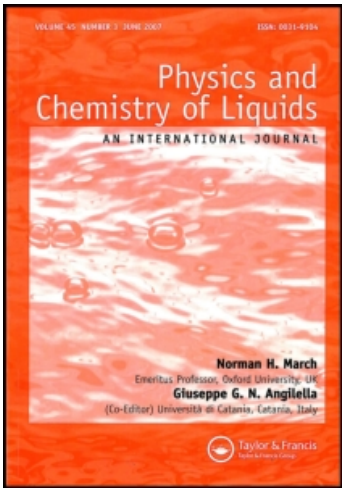

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Physicochemical Characteristics of Cerium(III) Caprylate

Anil Kumar[a]
[a] Department of Chemistry, Institute of Basic Sciences, Agra University, Agra, India

To cite this Article Kumar, Anil(1994) 'Physicochemical Characteristics of Cerium(III) Caprylate', Physics and Chemistry of Liquids, 28: 1, 57 — 62
To link to this Article: DOI: 10.1080/00319109408029541
URL: http://dx.doi.org/10.1080/00319109408029541

Phys. Chem. Liq., 1994, Vol. 28, pp. 57–62
Reprints available directly from the publisher
Photocopying permitted by license only

PHYSICOCHEMICAL CHARACTERISTICS OF CERIUM(III) CAPRYLATE

ANIL KUMAR

Department of Chemistry, Institute of Basic Sciences, Agra University, Khandari Road, Agra-282002, India

(Received 14 October 1993)

The respective values of critical micelle concentration, CMC (4.9×10^{-4} and 3.3×10^{-4}M) of cerium(III) caprylate in the solvent-mixture of 70/30 and 50/50 (v/v) methanol–benzene have been obtained by observing the inflexion exhibited by the plots of physical properties (viz. conductivity, density, viscosity and ultrasonic velocity) versus soap concentration, *C*.

KEY WORDS: Cerium Caprylate, Metal Soap, Critical Micelle concentration.

INTRODUCTION

Although there is no dearth of references on alkali, alkaline earth and transition metal soaps, literature survey[1–7], however, reveals that little work has appeared on lanthanide soap. In view of industrial applications, cerium(III) caprylate has been synthesised and, through the present study, its solution behaviour has been examined.

EXPERIMENTAL

Merck/BDH AnalaR grade chemicals were used in the present work. The fatty acid was purified by distillation under reduced pressure. Cerium(III) caprylate was prepared by direct metathesis of potassium caprylate with cerium(III) chloride at 50–55°C. The precipitated product was digested, filtered and washed, first with hot distilled water and, subsequently, with acetone. The initial drying in an air oven at 60–65°C was followed by drying under reduced pressure. The compound thus obtained was recrystallized twice from benzene and dried in vacuo for at least 48th before use. The purity of the compound was tested by determining its melting point (127.0°C) and by elemental analysis.

A digital conductivity meter (Toshniwal CL 01.10A) and a dipping type conductivity cell with platinized electrodes were used for making conductance measurements. An Ostwald type viscometer was used for measuring the viscosity. The density measurement (± 0.0001) was made with the help of a dilatometer. A multifrequency interferometer (M-83, Mittal Enterprises, New Delhi), operating at a frequency of 4 MHz was employed to measure the ultrasonic velocity. The maximum uncertainty

of the velocity results was $\pm 0.2\%$. All the measurements were carried out at $40 \pm 0.05°C$.

RESULTS AND DISCUSSION

I Conductivity

The increase in the specific conductance, k with increasing concentration (Fig. 1) of the solutions of cerium(III) caprylate in the solvent-mixture of methanol and benzene of varying composition (70/30 and 50/50, v/v) may be ascribed to the ionization of the metal soap into metal cations, Ce^{3+} and fatty acid anions, $C_7H_{15}COO^-$, (in dilute solutions) and to the formation of the micelles (in concentrated solutions). The inflexions at 4.9×10^{-4} and 3.3×10^{-4} M in the k–C plots (Fig. 1) refer to the respective values of critical micelle concentration, CMC of the soap solution in 70/30 and 50/50 (v/v) solvent-mixtures of MeOH–Benzene at 40°C.

The concave nature of the plots of molar conductance, μ vs. square root of soap concentration, $C^{1/2}$ suggests that the soap is behaving as a weak electrolyte in these

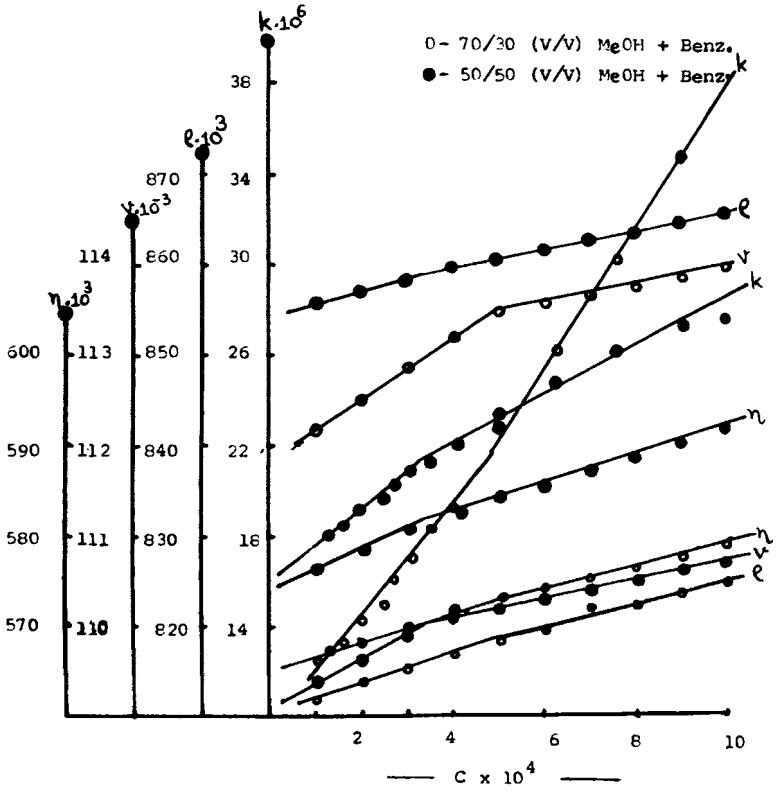

Figure 1 Plots of specific conductivity (k), density (ρ), viscosity (η) and ultrasonic velocity (v) as a function of concentration (C).

solutions and the limiting molar conductance. μ_0 cannot be obtained by extrapolation of the plot. The following expression[7] can, therefore, be derived:

$$\mu^3 C^3 = \frac{K\mu_0^4}{27\mu} - \frac{K\mu_0^3}{27} \tag{1}$$

The graphical value of μ_0 for soap solutions in 70/30 and 50/50 (v/v) solvent-mixtures of MeOH–Benzene has been evaluated (Table 1) from the plots of $\mu^3 C^3$ vs $1/\mu$. The degree of dissociation, α (Table 1) has been calculated (below the CMC) by assuming $\alpha = \mu/\mu_0$, employing the graphical value of μ_0. The values of dissociation constant, K (Table 1) for dilute soap solutions (below the CMC) have been calculated using the expression: $K = 27C^3\alpha^4/(1-\alpha)$ derived from the dissociation equilibrium following Ostwald's ideas. The values of both α and K (Table 1) evaluated for dilute soap solutions also suggest that cerium(III) caprylate behaves as a weak electrolyte in these solutions.

II Density and Viscosity

The density, ρ of the soap solutions at 40°C is found to increase with increasing soap concentration, C (Fig. 1). The $\rho - C$ plots (Fig. 1) for soap solutions are characterized by an intersection of two straight lines at 4.9×10^{-4} and 3.3×10^{-4} M, respectively, for soap solutions in 70/30 and 50/50 (v/v) solvent-mixture of methanol and benzene at 40°C. The density data have been explained in terms of Roots equation[8]. For dilute soap solutions (below the CMC), the higher value of Roots constant A than that of constant B (Table 1) suggest that the solute-solvent interaction predominates and that the aggregation of soap molecules commences at the CMC.

The plots of both viscosity, η vs. soap concentration, C (Fig. 1) and η_{sp} vs C (Einstein equation) are also characterised by an intersection of two straight lines in the vicinity of the CMC. The viscosity data have also been interpreted on the basis of the well known equation[9-12] proposed by Einstein[9], Vand[10], Moulik[11] and Jones–Dole[12]. The values for the molar volume (Table 1) of the soap have been obtained from Einstein (η_{sp} vs C) and Vand's ($1/C$ vs $1/\log(\eta/\eta_0)$) type plots. $(\eta/\eta_0)^2$ vs C^2 (Moulik's type plot) for dilute soap solution (below the CMC) is linear indicating that the equation[11] holds good in the premicellar region i.e. below the CMC. The values for Moulik's constants (M and K), evaluated from the intercept and the slope of the plot $(\eta/\eta_0)^2$ vs C^2 follow order $K > M$; whereas for dilute soap solutions (Premicellar region) constants of Jones–Dole's equation[12] (A and B) as evaluated from the intercept and the slope of the plot, $\eta_{sp}/C^{1/2}$ vs $C^{1/2}$ are found to accord with $B > A$ (Table 1). The above facts confirm that aggregation of the soap molecules begins at a definite soap concentration, CMC.

III Ultrasonic Velocity Measurements

The values of various acoustic parameters[13] viz. adiabatic compressibility (β), intermolecular free length (L_f), specific acoustic impedance (z), apparent molar compressibility (ϕ_k) for the solutions of cerium (III) caprylate in a solvent-mixture of methanol and benzene (70/30 and 50/50, v/v) at 40°C have been evaluated (Table 2).

Table 1 Parameters from conductivity, density and viscosity measurements of the soap solutions in solvent-mixtures of methanol and benzene at 40°C.

Parameters	*Derived from*	*Values for cerium(III) caprylate*	
		70% Methanol + 30% Benzene (v/v)	*50% Methanol + 50% Benzene* (v/v)
Critical micelle concentration, CMC (mol l^{-1})	k *vs* C, ρ *vs* C and η *vs* C	4.9×10^{-4} M	3.3×10^{-4} M
Specific conductance for solvent mixture, k_0 (mho cm^{-1})	k *vs* C	9.6×10^{-6}	16.0×10^{-6}
Molar conductance, μ_0 (mho cm^2)	μ^3C^3 *vs* $1/\mu$	1.4×10^{-2}	2.0×10^{-2}
Degree of dissociation, α below the CMC	μ/μ_0	0.30 – 0.59	0.27 – 0.53
Dissociation constant, K below the CMC	$(27C^3\alpha^4)/(1-\alpha)$	$(1.6 - 2.9) \times 10^{-11}$	1.0×10^{-11}
Density of solvent, ρ_0 ($g\,cm^{-3}$)	ρ *vs* C	0.8480	0.8502
Constants of Roots equation	A	13.3	5.3
	B	−200	−250
Viscosity of solvent, η_0 (Centipoise)	η *vs* C	0.565	0.574
Molar volume, $\bar{V}$ ($l.mol^{-1}$)	Einstein's plot	8.8	3.8
	Vand's plot	8.7	3.5
Constants of Moulik's equation	M	1.0	1.0
	K	3.8	4.0
Constants of Jones Dole's equation (below the CMC)	A	0.36	0.40
	B	3.2	33

Table 2 Ultrasonic velocity and derived parameters of cerium (III) caprylate in solvent mixture of methanol and benzene at 40°C.

Concentration	*70% methanol + 30% benzene* (v/v)					
$C \times 10^2$ (mol dm^{-3})	ρ (g cm^{-3})	$v \times 10^{-5}$ (cm sec^{-1})	$\beta \times 10^{10}$ (cm^2 dyne^{-1})	L_f(A°)	$z \times 10^{-5}$ (CGS Unit)	$-\phi_k \times 10^6$ (CGS Unit)
0.10	0.8251	1.140	0.932	0.119	0.940	7.67
0.09	0.8238	1.139	0.935	0.119	0.938	7.64
0.08	0.8224	1.138	0.938	0.119	0.933	8.19
0.07	0.8210	1.137	0.941	0.119	0.934	8.84
0.06	0.8198	1.136	0.942	0.119	0.929	10.33
0.05	0.8186	1.135	0.952	0.120	0.925	9.56
0.04	0.8170	1.132	0.954	0.120	0.923	10.95
0.03	0.8170	1.129	0.962	0.120	0.920	10.90
0.02	0.8139	1.125	0.970	0.121	0.915	11.95
0.01	0.8124	1.122	0.978	0.122	0.911	29.95
Concentration	*50% methanol + 30% benzene* (v/v)					
$C \times 10^2$ (mol dm^{-3})	ρ (g cm^{-3})	$v \times 10^{-5}$ (cm sec^{-1})	$\beta \times 10^{10}$ (cm^{2}dyne^{-1})	L_f(A°)	$z \times 10^{-5}$ (CGS Unit)	$-\phi_k \times 10^6$ (CGS Unit)
0.10	0.8658	1.106	0.942	0.119	0.958	5.32
0.09	0.8647	1.106	0.944	0.119	0.956	5.54
0.08	0.8637	1.105	0.947	0.120	0.954	6.29
0.07	0.8628	1.104	0.950	0.120	0.952	6.35
0.06	0.8616	1.103	0.953	0.120	0.948	6.59
0.05	0.8606	1.102	0.955	0.120	0.946	6.78
0.04	0.8595	1.102	0.958	0.120	0.946	7.72
0.03	0.8582	1.099	0.965	0.121	0.942	7.50
0.02	0.8568	1.096	0.970	0.121	0.939	7.49
0.01	0.8554	1.094	0.976	0.121	0.935	6.66

The ultrasonic velocity, v (cm · Sec^{-1}) of the soap solutions increases with increasing soap concentration, C (Fig. 1). The variation of ultrasonic velocity with concentration (dv/dC) depends on the concentration derivative of density (ρ) and adiabatic compressibility (β) through

$$dv/dC = -v/2[1/\rho(d\rho/dC) + 1/\beta(d\beta/dC)] \quad (2)$$

The derivatives $d\rho/dC$ are opposite in sign with the latter negative and numerically larger than the former. Thus the velocity usually increases with increasing, soap concentration. The v-C plot (Fig. 1) is also characterised by intersection at the CMC.

The decreasing adiabatic compressibility (β) with increasing soap concentration (Table 2) signifies that the internal pressure for the concentrated soap solutions is higher i.e. the solutions become harder to compress[14]. The increasing values for apparent molar compressibility (ϕ_k) and acoustic impedance, z (Table 2) as well as decreasing values of intermolecular free length (L_f) with increasing soap concentration, can be explained on the basis of lyophobic interaction between soap and solvent molecules, which increases the intermolecular distance leaving relatively wider gaps

between the molecules and thus becoming the main cause of obstruction to the propagation of ultrasound waves.

In summary, conductance measurements have been used to determine the CMC, electrolytic behaviour, degree of dissociation and dissociation constant of some soap solutions. The aggregation of soap molecules results in an increase in density and viscosity which vary widely with the nature of solute and solvent. The results of both density and viscosity are consistent in underlining the fact that the solute–solvent interactions predominate in these solutions. The knowledge of the change in the values of various acoustic parameters brought about by the addition of soap to solvent provides information concerning the structure of these electrolytic solutions.

Acknowledgement

The financial assistance from UGC, New Delhi is gratefully acknowledged.

References

1. R. C. Mehrotra, Z. Wiss, Friendrich-Schiller Univ., *Jena. Math. Naturwiss*, Reihe, **14**, 171 (1965).
2. F. Main, D. Mills and D. W. White, U.S. **3**, 320 (1967), 172.
3. A. M. Bhandari, S. Dubey and R. N. Kapoor, *J. Amer. Oil Chem. Soc.*, **4**, 47 (1970).
4. L. D. Skrylev, V. E. Sazonova, M. E. Kornelli and N. A. Shumitina, *Khim Khim. Technol.*, **21**, 491 (1978).
5. A. K. Solanki, and A. M. Bhandari, *Tenside Detergents*, **18**, 34 (1981).
6. K. N. Mehrotra, A. S. Gahiaut and M. Sharma; *J. Amer. Oil Chem. Soc.*, **63**, 1571 (1986).
7. K. N. Mehrotra, M. Saxena and A. Kumar, *An. Asoc. Quim. Argent.* **78**(5), 319 (1990).
8. W. C. Roots, *J. Amer. Chem. Soc.*, **55**, 850 (1933).
9. A. Einstein, *Ann. Physik*, **19**, 289 (1906), **34**, 591 (1911).
10. V. J. Vand, *Phys. Colloid. Chem.*, **52**, 277 (1948).
11. S. P. Moulik, *J. Phys. Chem.*, **72**, 4682 (1068).
12. G. Jones and M. Dole, *J. Am. Chem. Soc.*, **51**, 2950 (1929).
13. A. Kumar, *Phys. Chem. Liq.* **21**, 35 (1990).