Surfactants & Detergents

Surfactants & Detergents Technical

♣Conductometric Investigations on Lanthanum Soap Solutions

K.N. Mehrotra, A.S. Gahlaut and **Meera Sharma**
Department of Chemistry, Agra University, Agra 282004, India

The critical micelle concentration (CMC), degree of dissociation and dissociation constant of lanthanum caprate in benzene-methanol mixtures of varying composition were determined using conductometric measurements. The results show that the soap behaves as a weak electrolyte in these solutions below the CMC. The value of the CMC (0.0027 M) was found to be independent of the solvent composition but increases with the addition of dye.

While major developments have taken place in the study of alkali, alkaline earth and transition metal soaps, the studies on lanthanide soaps have remained almost untouched, with the result that only few references (1–14) are available in this relatively unexplored field. Studies on the nature and structure of these soaps are of great importance for their uses in industries and for explaining their characteristics under different conditions.

The present work deals with the conductometric studies of the solutions of lanthanum caprate in benzene-methanol mixtures of varying compositions, with the aim of finding out the nature of micelles formed in mixed solvents.

EXPERIMENTAL

Lanthanum caprate was prepared by the direct metathesis of potassium caprate with the required amount of aqueous solution of lanthanum nitrate at 50–55 C under vigorous stirring. The precipitated soap was washed several times with distilled water and finally with alcohol. The soap was recrystallized with a mixture of benzene and methanol, dried under reduced pressure and stored over calcium chloride. The absence of a hydroxyl group in the soaps was confirmed by studying their infrared (IR) spectra. The purity of the soap was checked by elemental analysis, and the results (Table 1) were in agreement with the theoretically calculated values.

The melting point of purified lanthanum caprate was 115.0 C. The reproducibility of the results was checked by preparing two samples of the soap under similar conditions.

A digital conductivity meter (Toshniwal CL 01.10A) and a dipping type conductivity cell with platinized electrodes were used for measuring the conductance of the soap solutions. All the measurements were made at constant temperature (40 ± 0.05 C) in a thermostat.

TABLE 1

Percentage of Elements in Lanthanum Caprate

Element	Found	Calculated
Carbon	55.1	55.2
Hydrogen	8.7	8.7
Lanthanum	21.5	21.4

RESULTS AND DISCUSSION

Specific conductance, k. The molecular conductance, μ, of the soap solutions involves the effects of both the simple ions and the micelles; thus, the specific conductance, k, of the soap solutions has been plotted against the soap concentration, C (g||mole l^{-1}) to determine the CMC. The specific conductance, k, of the solutions of lanthanum caprate in a series of mixtures of varying benzene:methanol compositions (70:30, 60:40, 50:50, 40:60) increases with the increase in the soap concentration (Fig. 1). The increase in the specific conductance with the increase in the soap concentration may be due to the ionization of lanthanum caprate into simple metal cation, La^{3+} and fatty acid anion, C$_9$H$_{19}$COO$^-$ in dilute solutions and due to the formation of micelles at higher concentration. The plots of specific conductance vs. concentration of the soap are characterized by an intersection of two straight lines showing a break at 0.0027 M which corresponds to the CMC of the soap. The specific conductance of the solutions of lanthanum caprate also increases with the increase in methanol concentration in the solvent mixture. It may be due to the high dielectric constant of methanol (32.63 at 25 C) compared to that of benzene (2.28 at 20 C). The CMC was found to be independent of solvent composition.
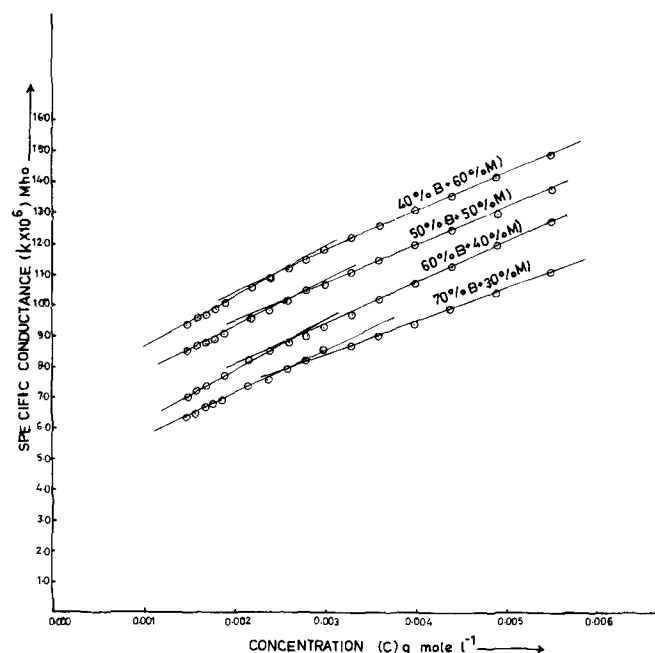
The specific conductance, k, of lanthanum caprate increases with the addition of 10^{-5} M solution of sudan (IV) dye. The results show that the nature of the curves remains the same, while the value of CMC increases by the addition of dye and is found to be 0.0036 M. This may be due to the fact that the molecules of the dye penetrate into the palisade layer of the micelle between the soap molecules, forming a larger, mixed micelle and resulting in the increase of the CMC.

Molecular conductance (μ) and dissociation constant (K). The molecular conductance, μ of the dilute solutions of lanthanum caprate in mixtures of benzene and methanol of varying compositions decreases with the increase in the soap concentration (Fig. 2). The decrease in molecular conductance may be due to the combined effects of ionic atmosphere, solvation of ions and decrease of mobility and ionization with the formation of micelles. The plot of molecular conductance, μ vs. square root of soap concentration, C$^{1/2}$ is not linear, which indicates that the soap behaves as a weak electrolyte in these solutions. The limiting-molecular conductance, μ_0 of these soap solutions cannot be obtained by the usual extrapolation method, and Debye-Huckel-Onsager's equation is not applicable to these soap solutions.

The molecular conductance of lanthanum caprate solutions also increases by the addition of 10^{-5} M Sudan (IV) dye, but the nature of the curves remains the same.

Because the soap in dilute solutions behaves as a weak electrolyte, an expression for the dissociation of lanthanum caprate can be developed in Ostwald's manner. If C is the concentration in g mol/l of lanthanum caprate and α is the degree of dissociation, the equivalent concentrations of different species can be represented as:

$$La(C_9H_{19}COO)_3 \rightleftharpoons La^{3+} + 3\ C_9H_{19}COO^-$$

$$C(1 - \alpha) \qquad C\alpha \qquad 3(C\alpha)$$

FIG. 1. Specific conductance (k) vs concentration (C). B, benzene; M, methanol.
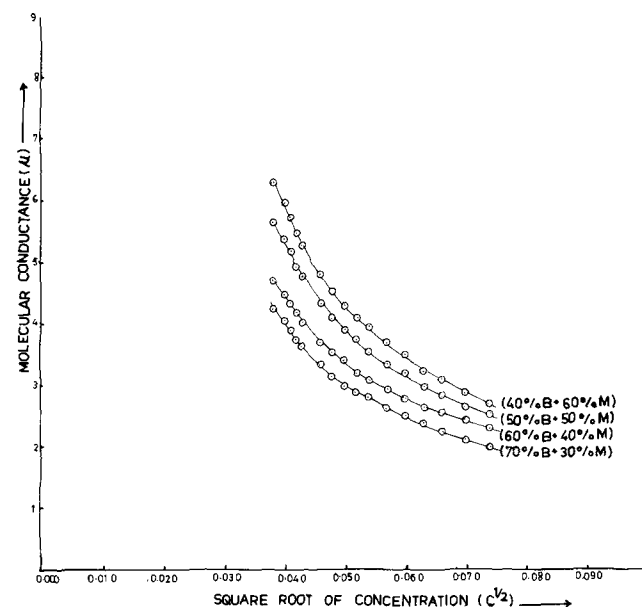
FIG. 2. Molecular conductance (μ) vs square root of concentration (C$^{1/2}$). B, benzene; M, methanol.

The dissociation constant, K can be expressed as:

$$K = \frac{[La^{3+}][C_9H_{19}COO^-]^3}{[La(C_9H_{19}COO)_3]}$$

$$= \frac{C\alpha \cdot (3C\alpha)^3}{C(1 - \alpha)} = \frac{27 \; C^3\alpha^4}{1 - \alpha} \qquad [1]$$

Because the degree of dissociation of lanthanum caprate in dilute solutions is small, ionic concentrations will be low and the interionic effects almost negligible. Therefore, the dilute soap solutions do not deviate appreciably from ideal behavior and the activities of ions can be taken as almost equal to the concentrations. The degree of dissociation, α may be replaced by the conductance ratio, μ/μ_0, where μ is the molecular conductance at finite concentration and μ_0 is the limiting molecular conductance at infinite dilution. On substituting the value of α and rearranging equation [1], one obtains:

$$\mu^3 \; C^3 = \frac{K \; \mu_0^4}{27 \; \mu} - \frac{K \; \mu_0^3}{27} \qquad [2]$$

The plots of $\mu^3 \; C^3$ vs $1/\mu$ (Fig. 3) are characterized by an intersection of two straight lines and show a break at a definite soap concentration which corresponds to the CMC of the soap. The values of the CMC are in agreement with the values obtained from the plots of specific conductance vs soap concentration. The values of K and μ_0 can be obtained from the slope, [K $\mu_0^4/27$] and intercept, [$-$ K $\mu_0^3/27$] of the linear plots of $\mu^3 \; C^3$ vs $1/\mu$ for dilute soap solutions.

The values of the degree of dissociation, α at different soap concentrations have been calculated by assuming it as equal to the conductance ratio, μ/μ_0 and using the value of μ_0 obtained from the plot of $\mu^3 \; C^3$ vs $1/\mu$. The plot of degree of dissociation, α vs soap concentration, C shows that lanthanum caprate behaves as a weak electrolyte (Fig. 4). The degree of dissociation of the soap decreases

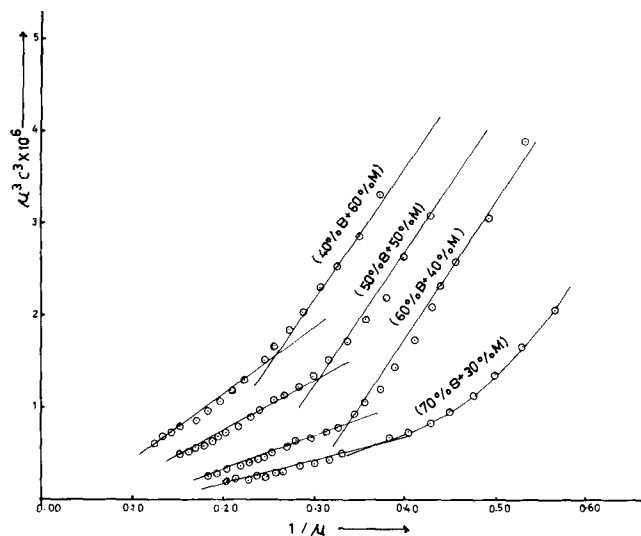rapidly in dilute solutions with the increase in soap concentration, whereas it decreases slowly above the CMC. The degree of dissociation of lanthanum caprate also decreases with the increase in methanol concentration in the solvent mixture and by the addition of 10^{-5} M Sudan (IV) dye.

The values of dissociation constant, K calculated by using equation [1] and assuming the degree of dissociation as equal to the conductance ratio are tabulated (Table 2). The values of the dissociation constant, K change slowly with the increase in the soap concentration below the CMC but increase rapidly above the CMC. The values of the dissociation constant, K increase with increasing concentration of benzene in the solvent mixture and decrease with the addition of dye to the soap solutions. The increase of the values of K with increasing benzene concentration in the solvent mixture may be due to the combined effects of ion association, micelle formation, solvation and change in the viscosity and dielectric constant of the solvent mixture. The decrease in the solvation of the micelles, degree of aggregation and viscosity of the medium has an increasing effect on the conductivity, degree of dissociation and dissociation constant, whereas the lowering of dielectric constant results in the decrease of conductivity, degree of dissociation and dissociation constant. The net result is the difference between these effects and, because the former predominates over the effect of the dielectric constant, the degree of dissociation and dissociation constant increases with increasing benzene concentration in the solvent mixture. Moreover, the effective dielectric around the soap is not due to the dielectric constant of the bulk of the mixture but is determined by the solvation sheath around the soap. The decrease in the values of the dissociation constant, K with the addition of 10^{-5} M Sudan (IV) dye is due
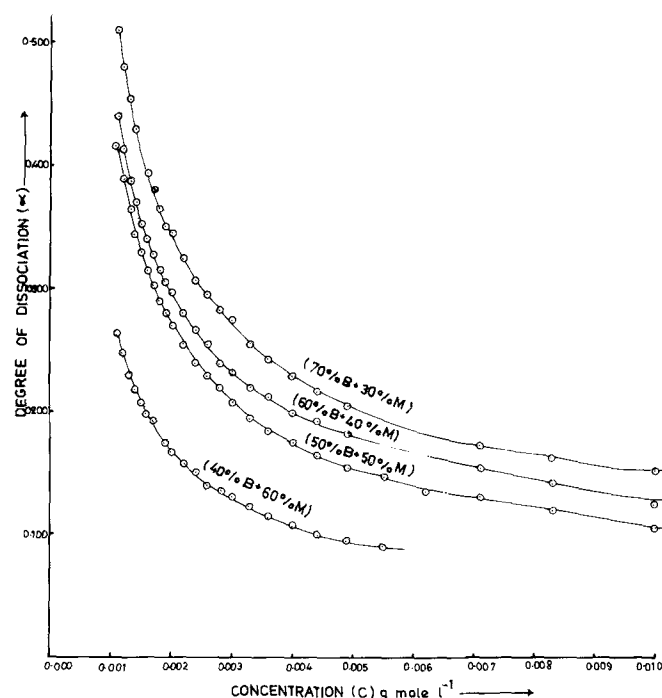

FIG. 3. $\mu^3 \; C^3$ vs $1/\mu$. B, benzene; M, methanol.

FIG. 4. Degree of dissociation (α) vs concentration (C). B, benzene; M, methanol.

TABLE 2

Conductance of Lanthanum Caprate in a Mixture of Benzene (70%) and Methanol (30%) at 40 ± 0.05 C

Concentration (g·mol l⁻¹) C	Specific conductance (in μ mhos) k	Molecular conductance (in mhos) μ	Degree of dissociation α	Dissociation constant K × 10⁹
0.0015	6.38	4.253	0.411	4.32
0.0016	6.52	4.075	0.394	4.32
0.0017	6.67	3.923	0.379	4.32
0.0018	6.78	3.766	0.364	4.32
0.0019	6.91	3.636	0.351	4.32
0.0022	7.39	3.359	0.325	4.73
0.0024	7.63	3.179	0.307	4.78
0.0026	7.92	3.046	0.294	5.00
0.0028	8.21	2.932	0.283	5.29
0.0030	8.52	2.839	0.274	5.29
0.0033	8.73	2.645	0.255	5.50
0.0036	9.02	2.505	0.242	5.69
0.0040	9.41	2.352	0.229	6.16
0.0044	9.89	2.247	0.217	6.51
0.0049	10.38	2.118	0.204	6.91
0.0055	11.11	2.019	0.195	8.06

to the fact that the molecules of the dye penetrate into the palisade layer of the micelle between the soap molecules, and a larger mixed micelle is formed; thus, the degree of dissociation and dissociation constant decrease with the addition of dye.

The plots of dissociation constant, K vs soap concentration, C show approximate constancy in dilute solutions but exhibit a drift with increasing soap concentration which shows that the soap does not behave as a very weak electrolyte (Fig. 5). The drift in the values of dissociation constant with increasing soap concentration may be due partly to the fact that the degree of dissociation, α is not exactly equal to the conductance ratio, μ/μ_0, but mainly because the activity coefficients of ions are not equal to unity. The deviations in the values of dissociation con-

stant at higher concentrations may be due to the failure of simple Debye-Huckel's activity equation at higher concentrations.

The dissociation constant, K′ of lanthanum caprate, when the activity coefficients of ions are not equal to unity, can be expressed as:

$$K' = \frac{27\ C^3\alpha^4}{1-\alpha} \cdot \frac{f_+\ f_-^3}{f_{soap}}$$

If the ionic strength is not too high, the activity coefficient of non-ionized molecules of soap, i.e. f_{soap}, may be taken as unity. Using Debye-Huckel's limiting law for activity coefficient, K′ can be expressed as:

$$\log K = \log K' + A'\ \sqrt{(C\alpha)}$$

The plots of log K vs $\sqrt{(C\alpha)}$ for lanthanum caprate solutions are linear. The values of K′ and A′ have been calculated from the intercept, log K′ and (Table 3) slope, A′ of the linear plots of log K vs $\sqrt{(C\alpha)}$. The results show that the values of K′ and A′ decrease with the increase in the concentration of methanol in the solvent mixture.

The results show that the soap behaves as a weak electrolyte in dilute solutions below the CMC, and the con-
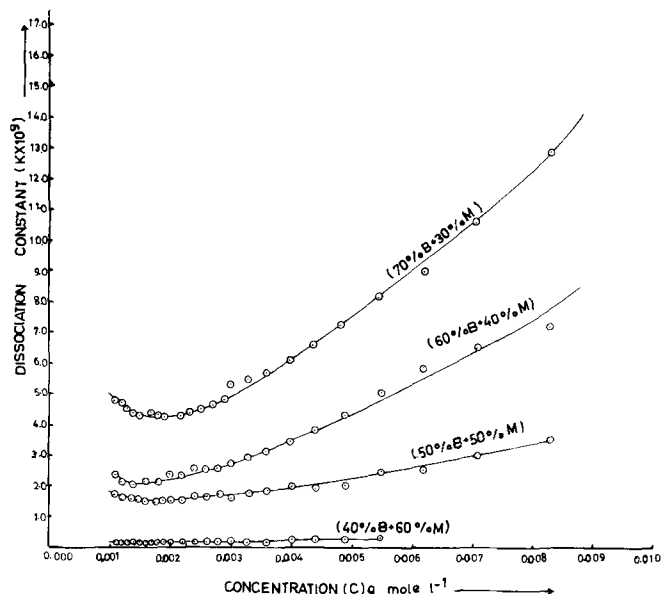

FIG. 5. Dissociation constant (k) vs concentration (C). B, benzene; M, methanol.

TABLE 3

Values of K′ and A′

Percentage of benzene in the solvent mixture	K′ × 10¹¹	A′
70% Benzene	5.4	34.4
60% Benzene	3.6	32.1
50% Benzene	3.1	30.8
40% Benzene	2.9	46.0

ductance results can be explained on the basis of Ostwald's formula and Debye-Huckel's theory of weak electrolytes.

REFERENCES

1. Ryan, L.W., and W.W. Plechnar, *Ind. Eng. Chem. 26*:909 (1934).
2. *Brit. 395-406*, Titanium Pigment Co. Inc. (1933) July 17.
3. Chatfield, H.W., *Paint Manuf. 6*:112 (1936).
4. Skellon, J.H., and J.W. Spence, *J. Soc. Chem. Ind.* (London) *67*:365 (1948).
5. Skellon, J.H., and J.W. Spence, *J. Appl. Chem.* (London) *3*:10 (1953).
6. Marwedel, G., *Farbe U. Lack 60*:530 (1954).
7. Marwedel, G., *Farbe U. Lack 62*:92 (1956).
8. Mishra, S.N., T.N. Mishra and R.C. Mehrotra, *J. Inorg. Nucl. Chem. 25*:195 and 201 (1963).
9. Skellon, J.H., and K.E. Andrews, *J. Appl. Chem.* (London) *5*:245 (1955).
10. Mehrotra, R.C., *Wiss. Z. Friedrich-Schiller Univ., Jena. Math. Naturwiss. Reth. 14*:171 (1965).
11. Main, F., D. Mills and D.W. White, *U.S.3, 320,172* (1967).
12. Bhandari, A.M., S. Dubey and R.N. Kapoor, *J. Amer. Oil Chem. Soc. 4*:47 (1970).
13. Skrylev, L.D., V.F. Sazonna, M.E. Kornelli and N.A. Shumitina, *Khim. Khim. Tekhnol 21*:491 (1978).
14. Solanki, A.K., and A.M. Bhandari, *Tenside Detergents 18*:34 (1981).
15. Varma, R.P., and R. Jindal, *Tenside Detergents 20*:193 (1983).

♣ Cobaltothiocyanate Colorimetric Analysis for Homologous Polyoxyethylated Alkyl Amides

John T. Lin, Donald G. Cornell and **Thomas J. Micich**

Eastern Regional Research Center, ARS/USDA, 600 East Mermaid Lane, Philadelphia, PA 19118

Cobaltothiocyanate colorimetry has been used for quantitative analysis of polyethoxylates in biodegradation and environmental studies. Usually, the calibration parameters (slope and intercept of a calibration line) for the cobaltothiocyanate colorimetry are dependent on ethylene oxide chain length. To make the colorimetric method useful for polyoxyethylated surfactant mixtures, where the average chain length is polydispersed, a condition was found yielding parameters independent of chain length in a homologous series of polyethoxylates within a limited chain length range. The dependency can be correlated to the thermodynamics of the ethylene oxide-cobaltothiocyanate complexation and the solvent extraction.

Recently, Micich and Linfield (1) developed a series of polyoxyethylated alkyl amides with outstanding wetting properties (see Table 1 for structured diagram). To evaluate their products as soil conditioners the adsorption of these nonionic surfactants on clay particles was studied. Such a study requires the measurement of the surfactant concentration in serum separated from the clay particles.

Polydispersity of the chain length distribution often prevents quantitative analysis of polyethoxylate surfactants. To be precise, two complimentary analytical methods must be devised, one for the hydrophobic head group and the other for the hydrophilic polyethoxylate chain, since the average chain length may change in the serum after adsorption. In our case, UV-VIS spectro-

TABLE 1

Cobaltothiocyanate Colorimetric Absorptivity of Homologous Polyoxyethylated Alkyl Amides[a]

	EO = 5	EO = 10	EO = 15	EO = 20
methyl chloride				
$a^b \cdot 10^{-4}$	1.71 ± 0.01	4.87 ± 0.01	7.27 ± 0.03	9.44 ± 0.12
$a'^c \cdot 10^{-3}$	3.41 ± 0.02	4.87 ± 0.01	4.85 ± 0.02	4.72 ± 0.06
f^d	99.0 ± 0.5	98.2 ± 0.5	97.0 ± 0.5	97.5 ± 0.5
benzene				
$a^b \cdot 10^{-4}$	1.58 ± 0.01	0.84 ± 0.03	0.08 ± 0.02	——
$a'^c \cdot 10^{-3}$	3.16 ± 0.02	0.84 ± 0.03	0.05 ± 0.01	——
f^d	97.5 ± 0.5	<31	——	——

[a]The homologous polyoxyethylated alkyl amide has a structure as $RCON(CH_2R)$ $(C_2H_5O)_nH$, where R is $-CH(C_4H_9)$ (C_2H_5) and n is the average E.O. chain length.
[b]a is apparent molar absorptivity in unit of mole$^{-1} \cdot$ cm^{-1}.
[c]a' is apparent molar absorptivity per E.O. in unit of equivalent$^{-1} \cdot$ cm^{-1}.
[d]f is the extraction efficiency.