Effect of Salt on the Micellar Behavior of Dysprosium Soap

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ABSTRACT

The critical micelle concentration (CMC), specific conductance, molar conductance and free energy of dysprosium soap in methanol and in a mixture of water methanol in the presence of salts were determined using conductometric measurements. The result show that dysprosium soaps behave as weak electrolytes in dilute solutions. The critical micelle concentration (CMC) was found to decrease with increasing ionic radii of counterions.

Keywords- Dysprosium Butyrate, CMC, Ionic Radii, Specific Conductivity, Molar Conductivity.

I. INTRODUCTION

The metallic soaps are being widely used in many industries and academic fields. Information on their nature and properties of metallic soaps is of great importance for their use in various industries and for explaining their characteristics under varying conditions [1-4]. Large numbers of studies have been carried out on dysprosium butyrate in methanol and mixture of water and methanol.

II. EXPERIMENTAL

All the chemicals used were BDH/AR grade. Dysprosium butyrate was prepared by direct metathesis of the corresponding potassium soap with slight-excess of the solution of dysprosium nitrate at 50-55°c under vigorous stirring [5-7]. The precipitated soap was washed several times with water and acetone. The metal soap thus obtained was first dried in an air oven at 50-60°C and the final drying of the soap was carried out under reduced pressure. The soap was purified by recrystallization with Benzene-methanol mixture. The purity of the soaps was confirmed by the determination of melting points.

Dysprosium butyrate was insoluble in water while salts were highly soluble in water. The solution of electrolytes and soap were prepared separately in methanol and water, respectively. These solutions were mixed in required amounts.

A digital conductivity meter (Toshniwal CL 01.10A) and a dipping type conductivity cell with platinized electrodes (cell constant 0.90) were used for measuring the conductance of the soap solutions. All measurements were made at 40°C (±0.05°C) in a thermostat.

III. RESULTS AND DISCUSSION

Specific Conductance

The specific conductance, k, of the solutions of dysprosium butyrate in methanol and water-methanol mixture increases with increasing soap concentration (Table 1). The increase in the specific conductance may be due to the fact that ionization of dysprosium butyrate into simple metal cations, DyH7, and fatty acid anions, C3H4O7− in dilute solutions and due to the formation of micelles of higher soap concentrations. The increasing of specific conductance at higher soap concentrations may be due to the formation of ionic micelles of higher conducting power than simple ions. The plots of specific conductance vs. soap concentrations (Fig.1) are characterized by an intersection of two straight lines at a concentration which corresponds to the CMC of dysprosium butyrate. It is suggested that these soaps are considerably ionized in dilute solutions and the anions begin to aggregate to form ionic micelles at CMC.

Molar Conductance and Ionization Constant

The molar conductance, μ of the solutions of dysprosium butyrate in methanol and water-methanol mixture (v/v) decreases with increasing soap concentration. The decrease is attributed to the combined effects of ionic atmosphere, solvation of ions and decrease of mobility and the formation of micelles. The plots of molar conductance μ vs. Square root of soap concentration, C1/2, are not linear which indicate that the soaps behave as weak electrolyte in dilute solutions. The limiting molar conductance, μ0, of these soap solutions cannot be obtained by usual extrapolation method and the Debye-Huckel-Onsager equation is not applicable to these soap solutions [8-9].

The molar conductance results show that the dilute solutions of dysprosium butyrate behave as weak electrolyte. Since the number of ions for a weak electrolyte is relatively small in dilute solutions and the interionic effects are negligible and so the activities of...
ions may be taken as almost equal to the concentrations and conductance ratio, \( \mu /\mu_0 \) is a reasonably good measure for the degree of ionization \( \alpha \), (where \( \mu \) is the molar conductance at infinite concentration and \( \mu_0 \) is the molar conductance at infinite dilution).

The molar conductance of the dilute solutions of dysprosium butyrate increases with the addition of additives but the nature of the curves (Fig.2) remains the same. The standard free energy of micellization, \( \Delta G \), at constant temperature is related to the critical micellar concentration by the following equation [10].

\[
\Delta G = 2RT \ln X_{\text{CMC}}
\]

Where, \( X_{\text{CMC}} \) is the CMC expressed as a mole fraction and is defined as:

\[
X_{\text{CMC}} = n_r / n_s + n_{\text{sol}} = n_r / n_{\text{sol}}
\]

Since number of moles of soap, \( n_s \) is very small in comparison to the number of moles of the solvent, \( n_{\text{sol}} \).

The values of free energy for micellization for dysprosium butyrate solutions in the absence of salts (KJ mol\(^{-1}\)) is lower than the corresponding values in the presence of salts. The free energy of micelle formation is less negative for ions of small ionic radii (Table 3). For the ionic system the free energy includes a contribution due to the involvement of the counterions with the micelles. This contribution may be taken into account either by a chemical approach based on binding of the some counterions to the micelles or by a physical approach using an electrostatic calculation based on a fully ionized model.

It is therefore, concluded that the nitrates of potassium, magnesium and aluminium are effective electrolytes in causing CMC lowering and that potassium nitrate is the most effective electrolyte. The main factor which causes a decrease in CMC appears to be the reduction of the free energy of the micelle due to the diluted surface charge density on the micelle.

### Table 1: The value of specific conductance (milli mhos) of dysprosium butyrate (D.B) solution in presence of different electrolytes at (40±0.005)\(^{\circ}\)C

| S. No. | Conc. Cx10\(^2\) mol/L | DB CH\(_3\)OH | DB H\(_2\)O-CH\(_3\)OH | DB H\(_2\)O-CH\(_3\)OH + Al(NO\(_3\))\(_3\) | DB H\(_2\)O-CH\(_3\)OH + Mg(NO\(_3\))\(_2\) | DB H\(_2\)O-CH\(_3\)OH + K NO\(_3\) |
|-------|-----------------|--------------|------------------|-----------------|-----------------|-----------------|
| 1     | 0.66            | 0.054        | 0.123            | 0.378           | 0.319           | 0.156           |
| 2     | 0.69            | 0.055        | 0.129            | 0.383           | 0.325           | 0.158           |
| 3     | 0.78            | 0.057        | 0.137            | 0.389           | 0.332           | 0.164           |
| 4     | 0.89            | 0.06         | 0.146            | 0.395           | 0.34            | 0.173           |
| 5     | 1.04            | 0.066        | 0.159            | 0.402           | 0.35            | 0.185           |
| 6     | 1.25            | 0.072        | 0.178            | 0.42            | 0.36            | 0.202           |
| 7     | 1.39            | 0.076        | 0.184            | 0.43            | 0.375           | 0.215           |
| 8     | 1.62            | 0.084        | 0.199            | 0.45            | 0.398           | 0.232           |
| 9     | 1.92            | 0.09         | 0.222            | 0.475           | 0.412           | 0.255           |
| 10    | 2.27            | 0.098        | 0.235            | 0.508           | 0.434           | 0.267           |
| 11    | 2.77            | 0.109        | 0.252            | 0.545           | 0.449           | 0.289           |
| 12    | 3.12            | 0.116        | 0.27             | 0.547           | 0.458           | 0.305           |
| 13    | 3.57            | 0.124        | 0.286            | 0.553           | 0.467           | 0.323           |
| 14    | 4.17            | 0.134        | 0.31             | 0.567           | 0.487           | 0.35            |
| 15    | 5               | 0.149        | 0.34             | 0.58            | 0.498           | 0.397           |

### Table 2: The value of molar conductance (\( \mu \)) of dysprosium butyrate (D.B) solution in presence of different electrolytes at (40±0.005)\(^{\circ}\)C

| S. No. | Conc. Cx10\(^2\) mol/L | DB CH\(_3\)OH | DB H\(_2\)O-CH\(_3\)OH | DB H\(_2\)O-CH\(_3\)OH + Al(NO\(_3\))\(_3\) | DB H\(_2\)O-CH\(_3\)OH + Mg(NO\(_3\))\(_2\) | DB H\(_2\)O-CH\(_3\)OH + K NO\(_3\) |
|-------|-----------------|--------------|------------------|-----------------|-----------------|-----------------|
| 1     | 0.66            | 8.182        | 18.636           | 57.424          | 48.333          | 23.636          |
| 2     | 0.69            | 7.971        | 18.696           | 55.507          | 47.391          | 22.899          |
| 3     | 0.78            | 7.308        | 17.564           | 50.256          | 43.462          | 20.513          |
| 4     | 0.89            | 6.742        | 16.404           | 45.618          | 39.101          | 19.213          |
| 5     | 1.04            | 6.346        | 15.288           | 40.673          | 34.327          | 17.308          |
Table 3: The value of CMC and free energy for micellization, ΔG of Dysprosium Butyrate at (40±0.005)0C

| S. No. | Additive | CMCx10^2 (mol/L) | -ΔG KJ mol⁻¹ |
|--------|----------|------------------|--------------|
| 1      | Without additive | 1.92             | 41.91        |
| 2      | Al⁺³     | 2.77             | 42.22        |
| 3      | Mg⁺²     | 2.27             | 42.92        |
| 4      | K⁺       | 1.62             | 43.27        |

Figure 1: Specific conductance k, vs. concentration of dysprosium butyrate
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Figure 2: Molar conductance µ, vs. square root of concentration of dysprosium butyrate