF TITANIUM(III) SOAPS AT 35-50 ºC

Temperature	$\chi \times 10^2$	$\gamma \times 10^2$	$A \times 10^{-5}$ (m^2)
Laurate			
35	7.605	2.329	5.061
40	7.902	2.056	5.005
45	8.210	1.724	4.799
50	8.503	1.022	4.552
Myristate			
35	7.502	1.733	4.851
40	7.806	1.712	4.796
45	8.106	1.059	4.618
50	8.405	1.044	4.579
Palmitate			
35	8.106	1.059	4.618
40	3.306	0.987	5.007
45	8.605	0.972	4.472
50	8.906	0.949	4.443
Stearate			
35	8.004	0.992	4.548
40	8.305	0.987	5.007
45	8.606	0.972	4.472
50	8.905	0.949	4.443

The surface area (A) covered by 1 g mole of the soap decreases with increase in temperature. However, the surface area, A covered by 1 g mole of the soap various chain and is showing order as:

Laurate > myristate > palmitate > stearate

Conclusion

The surface tension of titanium(III) soaps (laurate, myristate, palmitate and stearate) solutions in cyclohexane + benzene at various temperatures decreases with increase in soap concentration and temperatures. The plots of γ *vs.* C show a sharp change in the surface deficiency at CMC of the soaps. The CMC decreases with increasing chain length of the titanium soaps and is independent of temperature. The surface tension of soap solutions decreases with increase in chain length of soaps. This may be due to increase in the micelle size with increase in C-atoms of the soaps.

The plots of γ *vs.* log C are linear. Thus confirms that Szyszkoswki's empirical equation for the solution of fatty acids can be applied to the soap solution at different temperatures.

The values of χ, calculated from the liner plots, of γ *vs.* log C increase with increase in temperature and soap chain. However, it has been observed that the values of titanium soaps at various temperatures are showing increasing order.

The values of γ decrease with increasing temperature and chain length of fatty acids in the soaps. All data are showing that these surfactants definitely play the role of surface activity.

The surface area, A decreases with increasing temperature and soap chain. The surface area covered by 1 g mole of titanium soaps.

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