SURFACTANTS & DETERGENTS

Influence of Alkanols on the Micellar Behavior of Samarium Soaps

K.N. Mehrotra*, Mithlesh Chauhan and R.K. Shukla
Department of Chemistry, Institute of Basic Sciences (Agra University), Khandari Road, Agra-282004, India

The critical micelle concentration, degree of ionization, and ionization constant of samarium caproate in alcohols (methanol, ethanol, propanol-1, butanol-1 and pentanol-1) were determined by using conductometric measurements. The results show that the soap behaves as simple electrolyte in dilute solutions below the CMC. The viscosity results of samarium soap have been explained in terms of equations proposed by Einstein, Vand, Moulik and Jones-Dole. The critical micelle concentration (CMC) was found to decrease with increasing dielectric constant of the solvent.

Recently rare earth metal soaps have found wide applications in industries, however, the studies on these soaps have been limited, with the result that only few references (1–18) are available in this field. In view of the increasing interest in the study of heavy metal soaps, the conductometric and viscometric studies on samarium soaps have been carried out.

The present paper deals with the determination of critical micelle concentration (CMC), degree of ionization, ionization constant, molar volume and viscosity of the solutions of samarium caproate in alkanols (methanol, ethanol, propanol-1, butanol-1 and pentanol-1).

EXPERIMENTAL

Samarium nitrate hexahydrate (Indian Rare Earths, Ltd.Udoyogamandal, Kerala State, India) and caproic acid (BDH) were used for the preparation of samarium caproate. The solvents (alkanols) were purified by standard methods. The soap was prepared by the direct metathesis of potassium caproate with slight excess of an aqueous solution of samarium nitrate at 50–55°C under vigorous stirring. The precipitated soap was filtered off and washed with distilled water and alcohol, and then recrystallized with a mixture of benzene and methanol and dried under reduced pressure. The absence of hydroxyl group in soap was confirmed by studying its IR spectrum. The melting point of samarium caproate was 95°C. The reproducibility of the results was checked by preparing two samples of 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 conductivity of the solutions. The viscosity and density of the solutions of samarium caproate were measured by Ostwald's Viscometer and Pyknometer. The capacity of the viscometer and pyknometer was 10 and 15 ml, respectively. All measurements were made at 40 ± 0.5°C in a thermostat.

RESULTS AND DISCUSSION

Specific conductance. The specific conductance, k of the solutions of samarium caproate in organic solvents (viz. methanol, ethanol, propanol-1, butanol-1 and pentanol-1) increases with increasing soap concentration. The increase in specific conductance with the increase in soap concentration may be due to the ionization of samarium caproate into simple metal cations, Sm^{+3}, and fatty acid anions, $C_5H_{11}COO^-$, in dilute solutions as well as the formation of micelles at higher concentrations. The plots of specific conductance vs soap concentration (Fig. 1) for solutions in methanol, ethanol, propanol-1 and butanol-1 are characterized by an intersection of two straight lines at a definite soap concentration 0.0156, 0.0200, 0.0235 and 0.0283 M, respectively, corresponding to the CMC of samarium caproate in these solvents. The sharpness of breaks decreases with decreasing dielectric constant of solvents, so no break has been observed in case of pentanol-1. The specific conductance for soap solutions in pentanol-1 increases linearly with increasing soap concentration. The results show that the specific conductance of the soap solutions increases while CMC decreases with increasing dielectric constant of the solvent. This may be due to the fact that the high dielectric constant of the solvent reduces the electrostatic attractive forces between positive and negative ions, and thus favor ionization of the solute molecule, which ultimately results in micellization. The values of CMC show that the micelle formation occurs more easily in methanol than in other, higher alcohols showing the following trend:

$$\text{MeOH} > \text{EtOH} < \text{PrOH} < \text{BuOH}$$

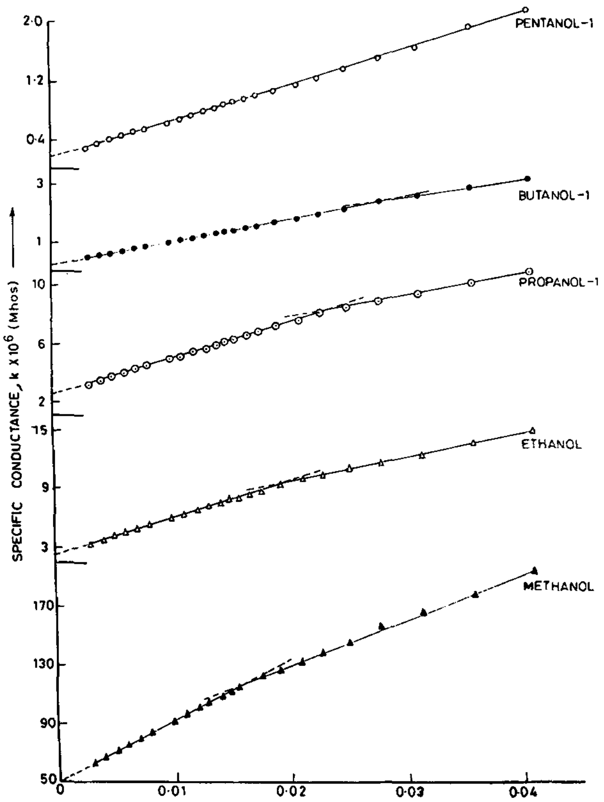

FIG. 1. Specific conductance (k) vs concentration (C).

---

*To whom correspondence should be addressed.

TABLE 1

A Comparative Chart of Molar Conductance, μ of Samarium Caproate

S. no.	Concentration C (g mol l^{-1})	Solvents				
		Methanol	Ethanol	Propanol-1	Butanol-1	Pentanol-1
1	0.0033	18.72	1.00	0.92	0.167	0.097
2	0.0036	17.65	0.94	0.87	0.158	0.094
3	0.0042	15.86	0.86	0.85	0.148	0.088
4	0.0045	15.11	0.84	0.74	0.144	0.087
5	0.0056	12.93	0.73	0.70	0.129	0.079
6	0.0062	12.07	0.69	0.66	0.124	0.077
7	0.0071	11.05	0.65	0.61	0.117	0.073
8	0.0083	10.01	0.61	0.56	0.108	0.069
9	0.0104	8.74	0.55	0.48	0.100	0.063
10	0.0125	8.00	0.52	0.44	0.095	0.059
11	0.0138	7.71	0.51	0.42	0.093	0.059
12	0.0156	7.28	0.48	0.40	0.091	0.058
13	0.0208	6.31	0.44	0.36	0.086	0.055
14	0.0250	5.85	0.41	0.33	0.084	0.054
15	0.0313	5.32	0.38	0.30	0.082	0.053
16	0.0417	4.68	0.35	0.26	0.077	0.052

Molar conductance μ and ionization constant K. The molar conductance, μ of the dilute solutions of samarium caproate in methanol, ethanol, propanol-1, butanol-1 and pentanol-1 decreases with the increase in the soap concentration (Table 1). The decrease seems to be due to the tendency of the soap to form aggregates at a higher soap concentration. It is suggested that the mobility of the soap decreases with the increase in the size of the molecules, and hence, the molar conductance decreases as the concentration increases. The plots of molar conductance, μ vs square root of soap concentration, $C^{1/2}$ are not linear, which indicates that the soap behaves as a weak electrolyte and the Debye-Huckel-Onsager's equation is not applicable to these soap solutions, and the limiting molar conductance, μ_0, for these soap solutions cannot be obtained by the usual extrapolation method.

Since the soap behaves as a simple electrolyte in dilute solutions, an expression for the ionization of samarium caproate can be developed in Ostwald's manner. If C is the concentration in g mol l^{-1} and α is the degree of ionization of samarium caproate, the equivalent concentrations of different species can be represented as:

$$\begin{array}{ccccc} Sm(C_5H_{11}COO)_3 & \rightleftharpoons & Sm^{3+} & + & 3C_5H_{11}COO^- \\ C(1-\alpha) & & C\alpha & & 3(C\alpha) \end{array}$$

The ionization constant, K, can be expressed as shown below in Eq. [1]:

$$K = \frac{[Sm^{3+}]\,[C_5H_{11}COO^-]^3}{[Sm(C_5H_{11}COO)_3]} = \frac{C\alpha\,(3C\alpha)^3}{C(1-\alpha)} = \frac{27\,C^3\,\alpha^4}{(1-\alpha)} \qquad [1]$$

The ionic concentrations in dilute solutions are low, and so the interionic effects may be treated as 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 ionization may be replaced by the conductance ratio, μ/μ_0, where μ is the molar conductance at finite concentration, and μ_0 is the limiting molar conductance at infinite dilution. On substituting the value of α and rearranging Eq. [1], we obtain:

$$\mu^3\,C^3 = \frac{K\,\mu_0^4}{27\,\mu} - \frac{K\,\mu_0^3}{27}$$

The values of K and μ_0 have been obtained from the slope, [K $\mu_0^4/27$], and intercept, [$-$K $\mu_0^3/27$], of the linear parts of the plots of μ^3 C^3 vs $1/\mu$ (Figs. 2 and 3) for dilute

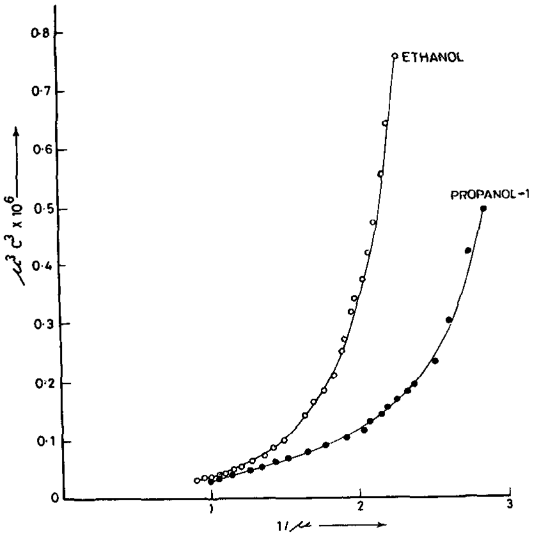

FIG. 2. μ^3C^3 vs $1/\mu$ for ethanol and propanol-1.

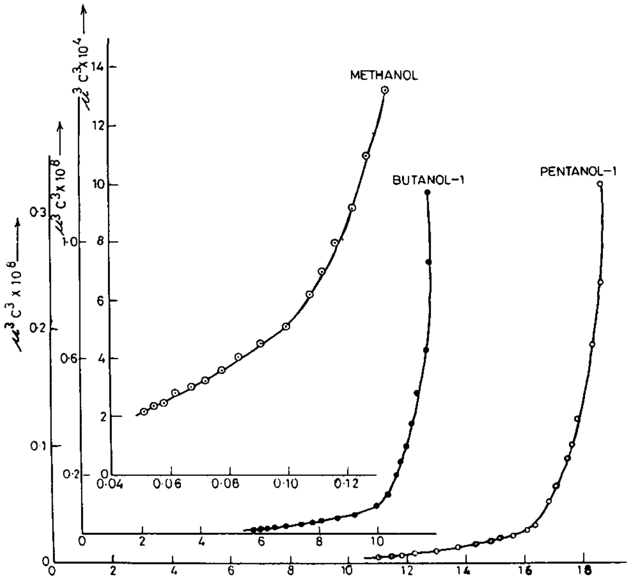

FIG. 3. μ^3C^3 vs $1/\mu$ for methanol, butanol-1 and pentanol-1.

TABLE 2

Values of CMC, Limiting Molar Conductance, μ_0 and Dissociation Constant, K

Solvent	CMC (g mol l^{-1})	μ_0	Dissociation constant, K × 10^7 Graphical (μ^3C^3 vs $1/\mu$)	Dissociation constant, K × 10^7 Calculated
Methanol	0.0156	64.70	0.10	0.09
Ethanol	0.0200	1.77	2.40	2.30
Propanol-1	0.0235	1.66	2.50	2.60
Butanol-1	0.0283	0.23	12.80	10.00
Pentanol-1	—	0.12	49.40	30.00

soap solutions and are recorded in Table 2. There is no doubt that the soap (samarium caproate) is in micellar and other aggregate forms at and above the CMC and possess different conductivities in these forms. However, the plots of μ^3 C^3 vs $1/\mu$ are linear below the CMC and the slope and intercept of linear portion have been used to evaluate μ_0 and K. The soap is in monomeric form below the CMC, and the value of C has been taken as equal to the total concentration of the surfactant. The plots of μ^3C^3 vs $1/\mu$ above the CMC have not been used for evaluating any parameter. The values of limiting molar conductance, μ_0, decrease in alkanol series. The values of ionization constant, K, increase in alkanol series. The values of degree of ionization, α, at different soap concentrations has been calculated by assuming it to be equal to the conductance ratio, μ/μ_0. The plots of degree of ionization, vs soap concentration show that the degree of ionization of the soap decreases rapidly in dilute solutions with the increase in soap concentration and dielectric constant of solvent. The values of ionization constant, K, have been calculated by using Eq. [1] and assuming the degree of ionization to be equal to the conductance ratio. The values of ionization constant, K, change slowly with the increase in the soap concentration in dilute solutions but increase rapidly in concentrated solutions, which shows that the soap does not behave as a very weak electrolyte. The drift in the values of ionization constant with increasing soap concentration may be due to these facts: The degree of ionization is not exactly equal to the conductance ratio, μ/μ_0; the activity coefficients of ions are not equal to unity; the soap is in micellar and other aggregate forms at and above the CMC; and the failure of Debye-Huckel's activity equation at higher soap concentrations.

The results show that the soap behaves as a simple electrolyte in dilute solutions below the CMC, and the conductance results can be explained on the basis of Ostwald's formula and Debye-Huckel's theory of electrolytes.

Molar volume, $\bar{V}$. The molar volume, $\bar{V}$, of the solutions of samarium caproate in methanol, ethanol, propanol-1, butanol-1 and pentanol-1 decreases with increasing soap concentration (Table 3). The plot (Fig. 4) of molar volume, $\bar{V}$ against the soap concentration C (g mol l^{-1}), are characterized by an intersection of two straight lines at a definite soap concentration, which corresponds to the CMC of soap. The results show that the CMC shifts to lower soap concentration with an increase in dielectric constant of the solvent (Table 4). This may be due to the fact that the solvent with high dielectric constant reduces the electrostatic attractive forces between positive and negative ions and favors the ionization of the soap molecules into cations, Sm^{3+}, and anions, C_5H_{11} COO^-, and the formation of ionic micelles.

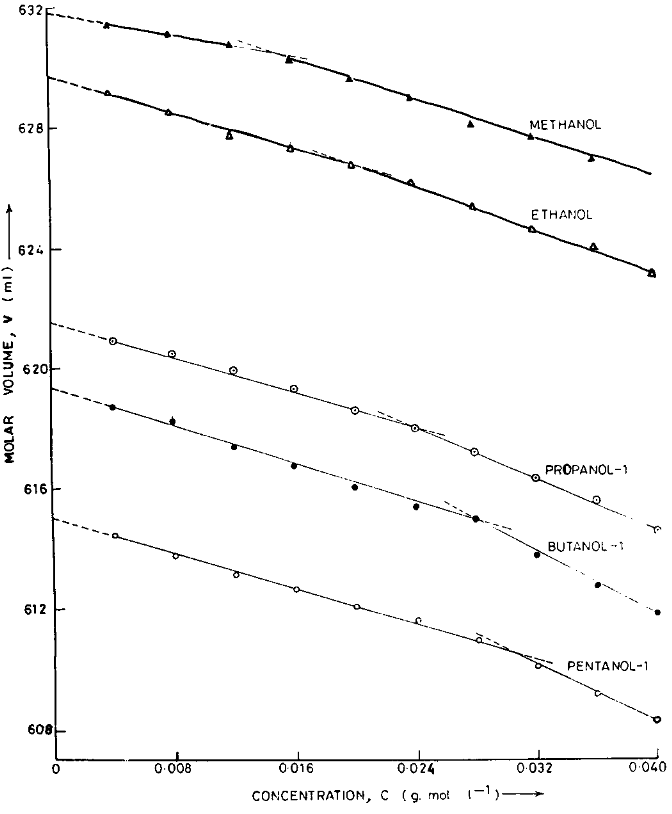

FIG. 4. Molar volume ($\bar{V}$) vs concentration (C).

TABLE 3

Molar Volume, $\bar{V}$ (ml) of Samarium Caproate

S. no.	Concentration C (g mol 1^{-1})	Solvents Methanol	Ethanol	Propanol-1	Butanol-1	Pentanol-1
1	0.004	631.50	629.25	620.90	618.65	614.51
2	0.008	631.17	628.53	620.51	618.19	613.83
3	0.012	630.69	627.74	619.89	617.27	613.07
4	0.016	630.21	627.34	619.27	616.73	612.69
5	0.020	629.49	626.71	618.50	615.96	612.01
6	0.024	628.85	626.07	617.88	615.43	611.56
7	0.028	627.98	625.28	617.11	614.97	611.03
8	0.032	627.58	624.57	616.26	613.75	610.05
9	0.036	626.79	623.95	615.58	612.77	609.15
10	0.040	626.63	623.08	614.51	611.93	608.26

TABLE 4

The Values of CMC, Molar Volume $\bar{V}$, Interaction Coefficient ϕ, Intrinsic-Viscosity η_I, Constant M and K (from Moulik's Equation) A and B (from Jones-Dole's Equation) and Values of Viscosity, η from the Extrapolation of Plots and from Pure Solvent

S. no.	Solvent	CMC in (g mol 1^{-1})	$\bar{V}$ in ml from Einstein's equation	$\bar{V}$ in ml from Vand's equation	ϕ	η_I	M	K	A	B	Viscosity of pure solvent (centipoise)	Viscosity from extrapolation of pt.
1	Methanol	0.0152	520	500	10	0.97	1.02	133	0.19	0.43	0.4571	0.4610
2	Ethanol	0.0200	420	460	8	1.04	1.02	123	0.10	0.50	1.0230	1.0260
3	Propanol-1	0.0240	560	580	10	1.07	1.02	108	0.15	0.22	1.6470	1.6440
4	Butanol-1	0.0280	480	460	10	1.24	1.02	46	0.03	0.82	2.0370	2.0400
5	Pentanol-1	0.0300	500	560	9	1.68	1.03	40	0.14	0.30	2.3200	2.3370

Viscosity, η. The viscosity, η, and specific viscosity, η_{sp}, of the solutions of samarium caproate in methanol, ethanol, propanol-1, butanol-1 and pentanol-1 increases with increasing soap concentration (Table 5), which may be due to the increasing tendency of the soap to form aggregates with increase in soap concentration. The plots of viscosity, η, vs soap concentration, C (Fig. 5), and specific viscosity vs soap concentration are characterized by an intersection of two straight lines at a concentration which corresponds to the CMC of the soap (Table 4), indicating a marked change in the aggregation of the soap molecules at the CMC. The results show that the CMC increases with decreasing dielectric constant of the solvent. The values of the CMC show that the micelle formation occurs more easily in methanol than in other alkanols. The values of the CMC are in agreement with those obtained from other measurements. The plots of viscosity vs soap concentration below the CMC have been extrapolated to zero soap concentration, and the extrapolated values of η_0 are in agreement with the viscosity of pure solvent (Table 4). The difference in the viscosity of solutions of samarium caproate in different solvents is mainly due to the difference in the viscosity of these solvents.

The results of viscosity have been explained on the basis of the following equations:

Einstein (19,20): $\eta_{sp} = 2.5\ \bar{V}\ C$

Vand (21): $1/C = \left[\dfrac{0.921}{\bar{V}}\right]^{-1} \dfrac{1}{\log \eta/\eta_0} + \phi\bar{V}$

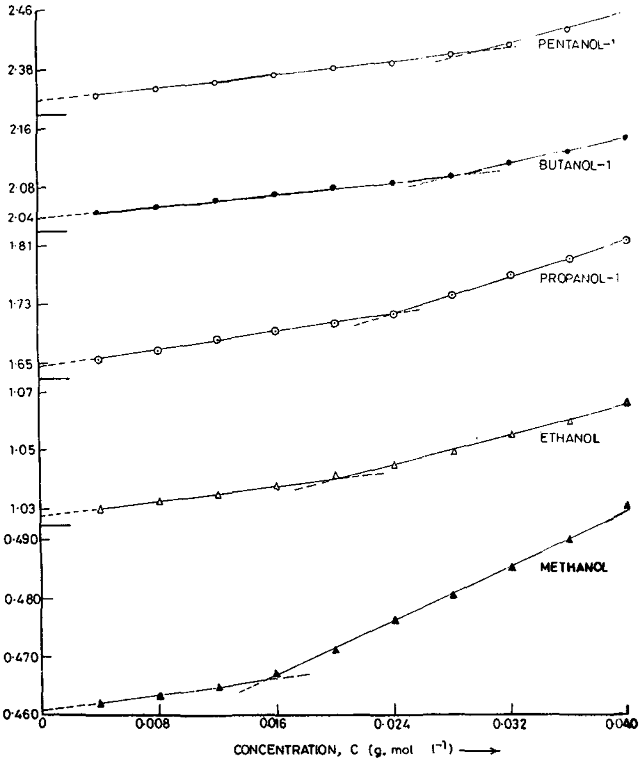

FIG. 5. Viscosity (η) vs concentration (C).

TABLE 5

Viscosity of Samarium Caproate

S. no.	Concentration, C (g mol 1^{-1})	Solvents				
		Methanol	Ethanol	Propanol-1	Butanol-1	Pentanol-1
1	0.004	0.4621	1.030	1.655	2.048	2.3453
2	0.008	0.4633	1.032	1.662	2.056	2.3541
3	0.012	0.4647	1.035	1.677	2.066	2.3602
4	0.016	0.4671	1.038	1.693	2.072	2.3699
5	0.020	0.4712	1.041	1.708	2.083	2.3798
6	0.024	0.4762	1.045	1.717	1.087	2.3852
7	0.028	0.4803	1.049	1.737	2.094	2.3938
8	0.032	0.4852	1.055	1.767	2.109	2.4083
9	0.036	0.4899	1.060	1.792	2.125	2.4274
10	0.040	0.4959	1.067	1.814	2.144	2.4513

Moulik (22): $(\eta/\eta_0)^2 = M + KC^2$

Jones-Dole (23): $(\eta_{sp}/C^{1/2}) = A + BC^{1/2}$

where $\overline{V}$, C, ϕ, η, η_0 and η_{sp} are the molar volume (ml), concentration (g mol 1^{-1}), interaction coefficient, viscosity of the solution, viscosity of pure solvent and specific viscosity, respectively, M and K are Moulik's constants. The constants A and B of Jones-Dole's equation refer to the soap-soap and soap-solvent interactions, respectively.

The plots of specific viscosity vs soap concentration below the CMC are linear with intercept equal to zero, which shows that Einstein's equation is applicable to dilute soap solutions. The values of the molar volume of the soap, $\overline{V}$, have been calculated from the slopes of the plots of η_{sp} vs C (Einstein's equation) and of 1/C vs 1/log (η/η_0) (Vand's equation), and the values obtained from both the equations are applicable to dilute soap solutions. The values of interaction-coefficient, ϕ, obtained from the intercept of Vand's plots lie between 8 and 10 for the solutions in alkanols, which shows that the interaction-coefficient is almost independent of the chainlength of alcohols. The plots of $(\eta/\eta_0)^2$ vs C^2 are linear, which indicates that Moulik's equation is applicable to these soap solutions. The value of Moulik's constant, M, is independent of the nature of the solvent and the values of K decrease with the increase in the chainlength of alcohols.

The applicability of Jones-Dole's equation is checked by the linearity of the plots of $\eta_{sp}/C^{1/2}$ vs $C^{1/2}$ below the CMC. The values of coefficients A and B have been calculated from the intercept and slope of the plot below the CMC (Table 4). The values of coefficient B (soap-solvent interaction) are larger than the values of coefficient A (soap-soap interaction), which confirms that the molecules of soap do not aggregate appreciably below the CMC, and that there is a sudden change in the aggregation above the CMC. The values of intrinsic viscosity, η_I, increase with increasing chainlength of alkanols.

Therefore, it is concluded that the equations of Einstein, Vand, Moulik and Jones-Dole are applicable to dilute solutions of samarium caproate in these solvents.

ACKNOWLEDGMENT

The authors would like to thank Professor S. K. Agrawal, Vice-Chancellor, Agra University, Agra, for providing necessary laboratory facilities. R.K.S. and M.C. are grateful to U.G.C., New Delhi, for financial support.

REFERENCES

1. Mehrotra, K.N., A.S. Gahlaut and Meera Sharma, *J. Am. Oil Chem. Soc. 63*:1571 (1986).
2. Mehrotra, K.N., A.S. Gahlaut and Meera Sharma, *J. Colloid Interface Sci. 120*(1):110 (1987).
3. Mehrotra, K.N., A.S. Gahlaut and Meera Sharma, *J. Indian Chem. Soc. 64*:103 (1987).
4. Mehrotra, K.N., Meera Sharma and A.S. Gahlaut, *J. Indian Chem. Soc. 64*:331 (1987).
5. Mehrotra, K.N., A.S. Gahlaut and Meera Sharma, *J. Indian Chem. Soc. 64*:285 (1987).
6. Varma, R.P., and R. Jindal, *Tenside Detergents 20*:193 (1983).
7. Main, F., D. Mills and D.W. White, *U.S.3 320*:172 (1967).
8. Lorant, B., *Seifen, Ole, Fette, Wachse 93*(16):547 (1967).
9. Chatfield, H.W., *Paint Manuf. 6*:112 (1936).
10. Bhandari, A.M., S. Dubey and R.N. Kapoor, *J. Amer. Oil Chem. Soc. 4*:47 (1970).
11. Solanki, A.K., and A.M. Bhandari, *Tenside Detergents 18*:34 (1981).
12. Mehrotra, R.C., *Wiss. Z. Friedrich-Schiller Univ., Jena. Math. Naturwiss. Reihe 14*:171 (1965).
13. Skrylev, L.D., V.F. Sazonna, M.E. Kornelli and N.A. Shumitina, *Khim. Khim. Tekhnol 21*:491 (1978).
14. Mishra, S.N., T.N. Mishra and R.C. Mehrotra, *J. Inorg. Nucl. Chem. 25*:195 (1963).
15. Mishra, S.N., T.N. Mishra and R.C. Mehrotra, *Ibid. 25*:201 (1963).
16. Marwedel, G., *Farbe U. Lack 60*:530 (1954).
17. Marwedel, G., *Ibid. 62*:92 (1956).
18. Skellon, J.H., and K.E. Andrews, *J. Appl. Chem. (London) 5*:245 (1955).
19. Einstein, A., *Ann. Physik. 19*:289 (1906).
20. Einstein, A., *Ibid. 34*:591 (1911).
21. Vand, V., *J. Phys. Colloid Chem. 52*:277 (1948).
22. Moulik, S.P., *J. Phys. Chem. 72*:4682 (1968).
23. Jones, G., and M. Dole, *J. Am. Chem. Soc. 51*:2950 (1929).

[Received April 17, 1989; accepted October 25, 1989]