Effect of temperature on Conductometric studies and thermodynamic behavior of anionic surfactant in non-aqueous media

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Abstract: The micellar behavior of anionic surfactants ie. cadmium hexanoate and decanoate as cadmium mono alkanoates and butanedioate and hexanedioate as dialkanoates in a mixture of benzene-methanol (50% v/v) have been determined by conductometric measurements at different temperatures to determine the critical micellar concentration (CMC), degree of dissociation and dissociation constant of dilute solutions. The results shows that alkanoate solutions of cadmium mono alkanoates behave as moderate electrolyte while, dialkanoates of cadmium behave as weak electrolytes in dilute solution. The values of CMC decreases with increasing chain length of fatty acid component. The various thermodynamic parameters have also been evaluated for both ionization and micellization process.

Key words: surface active agent, micellization, anionic surfactants, thermodynamic parameter.

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 alkanoates, can be called association colloids, indicating their tendency to associate in solution, forming particles of colloidal dimensions. In recent years, considerable work have been reported on mono-carboxylic metal alkanoates of alkaline earth, transition metal and lanthanides, whereas the studies on dicarboxylic metal alkanoates have remained almost untouched with the result that only few references are available in this relatively unexplored field. The studies on the nature and structure of these alkanoates are of great importance for their uses in industries and explaining their characteristics under different conditions. The application of metal alkanoates largely depends on their physico-chemical properties such as physical state, thermal stability, chemical reactivity and solubility in polar and non-polar solvents. Liu et al synthesized different metal dialkanoates such as calcium glutarate, zinc glutarate, calcium sebacate and zinc sebacate and discussed their use as thermal stabilizers for PVC material. Ikhuoria et al studied the effect of temperature on the stability of metal alkanoates of dicarboxylic acids. Barbara and Lacz studied the thermal decomposition of cadmium butanedioate dihydrate. Burrows et al synthesized di-carboxylic acid metal soap by metathesis. Kumari et al synthesized and studied physico-chemical behavior of metal alkanoates of mono-and dicarboxylic acid in solution. A number of workers have used ultrasonic measurements of metal alkanoates for the determination of ion-solvent interaction in organic solvents. Viscometric, conductometric and thermodynamic measurements of lanthanide and transition metal alkanoates have been reported in different organic solvents.

In this paper, we have presented effect of temperature on CMC alongwith dissociation and association constants with the determination of various thermodynamic parameters of anionic surfactants ie. cadmium mono-(hexanoate and decanoate) and di- (butanedioate and hexanedioate) alkanoates in mixed organic solvent of benzene and methanol (50% v/v) at different (20, 30 and 40±0.05ºC) temperature.

II. Experimental

All the chemicals were of BDH/AR grade. Solvents benzene and methanol were purified by distillation under reduced pressure. Cadmium mono-(hexanoate and decanoate) alkanoates were synthesized by direct metathesis of corresponding potassium alkanoates as mentioned in our earlier publications, while dialkanoates of cadmium were synthesized by metathesis in alcohol solution. The purity was checked by their melting points and absence of hydroxylic group was confirmed by IR spectra. The reproducibility of the results was checked by preparing two samples of the same alkanoates under similar conditions. The solutions of anionic surfactants of cadmium were prepared by dissolving a known amount of alkanoates in benzene-methanol mixture (50% v/v) and were kept for 2 hr in a thermostat at different (20, 30 and 40±0.05ºC) temperature. The cadmium alkanoates do not possess high solubility in pure solvents thus measurements were conducted in benzene - methanol mixture. A digital conductivity meter (Toshniwal CL 01.10A) and a dipping
type conductivity cell with platinized electrodes (cell constant 0.895) were used for measuring the conductance of solutions of cadmium alkanoates in mixed organic solvent at different temperature.

III. Results and Discussion

Specific conductance, $k$ of the solutions of anionic surfactants of cadmium in a mixture of benzene and methanol (50% v/v) increase with increase in concentration of soap concentration, $C$, as well as temperature (Table I). It may be due to the fact that anionic surfactant behave as moderate electrolyte in dilute solutions, and are considerably ionized into a simple metal cations, $\text{Cd}^{2+}$ and fatty acid anions, $\text{RCOO}^-$ (where $R$ is C$_4$H$_8$ and C$_6$H$_{12}$ for hexanoate and decanoate, respectively) and $R(\text{COO})_2^-$ (where $R$ is C$_3$H$_6$ and C$_4$H$_8$ for butanedioate and hexanedioate respectively) in dilute solutions due to the formation of micelles at higher soap concentrations. The decrease in specific conductance, $k$ with increase in chain length of fatty acid may be due to the increasing size and decreasing mobility of anions with increasing the number of carbon atoms in the cadmium alkanoates (Table I). 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 non-aqueous 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 cadmium mono alkanoates are considerably ionized in dilute solutions and the anions begin to aggregate to form micelles. These micelles are in thermodynamic equilibrium with the metal ions, $\text{Cd}^{2+}$ mono alkanoate ions, R$\text{COO}^-$ present in the solution. The increase in conductance above the CMC may be due to the liberation of some of attached counter ions from the micelles. The values of CMC decrease with increase in temperature of solution as well as chain length of fatty acids constituent of cadmium alkanoates molecule (Table I). In cadmium dialkanoates, critical micellar concentration has been characterized by two breaks at definite concentration which corresponds to CMC (I) and CMC (II). The appearance of CMC (I) and CMC (II) can be explained on the basis of the formation of ionic and neutral micelles in the surfactant solution (Table I). It is indicated that the soap is considerably ionized in dilute solution and the anions begin to aggregate, to form ionic micelles at CMC (I). The dialkanoates are largely present in the form of ionic micelles at moderate concentration between CMC (I) and CMC (II) and there is an interesting formation of neutral micelles takes place at the CMC (II). The dipole-dipole interactions between the head groups of the surfactant molecules act as a deriving force for the formation of micelles. The decrease in CMC with increasing temperatures may be due to the reduction in the thickness of ionic atmosphere surrounding the polar head groups and consequent decreased repulsion between them$^{11}$. The molar conductance, $\Lambda$ of the solutions of anionic surfactant decreases with increasing soap concentration may be due to the combined effects of ionic atmosphere, solvation of ions, decrease of mobility of ion and ionization and formation of micelles. Since the molar conductance of the solutions of anionic surfactant of cadmium does not vary linearly with the square root of soap concentration, the Debye-Huckel-Onsager’s equation$^{12}$ is not applicable to these solutions. Molar conductance results show that soap solutions of mono-alkanoates of cadmium behave as moderate electrolyte while, cadmium dialkanoates behave as weak electrolytes in dilute solutions and ionization of cadmium alkanoates may be explained by Ostwald’s manner.

If C, is the concentration and $\alpha$ is the degree of dissociation of cadmium alkanoates, molar concentration may be represented as follows: For mono alkanoates

$$\text{Cd}([\text{RCOO}])_2 \rightleftharpoons \text{Cd}^{2+} + 2\text{RCOO}^-$$

$$C(1- \alpha) = C \alpha = 2C$$

And for di-alkanoates-

$$\text{Cd}[R(\text{COO})_2]_2 \rightleftharpoons \text{Cd}^{2+} + 2R(\text{COO})_2^-$$

$$C(1- \alpha) = C \alpha = 2C$$

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

For mono alkanoates-

$$K_d = \frac{[\text{Cd}^{2+}][\text{RCOO}^-]^2}{[\text{Cd}([\text{RCOO}])_2]} = 4C^2\alpha^2/(1 - \alpha)$$

(1)

For di-alkanoate -

$$K_d = \frac{[\text{Cd}^{2+}][R(\text{COO})_2^-]^2}{[\text{Cd}([R(\text{COO})_2])]_2} = 4C^2\alpha^3/(1 - \alpha)$$

(2)

Since, ionic concentration are low and inter-ionic effects are almost negligible in dilute solutions, the solution of cadmium alkanoates do not deviate appreciably from ideal behavior, and the activities of ions can be taken as almost equal to the concentrations of anionic surfactant anionic surfactant solution. The degree of dissociation, $\alpha$, may be replaced by the conductance ratio, $\Lambda/\Lambda_x$, where $\Lambda$ and $\Lambda_x$(cm$^2$ mol$^{-1}$) are the molar conductance at finite and infinite dilution, respectively. By substituting the value of $\alpha$ and rearranging equation (1 and 2)
\[ \Lambda^2 \varepsilon^2 = \frac{K_d \Lambda^3}{4 \Lambda} - \frac{K_d \Lambda^2}{4} \]  

The values of dissociation constant, \( K_d \), and limiting molar conductance, \( \Lambda_c \) (Table II) were obtained from the slope, \( \frac{K_d \Lambda^3}{4} \) and intercept – \( \frac{K_d \Lambda^2}{4} \) of the linear part of the plots of \( \Lambda^2 \varepsilon^2 \) vs 1/T below critical micellar concentration. It is seen that dissociation constant, \( K_d \), decreases with an increase in the numbers of carbon atoms in soap molecules i.e., with increasing chain length of the mono-(hexanoate to decanoate) and di-(butanedioate to hexanedioate) alkanoates. However, the decrease in the values of dissociation constant with increasing temperature indicates the exothermic nature of the dissociation of cadmium alkanoates in benzene-methanol mixture (50% v/v).

The heat of dissociation, \( \Delta H_d^0 \) for anionic surfactant is determined with the following equation.

\[ \frac{\partial \log K_d}{\partial T} = \frac{\Delta H_d^0}{2RT} \]  

The values of heat of dissociation \( \Delta H_d^0 \) were obtained from the slope of the linear plots of \( \log K_d \) vs 1/T and are recorded in Table III. The negative values of heat of dissociation, \( \Delta H_d^0 \), indicate that the dissociation process for anionic surfactant of cadmium is endothermic in nature. The values of standard free energy change, \( \Delta G_d^0 \) and standard entropy change, \( \Delta S_d^0 \) per mole for dissociation process are calculated by using the relationship:

\[ \Delta G_d^0 = -RT \ln K \]  

Where, \( K \), is the equilibrium constant.

\[ T \Delta S_d^0 = \Delta H_d^0 - \Delta G_d^0 \]  

The calculated values of \( \Delta G_d^0 \) and \( \Delta S_d^0 \) are shown in Table IV. Careful scrutiny of thermodynamic parameters indicates that the positive values of \( \Delta G_d^0 \) and negative values of \( \Delta S_d^0 \) for the dissociation process (Table IV) show that the dissociation process is a non spontaneous process for mono-(hexanoate to decanoate) and di-(butanedioate to hexanedioate) alkanoates in benzene – methanol mixture (50% v/v).

For the micellization process, when counter ions are bound to micelles, the standard free energy of micellization per mole of monomer, \( \Delta G_a^0 \) (Table V), for the phase separation model is given by relationship:

\[ \Delta G_a^0 = 2RT \ln X_{cmc} \]  

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

\[ X_{cmc} = \frac{n_s}{n_0 + n_s} \]  

As the number of moles of free surfactant, \( n_s \), is small as compared to the number of moles of solvent, \( n_0 \), then

\[ X_{cmc} = \frac{n_s}{n_0} \]  

The standard enthalpy of micellization per mole of monomer, \( \Delta H_a^0 \) for the phase separation model is given by the relationship:

\[ \frac{\partial \ln X_{cmc}}{\partial T} = \frac{\Delta H_a^0}{2RT} \]  

The values of \( \Delta H_a^0 \) were obtained from the slope of linear plots of \( \ln X_{cmc} \) vs 1/T and are recorded in Table III. The positive values of \( \Delta H_a^0 \) indicate that the micellization process of cadmium alkanoates in benzene-methanol (50% v/v) is endothermic. The standard entropy change per mole for dissociation process is determined with the following equation:

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Where, \( K \), is the equilibrium constant.

\[ T \Delta S_d^0 = \Delta H_d^0 - \Delta G_d^0 \]  

The calculated values of \( \Delta G_d^0 \) and \( \Delta S_d^0 \) are shown in Table IV. Careful scrutiny of thermodynamic parameters indicates that the positive values of \( \Delta G_d^0 \) and negative values of \( \Delta S_d^0 \) for the dissociation process (Table IV) show that the dissociation process is a non spontaneous process for mono-(hexanoate to decanoate) and di-(butanedioate to hexanedioate) alkanoates in benzene – methanol mixture (50% v/v).

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\[ \Delta G_d^0 = -RT \ln K \]  

Where, \( K \), is the equilibrium constant.

\[ T \Delta S_d^0 = \Delta H_d^0 - \Delta G_d^0 \]  

The negative enthalpy change of dissociation (Table III) tends to make up for the unfavorable change in free energy and entropy of dissociation process (Table IV). On the other hand, the negative free energy and positive entropy (Table V) favor micellization and compensate for the unfavorable enthalpy change for the process (Table III). The results show that the association process is dominant over the dissociation process.

IV. Conclusion

It is therefore concluded that the thermodynamics of dissociation and association of anionic surfactant i.e., cadmium mono-(hexanoate and decanoate) and di-(butanedioate and hexanedioate) alkanoates can be satisfactorily explained in the light of the phase separation model by conductivity measurements. The results showed that dissociation of anionic surfactant was found to be exothermic while the association process was endothermic in nature and critical micellar concentration decreased with increase in temperatures as well as chainlength of fatty acid constituent of anionic surfactant.

References


### Table 1: CMC (mol dm$^{-3}$) values of anionic surfactants of anionic surfactants

<table>
<thead>
<tr>
<th>Cadmium alkanoates</th>
<th>Hexanoate</th>
<th>Decanoate</th>
<th>Butanedioate</th>
<th>Hexanedioate</th>
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<tbody>
<tr>
<td></td>
<td>CMC(I)</td>
<td>CMC(II)</td>
<td>CMC(I)</td>
<td>CMC(II)</td>
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<tr>
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<td>6.4</td>
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<td>5.2</td>
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<tr>
<td>40ºC</td>
<td>5.3</td>
<td>4.9</td>
<td>3.3</td>
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### Table 2: Values of limiting molar conductance, $\Lambda_{\infty}$ and dissociation constant, $K_d$ at different temperatures

<table>
<thead>
<tr>
<th>Cadmium alkanoates</th>
<th>20ºC</th>
<th>30ºC</th>
<th>40ºC</th>
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<tbody>
<tr>
<td></td>
<td>$\Lambda_{\infty}$</td>
<td>$K_d$</td>
<td>$\Lambda_{\infty}$</td>
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<tr>
<td>Hexanoate</td>
<td>8.68x10$^{-3}$</td>
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<tr>
<td>Decanoate</td>
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<td>1.61</td>
<td>4.69x10$^{-3}$</td>
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<tr>
<td>Butanedioate</td>
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<td>1.90</td>
<td>5.34x10$^{-3}$</td>
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<tr>
<td>Hexanedioate</td>
<td>3.57x10$^{-3}$</td>
<td>3.12</td>
<td>3.07x10$^{-3}$</td>
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### Table 3: Heat of dissociation, $\Delta H_{d}^{0}$ and Heat of association, $\Delta H_{a}^{0}$ of anionic surfactants

<table>
<thead>
<tr>
<th>Cadmium alkanoates</th>
<th>$\Delta H_{d}^{0}$ (kJ mol$^{-1}$)</th>
<th>$\Delta H_{a}^{0}$ (kJ mol$^{-1}$)</th>
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<tbody>
<tr>
<td>Hexanoate</td>
<td>27.33x10$^{-3}$</td>
<td>13.19x10$^{-3}$</td>
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<tr>
<td>Decanoate</td>
<td>14.90x10$^{-3}$</td>
<td>10.18x10$^{-3}$</td>
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<td>Butanedioate</td>
<td>15.99x10$^{-3}$</td>
<td>16.55x10$^{-3}$</td>
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<tr>
<td>Hexanedioate</td>
<td>17.61x10$^{-3}$</td>
<td>19.79x10$^{-3}$</td>
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### Table 4: Free energy of dissociation, $\Delta G_{d}^{0}$, Entropy of dissociation, $\Delta S_{d}^{0}$, at different temperatures

<table>
<thead>
<tr>
<th>Cadmium alkanoates</th>
<th>$\Delta G_{d}^{0}$ (kJ mol$^{-1}$)</th>
<th>$\Delta S_{d}^{0}$ (kJ mol$^{-1}$)</th>
<th>$\Delta G_{a}^{0}$ (kJ mol$^{-1}$)</th>
<th>$\Delta S_{a}^{0}$ (kJ mol$^{-1}$)</th>
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<tr>
<td>Hexanoate</td>
<td>22.785</td>
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<tr>
<td>Hexanedioate</td>
<td>36.170</td>
<td>36.19</td>
<td>37.785</td>
<td>39.841</td>
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### Table 5: Free energy of association, $\Delta G_{a}^{0}$, Entropy of association, $\Delta S_{a}^{0}$, at different temperatures

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<th>Cadmium alkanoates</th>
<th>20ºC</th>
<th>30ºC</th>
<th>40ºC</th>
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<tr>
<td></td>
<td>$\Delta G_{a}^{0}$</td>
<td>$\Delta S_{a}^{0}$</td>
<td>$\Delta G_{a}^{0}$</td>
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<td>Hexanoate</td>
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<td>47.749</td>
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<td>48.774</td>
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