Spectroscopic and Micellization of Uranyl Hexanoate in Organic Solvent
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Abstract: Micellization behavior of uranyl hexanoate in non-aqueous solvent was studied by using conductometric measurements. The critical micellar concentration (CMC), molar conductance and degree of ionization have been determined. The molar conductance, of the solutions of uranyl hexanoate decreases with increasing solute concentration. The decrease in molar conductance may be due to the combined effects of ionic atmosphere, solvation of ions, decrease of mobility and ionization and formation of micelles. The results show that the uranyl hexanoate behaves as a simple electrolyte in non-aqueous solvent below the CMC and the addition of Sudan dye increases the specific conductance of the alkanoates solution but the general behavior of the solution remains unaltered. The physico-chemical characteristics of uranyl hexanoate in solid state were investigated by FT-IR analysis. The IR results revealed that the fatty acids exist in dimeric state through hydrogen bonding and uranyl hexanoate possess partial ionic character.

Key words: Uranyl hexanoate, Sudan dye, critical micellar concentration, Specific conductance, molar conductance, degree of ionization.

I. Introduction
Surface active agents are characterized by the possession of both polar and non-polar regions in the same molecule. This dual nature is responsible for the phenomenon of surface activity, and micellization and solubilization. The dual nature of a surfactant is typified by metal soaps or alkanoates, can be called association colloids, indicating their tendency to associate in solution, forming particles of colloidal dimensions.

In spite of wide applications in many industries, the physico-chemical characteristics of rare earth alkanoates have not been thoroughly investigated. Wu et al\textsuperscript{1} and Kanan\textsuperscript{2} developed new technologies to synthesize metal alkanoates. Workers\textsuperscript{3,10} studied the spectroscopic and thermal behavior of metal alkanoates. Sawada et al\textsuperscript{11} characterized the fine metal alkanoate particles by x-ray diffraction, differential scanning calorimetry and specific surface area analysis. A number of workers\textsuperscript{12-24} studied their micellar behavior using conductometric, ultrasonic, viscosity and density measurements.

In the present work, the results of FT-IR analysis have been used to obtain structural information of uranyl hexanoate in solid state. Micellization behavior of uranyl hexanoate in DMF and effect of Sudan dye have been studied by conductometric investigations.

II. Experimental
All chemicals used were of BDH/AR grade. Solvent DMF was purified by distillation under reduced pressure. Uranyl hexanoate was synthesized by direct metathesis of corresponding potassium alkanoates as mentioned in our earlier publications\textsuperscript{12-13}. The insoluble deep yellow precipitate of uranyl hexanoate was digested for 1-2 hour and separated from the mother liquor by filtering through a Buchner funnel under reduced pressure and washed with water and then alcohol. The uranyl hexanoate thus obtained was dried in an air oven at 50-60°C and final drying of the alkanoate was carried out under reduced pressure. The purity of uranyl hexanoate was checked by elemental analysis and the absence of hydroxylic group was confirmed by FT-IR analysis.

The infrared absorption spectra of hexanoic acid and their corresponding uranyl hexanoate were recorded with a Perkin-Elmer ‘Model 577’ grating spectrophotometer in the region 4000-200 cm\textsuperscript{-1} using the potassium bromide disc method. A digital conductivity meter (Toshiba CL 01.10A) and a dipping type conductivity cell with platinized electrodes (cell constant 0.895) were used for measuring the conductance of uranyl hexanoate solution at 40±0.05 °C.
III. Results and Discussion

Infrared spectra

The infrared spectra of uranyl hexanoate shows marked differences with the spectrum of their corresponding hexanoic acid in some spectral regions. In the spectra of uranyl hexanoate characteristics $\nu_{O-H}$ stretch (2650-2660 cm$^{-1}$), $\nu_{C=O}$ (1690-1700 cm$^{-1}$), $\nu_{C=O-H}$ (1468-1470 cm$^{-1}$) stretch$^+$ in plane deformation and $\nu_{O-H}$ out of plane deformation (930-950 cm$^{-1}$) vibrations of free acids which are characteristic bands of dimeric carboxylic acids were found completely absent with the absorption maxima near 690 cm$^{-1}$ and 550 cm$^{-1}$ associated with carboxyl group bending and wagging modes. Beside it, two absorption bands are observed near 1480 cm$^{-1}$ and 1370 cm$^{-1}$ corresponding to asymmetric and symmetric vibration of carboxylate ion as pointed out by Duval, Lecomte and Douville with metal-oxygen bond near 435 cm$^{-1}$. In uranyl hexanoate stretching frequencies of the $\text{UO}_2^{2+}$ entity were also observed near 810 and 740 cm$^{-1}$.

Specific conductance, $k$ (mhos cm$^{-1}$) and CMC

The specific conductance, $k$ (mhos cm$^{-1}$) clearly depends on the concentration of the alkanoate. The specific conductance, $k$ of the dilute solutions of uranyl hexanoate in DMF increases with increasing solute concentration, C (mol dm$^{-3}$). The increase in the specific conductance, $k$ with the increase in solute concentration may be due to the ionization of uranyl hexanoate into simple metal cations, $\text{UO}_2^{2+}$ and fatty acids anions, $\text{C}_5\text{H}_{11}\text{COO}^-$ in dilute solutions and the formation of micelles at higher concentrations of alkanoate. The values of critical micellar concentration, CMC (0.03M) of the uranyl hexanoate have been determined by $k$-C plot (Fig.1). The concentration at which micelles formation starts known as critical micellar concentration (CMC), beyond this concentration the bulk properties of the surfactant, such as osmotic pressure, turbidity, solubilization, surface tension, viscosity, ultrasonic velocity and conductivity changes abruptly. If the micelles are formed in organic medium the aggregates are called “reversed micelles” in this case the polar head groups of the surfactant are oriented in the interior and the lyophilic groups extended outwards in to the solvent. It is suggested that the uranyl hexanoate is considerably ionized in dilute solutions and the anions begin to aggregate to form micelles. The addition of a surface active agent, i.e., sudan dye has no effect on the CMC value of uranyl hexanoate as apparent from the plot $k$-C (Fig.1). When the concentration of dye is increased from $10^{-6}$M to $10^{-3}$M, the specific conductance, $k$ (mhos cm$^{-1}$) increases but CMC remains unchanged (Fig.2).
The molar conductance, $\Lambda$ (cm$^2$ mol$^{-1}$) and ionization constant $K_d$,

The molar conductance, $\Lambda$ of the solutions of uranyl hexanoate decreases with increasing solute concentration. The decrease in molar conductance may be due to the combined effects of ionic atmosphere, solvation of ions, decrease of mobility and ionization and formation of micelles. Since the molar conductance, $\Lambda$ of the solutions of uranyl hexanoate solution does not vary linearly with the square root of alkanoate concentration, the Debye-Huckel-Onsager’s equation is not applicable to these solutions. Molar conductance results show that solution of uranyl hexanoate behaves as simple electrolyte and ionization of uranyl hexanoate solution may be explained by Ostwald’s manner.

If $C$ (mol dm$^{-3}$) is the concentration and $\alpha$ is the degree of ionization of uranyl hexanoate solution, molar concentration may be represented as follows:

$$(C_{H_2COO})_2UO_2 \rightleftharpoons UO_2^{++} + 2C_{H_11}COO^-$$

The ionization constant, $K_d$, for this equilibrium may be expressed as follows:

$$K_d = \frac{[UO_2^{2+}][C_{H_11}COO]^2}{[UO_2(C_{H_11}COO)_2]} = 4C^2\alpha^2/(1-\alpha)$$

(1)

The ionic concentrations are low in dilute solutions, so interionic effects are almost negligible. Therefore, the solution of alkanoate does not deviate appreciably from ideal behavior and the activities of ions can be taken as almost equal to the concentrations. The degree of ionization, $\alpha$ may be replaced by the conductance ratio, $\Lambda/\Lambda_\infty$ where $\Lambda$ and $\Lambda_\infty$ (cm$^2$ mol$^{-1}$) are the molar conductance at finite and infinite dilution, respectively. By substituting the value of $\alpha$ and rearranging, equation (1) can be written as:

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

(2)

The values of ionization constant, $K_d$, and limiting molar conductance, $\Lambda_\infty$ were obtained from the slope, $(K_d\Lambda^3_\infty/4\Lambda)$ and intercept $(-K_d\Lambda^2_\infty/4)$ of the linear part of the plot (Fig.3) of $\Lambda^2C^2$ vs $1/T$ below critical micellar concentration. The value of limiting molar conductance, $\Lambda_\infty$ was found to be 35.0.

![Fig.3 $\Lambda^2C^2$ vs. $1/T$](https://example.com/fig3.png)

The values of degree of ionization, $\alpha$ have been evaluated by assuming $\alpha$ as equal to the conductance ratio, $\Lambda/\Lambda_\infty$. The values of the degree of ionization lie between 0.513 and 0.802 (Table I), thereby confirming the fact that the uranyl hexanoate behaves as a simple electrolyte. The degree of ionization decreases rapidly in dilute solutions with the increase in uranyl hexanoate concentration (Table I).

It may thus conclude that the addition of Sudan dye increases the specific conductance, $k$ (mhos cm$^{-1}$) of the alkanoate solution (Table I and II) but the general behavior of the alkanoate remains unaltered.
Table I: Conductance of uranyl hexanoate in DMF at 40±0.05°C

<table>
<thead>
<tr>
<th>Concentration, C (mol dm⁻³)</th>
<th>Specific Conductance, k (mhos cm⁻¹)</th>
<th>Molar Conductance, Λ (cm² mol⁻¹)</th>
<th>Λ°C×10²</th>
<th>Degree of Ionization, α</th>
</tr>
</thead>
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<tr>
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<td>30.10</td>
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<td>15.44</td>
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<tr>
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<tr>
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<td>0.547</td>
<td>24.09</td>
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<tr>
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<td>0.0500</td>
<td>0.960</td>
<td>19.20</td>
<td>92.16</td>
<td>5.20</td>
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</table>

Table II: Conductance of uranyl hexanoate in Sudan dye (Conc. 10⁻⁴) and Sudan Red (Conc. 10⁻⁵) in DMF at 40±0.05°C

<table>
<thead>
<tr>
<th>Concentration, C (mol dm⁻³)</th>
<th>Specific Conductance, k×10⁶</th>
<th>Specific Conductance, k×10⁷</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0100</td>
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<tr>
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Acknowledgements

The authors are thankful to UGC, New Delhi for the financial assistance.

References