Thermodynamics of Dissociation of Strontium, Barium and Nickel Caproates in Water

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The critical micellar concentration (CMC) and thermodynamic parameters (heat ΔH_d, free energy ΔG_d, and entropy ΔS_d, of dissociation) of aqueous solutions of strontium, barium and nickel caproates were determined by conductivity measurements. A Kraus and Bray-type expression was used to evaluate molecular conductance at infinite dilution and theromdynamic parameters. The results confirm that CMC remains unaffected by temperature in the range of 25-55° C, and show that the dissociation of soaps is an exothermic reaction and nonspontaneous.

Key words: Critical micellar concentration, conductance, dissociation, barium, nickel and strontium caproate, thermodynamics.

Introduction

Bhatnagar and Prasad[1] determined the specific and equivalent conductivities of sodium and potassium soaps in alcohols, toluene and pyridine. Patrick *et.al.*[2] pointed out that sodium oleate in alcohols behaves as a simple electrolyte. Several researchers[3-6] have investigated soap solutions which bridge the transition from aqueous to nonaqueous solutions.

It was first demonstrated by Laing[7] that soaps dissolve in alcohols as simple rather than colloidal electrolytes. The values of the critical micellar concentration (CMC) of aqueous solutions of magnesium soaps have been determined by Varma and Kumar[8], and it has been shown that CMC is independent of temperature.

Varma and Dayal[9] studied the conductance behavior of aqueous solutions of barium, strontium and nickel soaps. The conductance and micellar behavior of praseodymium and neodymium linoleates in a mixture of 60% benzene and 40% methanol at different temperatures have been investigated by Mehrotra and Upadhyaya[10].

The purpose of this study was to determine the CMC and thermodynamic parameters of dissociation of strontium, barium and nickel by conductometric measurements.

Experimental

Sodium hydroxide, (NaOH), strontium nitrate $(Sr(NO_3)_2)$, barium sulfate $(BaSO_4)$, nickel sulfate hexahydrate $(NiSO_4.6H_2O)$, and n-caproic acid $(C_5H_{11}COOH)$, supplied by Merck, were "specially pure". Conductivity water was prepared in a glass apparatus, and in all cases, freshly distilled water (alkaline potassium permanganate) was used.

Firstly, sodium caproate $(NaC_5H_{11}COO)$ was obtained from the reaction between NaOH and $C_5H_{11}COOH$. Sr^{2+}, Ba^{2+} and Ni^{2+} caproates were then prepared by the replacement of $NaC_5H_{11}COO$ with the stoichiometrically required amount of $SrSO_4$, $BaSO_4$, and $NiSO_4$ in a water-alcohol medium (1:1).

The precipitated soaps were filtered in a Buchner funnel and washed with hot water until the filtrate gave a negative test for the metal salt used. After initial drying in an air oven (100-105°C), final drying was carried out in a vacuum desiccator.

The conductance of the soap solutions was measured with an Orion digital conductivity meter, Model 126 (Orion Research Inc., Boston, USA), and a dipping-type conductivity cell (cell constant 1.01) with platinized electrodes at different temperatures. The reproducibility of the measurements was ±0.1 %.

Results and Discussion

The specific conductance, **K**, of soap solutions increases with increasing soap concentration. **K** is equal to the multiplication of molar conductance with the concentration, i.e. **K** = Λ**C**. The plots (Figure 1) of specific conductance vs. soap concentration in moles/liter are characterized by the intersection of two straight lines at a concentration, indicating the probable formation of micelles[11,12] (Table 1).
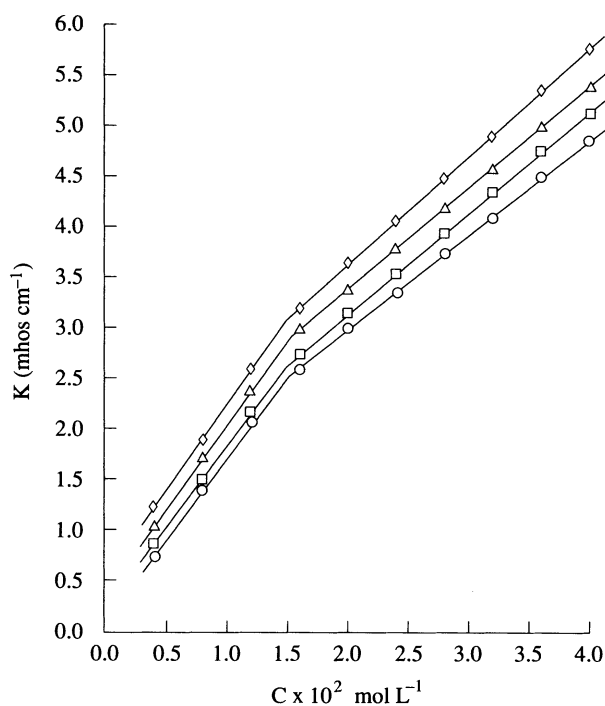

Figure 1. Specific conductance vs concentration plots of strontium caproate in water o :25° C; □ : 35° C; △ : 45° C and ◇ : 55° C.

Table 1. Values of critical micellar connectation and heat of dissociation of Sr^{2+}, Ba^{2+} and Ni^{2+} caproates in water at temperatures 25-55°C.

Soap	CMC $\times 10^3$ (mol L^{-1})	ΔH_d k J mol^{-1}
Strontium caproate	0.015	-65
Barium caproate	0.011	-63
Nickel caproate	0.012	-61

This may be because the long chain ions associate above the CMC, to form aggregates, and the number of free ions does not increase as rapidly as at concentrations < CMC. The CMC of these soaps is independent of temperature in the range of 25-55°C in water.

According to Kraus and Bray's expression[13], a soap behaves as an electrolyte in dilute solution, and it gives an equilibrium reaction during dissociation, which may be expressed as

$$M(RCOO)_n \quad \rightleftharpoons \quad M^{n+} \quad + + n \; RCOO^- \tag{1}$$
$$C\,(1-\alpha) \qquad\qquad C\,\alpha \qquad\quad C\,\alpha$$
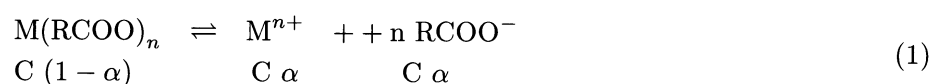
$$K_d = \frac{[M^{n+}][RCOO^-]^n}{[M(RCOO)_n]}$$

$$= \frac{(C\alpha)(nC\alpha)^n}{C(1-\alpha)} = \frac{n^n C^n \alpha^{(n+1)}}{(1-\alpha)} \tag{2}$$

where **C** is the concentration in moles/liter of a soap, α is the degree of dissociation and **n** is the oxidation state.

Since the soaps used in our experiments have two oxidation state (i.e. n = 2) Equation (2) may be rewritten as follows:

$$K_d = \frac{4C^2\alpha^3}{(1-\alpha)} \tag{3}$$

Since the degree of dissociation of soaps in solutions is very small, ionic concentrations will be low and, therefore, interionic effects are almost negligible. Such solutions do not deviate appreciably from ideal behavior, and hence the activity coefficient, γ, of ions is almost equal to 1, and the activity, a, can be taken as equal to the concentration, **c**. If $a = \gamma$ **c** and $\gamma = 1$ then $a = c$. Thus α may be defined by the conductance ratio, Λ/Λ_∞, where Λ is the molar conductance at a finite concentration that is attributable to the ions formed by the dissociation of soaps, and Λ_∞ is the limiting molar conductance at infinite dilution of these ions. On substituting the value of α in equation (3), one obtains

$$C^2\Lambda^2 = \frac{K_d\Lambda_\infty^3}{4\Lambda} - \frac{K_d\Lambda_\infty^2}{4} \tag{4}$$

It has been observed that the plots of $C^2\Lambda^2$ vs. $1/\Lambda$ are linear below the CMC, and equation (4) does not yield accurate results above this concentration. The values of dissociation constant K_d different temperatures are given in Table 2. The decrease in the values of K_d with increasing temperature indicates the exothermic nature of the dissociation of Sr^{2+}, Ba^{2+} and Ni^{2+} caproates in water.

Table 2. Values of dissociation constnat of Sr^{2+}, Ba^{2+} and Ni^{2+} caproates in water at different temperatures.

| Soap	Dissociation constant $K_d \times 10^3$			
	25°C	35°C	45°C	55°C
Strontium caproate	3.508	1.328	0.689	0.302
Barium caproate	5.821	2.399	1.148	0.560
Nickel caproate	2.114	0.955	0.457	0.218

The heat of dissociation, ΔH_d, for Sr^{2+}, Ba^{2+} and Ni^{2+} caproates was determined by the following equations:

$$\frac{\partial(\log K_d)}{\partial T} = \frac{\Delta T_d}{R\ T^2} \tag{5}$$

or

$$\log K_d = -\frac{\Delta H_d}{2.303R\ T} + C \tag{6}$$

The values of dissociation, ΔH_d, were obtained from the slope of the linear plots of **log K_d vs 1/T** (Fig. 2), and are mentioned in Table 1. The negative values of heat of dissociation, ΔH_d, again indicate that the dissociation process is exothermic in nature.
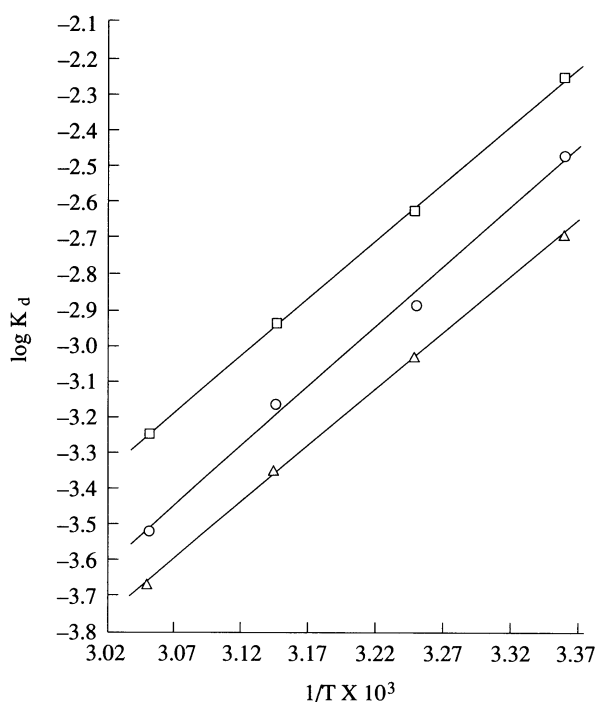
Figure 2. The log K_d vs 1/T in water: o: SR^{2+} caproate; □: Ba^{2+} caproate; △: Ni^{2+}.

The values of change in free energy, ΔG_d, and entropy ΔS_d per mole, for the dissociation process were calculated by the relationships

$$\Delta G_d = -R\ T \ln K_d \tag{7}$$

and

$$\Delta S_d = \frac{(\Delta H_d - \Delta G_d)}{T} \tag{8}$$

The calculated values of ΔG_d and ΔS_d are given in Table 3. It is apparent that CMC remains unaffected by temperature in the range of 25-55°C.

Table 3. Thermodynamic parameters of Sr^{2+}, Ba^{2+} and Ni^{2+} caproates in water for dissociation process at various temperatures.

Soap	ΔG_d k J mol^{-1}				$\Delta S_d \times 10^2$ kJ			
	25°C	35°C	45°C	55°C	25°C	35°C	45°C	55°C
Strontium caproate	14.01	16.96	19.25	22.10	-27	-27	-27	-27
Barium caproate	12.75	15.45	17.90	20.42	-25	-26	-25	-25
Nickel caproate	15.25	17.81	20.33	23.00	-26	-26	-26	-26

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