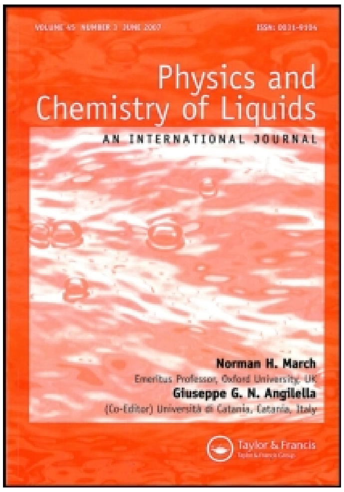

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CONDUCTOMETRIC, VISCOMETRIC AND ACOUSTICAL STUDIES ON GADOLINIUM CAPRYLATE AND CAPRATE IN NON-AQUEOUS MEDIUM

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The conductivity results showed that the gadolinium caprylate and caprate behave as weak electrolyte in dilute solutions (50% benzene + 50% methanol mixture v/v) below the critical micellar concentration and the micellization process of these soaps has been found to be predominant over the dissociation process. The viscosity results were interpreted in the light of some well known equations in order to determine the various constants and soap-solvent interaction. These results confirmed that the soap molecules do not aggregate below the CMC and there was a sudden change in the aggregation at the CMC. The ultrasonic velocity has been measured in non-aqueous solutions of gadolinium caprylate and caprate at different temperatures. The ultrasonic results were discussed in terms of different theories of propagation of ultrasonic waves. Jacobson's model was used to evaluate the various acoustic parameters and the effect of temperature on these parameters has also been studied.

KEY WORDS: Critical micellar concentration, phase-separation model, electrokinetic forces.

INTRODUCTION

A survey of literature[1–10] reveals that the physico-chemical properties and structure of rare-earth metal soaps have not yet been thoroughly investigated inspite of their considerable industrial applications. The study of metallic soaps in becoming increasingly important in technological as well as in academic fields. It has been a subject of intense investigation in the recent past on account of its role in such diversified fields as detergents, softeners, lubricants, plasticizers, stabilizers, catalysts, cosmetics, medicines, emulsifiers and water-proofing agents. However, the technological applications of these metallic soaps is based mostly on empirical know-how and the selection of a soap is dependent largely on economic factors.

In recent years, ultrasonic waves have acquired the status of an important probe, for the study of structure and properties of matter[11]. In the field of technology, the waves are being used for the detection of flows, testing of materials and mechanical cleaning of surfaces etc. In basic science they are used to provide information about the behaviour of microscopic particles of matter. Through the high order elastic constants of these waves, one gets an insight into the interaction in the solids. The absorption and dispersion of ultrasonic waves provides information on the relaxation processes and molecular interaction in liquids [12–14]. The ultrasonic velocities and the derived excess parameters can be used to determine the relative strength of homo- and hetero-molecular interactions in binary liquid mixtures[13]. All this type of information is very important for understanding the nature of the solute in liquids.

The present work deals with the conductivity, viscosity and acoustical studies of gadolinium caprylate and caprate in benzene-methanol mixture (50% v/v) at different temperatures.

EXPERIMENTAL

Gadolinium caprylate and caprate were prepared by the direct metathesis of corresponding potassium soaps with the required amount of gadolinium oxide in water-alcohol medium. The white precipitated soaps were washed with double distilled water and acetone to remove the excess of gadolinium ions and unreacted caprylic and capric acids. The purity of these salts was checked by the elemental analysis and IR and the results were found in good agreement with the theoretically calculated values. The reproducibility of the results was confirmed by preparing two samples of same salt under similar conditions. The purified gadolinium caprylate and caprate have the following melting points.

Gadolinium caprylate	110.0°C
Gadolinium caprate	115.0°C

The conductivity of the solutions of gadolinium caprylate and caprate in benzene-methanol mixture (50% v/v) was measured with the help of Systronics conductivity bridge 305 (SR No. 993) with a dipping type conductivity cell (Cell constant 1.6) at 35°, 40°, 45° and 50°C. The reproducibility (± 0.1%) of the measurements were examined by repeating the experiments several times.

Ostwald's type viscometer was used for measuring the viscosity of the solutions of gadolinium caprylate and caprate. The densities of the solutions were determined with a pyknometer calibrated with pure benzene.

The ultrasonic results were obtained on a multifrequency ultrasonic interferometer (MX-3, Mittal Enterprises, New Delhi) at different temperatures using a crystal of frequency 1 MHz. The uncertainty of velocity measurements is 0.2%.

RESULTS AND DISCUSSION

(i) *Conductometric Studies*

The specific conductance, k (Figure 1) of the solutions of gadolinium caprylate and caprate increases with an increase in concentration. The increase in specific conductance may be due to the fact that gadolinium caprylate and caprate behave as simple electrolyte in dilute solutions and are ionised to a considerable extent into gadolinium cations and caprylic and capric acid anions which increase the number of ions per unit volume of solutions. The increase in specific conductance is not very sharp because of

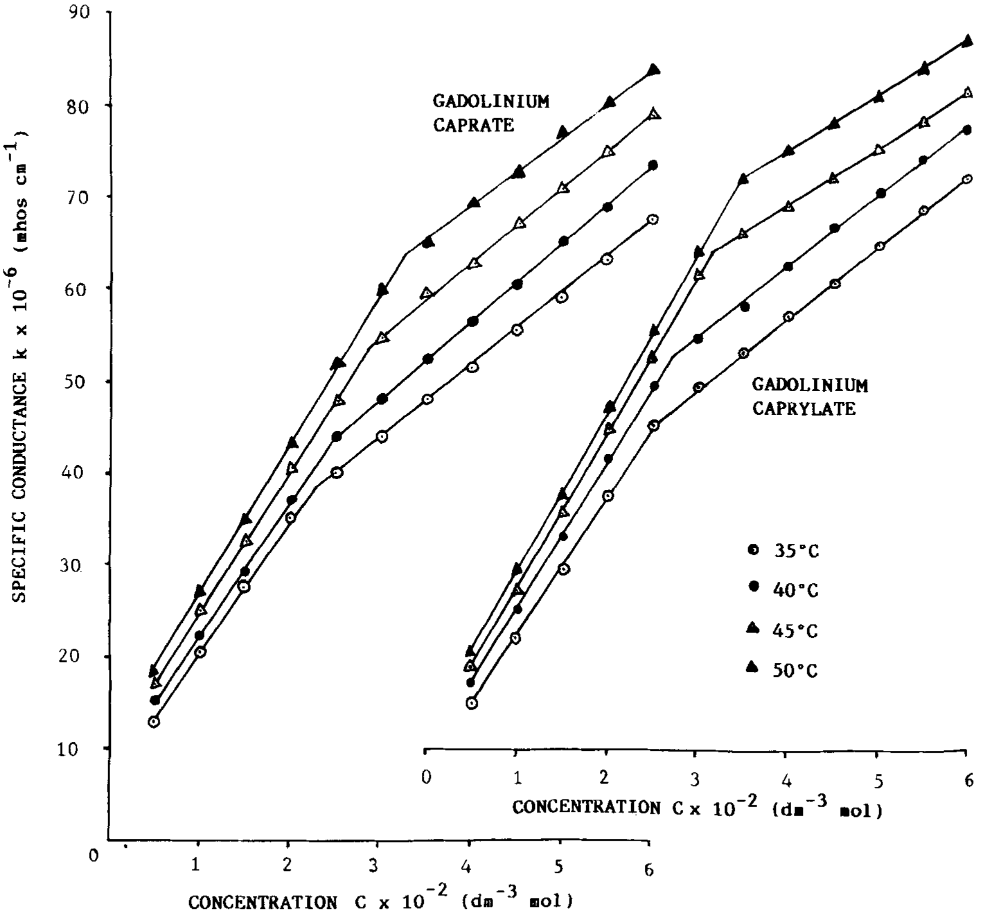

Figure 1 Specific conductance Vs Concentration 50% Benzene + 50% Methanol.

the changing partial ionization of the gadolinium caprylate and caprate below the *CMC* and consequently the conductance do not go up so rapidly like strong electrolytes. The plots of specific conductance Vs. concentration (Figure 1) are characterised by an intersection of two straight lines at critical micellar concentration (*CMC*) which indicates that the caprylate and caprate anions begin to aggregate together to form ionic micelles. Micelle formation in benzene-methanol mixture can be accounted for due to the hydrophobic character of the solute-solvent system and also due to dielectric constant of solvent, both these factors are responsible for various interactions in soap-solvent system and thus micelle formation. However, the results show that the increase in temperature shift the *CMC* to higher concentration (Table 1), because the process of micellization is assumed to occur when the energy released as a results of 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

Table 1 Criticle micellar concentration (*CMC*) limiting molar conductance (μ_o) and dissociation constant (K_D) of Gadolinium Caprylate and Caprate in Benzene-Methanol mixture (50% v/v).

	Gadolinium Caprylate			
Temperature °C	*35*	*40*	*45*	*50*
Critical micellar concentration CMC $\times 10^{-2}$ dm^{-3} mol	2.50	2.70	3.10	3.50
Limiting molar conductance, μ_o	4.8	5.4	6.2	6.6
Dissociation constant $K_D \times 10^{-4}$	2.40	1.82	1.48	1.12

	Gadolinium Caprate			
Temperature °C	*35*	*40*	*45*	*50*
Critical micellar concentration CMC $\times 10^{-2}$ dm^{-3} mol	2.25	2.50	2.80	3.25
Limiting molar conductance, μ_o	3.9	4.4	5.0	5.7
Dissociation constant $K_D \times 10^{-4}$	3.72	2.24	1.74	1.35

entropy accompanying aggregation. Therefore, increase in temperature would have been expected to shift the *CMC* values to higher concentration since the kindtic energy of the monomers would have been raised. Unlike the specific conductance the molar conductance, μ of the dilute solutions of gadolinum caprylate and caprate increases with dilution. The reason for this is that the decrease in specific conductance is more than compensated by the increase in the value of $1/C$ on dilution and hence molar conductance, μ goes up. The critical micellar concentration (*CMC*) can not be, however, obtained from the plots of molar conductance Vs square root of soap concentration, which are concave upwards with increasing slopes indicating that the Debye-Hückel Onsager's equation is not applicable to these solutions. Since below the critical micellar concentration (*CMC*) gadolinium caprylate and caprate behave like weak electrolyte in benzene-methanol mixture, the expression for their dissociation may be derived[15].

$$\begin{array}{ccccc} \mathrm{Gd(RCOO)_3} & \longrightarrow & \mathrm{Gd(RCOO)^{2+}} & + & \mathrm{2RCOO^-} \\ C(1-\alpha) & & C\alpha & & 2(C\alpha) \end{array} \tag{1}$$

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

Where R is C_7H_{15} and C_9H_{19} for caprylate and caprate, respectively and α and K are the degree of dissociation and dissociation constant. Since α in such systems is very

Table 2 Heat of Dissociation and Micellization of Gadolinium Caprylate and Caprate in 50% Benzene and 50% Methanol (v/v).

Soap	*Heat of dissociation* ΔH_D KJ mol^{-1}	*Heat of micellization* ΔH_m KJ mol^{-1}
Gadolinium Caprylate	-23.97	52.73
Gadolinium Caprate	-30.85	47.94

small, interionic effects may be treated as negligible. Thus considering α as μ/μ_0 and rearranging the Eq. (2) we get the following relationship.

$$\mu^2C^2 = \frac{K\mu_0^3}{4\mu} - \frac{K\mu_0^2}{4} \tag{3}$$

Where μ is the molar conductance at finite concentration and μ_0 is the limiting molar conductance at infinite dilution. The plots of μ^2C^2 Vs $1/\mu$ are linear below the *CMC*. However, the equation is not applicable in post micellization region as the process of aggregation takes place. The values of dissociation constant, K_D and limiting molar conductance, μ_0 have been obtained from the slope and intercept of the linear plots of μ^2C^2 Vs $1/\mu$, are mentioned in Table 1. The dissociation constant and limiting molar conductance at infinite dilution increase with increasing temperature and dielectric constant of the medium. This may be due to the increasing charge on the micelle due to easier dissociation of gadolinium caprylate and caprate. The values of heat of dissociation. ΔH_D^0 (Table 2) in benzene methanol mixture as obtained from the slope of the linear plots of $\log K_D$ Vs $1/T$ are -23.96 KJ mol^{-1} and -30.85 KJ mol^{-1} for gadolinium caprylate and caprate, respectively. The negative values of heat of dissociation, ΔH_D^0 indicate that the dissociation process of gadolinium caprate is more exothermic than gadolinium caprylate.

Table 3 Thermodynamic Parameters of Dissociation and Micellization of Gadolinium Caprylate and Caprate in 50% Benzene 50% Methanol (v/v).

		Gadolinium Caprylate		
	Dissociation process		*Micellization process*	
Temperature °C	ΔG_D^0 KJ mol^{-1}	$\Delta S_D^0 \times 10^2$ KJ mol^{-1}	ΔG_m^0 KJ mol^{-1}	$\Delta S_m^0 \times 10^2$ KJ mol^{-1}
35	10.69	-11.25	-16.87	22.60
40	11.22	-11.24	-16.95	22.26
45	11.67	-11.21	-16.85	21.88
50	12.23	-11.21	-16.79	21.52
		Gadolinium Caprate		
35	10.13	-13.31	-17.14	21.13
40	10.95	-13.35	-17.15	20.80
45	11.46	-13.31	-17.12	20.46
50	11.98	-13.26	-16.99	20.10

The free energy (Table 3) for the dissociation process, ΔG_D^0, was evaluated from the expression $\Delta G_D^0 = -RT \ln K_m$. Where K_m is the equilibrium constant for the micellization process. Thus

$$\begin{aligned}\Delta G_D^0 &= -RT \ln K_m \\ &= RT \ln K_D.\end{aligned} \tag{4}$$

Where K_D is the equilibrium constant for the process of dissociation. The entropy, ΔS_D per mole for the dissociation process (Table 3) have been evaluated by using the relationship.

$$\Delta S_D = (\Delta H_D - \Delta G_D)/T \tag{5}$$

For micellization i.e. aggregation process, when counter ions are bound to a micelle, the standard free energy change of micellization per mole of monomer, ΔG_M^0 for the phase separation model[16,17] is expressed by the relationship.

$$\Delta G_M^0 = 2RT \ln x_{CMC} \tag{6}$$

Where x_{CMC} is the *cmc* expressed in terms of mole fraction and is given by the relationship.

$$x_{CMC} = n_s/(n_s + n_0) \tag{7}$$

Where n_s and n_0 are the number of moles of solute and solvent, respectively. Since the number of moles of free solute, n_s is very small as compared to the number of moles of solvent n_0' it follows that

$$x_{CMC} = n_s/n_0 \tag{8}$$

The standard enthalpy change of micellization per mole of monomer for the phase separation model[16,17], ΔH_m is given by the relationship.

$$\frac{\partial(\ln x_{CMC})}{\partial T} = \frac{\Delta H_m}{2RT^2}$$

$$\ln x_{CMC} = \frac{\Delta H_m}{2RT} + C \tag{9}$$

The values of ΔH_m^0 of gadolinium caprylate and caprate (Table 2) have been obtained from the slope of the linear plots of ln X_{CMC} Vs $1/T$.

The negative values of ΔG_m and positive values of ΔS_m for the micellization process (Table 3) and positive values of ΔG_D and negative values of ΔS_D for the dissociation process (Table 3) indicate that the micellization is favoured over the dissociation process.

It is, therefore, concluded that the thermodynamics of dissociation and micellization can satisfactorily be explained in the light of phase separation model and conductivity measurements. The results showed that the micellization process is predominant over the dissociation process and gadolinium caprylate and caprate behaved as weak electrolyte in benzene-methanol mixture (50% v/v).

ii) Viscometric Studies

The viscosity, η (millipoise) is plotted against the soap concentration, C at different temperatures (Figure 2). The plots show an intersection of two straight lines at *CMC*. Which increases with increasing temperature. These results are in good agreement with those obtained from conductivity and ultrasonic measurements.

The viscosity behaviour of gadolinium caprylate and caprate in benzene-methanol mixture (50% v/v) was analysed in the light of the following well known equations:

$$\text{(a) Einstein}^{18}\text{: } \eta_{sp} = 2.5\,\bar{V}C \qquad (10)$$

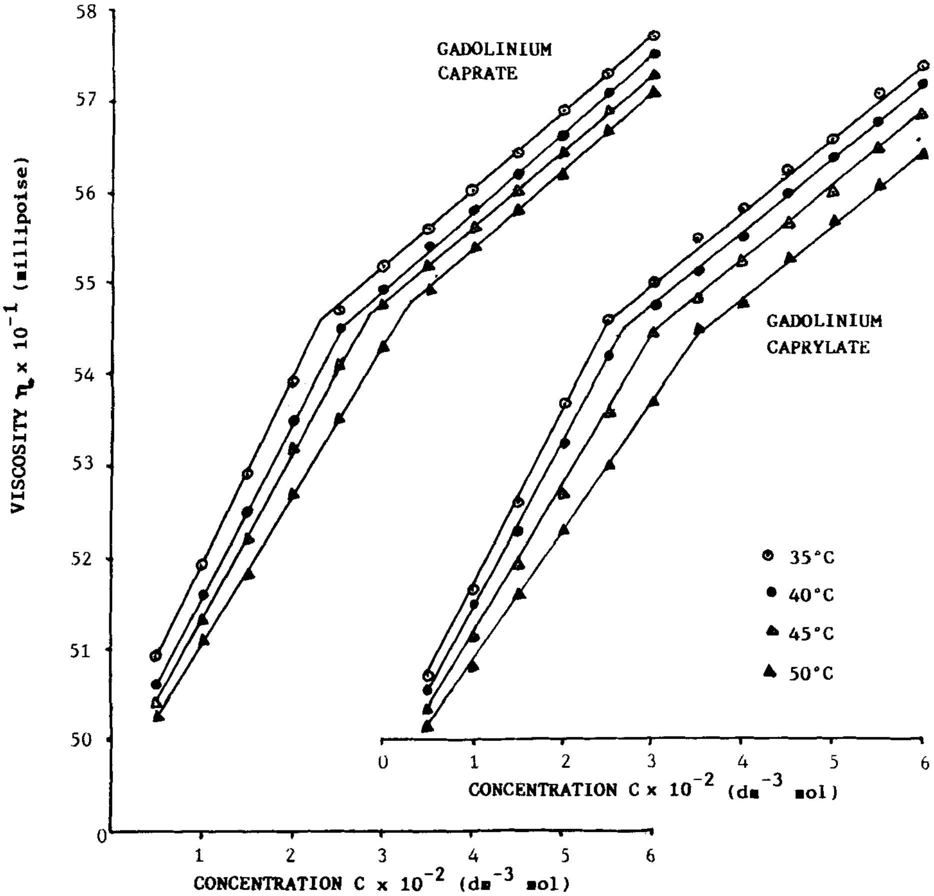

Figure 2 Viscosity Vs Concentration 50% Benzene + 50% Methanol.

Where η_{sp} and $\bar{V}$ are the specific viscosity and molar volume of the solute in $1\,mol^{-1}$ and C is the concentration in dm^{-3} mol.

$$\text{(b) Moulik}^{19}\text{: } (\eta/\eta_o)^2 = M + K'C^2 \tag{11}$$

Where M and K' are constants.

$$\text{(c) Jones-Dole}^{20}\text{: } \eta_{sp}/C^{1/2} = A + BC^{1/2} \tag{12}$$

Where the coefficients A and B refer to the soap–soap and soap–solvent interaction, respectively.

The plots of specific viscosity, η_{sp} against the soap concentration, C are linear below the *CMC* with intercept equal to zero which shows that Einstein's equation is applicable to these soap solutions. The molar volume, $\bar{V}$ of these soaps solutions calculated from the slope of the plots of η_{sp} Vs C at different temperatures are recorded in Table 4. The values of molar volume decrease with increasing temperature.

The plots of $(\eta/\eta_o)^2$ Vs C^2 are linear below the *CMC* which indicates that Moulik's equation is applicable to the solutions of gadolinium caprylate and caprate in a mixture of benzene and methanol (50% v/v), below the *CMC*. The values of the constants M and K' of Moulik's equation have been determined form the intercept and slope of the plots of $(\eta/\eta_o)^2$ Vs C^2 below the *CMC* (Table 4). These results show that the values of M and K' increase with increasing temperature.

The applicability of the Jones-Dole equation was checked by plotting $\eta_{sp}/C^{1/2}$ Vs $C^{1/2}$. The intercept and the slope of the linear plots give the values of coefficients A and B which are recorded in Table 4. The values of coefficients B (Soap–solvent interaction) are larger than the values of coefficients A (Soap–soap interaction) which confirms that the molecules of the soap do not aggregate appreciably below the *CMC* and there is a sudden change in the aggregation at the *CMC*. The values of constant B differ widely below and above the *CMC* which may be attributed to the fact that the aggregation of

Table 4 Viscosity Parameters for Gadolinium Caprylate and Caprate in 50% Benzene and 50% Methanol.

Temperature	$\bar{V}$	*M*	$K' \times 10^{-2}$	*A*	*B*
		Gadolinium Caprylate			
35	1.75	1.06	2.80	0.30	2.86
40	1.34	1.11	2.81	0.60	1.35
45	1.45	1.24	3.20	2.30	2.42
50	1.28	1.36	2.57	2.53	3.44
		Gadolinium Caprate			
35	1.76	1.05	2.46	−0.30	4.28
40	1.69	1.16	3.65	1.33	3.25
45	1.52	1.30	3.14	1.65	2.50
50	1.50	1.37	2.09	2.00	3.14

the soap molecules above the *CMC* boosts up the electrokinetic forces causing more intake of the solvent resulting in an increasing viscosity of the system. The values of constant *B* increase with the increase in the chain-length of the soap molecule.

iii) Acoustical Studies:

The ultrasonic velocity v (± 0.2%) and various acoustical and soap–solvent interaction parameters for gadolinium caprylate and caprate in benzene-methanol mixture (50% v/v) are tabulated in Table 6. The variation in ultrasonic velocity, v with concentration C follows the relationship.

$$v = vo + GC \tag{13}$$

Where vo is the ultrasonic velocity in pure solvent and G is Garnsey's constant[21].

The values of Garnsey's constant, G for gadolinium caprylate and caprate at different temperatures are mentioned in Table 5. When ultrasonic velocity $v(\pm 0.2\%)$ and adiabatic compressibility, $\beta(\pm 3.5\%)$ both plotted as a function of concentration, C show an intersection of two straight lines at a definite soap concentration. The values of the *CMC* of gadolinium caprylate and caprate are consistant with the values determined from conductivity, viscosity and density measurements. The plots of v Vs C (Figure 3) and β Vs C when extrapolated to zero soap concentration (Table 5) give the values of pure solvent which are in accordance with the experimental values, indicating that the soap molecules do not aggregate to an appreciable extent below the *CMC*.

Table 5 Values of Various Constants Obtained from Ultrasonic Studies (50% Benzene + 50% Methanol v/v).

Gadolinium Caprylate				
	Temperature °C			
	35	*40*	*45*	*50*
Garnsey's Constant $R \times 10^3$	1.40	1.50	1.50	1.40
$S_k \times 10^{-8}$	4.1	4.8	5.2	7.4
Extrapolated values of v_0 (m/sec)	1048	1040	1033	1028
Extrapolated values of $\beta_0 \times 10^{-10}$	10.28	10.42	10.55	10.65
Extrapolated values of $\phi_k^0 \times 10^{-8}$	−36.2	−37.1	−37.9	−38.6
Extrapolated values of L_f (Å)	0.649	0.658	0.661	0.664
Extrapolated values of $Z_0 \times 10^5$	9.30	9.23	9.15	9.13
Gadolinium Caprate				
Garnsey's constant $R \times 10^3$	1.80	2.00	1.75	1.67
$S_k \times 10^{-8}$	4.7	5.0	6.9	9.2
Extrapolated values of v_0 (m/sec)	1050	1040	1034	1028
Extrapolated values of $\beta_0 \times 10^{-10}$	10.21	10.38	10.50	10.60
Extrapolated values of $\phi_k^0 \times 10^{-8}$	−37.4	−37.6	−38.0	−39.0
Extrapolated values of L_f (Å)	0.650	0.655	0.658	0.661
Extrapolated values of $Z_0 \times 10^5$	9.33	9.23	9.17	9.14

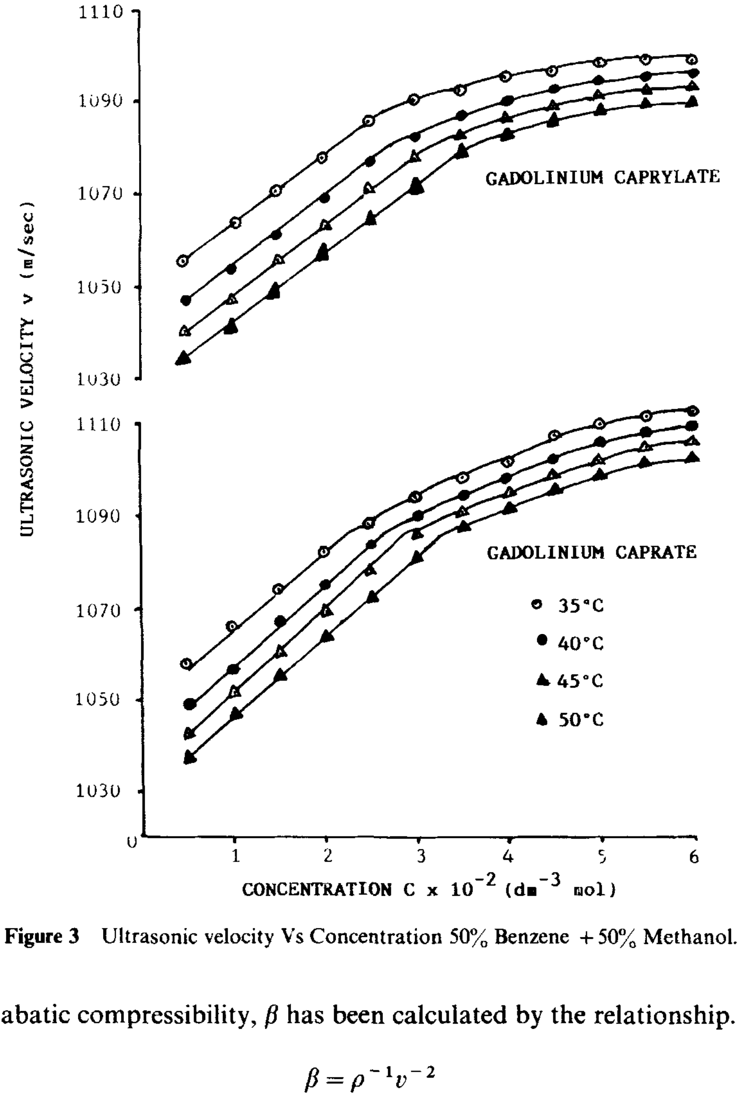

Figure 3 Ultrasonic velocity Vs Concentration 50% Benzene + 50% Methanol.

The adiabatic compressibility, β has been calculated by the relationship.

$$\beta = \rho^{-1} v^{-2} \tag{14}$$

The adiabatic compressibility of gadolinium caprylate and caprate in benzene-methanol mixture decreases with increasing concentration of salts (Table 6). The decrease in adiabatic compressibility is attributed to the fact that the gadolinium soaps in dilute solutions are considerably ionized into gadolinium cations and caprylic and capric 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 the soap solutions i.e. solutions become harder to compress[22]. The decrease in adiabatic compressibility in post-micellization region 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.

Table 6 Ultrasonic velocity and other acoustic Parameters of Gadolinium soaps in 50% Benzene + 50% Methanol (v/v) Mixture at 35 °C.

S. No.	*Concentration* $C \times 10^2$ dm^{-3} mol	*Ultrasonic Velocity* v ms^{-1}	*Adiabatic Compressibility* $\beta \times 10^{10}$ $m^2 N^{-1}$	*Intermolecular Free length* L_f(Å)	*Specific Acoustic Impedance* $Z \times 10^{-5}$ $kg m^{-2} S^{-1}$	*Apparant molar Volumes* (ϕ_v) $m kg^{-1} S^2$	*Apparant Compressibility* $\phi_k \times 10^8$ $m^5 N^{-1}(K mol)$	*Rao's Number* $(R \times 10^{-3})$	*Relative association* (R_A)	*Solvation Number* (S_n)	*Available Volume* (Va)
Gadolinium Caprylate											
1.	0.5	1056.2	10.085	0.6445	9.388	226.77	−42.7	16.031	0.9919	24.34	115.27
2.	1.0	1063.5	9.942	0.6397	9.458	238.03	−35.7	16.061	0.9844	11.88	113.67
3.	1.5	1071.1	9.795	0.6355	9.530	234.28	−34.1	16.091	0.9780	7.16	111.99
4.	2.0	1078.3	9.661	0.6309	9.599	238.08	−32.5	16.118	0.9711	4.83	110.42
5.	2.5	1085.6	9.526	0.6267	9.669	235.78	−31.7	16.146	0.9664	3.42	108.82
6.	3.0	1090.6	9.437	0.6234	9.716	245.54	−29.3	16.167	0.9612	2.60	107.73
7.	3.5	1093.1	9.391	0.6221	9.740	252.51	−26.3	16.175	0.9577	2.12	107.18
8.	4.0	1095.7	9.345	0.6203	9.765	257.73	−23.9	16.185	0.9544	1.76	106.20
9.	4.5	1097.5	9.312	0.6193	9.784	261.80	−21.8	16.190	0.9499	1.50	106.07
10.	5.0	1098.0	9.302	0.6190	9.790	265.05	−19.5	16.189	0.9484	1.33	106.07
11.	5.5	1098.8	9.286	0.6185	9.800	267.71	−17.9	16.189	0.9468	1.18	105.88
12.	6.0	1098.8	9.285	0.6185	9.802	271.80	−16.2	16.187	0.9467	1.07	105.87
Godolinium Caprate 35°C											
1.	0.5	1058.1	10.046	0.6434	9.407	81.32	−36.1	9.164	0.9919	5.18	65.62
2.	1.0	1066.7	9.878	0.6380	9.488	92.57	−36.5	9.184	0.9814	5.25	64.55
3.	1.5	1074.2	9.732	0.6333	9.560	88.82	−35.0	9.201	0.9780	5.04	63.61
4.	2.0	1082.5	9.574	0.6281	9.639	86.95	−35.0	9.219	0.9711	5.03	62.57
5.	2.5	1088.1	9.476	0.6249	9.692	94.82	−32.1	9.232	0.9664	4.64	61.87
6.	3.0	1094.3	9.369	0.6214	9.750	103.83	−30.5	9.247	0.9612	4.43	61.11
7.	3.5	1098.5	9.298	0.6190	9.789	110.26	−28.3	9.257	0.9577	4.12	60.59
8.	4.0	1102.5	9.230	0.6167	9.827	115.08	−26.5	9.266	0.9544	3.87	60.09
9.	4.5	1108.0	9.131	0.6134	9.878	118.83	−25.9	9.280	0.9499	3.77	59.41
10.	5.0	1110.0	9.098	0.6123	9.898	121.83	−23.9	9.283	0.9484	3.51	59.16
11.	5.5	1112.1	9.063	0.6111	9.919	124.29	−22.4	9.287	0.9468	3.30	58.89
12.	6.0	1112.5	0.057	0.6109	9.925	126.33	−20.5	9.286	0.9467	3.04	58.83

The values of apparent molar compressibility, ϕ_k (Table 6) at different soap concentration have been calculated by the following relationship.

$$\phi_k = \frac{10^3(\beta - \beta_o)}{Cp_o} + \beta\phi_v \tag{15}$$

Where β, β_o, p_o, C and ϕ_v are the adiabatic compressibility of the solution, adiabatic compressibility of the solvent, density of the solvent, soap concentration and apparent molar volume of the solution respectively.

From the Debye-Hückel theory it follows that the apparent molar compressibility, ϕ_k is related to the molar concentration of soap C by

$$\phi_k = \phi_k^0 + S_k C^{1/2} \tag{16}$$

The values of limiting apparent molar compressibility ϕ_k^0 and constant S_k have been evaluated (Table 5) from the intercept and slope of the plots of ϕ_k vs $C^{1/2}$ below the CMC and compared with the results of different electrolytes.[23,24] The plots are also characterized by a break at the CMC. The positive values of S_k signify a considerable soap–solvent interaction below the CMC. The negative values of apparent molar compressibility decrease linearly with concentration in pre-micellization region, but this decrease is sharp in pre-micellization region as compared to post-micellization region, indicating the poor compressibility may be due to the decreasing internal pressure.

The intermolecular free length[25] (L_f) and specific acoustic impedance[26] (Z) have been calculated using the relationships:

$$L_f = K\sqrt{\beta} \tag{17}$$

$$Z = pv \tag{18}$$

where K is the temperature-dependent Jacobson's constant. The decrease in the values of the intermolecular free length L_f ($\pm 0.2\%$) (Table 6) and increase in the values of specific acoustic impedance Z ($\pm 2.2\%$) with increasing concentration of gadolinium caprylate and caprate can be explained on the basis of hydrophobic interaction between salts and solvent molecules, which increases the intermolecular distance, leaving a relatively wider gap between the molecules and thus becoming the main source of impediment to the propagation of ultrasound waves.

The solvation number[27] (S_n) and relative association[18] (R_A) of gadolinium caprylate and caprate (Table 6) have been determined by the relationships:

$$S_n = \frac{n_1}{n_2}\left(1 - \frac{\beta}{\beta_o}\right) \tag{19}$$

$$R_A = \frac{p}{p_o}\left(\frac{v_o}{v}\right) \tag{20}$$

Where $n_1, n_2; p_o\ p; \beta_o\ \beta; v_o, v$ are the number of moles, density, adiabatic compressibility and ultrasonic velocity of solvent and solutions, respectively. The values of solvation number and relative association (Table 6) decrease with increasing soap concentration. However the values of solvation number increase while relative association decrease with increasing temperature.

The values of solvation number, S_n correspond to the number of solvent molecules in the primary solvation sheaths of the ions. On account of electrostriction, molecules in the primary 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 decrease in the values of relative association, R_A has been attributed either to the decreased association between salt and organic solvent molecules at higher concentration or decreasing solvation of ions. The values of apparent molar volume increase while the values of available volume decrease with increasing concentration. The values of apparent molar volume and available volume increase with increasing temperature. The plots of apparent molar volume, ϕ_v Vs square root of soap concentration, $C^{1/2}$ and available volume, Va Vs concentration C are characterized by the break at the *CMC*.

The results of conductivity, viscosity and ultrasonic studies indicate that the godolinium caprylate and caprate behave as weak electrolytes in benzene-methanol mixtures. These results have been interpreted in the light of some well known equations indicating that there is a significant interaction between soap and solvent molecules.

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