Spectroscopic and Conductometric Studies of Lanthanide Soaps

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Infrared spectral studies of lanthanide soaps (octanoates of cerium, didymium, neodymium, and samarium) reveal that fatty acids exist with a dimeric-type structure through hydrogen bonding between two molecules of fatty acids, whereas the metal-to-oxygen bonds in these soaps have an ionic character. The X-ray diffraction results confirm that these soaps have a double-layer structure with molecular axes slightly inclined to the basal plane. The premicellar association and the formation of micelles in lanthanide soap solutions have been investigated by conductometric measurements in a nonaqueous medium. The molar conductance at infinite dilution, the degree of ionization and the ionization constant have been evaluated. The results show that these soaps behave as weak electrolytes in dilute solutions.

The most striking feature of metal soaps has been their increasing importance in industries as detergents, softners, stabilizers, plasticizers, driers, thickners, catalysts, antioxidants, greases, lubricants, medicines, fungicides, germicides, insecticides, emulsifiers, water proofing, and wetting agents. A survey of the literature reveals that although an enormous amount of work has been reported concerning the formation, characterization, and application of alkali, alkaline earth, and transition metal soaps but comparatively less work has been reported[1—20] concerning rare earth metal soaps. Rare earth metal soaps have been prepared by several workers[1—11] by double decomposition, metathesis, the direct reaction of metal oxide or hydroxide with an organic acid, the adding of an organic or inorganic salt of fatty acid and crystallization of the hydrated soaps with a dried organic solvent. Varma and Jindal,[12] Solanki and Bhandari,[13] and Mehrotra[14] characterized cerium, uranyl, and lanthanum soap by using the infrared and electronic absorption spectra. Mehrotra et al.[17—20] studied the nature of formed micelles, cmc, and molecular interactions of lanthanide and actinide soaps in different solvents by using conductivity, viscosity, and ultrasonic-velocity measurements. Mains et al.[15] found that the detergency and foaming of synthetic detergents are greatly enhanced by embodying a small amount of water-soluble cerium salts in the detergents. Chatfield[16] summarized the properties and uses of cerium and thorium soaps.

In view of the increasing interest in the field of heavy metal soaps, the present work was initiated with the view to study the nature of the bonding structure and to determine the critical micelle concentration and nature of electrolytes in dilute solutions of lanthanide soaps (octanoates of cerium, neodymium, samarium, and didymium). Didymium is a mixture of cerium lean rare earths having atomic weights of approximately 141. The precise composition of didymium is 70% cerium and 30% other lanthanides.

Experimental

All of the chemicals used were of BDH/AR grade. Lanthanide soaps were prepared by the direct metathesis of the corresponding potassium soap with a slight excess of a solution of chloride/nitrate of lanthanides at 50—60 °C under vigorous stirring. The precipitated soaps were digested, filtered, washed with distilled water–ether, and dried. The soaps were purified by recrystallization with a benzene–methanol mixture. The purity of the soaps was confirmed by elemental analysis and determining their melting points (didymium octanoate, 154 °C; cerium octanoate, 138 °C; neodymium octanoate, 105 °C; and samarium octanoate, 102 °C). The infrared absorption spectra of lanthanide soaps together with the corresponding fatty acids were recorded on a Perkin–Elmer grating spectrophotometer (Model 577) in the 4000—400 cm^{-1} region using the potassium bromide disc method. The X-ray diffraction patterns of lanthanide soaps were obtained over a range of diffraction angles of $2\theta=5$ to 80° using a Philips PW 1730 diffractometer and Cu-$K\alpha$ radiation filtered through a nickel foil. The conductivity measurements of the solutions of lanthanide soaps in a mixture of benzene–DMF (50% v/v) were carried out using a Toshniwal digital conductivity meter (Model CL 01.10 A) and a dipping-type conductivity cell with platinized electrodes.

Results and Discussion

Infrared Absorption Spectra. The IR spectra of lanthanide soaps (octanoates of cerium, didymium, neodymium, and samarium) were recorded (Figs. 1, 2, 3, and 4) and compared with the results of the corresponding fatty acids (Table 1). The absorption

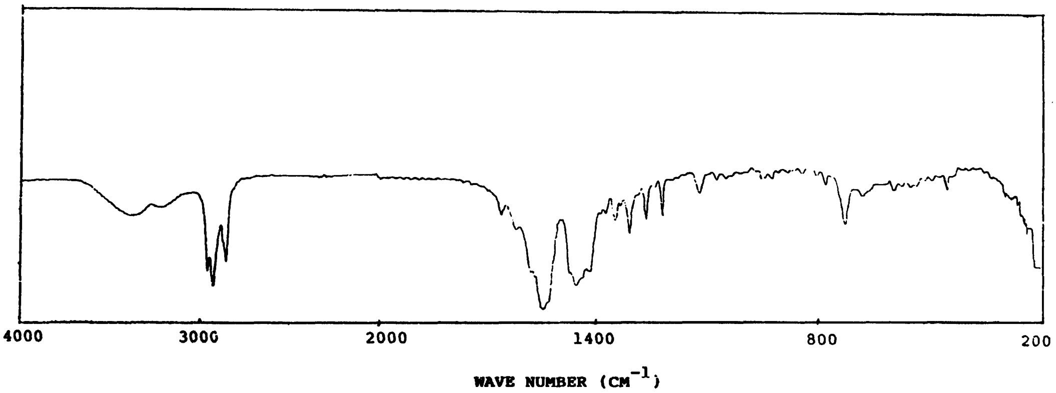

Fig. 1. Infrared absorption spectrum of cerium octanoate.

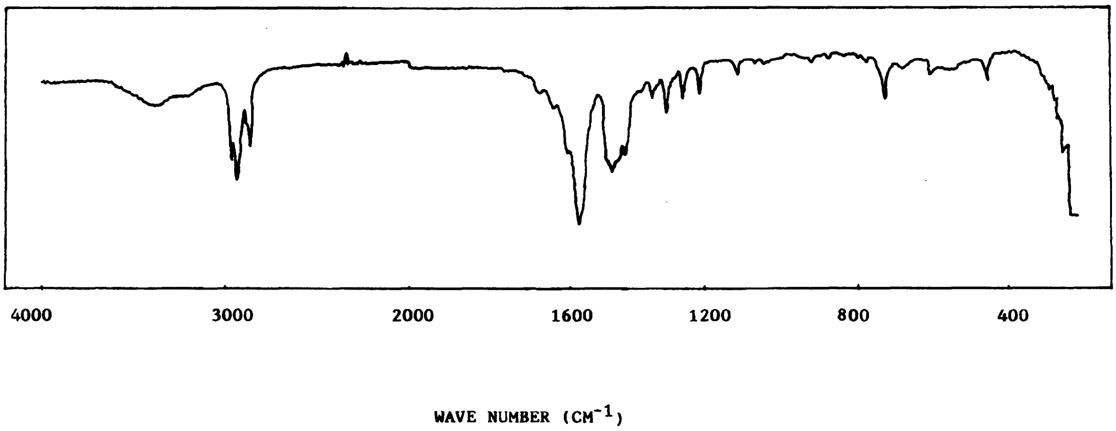

Fig. 2. Infrared absorption spectrum of didymium octanoate.

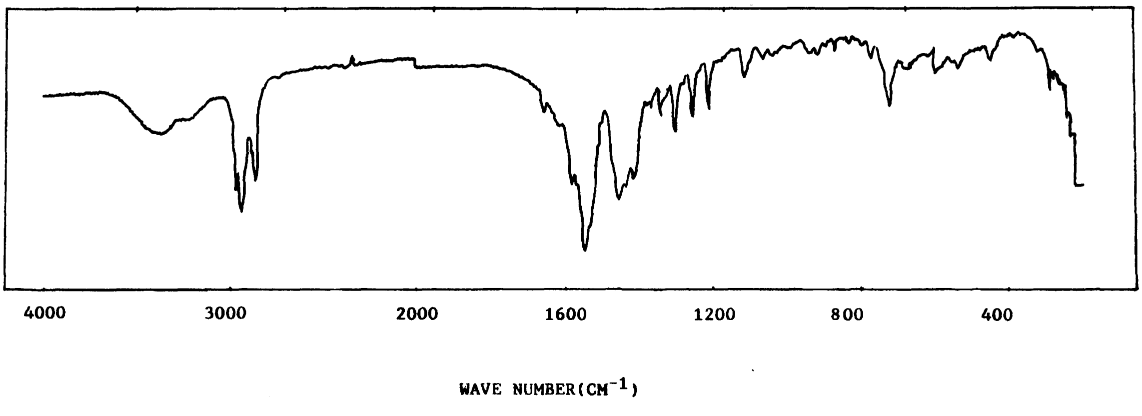

Fig. 3. Infrared absorption spectrum of neodymium octanoate.

maxima observed near to 2650, 1700, 1440, 950, 690, and 550 cm^{-1} in the spectra of the fatty acid are associated with the localized (–COOH) carboxyl group[21] of the acid molecule in the dimeric state, and confirm the presence of hydrogen bonds between two molecules of fatty acids. The absorption bands observed near to 2580, 1700, and 910 cm^{-1}, corresponding to the OH group in the spectra of the fatty acids, disappeared from the spectra of the corresponding potassium and lanthanide soaps. Evenly spaced progressive bands near to 1370—1140 cm^{-1}, which are characteristic of the hydrocarbon chain of the acid, remained almost unchanged upon preparing soap from the acid. The appearance of two absorption bands of the carboxyl group corresponding to the symmetric and asymmetric stretching vibrations of the carboxylate anion near to 1450 and 1550 cm^{-1} in the spectra of lanthanide soaps confirm that these soaps possess an ionized structure.

The results show that fatty acids in the solid state exist with a dimeric structure through hydrogen bonding between two molecules of fatty acids, whereas the M–O bonds in these soaps have an ionic character. The IR

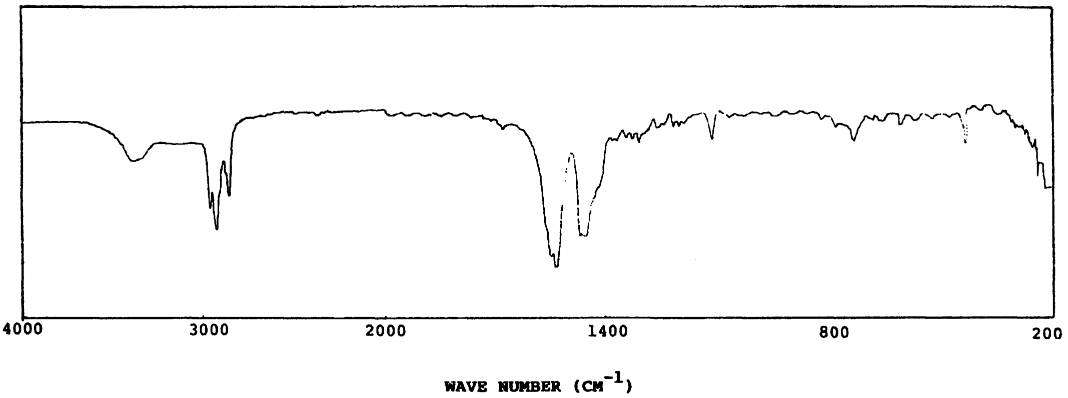

Fig. 4. Infrared absorption spectrum of samarium octanoate.

Table 1. Infrared Absorption Spectral Frequencies (cm^{-1}) with Their Assignments

Sl. No.	Assignments	Octanoic acid	Cerium octanoate	Didymium octanoate	Neodymium octanoate	Samarium octanoate
1.	CH_3, C–H asym. Stretch	2950 W	2960 M	2960 W	2960 W	2960 M
2.	CH_2, C–H asym. Stretch	2920 M	2920 S	2925 S	2925 S	2925 W
3.	CH_2, C–H sym. Stretch	2850 M	2860 M	2850 M	2855 M	2860 M
4.	OH, Stretch.	2580 W	—	—	—	—
5.	C=O, Stretch	1700 S	—	—	—	—
6.	COO^-, C–O asym. Stretch	—	1540 S	1550 S	1540 S	1540 S
7.	COO^-, C–O sym. Stretch	—	1450 M	1445 S	1430 S	1460 M
8.	C–O, Stretch, OH in-plane deformation	1430 M	—	—	—	—
9.	Progressive bands (CH_2 twisting and wagging)	1370—1140 M	1365—1210 M	1360—1210 M	1360—1210 M	1360—1190 M
10.	CH_3, Rocking	1110 M	1115 M	1115 M	1115 M	1110 M
11.	OH-out of plane deformation	910 M	—	—	—	—
12.	CH_2, Rocking	720 M	720 M	725 M	725 M	720 W
13.	COO^-, Bending mode	690 M	—	—	—	—
14.	COO^-, Wagging mode	550 M	—	—	—	—
15.	M–O, bond	—	420 M	450 W	440 M	450 M

spectra of lanthanide soaps do not show any absorption maxima in the 3500—3300 cm^{-1} region which confirms the absence of any co-ordinated water molecule in these soap molecules.

X-Ray Analysis.

The intensities of diffracted X-rays as a function of the diffraction angle, 2θ for lanthanide soaps (cerium, didymium, neodymium, and samarium octanoate), were recorded over the 5—80° range. The interplanar spacings (d) were calculated from the positions of intense peaks using Bragg's relationship, $n\lambda=2d\ \sin\theta$, where λ is the wavelength of radiation. A large number of peaks arising from the diffraction of X-rays by planes of metal ions (known as basal planes) were observed in the diffraction patterns of these metal soaps.

The appearance of diffraction up to the 13th, 14th, 19th, and 20th order for octanoates of cerium, samarium, neodymium, and didymium, respectively, suggested good crystallinity. The observed values of long spacing for lanthanide soaps (Table 2) (cerium octanoate, 24.40 Å; neodymium octanoate, 24.50 Å; samarium octanoate, 24.74 Å; and didymium octanoate, 24.51 Å) were smaller than the calculated dimensions of the octanoate ion (27.0 Å) from Pauling's values of the atomic radii and bond angles. This suggests that the molecular axes of these soaps are somewhat inclined to the basal planes. The metal ions Ce^{3+}, Nd^{3+}, Sm^{3+}, and didymium fit into spaces between the oxygen atom of the ionized carboxylate group without a large strain of the bond. On the basis of the long spacings, it is proposed that the metal ions in these soaps are arranged in a parallel plane, and that these soaps have a double-layer structure, as proposed by Vold and Hattiangdi.[22)]

Conductivity. The increase in the specific conductance (k/mho cm^{-1}) of the solutions of lanthanide soaps (cerium, didymium, neodymium, and samarium octanoate) in a mixture of benzene and dimethylformamide (DMF) (50% v/v) with increasing soap concentration, (C/mol dm^{-3}) at 40 °C may be ascribed to the ionization of the lanthanide soaps into metal cations, (M^{3+}; M=Ce, Nd, Sm, and didymium) and fatty acid anions ($C_7H_{15}COO^-$; in dilute solutions) and to the formations of micelles at higher soap concentrations. The cmc of these solutions at 40 °C (Table 3) have been de-

Table 2. X-Ray Diffraction Analysis of Lanthanide Soaps

	θ	Sin θ	$\lambda/2$ Sin θ	d	n	I/I_0
Cerium octanoate	1.899	0.0319	24.1521	24.152	1	1.00
	3.628	0.0633	12.1855	24.371	2	0.25
	5.437	0.0948	8.1364	24.409	3	0.29
	7.252	0.1262	6.1072	24.429	4	0.05
	9.068	0.1576	4.8912	24.459	5	0.06
	10.901	0.1891	4.0765	24.459	6	0.02
	12.741	0.2205	3.4956	24.469	7	0.02
	24.178	0.4096	1.8823	24.470	13	0.07
Didymium octanoate	5.428	0.0945	8.1437	24.431	3	1.00
	7.240	0.1260	6.1121	24.448	4	0.13
	9.048	0.1573	4.8983	24.492	5	0.14
	10.760	0.1867	4.1259	24.755	6	0.14
	12.730	0.2204	3.4956	24.469	7	0.03
	18.559	0.3183	2.4101	24.202	10	0.03
	20.114	0.3439	2.2399	24.639	11	0.04
	24.313	0.4117	1.8709	24.322	13	0.03
	25.833	0.4357	1.7677	24.748	14	0.03
	36.604	0.5963	1.2918	24.544	19	0.03
Neodymium octanoate	5.415	0.0944	8.1624	24.487	3	1.00
	7.222	0.1257	6.1279	24.512	4	0.20
	9.047	0.1572	4.8990	24.495	5	0.22
	10.889	0.1889	4.0777	24.466	6	0.08
	12.713	0.2201	3.5003	24.502	7	0.07
	14.568	0.2515	3.0625	24.500	8	0.03
	16.429	0.2828	2.7235	24.512	9	0.05
	18.320	0.3143	2.4506	24.506	10	0.03
	20.302	0.3470	2.2201	24.421	11	0.01
	22.235	0.3784	2.0356	24.427	12	0.02
	24.150	0.4091	1.8827	24.475	13	0.01
	26.009	0.4385	1.7566	24.592	14	0.01
	28.138	0.4716	1.6334	24.501	15	0.01
	32.302	0.5344	1.4415	24.506	17	0.01
	38.923	0.6283	1.2260	24.520	20	0.01
Samarium octanoate	1.797	0.0313	24.5905	24.590	1	1.00
	3.575	0.0624	12.3642	24.728	2	0.14
	5.364	0.0935	8.2464	24.739	3	0.07
	8.955	0.1557	4.9522	24.761	5	0.01
	10.755	0.1866	4.1310	24.786	6	0.03
	12.577	0.2178	3.5404	24.783	7	0.02
	14.415	0.2489	3.0967	24.774	8	0.01
	25.858	0.4361	1.7676	24.746	14	0.01

termined by k–C plots (Fig. 5). The values of the cmc decrease with increasing molecular weight of the soap molecule. This suggests that these soaps are considerably ionized in dilute solutions, and that the anions begin to aggregate to form ionic micelles at the cmc of the soap.

The molar conductance (μ) of the solution of lanthanide soaps in a mixture of benzene and DMF (50% v/v) decreases in dilute solutions with increasing soap concentration and molecular weight of the soap. The decrease is attributed to the combined effects of the ionic atmosphere, the solvation of ions, a decrease in the mobility and the formation of micelles. The concave nature of plots of the molar conductance (μ/mho cm^2 g^{-1}) vs. the square root of soap concentration, ($C^{1/2}$) suggests that these soaps behave as weak electrolytes in dilute solutions. An expression for the ionization of lanthanide soaps can be developed according to Ostwald's technique. If C is the concentration and α is the degree of ionization of lanthanide soaps, the equivalent concentrations of different species can be represented as

$$\mathrm{Ln(C_7H_{15}COO)_3} \rightleftharpoons \mathrm{Ln^{3+}} + \mathrm{3C_7H_{15}COO^-}$$

(Ln = Ce, Nd, Sm, and didymium)

The ionization constant (K) can be expressed as

$$K=\frac{[\mathrm{Ln^{3+}}][\mathrm{C_7H_{15}COO^-}]^3}{[\mathrm{Ln(C_7H_{15}COO)_3}]}$$

Table 3. Conductometric Data of Lanthanide Octanoate in Benzene–DMF (50% v/v) at (30±0.05) °C

$C\times10^3$	Cerium octanoate			Didymium octanoate			Neodymium octanoate			Samarium octanoate		
mol dm^{-3}	$k\times10^6$ mho cm^{-1}	μ	α	$k\times10^6$ mho cm^{-1}	μ	α	$k\times10^6$ mho cm^{-1}	μ	α	$k\times10^6$ mho cm^{-1}	μ	α
1.000	22.7	22.70	0.421	15.5	15.50	0.358	7.09	7.09	0.282	3.45	3.45	0.197
0.909	20.8	22.88	0.424	14.0	15.40	0.355	6.35	6.98	0.277	3.15	3.46	0.198
0.833	18.8	22.57	0.419	12.6	15.13	0.349	5.70	6.84	0.272	2.89	3.47	0.199
0.769	17.4	22.63	0.420	11.7	15.21	0.351	5.22	6.79	0.270	2.68	3.49	0.200
0.714	15.9	22.27	0.413	10.9	15.27	0.352	4.72	6.61	0.263	2.55	3.53	0.202
0.625	14.0	22.40	0.415	9.6	15.36	0.354	4.00	6.40	0.254	2.24	3.58	0.205
0.556	12.5	22.48	0.417	8.6	15.47	0.357	3.40	6.12	0.243	2.04	3.67	0.210
0.500	11.5	23.00	0.427	7.8	15.60	0.360	2.90	5.80	0.230	1.85	3.70	0.212
0.455	10.6	23.30	0.432	7.2	15.82	0.365	2.70	5.93	0.236	1.70	3.74	0.214
0.417	10.0	23.98	0.445	6.7	16.07	0.371	2.55	6.11	0.243	1.57	3.76	0.215
0.385	9.5	24.68	0.458	6.3	16.36	0.378	2.50	6.49	0.258	1.52	3.95	0.226
0.357	9.0	25.21	0.468	6.1	17.09	0.394	2.45	6.86	0.272	1.50	4.20	0.240
0.333	8.5	25.53	0.473	5.8	17.42	0.402	2.40	7.21	0.286	1.48	4.44	0.254
0.313	8.0	25.56	0.474	5.6	17.89	0.413	2.35	7.51	0.298	1.45	4.63	0.265
0.278	7.5	26.98	0.500	5.3	19.06	0.440	2.30	8.27	0.328	1.43	5.14	0.294
0.250	7.0	28.00	0.519	5.0	20.00	0.462	2.25	9.00	0.357	1.40	5.60	0.321
0.227	6.6	39.07	0.539	4.8	21.15	0.488	2.22	9.78	0.388	1.38	6.08	0.348
0.192	6.0	31.25	0.580	4.4	22.92	0.529	2.15	11.20	0.445	1.36	7.08	0.405
0.167	5.6	33.53	0.622	4.2	25.15	0.580	2.10	12.57	0.499	1.34	8.02	0.459
0.147	5.2	35.37	0.656	4.0	27.21	0.628	2.06	14.01	0.556	1.32	8.98	0.514

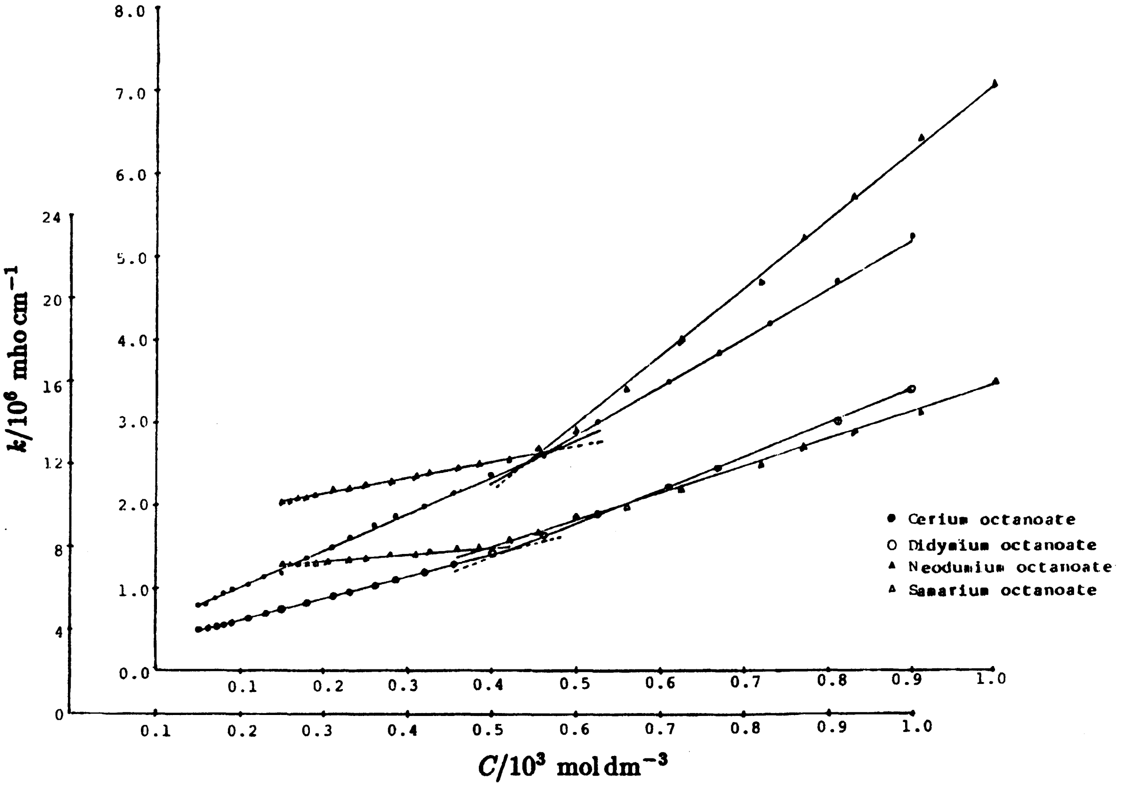

Fig. 5. Specific conductance, k vs. soap concentration, C.

$$=\frac{C\alpha\cdot(3C\alpha)^3}{C(1-\alpha)}=\frac{27C^3\alpha^4}{1-\alpha}. \tag{1}$$

The degree of ionization, (α) may be replaced by the conductance ratio (μ/μ_0), where μ is the molar conductance at finite dilution and μ_0 is the limiting molar conductance at infinite dilution. Upon substituting the value of α and rearranging Eq. 1, one obtains

$$\mu^3c^3=\frac{K\mu_0{}^4}{27\mu}-\frac{K\mu_0{}^3}{27}. \tag{2}$$

The graphical values of K and μ_0 (Table 4) for

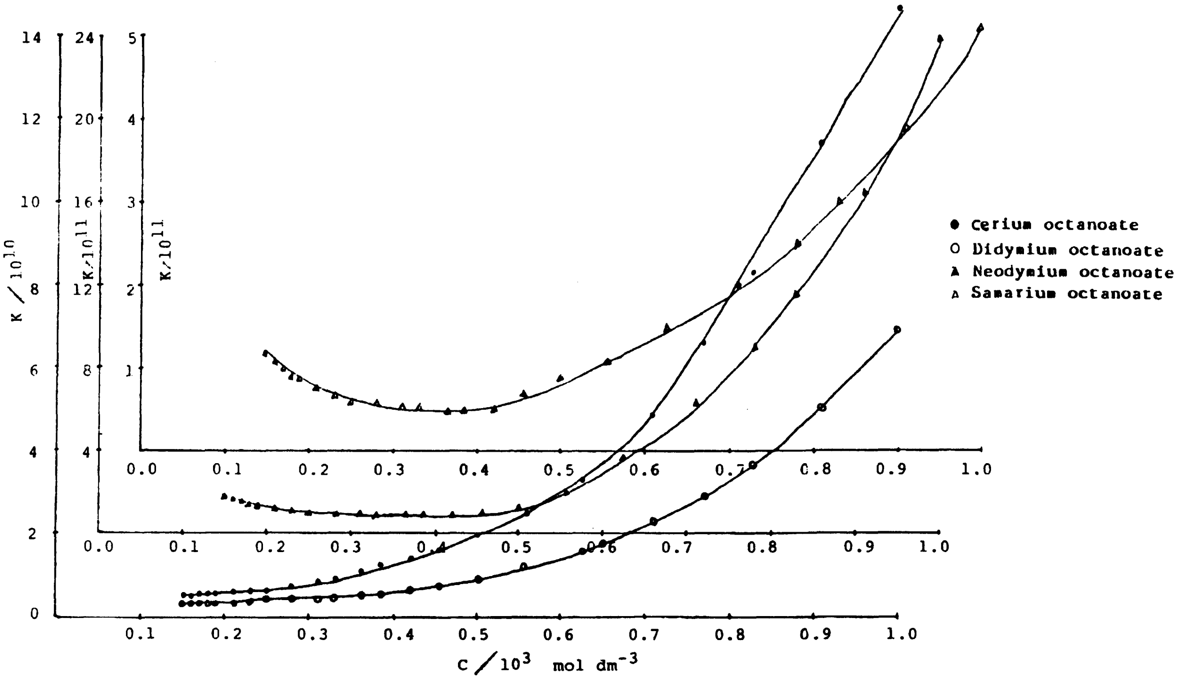

Fig. 6. Ionization constant, K vs. soap concentration, C.

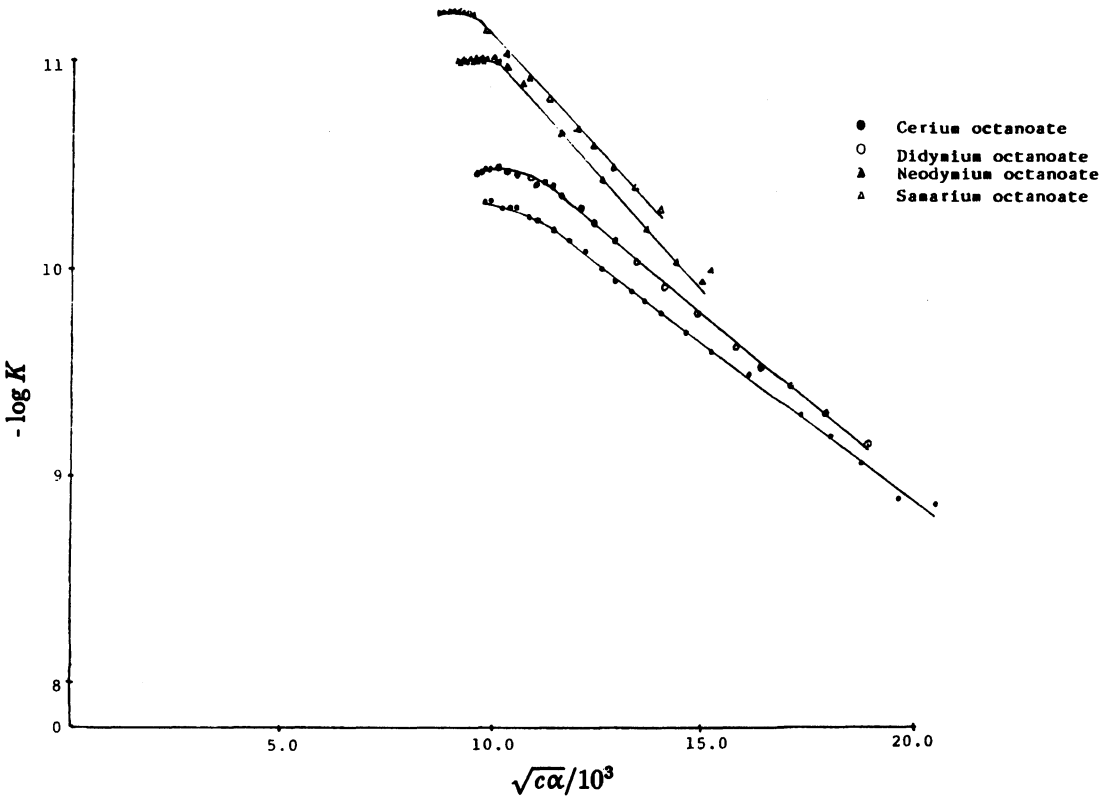

Fig. 7. $-\log K$ vs. $\sqrt{C\alpha}$.

these soap solutions in benzene–DMF (50% v/v) were obtained from the slope $[K\mu_0{}^4/27]$ and intercept $[-K\mu_0{}^3/27]$ of linear plots of μ^3c^3 vs. $1/\mu$ below the cmc. The values of the ionization constant, (K) for different soap concentrations were also evaluated by using the expression $K=27C^3\alpha^4/(1-\alpha)$. The values of the degree of ionization, (α) required to evaluate the ionization constant were computed using the expression $\alpha=\mu/\mu_0$; the values of both these paramaters, (α, K) also suggest that lanthanide octanoate behaves as a weak electrolyte in this solvent mixture. The drift in the values of K (Fig. 6), however, suggest that the de-

Table 4. Values of cmc, Limiting Molar Conductance, μ_0, and Ionization Constant, K of Lanthanide Soaps

Name of soap	cmc mol dm^{-3}	μ_0	$K\times10^{11}$
Cerium octanoate	56×10^{-5}	53.92	8.267
Didymium octanoate	51×10^{-5}	33.33	10.940
Neodymium octanoate	46×10^{-5}	18.18	15.730
Samarium octanoate	40×10^{-5}	7.47	9.716

gree of ionization (α) cannot be assumed to be equal to the conductance ratio (μ/μ_0), since the activity coefficients, in this case, may not be exactly equal to unity. The value of the true ionization constant (K^1) can then be expressed as $K^1=(27C^3\alpha^4/1-\alpha)(f_+f_-/f_{\text{soap}})$, where f_+, f_-, and f_{soap} represent the activity coefficients of the cation, anion, and soap, respectively.

Since the activity coefficient of the nonionized molecules of soap, i.e. f_{soap}, may be taken as unity, the Debye–Hückel's limiting law enables us to obtain $\log K=\log K^1+A\sqrt{C\alpha}$, where A is a constant for the solvent at a specific temperature. Plots of $\log K$ vs. $\sqrt{C\alpha}$ (Fig. 7) for the soap solution (below the cmc) were found to be linear, and the values of the true ionization constant (6.31×10^{-10}, 7.94×10^{-10}, 1.00×10^{-11}, and 1.74×10^{-11} for cerium, didymium, neodymium, and samarium, respectively.) for benzene–DMF (50% v/v) were obtained from the intercept of these plots. The data again support the conclusion that the metal soap behaves as a weak electrolyte in dilute solutions below the cmc, and that the conductivity results can be explained on the basis of Ostwald's formula and Debye–Hückel's theory of weak electrolytes.

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References

1) L. D. Skrylev, V. F. Sazonova, M. E. Kornelli, and N. A. Shumitina, *Khim. Khim. Tekhnol.*, (*Alma-Ata*), **21**(4), 491 (1978).

2) R. C. Mehrotra, *Wiss. Z. Friedrich-Schiller Univ. Jena, Math. Naturwiss. Reihe*, **14**(2), 171 (1965).

3) S. N. Misra, T. N. Misra, and R. C. Mehrotra, *J. Inorg. Nucl. Chem.*, **25**, 195 and 201 (1963).

4) A. M. Bhandari, S. Dubey, and R. N. Kapoor, *J. Am. Oil Chem. Soc.*, **47**, 4 (1970).

5) K. W. Bagnall, *Int. Rev. Sci.*, *Inorg. Chem.*, *Ser. 2*, **7**, 41 (1975).

6) J. H. Skellon and K. E. Anderws, *J. Appl. Chem.* (*London*), **5**, 245 (1955).

7) G. Marwedel and F. U. Lack, **60**, 530 (1954), **62**, 92 (1956).

8) J. H. Skellon and J. W. Spence, *J. Appl. Chem.* (*London*), **3**, 10 (1953).

9) W. Casellato, P. A. Vigato, and M. Vidali, *Coord. Chem. Rev.*, **26**, 85 (1978).

10) G. Sbrignadello, G. Battiston, G. Tomat, and O. Traverso, *Inorg. Chim. Acta*, **24**, 143 (1977).

11) R. L. Martin and H. Waterman, *J. Chem. Soc.*, **1957**, 2545.

12) R. P. Varma and R. Jindal, *Tenside Deterg.*, **20**, 193 (1983).

13) A. K. Solanki and A. M. Bhandari, *Tenside Deterg.*, **18**, 34 (1981).

14) K. N. Mehrotra, A. S. Gahlaut, and M. Sharma, *J. Indian Chem. Soc.*, **64**, 309 (1987).

15) F. Mains, D. Mills, and D. W. White, U. S. Patent 3320172 (1967).

16) H. W. Chatfield, *Paint Manuf.*, **6**, 112 (1936).

17) K. N. Mehrotra, A. S. Gahlaut, and M. Sharma, *J. Am. Oil Chem. Soc.*, **63**, 1571 (1986).

18) K. N. Mehrotra, A. S. Gahlaut, and M. Sharma, *J. Colloid Interface Sci.*, **120**, 110 (1987).

19) K. N. Mehrotra, R. K. Shukla, and M. Chauhan, *Acoust. Lett.*, **12**, No. 4, 66 (1988).

20) K. N. Mehrotra, M. Chauhan, and R. K. Shukla, *J. Phys. Chem. Liq.*, **18**, 295 (1988).

21) K. Nakanishi "Infrared Absorption Spectroscopy," Holden Day, San Francisco (1977), p. 39.

22) R. D. Vold and G. S. Hattiangdi, *Ind. Eng. Chem.*, **41**, 2311 (1949).