

Conductivity of Strontium Soaps in Water

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Conductivity data of strontium soaps (valerate, caproate and caprylate) solutions have been used to evaluate the true dissociation constant, limiting molar conductivity and thermodynamic parameters, viz., enthalpy, free energy and entropy changes of dissociation. The soaps behave as a weak electrolyte in water and Debye-Hückel-Onsager equation is not applicable for these soap solutions.

INTRODUCTION

The importance of alkaline earth metal soaps has already been realised due to their proven utility as catalysts^{1,2}, corrosion inhibiting agents^{3,4}, driers, fungicides and stabilizers⁵. The soaps are useful for a specific purpose on account of their fundamental properties and state of molecule in the solution. The micellar behaviour of strontium soaps in water has been studied conductometrically⁶.

In the present study the true mode of dissociation, dissociation constant, limiting molar conductivity and other thermodynamic parameters of strontium soaps have been determined.

EXPERIMENTAL

AnalaR (BDH) *n*-caprylic, caproic and valeric acids were used and purified by distillation under reduced pressure and the purity was confirmed by determination of boiling points. Conductivity water was prepared in glass apparatus and in all cases freshly distilled water (alkaline KMnO_4) was used.

A conductivity meter (Toshniwal CL 01 10A, India) and a dipping type conductivity cell with platinised electrodes of cell constant 0.9110 were used for measuring the conductivity of the soap solutions. All the measurements were made at constant temperature ($\pm 0.05^\circ\text{C}$). The specific and molar conductivities were expressed in $\text{ohm}^{-1} \text{cm}^{-1}$ and $\text{ohm}^{-1} \text{cm}^2 (\text{g mol})^{-1}$.

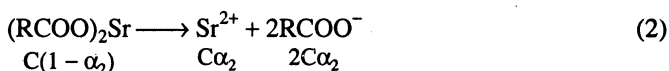
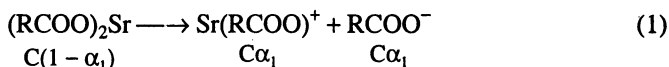
Method of preparation of soap

The calculated amount of strontium carbonate was weighed and suspended in water and the suspension was heated at 80°C . The required amount of acid was added in portions to the suspension under constant stirring. After the evolution of CO_2 ceased, the product was crystallised in alcohol and dried in air oven at $100\text{--}105^\circ\text{C}$.

RESULTS AND DISCUSSION

The critical micelle concentration (CMC) obtained from specific conductivity k vs. soap concentration, C plots are found the same as reported earlier⁶. The CMC however cannot be obtained from molar conductivity μ vs. square root of concentration $C^{1/2}$ plots which are concave upwards with increase of soap concentration indicating that strontium soaps behave as weak electrolyte in solution, and Debye-Hückel-Onsager's equation is not applicable to these soap solutions.

The probable mode of dissociation of these soaps in water can be represented in two ways⁷ below CMC:



where $R = \text{C}_4\text{H}_9$, C_5H_{11} and C_7H_{15} ; α_1 and α_2 are the degrees of dissociation of soaps. The dissociation constant K_1 for the equilibrium represented by the equation (1) can be expressed as:

$$K_1 = K_1' \frac{f_+ f_-}{f_{\text{soap}}} \quad (3)$$

where f_+ and f_- are the activity coefficients of the two ions, f_{soap} is activity coefficient of the undissociated soap molecule, and K_1' represents $C\alpha_1^2/(1 - \alpha_1)$. Since the ionic strength of the solution is not too high, the f_{soap} does not differ much from unity. Now writing equation (3) as:

$$K_1 = K_1' f_{\pm}^2 \quad (4)$$

where f_{\pm} is the mean activity coefficient of the ion. Similarly K_2 can be expressed as:

$$K_2 = K_2' \frac{f_+ f_-}{f_{\text{soap}}} \quad (5)$$

$$K_2 = K_2' f_{\pm}^2 \quad (6)$$

By employing Debye-Hückel theory the value of mean activity coefficient f_{\pm} for the dissociation equilibrium represented by equations (1) and (2) may be evaluated.

$$\ln f_{\pm} = -(Z_+ Z_-) \frac{e^2 k}{2\epsilon k_B T} \quad (7)$$

$$K = \left(\frac{8\pi N_A e^2}{100\epsilon k_B T} \right)^{1/2} I^{1/2} \quad (8)$$

$$I = (1/2)[C_1 Z_+^2 + C_2 Z_-^2 + \dots] \quad (9)$$

where e , ϵ , I and N_A signify the protonic charge (4.803×10^{-10} esu), solvent dielectric constant, ionic strength of the solution and Avogadro's number respectively. The quantity 1.38×10^{-16} ergs K^{-1} has been used for k_B . The symbol K in equation (8) signifies the inverse of Debye radius.

When activity coefficients are unity, it may be conveniently written from equations (3) and (5) as

$$K'_1 = \frac{C\alpha_1^2}{1 - \alpha_1} \quad \text{and} \quad K'_2 = \frac{4C^2\alpha_2^3}{1 - \alpha_2} \quad (10)$$

On substituting the value of α_1 as μ/μ_1^0 and α_2 as μ/μ_2^0 and rearranging, the K'_1 and K'_2 may be expressed as:

$$\mu C = \frac{K'_1 \mu_1^{02}}{\mu} - K'_1 \mu_1^0$$

and

$$\mu^2 C^2 = \frac{K'_2 \mu_2^{03}}{4\mu} - \frac{K'_2 \mu_2^{02}}{4} \quad (11)$$

The value of dissociation constants K'_1 and K'_2 and limiting molar conductivities μ_1^0 and μ_2^0 have been obtained from the linear plots of μC vs. $1/\mu$ and $\mu^2 C^2$ vs. $1/\mu$ for soap solutions below CMC (Table-1). The values of limiting molar conductivities increase with temperature due to decrease in viscosity of the solvent but decrease with chain length of the soap. It is observed that the values of μ_1^0 are higher than μ_2^0 . From these values α_1 and α_2 (Table-2) have been calculated at 40°C .

TABLE-1

VALUES OF μ_1^0 , μ_2^0 , K'_1 AND K'_2 OF STRONTIUM SOAPS IN WATER AT DIFFERENT TEMPERATURES OBTAINED FROM LINEAR PLOTS

Soaps	Temperature ($^\circ\text{C}$)			50°
	35°	40°	45°	
Valerate	$\mu_1^0 = 249.0$	$\mu_1^0 = 286.5$	$\mu_1^0 = 331.6$	$\mu_1^0 = 364.6$
	$\mu_2^0 = 229.3$	$\mu_2^0 = 261.1$	$\mu_2^0 = 294.1$	$\mu_2^0 = 331.4$
	$K'_1 = 2.33 \times 10^{-2}$	$K'_1 = 1.92 \times 10^{-2}$	$K'_1 = 1.48 \times 10^{-2}$	$K'_1 = 1.26 \times 10^{-2}$
	$K'_2 = 1.70 \times 10^{-3}$	$K'_2 = 1.69 \times 10^{-3}$	$K'_2 = 6.30 \times 10^{-4}$	$K'_2 = 4.15 \times 10^{-4}$
Caproate	$\mu_1^0 = 226.9$	$\mu_1^0 = 247.7$	$\mu_1^0 = 270.3$	$\mu_1^0 = 346.0$
	$\mu_2^0 = 212.8$	$\mu_2^0 = 224.4$	$\mu_2^0 = 276.1$	$\mu_2^0 = 309.6$
	$K'_1 = 3.61 \times 10^{-2}$	$K'_1 = 3.44 \times 10^{-2}$	$K'_1 = 3.42 \times 10^{-2}$	$K'_1 = 3.40 \times 10^{-2}$
	$K'_2 = 1.66 \times 10^{-3}$	$K'_2 = 1.05 \times 10^{-3}$	$K'_2 = 7.74 \times 10^{-4}$	$K'_2 = 5.70 \times 10^{-4}$
Caprylate	$\mu_1^0 = 228.9$	$\mu_1^0 = 246.5$	$\mu_1^0 = 260.4$	$\mu_1^0 = 295.5$
	$\mu_2^0 = 208.3$	$\mu_2^0 = 240.4$	$\mu_2^0 = 251.5$	$\mu_2^0 = 287.2$
	$K'_1 = 3.41 \times 10^{-2}$	$K'_1 = 2.88 \times 10^{-2}$	$K'_1 = 2.48 \times 10^{-2}$	$K'_1 = 2.04 \times 10^{-2}$
	$K'_2 = 2.40 \times 10^{-3}$	$K'_2 = 1.30 \times 10^{-3}$	$K'_2 = 1.10 \times 10^{-4}$	$K'_2 = 7.20 \times 10^{-4}$

TABLE-2
VALUES OF f_{\pm} , α_1 , α_2 , K'_1 , K'_2 , K_1 AND K_2 OF STRONTIUM SOAPS
IN WATER AT 313 K

Conc. (M) $C \times 10^3$	f_{\pm}	α_1	$K'_1 \times 10^3$	$K_1 \times 10^3$	f_{\pm}	α_2	$K'_2 \times 10^3$	$K_2 \times 10^3$
Valerate								
2.0	0.950	0.96	43.7	9.5	0.948	1.050	—	—
3.0	0.914	0.86	16.3	10.6	0.939	0.950	0.6	0.5
5.0	0.899	0.81	17.0	10.3	0.925	0.817	0.6	0.5
8.0	0.878	0.75	17.4	11.0	0.909	0.818	0.8	0.6
10.0	0.867	0.72	18.9	9.9	0.901	0.793	1.0	0.7
Caproate								
2.0	0.948	1.08	—	—	0.947	1.080	—	—
3.0	0.939	0.95	54.2	47.8	0.939	0.960	0.9	0.7
5.0	0.924	0.89	37.3	31.8	0.924	0.915	0.8	0.6
10.0	0.901	0.79	29.1	23.6	0.900	0.800	1.0	0.7
Caprylate								
2.0	0.950	0.94	28.9	26.0	0.950	0.960	0.4	0.3
5.0	0.925	0.85	34.4	29.4	0.926	0.870	0.5	0.4
8.0	0.910	0.78	29.4	24.4	0.911	0.800	0.7	0.5
10.0	0.902	0.75	28.7	23.4	0.903	0.770	0.8	0.6

TABLE-3
VALUES OF FREE ENERGY, ΔG_D^0 , (kJ mol⁻¹) ENTROPY ΔS_D^0 , (kJ mol⁻¹) AND HEAT
 ΔH_D^0 , (kJ mol⁻¹) OF DISSOCIATION OF STRONTIUM SOAPS IN WATER

Soaps	35°C		40°C		45°C		50°C		$-\Delta H_D^0$
	ΔG_D^0	$-T\Delta S_D^0$	ΔG_D^0	$-T\Delta S_D^0$	ΔG_D^0	$-T\Delta S_D^0$	ΔG_D^0	$-T\Delta S_D^0$	
Valerate	9.63	6.93	10.29	7.55	11.14	8.05	11.75	8.73	1.727
Caproate	8.51	7.50	8.77	7.77	8.92	7.92	9.08	8.08	1.005
Caprylate	8.65	7.96	9.28	8.60	9.78	9.50	10.46	10.08	1.667

Dissociation constants K'_1 and K'_2 decrease with increase in temperature. From the values of mean activity coefficients (Table-2) K_1 and K_2 have been calculated using equations (4) and (6). It may be mentioned that the values of K'_1 and K'_2 obtained graphically are almost the same as the values calculated (Table-2) from degree of dissociation values using equation (10).

According to Debye-Hückel limiting law the logarithmic form of mean activity coefficient of ions for two equilibria represented by equations (1) and (2) may be expressed as:

$$\log f_{\pm} = -AI^{1/2} \quad \text{and} \quad \log f_{\pm} = -2AI^{1/2} \quad (12)$$

Now taking the logarithm of equation (4) and (6) and substituting the respective values of $\log f_{\pm}$, the results after the rearrangement are:

$$\log K'_1 = \log K_1 + 2AI^{1/2} \quad \text{and} \quad \log K'_2 = \log K_2 + 6AI^{1/2} \quad (13)$$

where A is constant for the solvent at specified temperature and I is the ionic strength of the solution. The value of constant A obtained from equation (13) by putting the values of K_1 , K'_1 and K_2 , K'_2 are compared with the standard value of A for water at 40°C (= 0.50). It is observed that the value of A for solvent at 40°C given by the first expression of equation (13) is the same (*i.e.* 0.50). Thus it is concluded that strontium soaps ionise in water according to equation (1).

The enthalpy of dissociation, ΔH_D^0 (Table 3), for soaps is obtained from slopes of the linear plots of $\log K_1$ vs. $1/T$. The negative ΔH_D^0 suggests that the dissociation of these soaps in water is exothermic.

The standard free energy change ($\Delta G_D^0 = -RT \ln K_1$) and standard entropy change ($T\Delta S_D^0 = \Delta H_D^0 - \Delta G_D^0$) are also evaluated for the dissociation process represented by equation (1) and the values are recorded in Table-3. These values are found to increase with increase in temperature for the soaps.

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REFERENCES

1. E.S. Lower, *Ind. Perfum.*, **2**, 319 (1947).
2. M.P. Bespyatov and V.I. Polstyanoi, *Maslob. Zhir. Prom.*, **28**, 14 (1962).
3. J.E.O. Mayne and D.V. Rooyen, *Appl. Chem. London*, **4**, 384 (1954).
4. W.C. Johnson, US 2, 858, 285 (Aug 13, 1953); *Chem. Abstr.*, 3733 (1959).
5. A.J. Lehmann, *Assoc. Food and Drug Officials US Quart. Bull.*, **15**, 82 (1951).
6. R.P. Varma and R. Dayal, *J. Am. Oil Chemist's Soc.*, **53**, 39 (1976).
7. K.N. Mehrotra and A. Kumar, *Colloid Polym. Sci.*, **267**, 80 (1989).

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