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SURFACE TENSION AND PARACHOR STUDIES OF LITHIUM SOAPS IN NON-AQUEOUS MEDIA AT 313 K

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ABSTRACT

Surface tension studies of lithium soap solutions confirm that CMC values depend upon the composition of the solvent mixtures and are found to decrease with increasing chain length of the soap anion. In regards to chain length of the soap the CMC values follow the order : laurate < caprate. The results of the surface tensions have been explained on the basis of Szyszkowski's empirical equation and it is observed that the values X, Y and (-X ln Y) lead to the confirmation of the fact that the change in the behaviour of the soap takes place at 40% methanol concentration whereas this consistency disappears above this concentration. The plots of the parachor against the mole fraction of the soap are characterized by an intersection of two straight lines at the CMC of the soap. Hammic and Andrew's equation has been successfully applied to explain the behaviour of soap in benzene-methanol mixtures.

Key words: Surface tension, Parachor, Lithium soap, Non-aquous media.

INTRODUCTION

Anionic surfactants containing lithium ions are ideal for investigations because of their valuable characteristics such as foaming, detergency, emulsification, spreading, wetting etc. Study of micellar characteristics and surface tension parameters will play a significant role for exploring their applications and possible uses in various industries.

Blackley and Haynes evaluated the effectiveness of lithium laurant to enhance the mechanical stability of natural rubber latex[1]. Lithium soap plus sodium silicate gave extra ordinary results in protecting ferrous and non-ferrous metals in the form of inhibitors[2]. Sinitsyn et al. developed lubricants melts by introducing sodium and lithium soaps of saturated carboxylic acid ranging from C_{12} to C_{20}[3]. Lithium caprate has been found as excellent drinking agent for repulping waste paper[4]. The United States eventually is

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projected to lead in the manufacture of electric vehicles, a domestic base of lithium ion battery manufacturing capacity will be critical[5]. Lithium chloride and lithium bromide are extremely hygroscopic and are used as desicants. Lithium hydroxide is an important compound of Li obtained from Li_2CO_3[6]. Metallic lithium and its complex hydride, such as $LiAlH_4$ are used high energy additives to rocket propellants[7]. Lithium soaps play a significant role in various fields like preparation of paints, lubricants, grease and in rubber industry etc.

EXPERIMENTAL

Surface tension

The surface tension of the soap solutions was measured by drop weight method. In all the measurements Traube's stalagmometer was used. Harkins and brown method was employed for controlling the drops. Ostwald's modification of the sprengal pyknometer was used for measuring the density of soap solution at constant temperature (313 K) in a thermostatic bath. The results were calculated by the following formula :

$$\frac{\gamma_0}{\gamma_1} = \frac{n_1 d_0}{n_0 d_1} \qquad \ldots(1)$$

Where γ_0 and γ_1 are the surface tensions of the standard and unknown solutions. n_o, n_1 and d_0, d_1 are the corresponding number of drops and densities, respectively. The accuracy of the results was checked by measuring the surface tension of pure and dried benzene. The difference in the results was below 0.5%. The results are in dynes cm^{-1}.

RESULTS AND DISCUSSION

The surface tension γ of the solutions of lithium caprate and laurate in mixtures of varying compositions of benzene and methanol decreases with increase in soap concentration. This may be due to the increasing tendency of soap molecules to form aggregates as micelles and the decreasing effects in the surface energy of the solvent[8].

The plots of surface tension against soap concentration are characterized by two straight lines corresponding to CMC of soap (Table 1). The values of CMC in the solution containing methanol up to 40% are lower as compared with the CMC values in solution containing higher volume percent of methanol. This may be ascribed to the predominance of non hydrogen bonded solvent (benzene) below 40% methanol. It is suggested that the methanol takes quite difference position in the palisade layers and soap exhibits different degrees of aggregations in the mixed solvent of varying compositions. The value of CMC of soap agrees with that determined from the studies of other physical properties (viz. density, viscosity, ultrasonic velocity and conductance).

Table 1: Values of CMC (in g mole L^{-1}) for lithium soaps in benzene and methanol mixtures at 313 K.

Name of Soap	Parameter	Volume percent of methanol in solvent mixture						
		10	20	30	40	50	60	70
Caprate	Surface tension	0.0280	0.0310	0.0335	0.0330	0.0340	0.0350	0.0355
	Parachor	0.0290	0.0310	0.0320	0.0325	0.0340	0.0350	0.0355
Laurate	Surface tension	0.0275	0.0300	0.0330	0.0335	0.0340	0.0350	0.0360
	Parachor	0.0280	0.0300	0.0320	0.0335	0.0350	0.0345	0.0360

The plot of γ v/s. log c (Fig. 1) are characterized by an intersection of two straight lines for all the compositions of the solvent mixture.

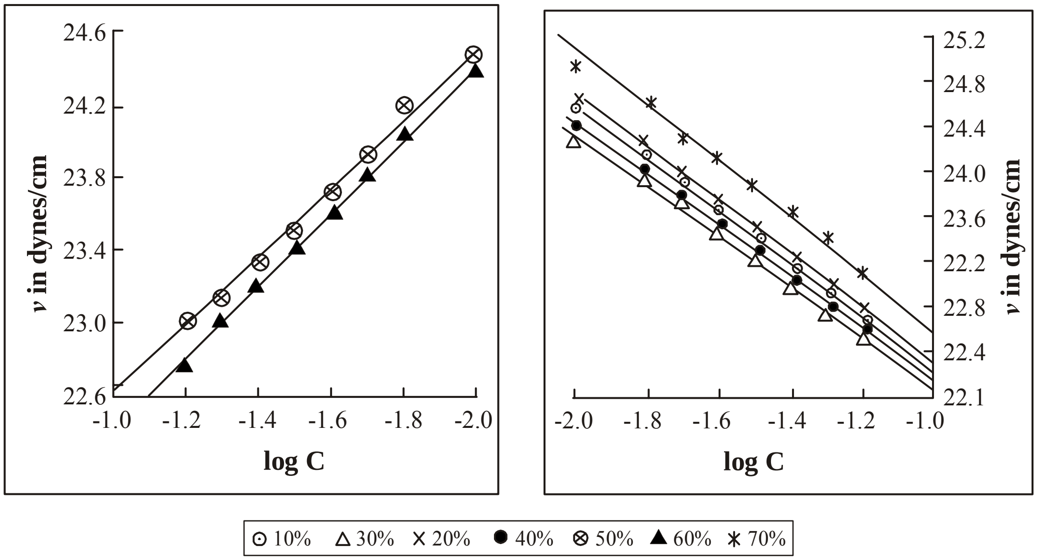

Fig. 1: Surface tension of the system : Lithium laurate benzene plus methanol

The linear variation of γ against log c is in agreement with Szyszkowski's[9] empirical equation for fatty acids.

$$\frac{\gamma}{\gamma_1} = 1 - x \ln \frac{c}{Y} \qquad \ldots(2)$$

Where γ and γ_o are surface tensions of the solution of concentration c (g mol L^{-1}) and of the pure solvent respectively and X and Y are constants.

Equation (2) can be written as :

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

Hence

$$\frac{d\gamma}{d - \ln c} = -x \gamma_0 \qquad \ldots(4)$$

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

$$e = -\frac{1}{RT} \frac{d\gamma}{d \ln c} = \frac{x \gamma_0}{RT} \qquad \ldots(5)$$

Hence the surface area, A, covered by the soap micelles formed by 1 g. mol of the soap is:

$$A = \frac{RT}{x \gamma_0} \qquad \ldots(6)$$

The values of X evaluated from the slopes (-2.303 γ_0 X) and values of Y and (-X ln Y) calculated from the intercept {γ_0 (1 + X ln Y)} of the plots of γ v/s log C are summarized in Table 2. A perusal of Table 2 shows that the parameters X_1Y and –X ln Y are not independent of the composition of the solvent mixtures. It is interesting to point out that :

(i) X increases upto 40 percent methanol and then the trend vanishes.

(ii) Y decreases upto 40 percent methanol and then the trend vanishes.

(iii) -X ln Y increases upto 40 percent methanol and then the trend vanishes.

Obviously these observations support the fact that the change in behaviour of the soap takes place in the proximity of 40% methanol concentration.

However, this conclusion reveals that the process of agglomeration of soap molecules into micelle above and below 40% methanol is quite dis-similar. Furthermore it is argued that the ordering of micellar structure is less pronounced above 40% methanol because methanol being polar solvent having a resultant dipole moment, exhibit a perturbing effect on the micelles due to its electric field[10]. A theoretical subscription to the orderly orientation of the micelles below 40% methanol may be ascribed the fact that the hydrocarbon head group of the soap anion within the adsorbed monolayer at the air solvent interface penetrating towards more non-polar benzene phase exhibits inter molecular attraction[11].

The approximate values of the surface area occupied by the micelle formed by 1 g mole of the soap in the mixed solvents are recorded in (Table 2). It is noteworthy to point out that the area covered by 1 g mole of the caprate decreases up to 40% methanol and then the trend disappears. Therefore it is pertinent to suggest that beyond 40% methanol the disarray in the clustering of methanol molecules in the peripheral region of the micelles and their incorporation in the micelle lead to scattering of agglomerates. From this consideration it may be concluded that the nature and size of the micelles below and above 40% methanol is quite different. The values of X, Y, (-X ln Y) and A for lithium caprate and laurate show a marked change at 40% methanol concentration. Hence there is a justification in applying Szyskowski's equation to find out the nature of the micelles formed in this system.

Table 2: Values of X, Y, X ln Y and A for lithium caprate solution and lithium laurate solution in benzene and methanol mixtures at 313 K

Volume % of methanol in the solvent mixtures	**$X \times 10^3$**		**$Y \times 10^{-6}$**		**($-X \ln Y \times 10^3$)**		**$A \times 10^{-10}$**	
	Caprate	**Laurate**	**Caprate**	**Laurate**	**Caprate**	**Laurate**	**Caprate**	**Laurate**
10	6.379	5.419	1.540	379.140	90.90	107.07	16.482	19.401
20	7.217	6.065	0.570	52.047	95.68	107.79	14.556	17.320
30	8.539	7.259	0.081	3.730	96.60	109.86	12.351	14.554
40	9.047	8.715	0.078	0.298	101.94	109.94	11.634	12.078
50	9.036	6.037	0.028	2.405	92.74	88.70	11.612	17.381
60	10.386	2.733	0.008	24.243	93.47	97.50	10.094	38.363
70	7.828	6.889	0.200	5.949	95.56	107.49	13.186	14.983

Parachor

The parachor, P of the solution is written as :

$$P = \frac{M\gamma^{1/4}}{D} = V.\gamma^{1/4} \qquad \dots(7)$$

Where M, D, V and γ are respectively the molecular weight, density, molar volume and surface tension of the solution respectively.

According to Hammic and Andrew's[12] mixture law equation, the parachor of the solution may be written as :

$$P = X\, P_{soap} + (1-X)\, P_{solvent} \qquad \dots(8)$$

Where P, P_{soap} and $P_{solvent}$ refer to the parachor of the soap solution, soap and solvent respectively and X is the more fraction of the soap in the solution.

Since P_{soap} and $P_{solvent}$ are constants the equation (8) can be written as :

$$P = X\, [P_{soap} - P_{solvent}] + P_{solvent} = X\, K_1 + K_2 \qquad \dots(9)$$

Where K_1 is equal to $[P_{soap} - P_{solvent}]$ and K_2 is equal to $P_{solvent}$. Hence, from equation (7) and (8) we have :

$$P = X\, K_1 + K_2 = V.\gamma^{1/4} \qquad \dots(10)$$

The equation shows that the plots of $V.\gamma^{1/4}$ against X should be linear. On differentiating Eq. (10) we get :

$$P = \frac{d\,(V.\gamma^{1/4})}{dx} = K_1 \qquad \dots(11)$$

This shows that quantity $d\,(V.\gamma^{1/4}) / dX$ should be equal to K_1 i.e. $(P_{soap} - P_{solvent})$.

The values of K_1 have been calculated by using Equation (11) for the solutions of lithium caprate and laurate in mixtures of benzene and methanol and have been compared with the values obtained graphically by plotting $V.\gamma^{1/4}$ against X.

It is observed that the values of parachor of the soap solution (Caprate and Laurate) decreases with the increase in the mole fraction and volume percent of methanol in the soap.

The plots of the parachor against the mole fraction of the soap (Fig. 2) show a change at a point corresponding to the CMC of the soap which may be due to the fact that the soap exists in different forms below and above the CMC. The parachor behaviour may be represented by two linear equations having different values of the constant, K_1 and K_2 below and above the CMC. It is observed that the calculated values of K_1 using equation (11) are in close agreement with the values obtained graphically are in complete agreement with the corresponding experimental values of the parachor of the solvent mixtures of benzene and methanol. Hence there is a justification in applying Hammic and Andrew's equation to the solution of lithium caprate/laurate in mixtures of benzenes and methanol.

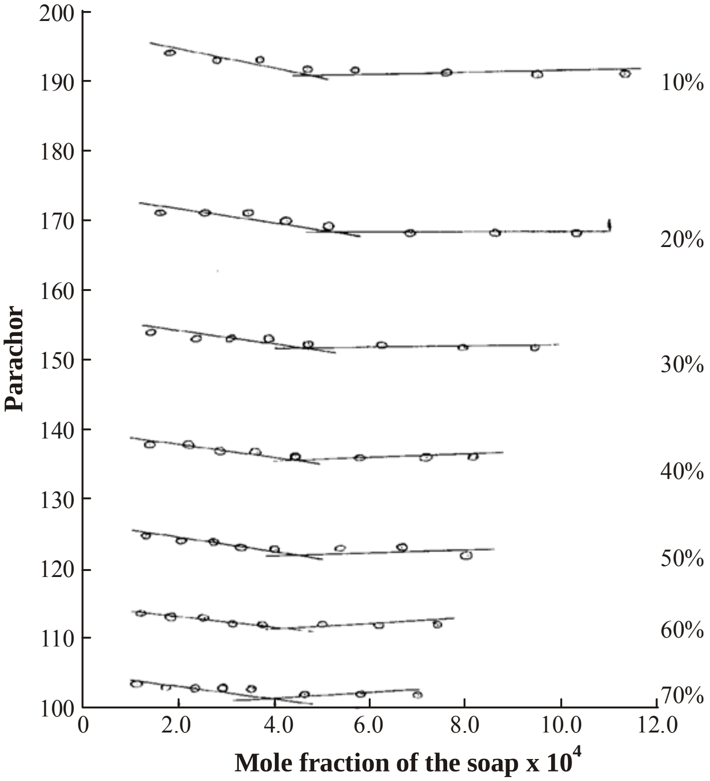

Fig. 2: Parachor of lithium laurate solutions against mole fraction in benzene plus methanol

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REFERENCES

1. D. C. Blackley and A. C. Haynes, Plast. Rubber Process Appl., **1(1)**, 73 (1981).
2. I. I. Garaslmov, N. A. Zakharov, A. P. Patapova, T. A. Chumachenko and D. A. Tseberg, USSR, **177**, 255 (1965).
3. V. V. Sinitsyn, E. L. Ponomareva, K. I. Penyaeva, Dokl. Akad. Nauk SSSR, **181(1)**, 160 (1968).
4. Hoshimoto, Kenichi, Highchi, Hisav, Tachibana, Hideko, Ito, Yutaka, Jpn. Kokai Tokkyo Koho JP 6350, 591 (1988).
5. Nishino, Hirashi, Key Technology for EVS, Lithium-Ion Secondary Battery Retrieved June 25, 2010 (2010).
6. E. T. George, R. S. Westbrook and R. J. Shah, Fuels and Lubricants Handbook Technology, Properties, Performance and Testing, Vol. 1, ASTM International (2003) p. 559.
7. J. Emsley, Nature's Building Blocks, Oxford University Press, Oxford (2001).
8. R. P. Verma and R. Dayal, J. Indian Chem. Soc., **57**, 1086 (1980).
9. B. Szyszkowski, Z. Phys. Chem.., **64**, 385 (1908).
10. K. N. Mehrotra, V. P. Mehta and T. N. Nagar, J. Am. Oil Chem. Soc., **47**, 329 (1970).
11. A. K. Biswas, Frontier in Applied Chemistry, Springer Verlag (1986) p. 186.
12. D. I. Hammic and L. W. Andrews, J. Chem. Soc., 754 (1927).

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