

Conductometric Studies of Dysprosium Butyrate and Valerate in Methanol

S.K. UPADHYAY, R.K. SHUKLA and GOVIND SHARMA*

Department of Chemistry, Faculty of Engineering and Technology

R.B.S. College, Bichpuri Campus, Agra-283 105, India

E-mail: sanjay_upadh11J@rediffmail.com

The critical micelle concentration of dysprosium soaps (butyrate, valerate) in methanol have been determined by conductometric measurement. The value of critical micelle concentration decreases with increasing chain length of fatty acid component. The molar conductance at infinite dilution, degree of ionization have been evaluated. The results show that dysprosium soaps behave as weak electrolyte at dilute solutions.

Key Words: Conductivity, Critical micelle concentration, Dysprosium soaps, Weak electrolyte.

INTRODUCTION

The study of metallic soaps is becoming increasingly important in technological as well as in academic fields. The soaps have attracted much attention in industries and are finding application in many diversified fields. The physico-chemical characteristics and structure of these soaps depend on the method and conditions of preparation. Information about the structure and properties of these soaps is of great significance for their use in industries under varying conditions. Little work has, however, been done on lanthanide soaps, so that no much has been published in the literature¹⁻⁸.

The present work discusses the conductometric studies of solutions of dysprosium soaps (butyrate and valerate) in methanol to examine their micellar behaviour and the nature of the soap in non-aqueous media.

EXPERIMENTAL

All the chemicals used were of BDH/AR grade. Solvent methanol was purified by distillation under reduced pressure. Dysprosium soap (butyrate and valerate) were synthesized by reported method^{6,8}. The metal soaps thus obtained were recrystallized twice from methanol and dried under vacuum for at least 48 h before use.

The conductance of soap solutions in methanol was measured with digital conductivity meter (Toshniwal CL 01.10 A) and dipping type conductivity cell with platinised electrodes (cell constant 0.875) at $40 \pm 0.05^\circ\text{C}$ in a thermostat.

RESULTS AND DISCUSSION

The specific conductance K of the solution of dysprosium soaps (butyrate and valerate) in methanol increases with increasing concentration and decreasing chain length of the soap (Table-2). The increase in the specific conductance may be due to the fact dysprosium soaps behave as simple electrolytes in dilute solutions and are ionized into simple metal cations, Dy^{3+} and fatty acid anions, $RCOO^-$ (where R is C_3H_7 and C_4H_9 for butyrate and valerate). The decrease in specific conductance with increasing chain length of the soap may be due to increasing size and decreasing mobility of anions in the soap molecule. It may be pointed out that the micellization process in organic solvents is somewhat different from that in aqueous solutions. The aggregation begins at very low concentration in organic solvent and results in the formation of very much smaller aggregate and than in aqueous solutions. The main cause of micellization in organic solvent is the energy change due to dipole-dipole interaction between the polar head groups of soap molecules. The plots of specific conductance *vs.* soap concentration are characterized by a break at definite soap concentration which corresponds to the CMC of dysprosium soaps. The results show that the CMC decreases with increasing chainlength of fatty acid constituent of the soap (Table-2) (Fig. 1).

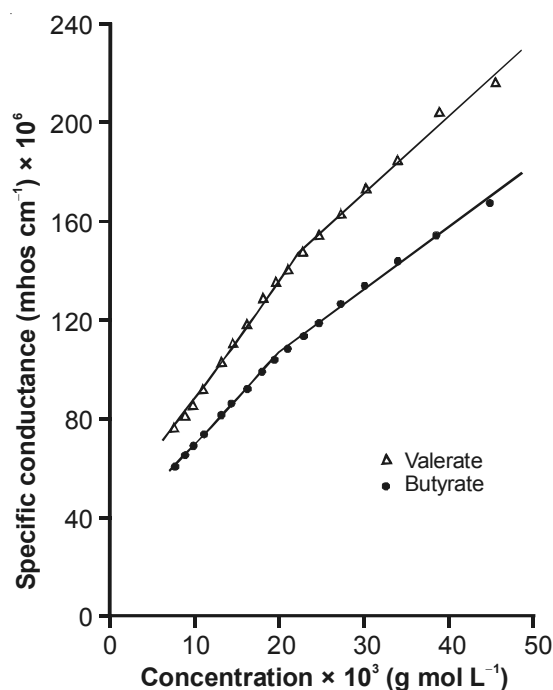
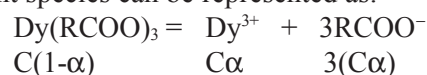


Fig. 1. Specific conductance *vs.* concentration of dysprosium soaps in methanol

Molar conductance and ionisation constant

The molar conductance, μ of the solutions of dysprosium soaps in methanol decreases with increasing concentration and chain length of the soap. The decrease may be attributed to the combined effects of the ionic atmosphere, solvation of ions and decrease of mobility and formation of micelles. The plots of molar conductance μ vs square root of soap concentration $C^{1/2}$ (Fig. 2) are concave upwards, indicating that the soaps behave as weak electrolytes in dilute solutions. The limiting molar conductance μ_0 of these soap solutions cannot be obtained by the usual extrapolation method and the Debye-Huckel-Onsager^{9,10} equation is not applicable to these soap solutions in methanol. The soaps in dilute solutions behave as weak electrolytes and so an expression for the ionization of dysprosium soaps can be developed using the Ostwald model. If C is the concentration in mol/lit and α is the degree of ionization, the equivalent concentration of different species can be represented as:



where R = C₃H₇ and C₄H₉ for butyrate and valerate, respectively.

The ionization constant can be expressed as:

$$\begin{aligned} K &= [\text{Dy}^{3+}][\text{RCOO}^-]^3/[\text{Dy(RCOO)}_3] \\ &= (C\alpha)(3C\alpha)^3/C(1-\alpha) \\ &= 27C^3\alpha^4/(1-\alpha) \end{aligned} \quad (1)$$

Since the number of ions for a weak electrolyte in dilute solutions is relatively small and interionic effects are almost negligible the activities of ions may be taken as proportional to the concentration and the conductance ratio (Arrhenius dissociation), μ/μ_0 , is reasonably good measure for the degree of ionization α (where μ is the molar conductance at finite concentration and μ_0 is the molar conductance at infinite dilution). On substituting the value of α and rearranging eqn. 1, one obtains

$$\mu^3 C^3 = \frac{K\mu_0^4}{27\mu} - \frac{K\mu_0^3}{27} \quad (2)$$

The values of the ionization constant, K and μ_0 (Table-2) can be obtained from the slope ($K\mu_0^4/27$) and intercept ($-K\mu_0^3/27$) of the linear portion of the plots of $\mu^3 C^3$ vs $1/\mu$ (Fig. 3) for dilute soap solutions. The values of the degree of ionization α at different soap concentrations have been calculated by assuming that it is equal to the conductance ratio, μ/μ_0 . The low values of the degree of ionization α (Table-1) show that the solutions of dysprosium soaps in methanol behave as weak electrolytes. The degree of ionization decreases rapidly in dilute solutions with increasing soap concentration whereas the values of α decrease slowly above the CMC.

TABLE-1
 CONDUCTIOMETRIC DATA OF DYSPROSIUM SOAPS IN
 METHANOL AT $40 \pm 0.05^\circ\text{C}$ VALUES OF SPECIFIC CONDUCTANCE
 K, MOLAR CONDUCTANCE, DEGREE OF IONIZATION AND
 IONIZATION CONSTANT K AT DIFFERENT CONCENTRATIONS

Conc.		Butyrate			Valerate			
$C \times 10^3$ (g mol L ⁻³)	$k \times 10^6$ (mohs)	μ	α	$10^6 K$	$k \times 10^6$ (mohs)	μ	α	$10^6 K$
7.1	77.0	10.84	0.633	4.4	64.3	9.06	0.599	3.1
8.0	82.0	10.25	0.603	4.6	68.3	8.54	0.564	3.2
8.9	86.0	9.66	0.568	4.6	71.9	8.08	0.534	3.3
10	82.0	9.20	0.541	5.0	75.9	7.59	0.502	3.4
11.9	102.0	8.57	0.504	3.9	83.1	6.98	0.461	4.1
13.1	108.0	8.24	0.485	6.5	87.4	6.67	0.441	4.1
14.7	114.0	7.76	0.456	6.8	92.7	6.31	0.417	4.4
16.6	123.0	7.41	0.436	7.9	98.7	5.95	0.393	4.5
17.8	128.0	7.19	0.423	8.4	102.3	5.75	0.380	5.1
19.2	133.0	6.93	0.408	8.9	106.0	5.43	0.366	5.4
20.8	139.0	6.68	0.393	9.5	110.8	5.33	0.352	5.8
22.7	145.0	6.39	0.376	10.1	115.8	5.10	0.337	6.1
25.0	153.0	6.12	0.360	11.1	121.5	4.86	0.321	6.6
27.7	162.0	5.85	0.328	9.9	128.2	4.63	0.306	7.2
31.3	172.0	5.50	0.324	13.5	136.0	4.35	0.288	8.0
35.7	184.0	5.15	0.303	14.9	145.5	4.10	0.271	9.1
41.7	199.0	4.77	0.281	17.0	156.8	3.74	0.247	9.7
50.0	224.0	4.48	0.264	22.3	180.0	3.60	0.238	14.2

TABLE-2
 VALUES OF CMC, LIMITING MOLAR CONDUCTANCE, μ_0 AND
 IONIZATION CONSTANT K, OF DYSPROSIUM SOAPS IN
 METHANOL AT 40°C

Soap	CMC (mol L ⁻¹)	μ_0	K
Dy-butyrate	1.8×10^3	3.13	0.35×10^5
Dy-valerate	2.1×10^3	2.96	0.94×10^5

The values of the ionization constant K have been calculated by using eqn. 1 and assuming the degree of ionization as equal to the conductance ratio. The values of k remain nearly constant with increase in the soap concentration below the CMC, as expected for weak electrolytes, but increase rapidly above the CMC. K is related to the concentration C and degree of ionization α ($=\mu/\mu_0$) according to eqn. 1. The rapid increase in ionization constant at higher soap concentration may be due to the predominating effects of the concentration as compared that of degree of ionization. The deviations observed at higher soap concentrations in methanol

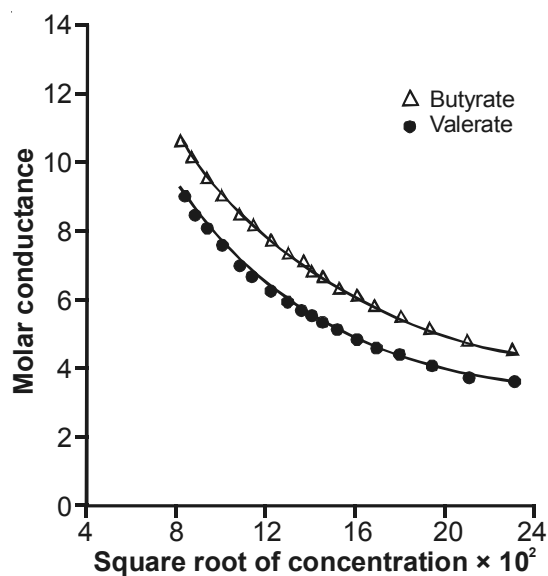


Fig. 2. Molar conductance vs. square root of concentration of dysprosium soaps in methanol

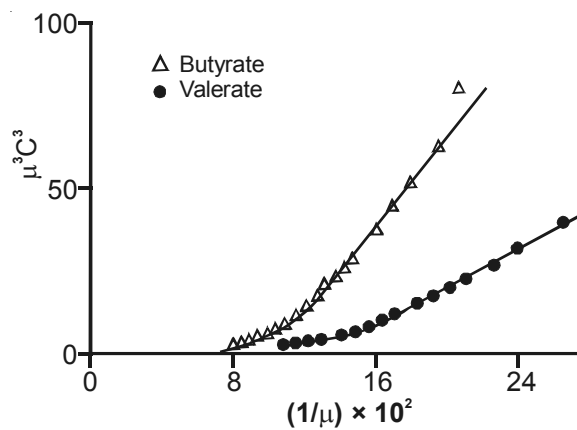


Fig. 3. $\mu^3 C^3$ vs. $1/\mu$ of Dysprosium soaps in methanol

from the Debye-Huckel treatment are in agreement with the Bjerrum¹¹ and Fuoss and Kraus¹² extensions of the Debye-Huckel theory.

The results show that the soaps behave as weak electrolytes in dilute solutions below the CMC and the conductance results can be explained on the basis of Ostwald's formula and the Debye-Huckel theory of weak electrolytes.

ACKNOWLEDGEMENTS

We are thankful to Dr. B.K. Agarwal Principal, Raja Balwant Singh College, Agra for providing necessary facilities and encouragement for carrying out the work.

REFERENCES

1. R.P. Verma and R. Jindal, *Tenside Detergents*, **20**, 193 (1983).
2. A.K. Solanki and A.M. Bhandari, *Tenside Detergents*, **18**, 34 (1981).
3. K.N. Mehrotra, R.K. Shukla and M. Chauhan, *Acustica*, **75**, 82 (1991).
4. M. Chauhan, *J. Chem. Eng. Data.*, **37**, 4 (1992).
5. K.N. Mehrotra, M. Chauhan and R.K. Shukla, *J. Phys. Chem. Liq.*, **21**, 293 (1990).
6. K.N. Mehrotra, M. Chauhan and R.K. Shukla, *Monatsh. Chem.*, **120**, 1063 (1989).
7. K.N. Mehrotra, M. Chauhan and R.K. Shukla, *Bull. Chem. Soc. (Japan)*, **68**, 1825 (1995).
8. K.N. Mehrotra, M. Chauhan and R.K. Shukla, *J. Am. Oil Chem. Soc.*, **67**, 446 (1990).
9. P. Debye and E. Huckel, *Z. Phys.*, **24**, 305 (1923)
10. P. Debye and E. Huckel, *Onsager Z. Phys.*, **27**, 388 (1926).
11. K. Bjerrum and K.D. Vidensk, *Selsk. Mat.-Fys. Medd.*, **7**, 9, (1926).
12. R.M. Fuoss and C.A. Kraus, *J. Am. Chem. Soc.*, **55**, 1019 (1933).

(Received: 24 March 2006;

Accepted: 26 February 2007)

AJC-5448