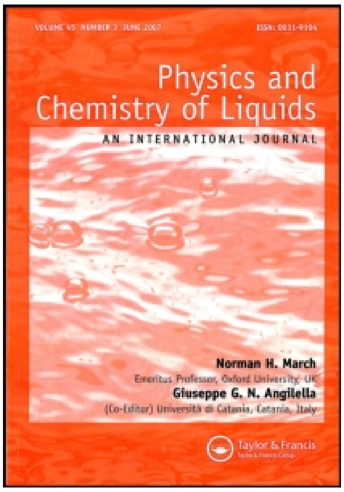

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

# Acoustical Study and Thermodynamics of Dissociation and Micellization of Lanthanum and Cerium Linoleates in A Mixture of Benzene and Methanol

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**To cite this Article** Upadhyaya, S. K.(1993) 'Acoustical Study and Thermodynamics of Dissociation and Micellization of Lanthanum and Cerium Linoleates in A Mixture of Benzene and Methanol', Physics and Chemistry of Liquids, 25: 3, 185 — 199

**To link to this Article: DOI:** 10.1080/00319109308030360

**URL:** http://dx.doi.org/10.1080/00319109308030360

*Phys. Chem. Liq.*, 1993, Vol. 25, pp. 185–199
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# ACOUSTICAL STUDY AND THERMODYNAMICS OF DISSOCIATION AND MICELLIZATION OF LANTHANUM AND CERIUM LINOLEATES IN A MIXTURE OF BENZENE AND METHANOL

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*(Received 1 February 1992)*

Ultrasonic measurements on lanthanum and cerium linoleates were made in a mixture of 60% benzene and 40% methanol (V/V), to determine the CMC, soap-solvent interaction and various acoustic and thermodynamic parameters. The values of the CMC increase with the increase in temperature. The ultrasonic velocity, specific acoustic impedance, apparent molar compressibility, relative association and Rao's number increase while the adiabatic compressibility, intermolecular free length, apparent molar volume, solvation number and available volume decrease with increasing soap concentration. The dissociation constant and thermodynamic parameters for dissociation and micellization processes of lanthanum and cerium linoleates were evaluated from conductivity measurements. The results showed that these soaps behave as weak electrolytes in dilute solutions and the micellization process is dominant over the dissociation process.

KEY WORDS: Sound velocity, specific acoustic impedance, available volume, CMC, dissociation constant.

## INTRODUCTION

The proven utility of metallic soaps as dispersants[1], lubricants[2–4], catalysts[5,6], stabilizers[7] and corrosion inhibiting agents[8,9], has fascinated research workers[10,11], in the past. A great deal of work has been reported on the alkali, alkaline earth and transition metal soaps but the studies on rare earth metal soaps[12–15] remained almost unexplored inspite of their large applications. The technological applications of these soaps are mostly based on empirical know-how and the selection of soap is dependent largely on economic factors. The physico-chemical characteristic and the structure of metal soaps depend largely on the method and conditions of preparation. A metal soap is largely present in dilute solutions as metal cations and fatty acid anions. The anions begin to associate on increasing the soap concentration and form micelles, which are in thermodynamic equilibrium with the ions. Their formation occurs over a narrow range of concentration. The initial concentration at which micelles first appear in the solution is known as critical micelle concentration, (CMC). The physical properties of the soap solutions exhibit a discontinuity at the CMC.

The present work deals with the ultrasonic and conductivity measurements of solutions of lanthanum and cerium linoleates in a mixture of 60% benzene and 40% methanol (V/V) and with the evaluation of various acoustic and thermodynamics parameters.

## EXPERIMENTAL

The lanthanum and cerium linoleates soaps were prepared by the direct metathesis of potassium linoleates with the required amount of metal nitrate/chloride in water alcohol medium (1:1). The precipitated soaps were washed with water and acetone to remove the excess of metal ions and unreacted linoleic acid. Both the preparation and purification processes were carried out under nitrogen atmosphere to protect against possible oxidation of these soaps. The purity of the soaps was checked by the elemental analysis and the results were found in agreement with the theoretically calculated values. The reproducibility of the results was checked by preparing two samples of the same soap under similar conditions. The solutions of soaps were prepared by dissolving a known amount of soap in a mixture of 60% benzene and 40% methanol (V/V) and were kept for 2 in a thermostat at the desire constant temperature.

The ultrasonic velocity measurements were recorded on a multifrequency ultrasonic interferometer (M-83, Mittal Enterprises, New Delhi) at 40 ± 0.05°C using a crystal of frequency 4 $MH_z$. The uncertainty of velocity measurements is 0.2%. The densities of the solvent and solution were determined with a pyknometer calibrated with pure benzene. The volume of the pyknometer was 10 ml and the accuracy of the density results was $\pm 0.1$ $Kg.m^{-3}$.

The conductance of the solutions was measured with a Toshniwal digital conductivity meter, Model CL 01 10A, and dipping type conductivity cell (Cell constant 0.90) with platinized electrodes at different temperatures. The reproducibility (±0.1%) of the measurements were examined by repeating them several times.

## CALCULATIONS

The various acoustic parameters, namely adiabatic compressibility ($\beta$), intermolecular free length[16] (Lf) specific acoustic impedance[17] ($Z$), apparent molar volume ($\phi_v$), available volume[19] ($V_a$), relative association[20] ($R_A$), apparent molar compressibility[18] ($\phi_k$), Rao's number[21] ($R$) and primary solvation number ($S_n$) have been evaluated using the following relationships

$$\beta = \rho^{-1} v^{-2} \tag{1}$$

$$L_f = K\sqrt{\beta} \tag{2}$$

$$Z = v \cdot \rho \tag{3}$$

$$\phi_v = \frac{10^3(\rho - \rho_0)}{C\rho\rho_0} + \frac{M}{\rho_0} \tag{4}$$

$$V_a = \bar{V}\left(1 - \frac{v}{v_\alpha}\right) \tag{5}$$

$$R_A = \left(\frac{\rho}{\rho_0}\right)\left(\frac{v_0}{v}\right)^{1/3} \tag{6}$$

$$\phi_k = \frac{10^3(\beta - \beta_0)}{c\rho_0} + \beta\phi_v \tag{7}$$

$$R = \frac{\bar{M}}{\rho} v^{1/3} \tag{8}$$

$$\left[\bar{M} = \frac{n_0 M_0 + nM}{n_0 + n}\right]$$

and

$$S_n = -\phi_k/\bar{V}_0\beta_0 \tag{9}$$

Where $\rho_0$, $\rho$; $\beta_0$, $\beta$; $\bar{V}_0$, $\bar{V}$ and $v_0$, $v$ are the density, adiabatic compressibility, molar volume and ultrasonic velocity of solvent and solution respectively. $n_0$, $n$ and $M_0$, $M$ are the number of moles and molecular weight of solvent and solute respectively and $K$ and $\bar{M}$ are the temperature dependent Jacobson's constant and effective molecular weight of the solutions. $v_\alpha$ equivalent to 1600 $\mathrm{ms}^{-1}$.

## RESULTS AND DISCUSSION

The ultrasonic velocity $v$ ($\pm 0.2\%$) and other acoustic and solute-solvent interaction parameters for the lanthanum and cerium linoleates in 60% benzene and 40% methanol (V/V) are recorded in Tables 1 and 2. The variation of ultrasonic velocity with concentration ($dv/dc$) depends on the concentration derivatives of density and adiabatic compressibility

$$(dv/dc) = -v/2 \ 1/\rho(d\rho/dc) + 1/\beta(d\beta/dc)$$

The quantity of $d\rho/dc$ is always positive, while $d\beta/dc$ is negative. Since the values of $1/\beta$ ($d\beta/dc$) are higher than $1/\rho$ ($d\rho/dc$) for these solutions, the quantity $dv/dc$ is positive, i.e. ultrasonic velocity increases with the increase in concentration.

The variation in ultrasonic velocity $v$ with soap concentration. $C$ follows the relationship

$$v = v_0 + GC.$$

**Table 1** Ultrasonic velocity and other allied parameters of lanthanum linoleate in 60% benzene and 40% methanol (V/V) at 40 ± 0.05°C.

| *S. no.* | *Concentration* $C \times 10^3$ $dm^{-3}$ *mol* | *Density* $\rho$ $Kg\ m^{-3}$ | *Velocity* $v \times 10^{-3}$ $ms^{-1}$ | *Adiabatic compressibility* $\beta \times 10^{10}$ $m^2\ N^{-1}$ | *Apparent molar compressibility* $-\phi_k \times 10^8$ $m^5\ N^{-1}(k\ mol)$ | *Specific acoustic impedance* $Z \times 10^{-5}$ $Kg\ m^{-2}\ s^{-1}$ | *Intermolecular free length* $L_f$ Å | *Apparent molar volume* $\phi_v$ $m\ kg^{-1}\ s^2$ | *Available volume* $V_a \times 10^2$ | *Relative association* $R_a$ | *Solvation number* $S_n$ | *Rao's number* $R \times 10^3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *1* | *2* | *3* | *4* | *5* | *6* | *7* | *8* | *9* | *10* | *11* | *12* | *13* |
| 1 | 1.0 | 847.6 | 1.132 | 9.207 | 2.34 | 9.595 | 0.6160 | 19.26 | 1.75 | 1.0117 | 403.4 | 622.7 |
| 2 | 2.0 | 851.2 | 1.144 | 8.977 | 2.29 | 9.738 | 0.6083 | 12.71 | 1.70 | 1.0125 | 394.8 | 624.2 |
| 3 | 3.0 | 854.7 | 1.156 | 8.755 | 2.26 | 9.880 | 0.6007 | 10.47 | 1.65 | 1.0131 | 389.7 | 624.5 |
| 4 | 4.0 | 858.4 | 1.168 | 8.540 | 2.22 | 10.025 | 0.5933 | 9.41 | 1.60 | 1.0139 | 382.9 | 624.8 |
| 5 | 5.0 | 861.1 | 1.178 | 8.369 | 2.12 | 10.144 | 0.5873 | 8.49 | 1.56 | 1.0143 | 365.3 | 625.1 |
| 6 | 6.0 | 862.5 | 1.182 | 8.299 | 1.87 | 10.195 | 0.5849 | 7.58 | 1.55 | 1.0148 | 322.2 | 625.5 |
| 7 | 7.0 | 863.6 | 1.185 | 8.246 | 1.66 | 10.234 | 0.5830 | 6.88 | 1.53 | 1.0152 | 286.9 | 625.9 |
| 8 | 8.0 | 864.8 | 1.187 | 8.207 | 1.49 | 10.265 | 0.5816 | 6.37 | 1.52 | 1.0161 | 256.6 | 626.1 |
| 9 | 9.0 | 866.0 | 1.191 | 8.141 | 1.39 | 10.314 | 0.5793 | 5.97 | 1.51 | 1.0163 | 239.5 | 626.7 |
| 10 | 10.0 | 868.3 | 1.194 | 8.078 | 1.30 | 10.368 | 0.5770 | 5.79 | 1.50 | 1.0182 | 223.4 | 626.1 |

**Table 2** Ultrasonic velocity and other allied parameters of cerium linoleates in 60% benzene and 40% methanol (v/v) at 40 ± 0.05°C.

| *S. no.* | *Concentration* $C \times 10^3$ $dm^{-3}$ *mol* | *Density* $\rho$ $Kg\ m^{-3}$ | *Velocity* $v \times 10^{-3}$ $ms^{-1}$ | *Adiabatic compressibility* $\beta \times 10^{10}$ $m^2\ N^{-1}$ | *Apparent molar compressibility* $-\phi_k \times 10^8$ $m^5\ N^{-1}(k\ mol)$ | *Specific acoustic impedance* $Z \times 10^{-5}$ $Kg\ m^{-2}\ s^{-1}$ | *Intermolecular free length* $L_f$ Å | *Apparent molar volume* $\phi_v$ $m\ kg^{-1}\ s^2$ | *Available volume* $V_a \times 10^2$ | *Relative association* $R_a$ | *Solvation number* $S_n$ | *Rao's number* $R \times 10^3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *1* | *2* | *3* | *4* | *5* | *6* | *7* | *8* | *9* | *10* | *11* | *12* | *13* |
| 1 | 1.0 | 848.4 | 1.128 | 9.264 | 1.54 | 9.570 | 0.6179 | 20.37 | 1.76 | 1.0139 | 265.5 | 622.7 |
| 2 | 2.0 | 851.9 | 1.141 | 9.017 | 2.00 | 9.720 | 0.6096 | 13.19 | 1.76 | 1.0142 | 245.4 | 623.1 |
| 3 | 3.0 | 855.5 | 1.156 | 8.747 | 2.26 | 9.890 | 0.6004 | 10.83 | 1.65 | 1.0141 | 389.5 | 623.9 |
| 4 | 4.0 | 859.1 | 1.166 | 8.562 | 2.49 | 10.017 | 0.5941 | 8.42 | 1.61 | 1.0154 | 429.3 | 623.8 |
| 5 | 5.0 | 861.8 | 1.175 | 8.405 | 2.01 | 10.126 | 0.5886 | 8.62 | 1.57 | 1.0160 | 346.6 | 624.1 |
| 6 | 6.0 | 863.0 | 1.178 | 8.350 | 1.76 | 10.166 | 0.5866 | 7.70 | 1.56 | 1.0165 | 301.7 | 624.5 |
| 7 | 7.0 | 864.4 | 1.182 | 8.280 | 1.59 | 10.217 | 0.5842 | 7.03 | 1.52 | 1.0170 | 274.1 | 624.8 |
| 8 | 8.0 | 865.7 | 1.185 | 8.226 | 1.45 | 10.259 | 0.5823 | 6.52 | 1.53 | 1.0177 | 250.0 | 625.1 |
| 9 | 9.0 | 866.9 | 1.188 | 8.173 | 1.33 | 10.299 | 0.5804 | 6.10 | 1.52 | 1.0182 | 229.3 | 625.5 |
| 10 | 10.0 | 868.5 | 1.192 | 8.104 | 1.26 | 10.353 | 0.5779 | 5.82 | 1.51 | 1.0190 | 217.2 | 625.7 |

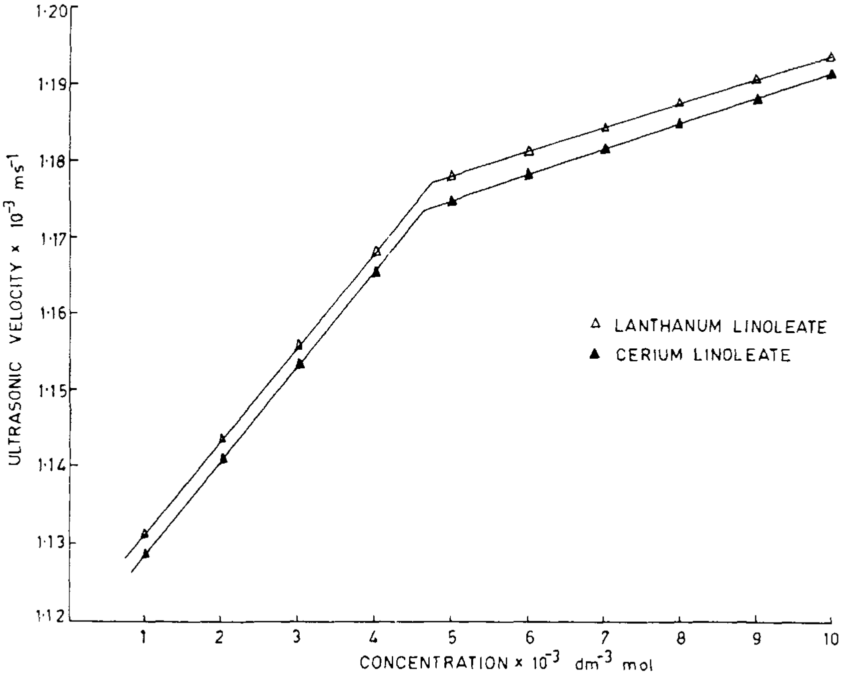

**Figure 1** Ultrasonic velocity vs concentration in 60% benzene and 40% methanol.

where $v_0$ is the ultrasonic velocity in pure solvent and $G$ is Garnsey's constant.[22] The plots of ultrasonic velocity $v$, against soap concentration $C$ (Figure 1) are characterised by an intersection of two straight lines at a definite soap concentration which corresponds to the CMC of these soaps (Lanthanum Linoleates: $4.8 \times 10^{-3}$ M Cerium Linoleate: $4.6 \times 10^{-3}$ M). The existence of the micelles has also been confirmed by conductivity and density measurements. The micellization process is due to the energy change arising from the polar head groups of the soap molecules. The micelles are held together by Vander Waal's forces acting between the hydrocarbon chains of parallel layers and strong dipole–dipole interactions between polar heads. The values of CMC decrease with the increase in the size of the cations and are in agreement with the results of measurements of other micellar properties[23–25]. The plots (Figure 1) are extrapolated to zero soap concentration and the extrapolated value of velocity, $v_0$ ($1.119 \times 10^3$ $ms^{-1}$) is in close agreement with the experimental velocity in solvent, indicating that the soap molecules do not aggregate up to an appreciable extent below the CMC. The values of Garnsey's constant, $G$ for lanthanum and cerium linoleates in 60% benzene and 40% methanol are $12.5 \times 10^3$ and $13.5 \times 10^3$, respectively.

The adiabatic compressibility, $\beta$ of these rare earth metal soap solution decreases with increasing soap concentration (Tables 1 and 2). The decrease in adiabatic compressibility is attributed to the fact that the lanthanum and cerium linoleate soaps molecules in dilute solutions are considerably ionised into metal cations and linoleic acid anions. These ions are surrounded by a layer of solvent molecules firmly bound and oriented towards the ions. The orientation of solvent molecules around the ions is attributed to the influence of electrostatic field of the ions and thus the internal pressure increases, which lowers the compressibility of these soap solutions, i.e. solutions become harder to compress[26]. The decrease in adiabatic compressibility at higher soap concentrations may be explained on the basis of closed packing of ionic head groups in the micelles, resulting in an increase in ionic repulsion and finally internal pressure.

The plots of adiabatic compressibility, $\beta$, Vs soap concentration, $C$, indicate a break at a definite soap concentration which corresponds to the CMC of these soaps and these plots are extrapolated to zero soap concentration and the extrapolated value of adiabatic compressibility. $\beta_0$ ($9.43 \times 10^{-10}\,\mathrm{m^2\,N^{-1}}$) is in good agreement with the experimental value of adiabatic compressibility of the solvent ($9.55 \times 10^{-10}\,\mathrm{m^2\,N^{-1}}$).

The results of adiabatic compressibility have also been explained in terms of Bachem's relationship[27].

$$\beta = \beta_0 + AC - BC^{3/2} \tag{10}$$

where $A$ and $B$ are constants, $C$ is the molar soap concentration and $\beta$ and $\beta_0$ are the adiabatic compressibility of the solution and solvent respectively. The plots of $(\beta - \beta_0)/C$ against square root of soap concentration, $C^{1/2}$ show a break at the CMC. The intercept and slope of the plots have been used to obtain the values of constant A (lanthanum linoleate: $-3.74 \times 10^{-8}$ and cerium linoleate: $-3.42 \times 10^{-8}$) and B (lanthanum linoleate: $1.9 \times 10^{-7}$ and cerium linoleate: $1.6 \times 10^{-7}$).

The negative values of the apparent molar compressibility decrease linearly with concentration, but this decrease is sharp for pre micellization region as compared to post micellization region, indicating poor compressibility at higher concentrations. However, this negative value of the apparent molar compressibility is probably due to the decreasing internal pressure.

The values of $S_k$ at infinite dilution were obtained from the Masson's[28] equation.

$$\phi_k = \phi_k^0 + S_k C^{1/2} \tag{11}$$

where $\phi_k^0$ is apparent molar compressibility of the solvent and $S_k$ is a constant. The plots of apparent molar compressibility, $\phi^k$ Vs. square root of soap concentration, $C^{1/2}$ show a break at the CMC. The values of limiting apparent molar compressibility, $\phi_k^0$, have been obtained from the intercept of the plots of $\phi_k$ Vs. $C^{1/2}$ and are found to be $-2.46 \times 10^{-8}$ and $-0.7 \times 10^{-8}$ for lanthanum and cerium linoleates, respectively. The values of constant $S_k$, for these soaps (Lanthanum linoleate: $4.0 \times 10^{-7}$ and cerium linoleate: $3.1 \times 10^{-6}$) have been obtained from the slope of the plots. The positive value of $S_k$ signifies a considerable soap solvent interaction below the CMC. The comparison of the results with the results of other metal soaps[25] and electrolytes[26] shows that these soaps behave as weak electrolytes in dilute solutions.

The intermolecular free length, $L_f$, decreases while specific acoustic impedance, $Z$, increases with the increase in soap concentration (Tables 1 and 2), which indicates that there is a significant interaction[29] between the soap and solvent molecules which considerably affects the structural arrangement. The increase in the value of specific acoustic impedance, $Z$, with increasing soap concentration, $C$, can be explained on the basis of lyophobic interaction between soap and solvent molecules which increases the intermolecular distance, making relatively wider gaps between the molecules and becoming the main cause of impedance in the propagation of ultrasound waves.

The plots of intermolecular free length, $L_f$, and specific acoustic impendance, $Z$, against the soap concentration, $C$, show a break at a definite soap concentration which corresponds to the CMC of these soaps. The extrapolated values of intermolecular free length $L_f^0$ (0.6245 Å) and specific acoustic impendance $Z_0$ ($9.455 \times 10^5$ Kg.m$^{-2}$ s$^{-1}$), are in agreement with the values for the solvent mixture. This again confirms the fact that the soap molecules do not aggregate to an appreciable extent below the CMC, whereas there is a marked change in aggregation at the CMC.

The values of apparent molar volume decrease with increasing soap concentration (Tables 1 and 2). The values of apparent molar volume of the cerium linoleates in 60% benzene and 40% methanol (V/V) are somewhat higher than the values of lanthanum linoleates because the former does not penetrate the dimensional structure of mixed organic solvent. The values of limiting apparent molar volume are positive which indicate that this does not restrict molecular motion within the solutions.

The values of available volume, $V_a$ decrease while the values of relative association increase with increasing soap concentration (Tables 1 and 2). The plots of $V_a$ and $R_A$ Vs. soap concentration are characterized by a break at the CMC. The increase in the values of $R_A$ has been attributed either to the increased association between soap and mixed organic solvent molecules at higher concentration or increasing solvation of ions[30], but the former seems to be predominant because the solvation number, Sn, decreases with increase in soap concentration.

The solvation number decreases with increase in soap concentration. The values of Sn correspond to the number of solvent molecules in the primary solvation sheaths of the ions. On account of electrostriction, molecules in the solvation sheath will be highly compressed so that these molecules will be less compressible than those in the bulk of the solution when an external pressure is applied. The compressibility of solvent molecules near but not in the primary solvation sheaths is the same as that of pure solvent. The solvation numbers are in indication more of electrostriction effects of the ions on surrounding solvent molecules than of the actual primary solvation numbers. The ionic solvation numbers based on compressibility data might be anticipated to depend on the size and the charge density of the ions. The molar sound velocity, $R$ show a regular, almost linear increase with soap concentration, $C$.

## CONDUCTANCE

The specific conductance, $k$ of the solutions of lanthanum and cerium linoleates in 60% benzene and 40% methanol (V/V) increases with increase in soap concentration

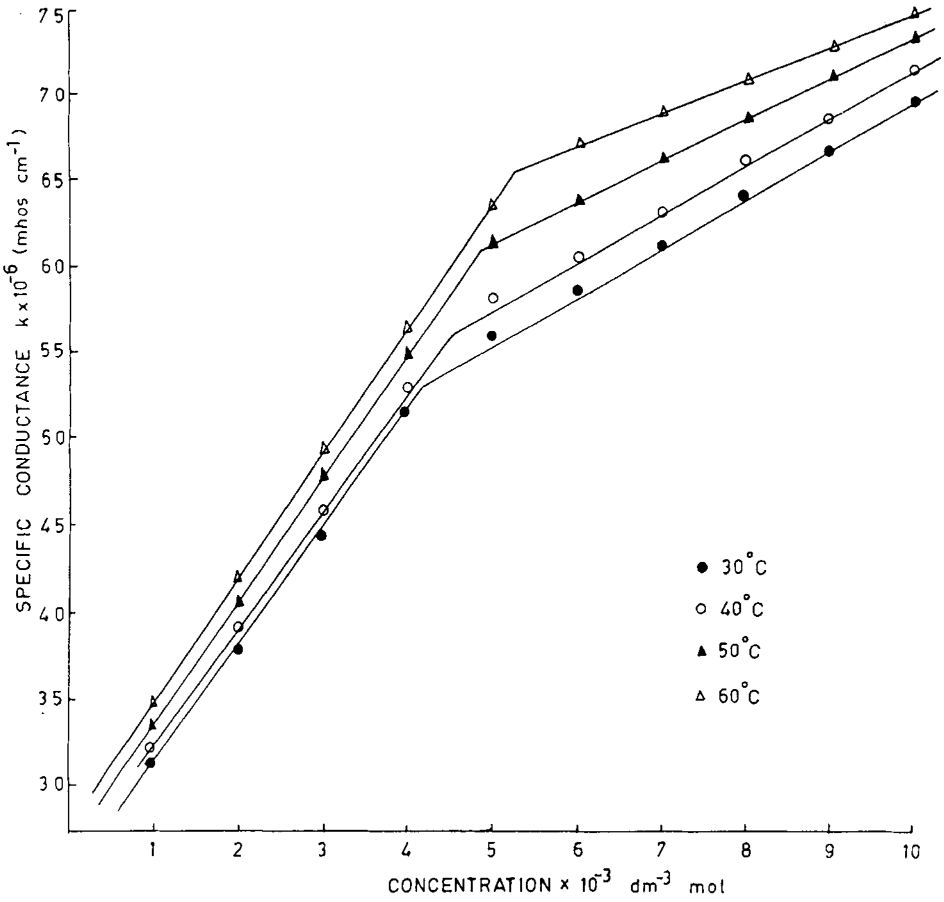

**Figure 2** Specific conductance vs concentration of lanthanum linoleate in 60% benzene and 40% methanol.

and temperature. The plots of specific conductance Vs soap concentration are characterized by an intersection of two straight lines at a concentration which corresponds to the CMC (Figure 2). The results show that the increase in temperature and decrease of the size of cation results in the increase of the CMC. (Table 3) because the micellization is assumed to occur when the energy released as a results of

**Table 3** Critical micelle concentration of lanthanum and cerium linoleates in 60% benzene and 40% methanol

| *Soap* | *CMC* × 10$^3$ *dm*$^{-3}$ *mol* | | | |
|---|---|---|---|---|
| | *30°C* | *40°C* | *50°C* | *60°C* |
| Lanthanum linoleate | 4.3 | 4.8 | 5.1 | 5.4 |
| Cerium linoleate | 4.2 | 4.6 | 4.9 | 5.3 |

aggregation of the hydrocarbon chains of the monomer is sufficient to overcome to the electrical repulsion between the ionic head groups and to balance the decrease in entropy accompanying aggregation. Therefore, increase in temperature would have been expected to increase the CMC value since the kinetic energy of the monomers would have been raised.

The molar conductance, $\mu$ of the dilute solutions of soaps decrease with increasing soap concentration. The decrease in molar conductance may be due to the combined effects of ionic atmosphere, solvation of ions and decrease of mobility and ionisation with the formation of micelles. However, the CMC values can not be obtained from the plots of molar conductance Vs. square root of soap concentration because the plots are concave upwards with increasing slopes, indicating that these soaps behave as weak electrolytes in dilute solution and Debye–Huckels–Onsagers equation is not applicable to these soap solutions. Since the lanthanide linoleates behave as weak electrolytes in dilute solutions, an expression for the dissociation may be developed in Ostwald's manner. The dissociation of these soaps can be represented as follows:

$$\underset{C(1-\alpha)}{M(C_{17}H_{31}COO)_3} \rightleftarrows \underset{C\alpha}{M(C_{17}H_{31}COO)_2^+} + \underset{C\alpha}{C_{17}H_{31}COO^-} \tag{12}$$

where $C$ is the concentration of soap ($dm^{-3}$ mol)$\alpha$, is the degree of dissociation and $M$ stands for lanthanum and cerium, respectively. The dissociation constant $K$ for the above mentioned dissociation of soap can be expressed as

$$K = \frac{[M(C_{17}H_{31}COO)_2^+][C_{17}H_{31}COO^-]}{[M(C_{17}H_{31}COO)_3]} \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \tag{13}$$

Since the degree of dissociation of lanthanide linoleates in dilute solutions is small, the ionic concentrations are low and interionic effects are almost negligible. Therefore, the dilute soap solutions do not deviate appreciably from ideal behaviour and the activities of ions can be taken as almost equal to the concentration. The degree of dissociation, $\alpha$, may be determined by the conductance ratio, $\mu/\mu_0$ where $\mu$ is the molar conductance at finite concentration and $\mu_0$ is the limiting molar conductance at infinite dilution. On substituting the value of $\alpha$ and rearranging, Eq. (13) can be written as

$$\mu C = \frac{K\mu_0^2}{\mu} - K\mu_0 \tag{14}$$

The values of $\mu_0$ and $K$ have been calculated from the slope, $[K\mu_0^2]$ and intercept $[-K\mu_0]$ of the linear plots of $\mu C$ Vs. $1/\mu$ below the CMC (Table 4).

The results show that the values of molar conductance at infinite dilution increase while the values of dissociation constant decreases with increasing temperature. The values of limiting molar conductance and dissociation constants decrease with the increase in the size of the cations. The values of degree of dissociation, $\alpha$, at different

**Table 4** Values of dissociation constant of lanthanide metal linoleates soaps in 60% benzene and 40% methanol (V/V)

| *Soap* | *Dissociation constant K* | | | |
|---|---|---|---|---|
| | *30°C* | *40°C* | *50°C* | *60°C* |
| Lanthanum linoleate | $1.445 \times 10^{-6}$ | $9.441 \times 10^{-7}$ | $6.095 \times 10^{-7}$ | $4.786 \times 10^{-7}$ |
| Celium linoleate | $1.738 \times 10^{-6}$ | $1.122 \times 10^{-6}$ | $6.761 \times 10^{-7}$ | $5.129 \times 10^{-7}$ |

soap concentrations and temperatures have been determined by assuming it as equal to the conductance ratio, $\mu/\mu_0$. The results show that these soaps behave as a weak electrolyte in solutions. The values of degree of dissociation of the soaps decrease rapidly in dilute solution with the increase in soap concentrations whereas it decreases slowly above the CMC.

The values of dissociation constant, $K$ show approximate constancy in dilute solutions but exhibit a drift with increasing soap concentration which indicates that

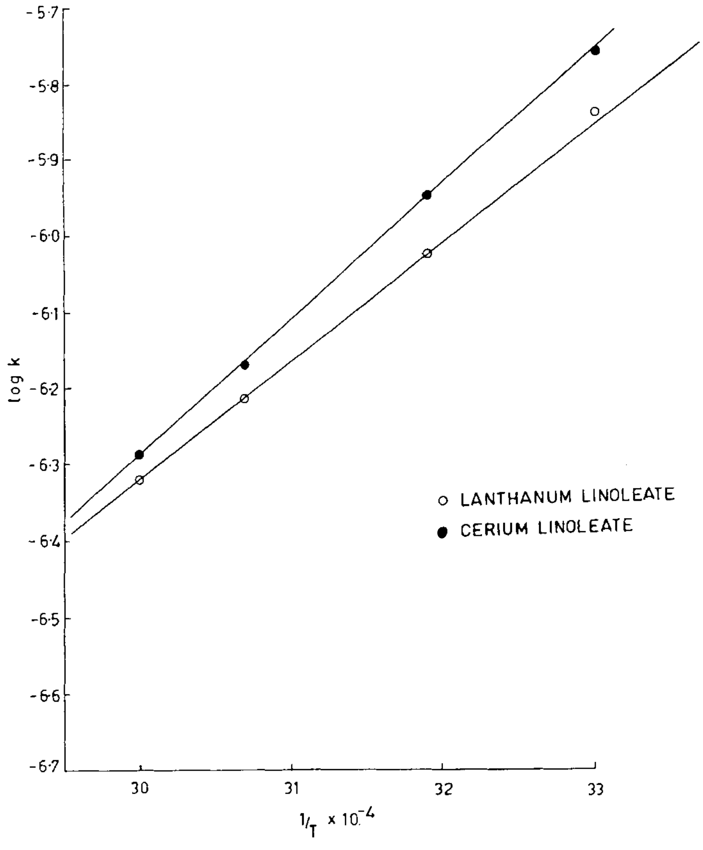

**Figure 3** 60% benzene and 40% methanol, log $k$ vs $1/T$.

**Table 5** Thermodynamic parameters of lanthanide linoleates per mole of monomers

| *Soap* | *Heat of dissociation* $\Delta H_D$ *kJ mol*$^{-1}$ | *Heat of micellization* $\Delta H_A$ *kJ mol*$^{-1}$ |
|---|---|---|
| Lanthanum linoleate | −11.03 | −10.61 |
| Cerium linoleate | −11.51 | −9.85 |

these soaps do not behave as very weak electrolyte in these solutions. The drift in the values of dissociation constant with increasing soap concentration may be partly due to the fact that the degree of dissociation, is not exactly equal to the conductance ratio, $\mu/\mu_0$ but mainly due to the fact that the activity coefficient of ions are not equal to unity at higher soap concentrations. The deviation in the values of dissociation constant at higher soap concentration may be due to the failure of simple Debye–Huckel's activity equation at higher concentrations. The decrease in the values of dissociation constants with increasing temperature indicates the exothermic nature of the dissociation of lanthanum and cerium linoleates in solutions.

The heat of dissociation, $\Delta H_D^0$ for lanthanide linoleates have been calculated by using the following expression

$$\frac{\partial(\log K)}{\partial T} = \frac{\Delta H_D}{RT^2} \tag{15}$$

or

$$\log K = -\frac{\Delta H_D}{2.303RT} + C$$

The values of heat of dissociation, $\Delta H_D^\circ$, have been obtained from the slope of the linear plots of log $K$ Vs. $1/T$ (Figure 3) and are recorded in (Table 5). The negative values of heat of dissociation $\Delta H_D$ indicate that the dissociation process is exothermic in nature.

The value of change in free energy, $\Delta G_D^\circ$, and entropy, $\Delta S_D^\circ$ per mole for the dissociation process have been calculated by using the relationship

$$\Delta G_D = -RT \ln K_D \tag{16}$$

$$\Delta S_D = (\Delta H_D - \Delta G_D)/T \tag{17}$$

The calculated values of $\Delta G_D^\circ$ and $\Delta S_D^\circ$ are recorded in Table 6.

For the aggregation process, when counter ions are bound to a micelle, the standard free energy of micellization (per mole of monomer), $\Delta G_A^\circ$, for the phase separation model[31,32] is given by the relationship

$$\Delta G_A = 2RT \ln X_{\text{CMC}} \tag{18}$$

**Table 6** Thermodynamic parameters of lanthanide linoleate soaps (60% benzene and 40% methanol) for dissociation process

| *S. no.* | *Soap* | $\Delta G_D$ *KJ mol*$^{-1}$ | | | | $\Delta S_D \times 10^2$ *KJ mol*$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | *30°C* | *40°C* | *50°C* | *60°C* | *30°C* | *40°C* | *50°C* | *60°C* |
| 1 | Lanthanum linoleate | 11.31 | 12.06 | 12.84 | 13.46 | −7.37 | −7.38 | −7.39 | −7.35 |
| 2 | Cerium linoleate | 11.16 | 11.91 | 12.74 | 13.39 | −7.48 | −7.48 | −7.51 | −7.481 |

where $X_{CMC}$ is the CMC expressed in terms of mole fraction and is given by the relationship

$$X_{CMC} = n_s/(n_s + n_0) \tag{19}$$

where $n_s$ and $n_0$ are the number of moles of surfactants and solvent, respectively. Since the number of moles of free surfactant, $n_s$ is small as compared to the number

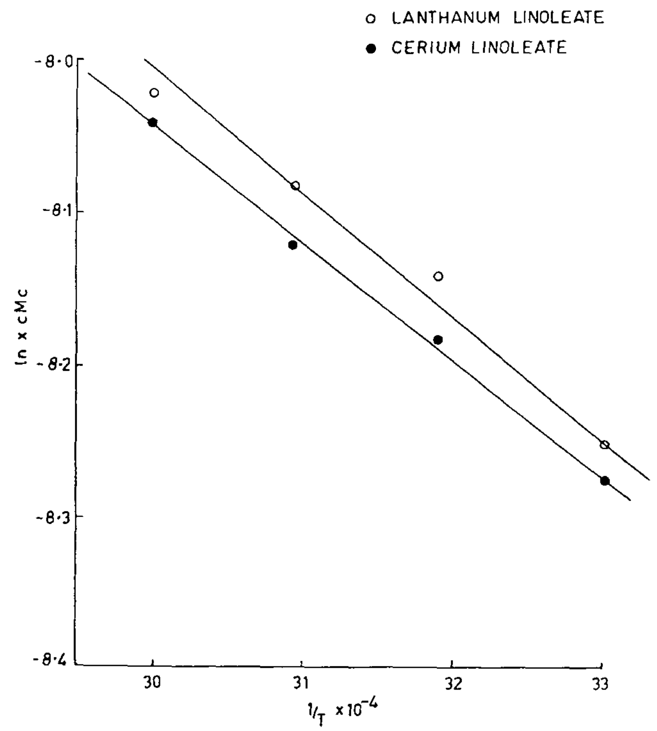

**Figure 4** 60% benzene and 40% methanol, ln $x$ CMC vs $1/T$.

**Table 7** Thermodynamic parameters of lanthanide linoleate soaps (60% benzene and 40% methanol) for micellization process

| *S. no.* | *Soap* | $\Delta G_A$ *KJ mol*$^{-1}$ | | | | $\Delta S_A \times 10^3$ *KJ mol*$^{-1}$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | *30°C* | *40°C* | *50°C* | *60°C* | *30°C* | *40°C* | *50°C* | *60°C* |
| 1 | Lanthanum linoleate | −13.88 | −14.15 | −14.49 | −14.84 | 10.79 | 11.31 | 12.01 | 12.70 |
| 2 | Cerium linoleate | −13.92 | −14.22 | −14.56 | −14.87 | 13.43 | 13.96 | 14.58 | 15.08 |

of moles of solvent, $n_0$ it follows that

$$X_{\mathrm{CMC}} = n_s/n_0 \tag{20}$$

The standard enthalpy change of micellization per mole of monomer for the phase separation model[31,32] $\Delta H_A$ is given by the relationship;

$$\frac{\partial(\ln X_{\mathrm{CMC}})}{\partial T} = -\frac{\Delta H}{2RT^2} \tag{21}$$

$$\ln X_{\mathrm{CMC}} = \frac{\Delta H_A}{2RT} + C$$

The values of $\Delta H_A$ of lanthanide linoleates have been obtained from the slope of linear plots of ln $X_{\mathrm{CMC}}$ Vs. $1/T$ (Figure 4) and are recorded in Table 5.

A careful scrutiny of the thermodynamic parameters indicates that negative values of $\Delta G^\circ$ and positive values of $\Delta S^\circ$ for the micellization process (Table 7) and positive values of $\Delta G^\circ$ and negative values of $\Delta S^\circ$ for the dissociation process (Table 6), that the association process is favoured over the dissociation process.

The results of ultrasonic velocity show that the lanthanum and cerium linoleates behave as weak electrolytes in 60% benzene and 40% methanol (V/V). These results also confirm that there is a significant interaction between soap and solvent molecules and the values of various acoustic parameters are in agreement with the results of other workers[25–30]. The conductivity results show that the thermodynamics of dissociation and association can satisfactorily be explained in the light of phase separation model. These results showed that the micellization process is predominant over the dissociation process and lanthanum and cerium linoleates behaved as a weak electrolyte in mixed organic solvents.

### *Acknowledgements*

Financial support for this work by Council of Scientific and Industrial Research (CSIR), India is gratefully acknowledged. The author wishes to express his sincere thanks to Prof. K. N. Mehrotra, Dr. Pritam Singh and Dr. Archana Vyas for valuable suggestions and encouragement.

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