Ultrasonic Measurements on Nonaqueous Solutions of Samarium Soaps

Mithlesh Chauhan

Department of Chemistry, Institute of Basic Sciences, Khandari Road, Agra 282 004, India

Ultrasonic measurements on solutions of samarium soaps (pentanoate, hexanoate, octanoate, and decanoate) in a mixture of 60% volume benzene + 40% volume methanol show that the value of the critical micellar concentration (cmc) decreases with increasing chain length of the fatty acid constituent of the soap molecule. The values of the critical micellar concentration agree with values obtained from other micellar properties. The results suggest that there is a significant interaction between soap and solvent molecules in dilute solutions, and soap molecules do not aggregate appreciably in dilute solutions.

Introduction

The complimentary use of ultrasonic measurements can provide interesting information on the specificities of the ion–solvent interaction related to the structure of the solute and on the reciprocal effects which arise in the solvents. However, the studies on ultrasonic measurements of the soap solutions have not drawn adequate attention, although such a study is likely to give more information on the soap–solvent interaction. A number of researchers (*1–8*) have used the ultrasonic measurements for the determination of the ion–solvent interaction, and the results were found to be in agreement with those computed by other techniques.

The present work is supplementary to previous papers on the structure of soap molecules in the solid state (*9*) and the conductivity (*10*) and viscosity (*11*) of nonaqueous solutions of samarium soaps. The ultrasonic measurements furnish extra information on ion–solvent interactions and the micellar behavior of these solutions. The results have been used to determine the critical micellar concentration, the soap–solvent interaction, and various acoustic parameters and to study the effect of the soap concentration and chain length of the fatty acid constituent of the soap molecule on the various acoustic parameters.

Experimental Section

All the chemicals used were of analytical reagent (E. Merck) grade. Samarium soaps (pentanoate, hexanoate, octanoate, and decanoate) were prepared and purified as described in our papers (*10–12*). The purity of the soaps was confirmed by their infrared spectra, elemental analysis, and melting points. The absence of the hydroxyl group was confirmed by infrared spectra. The melting points of samarium pentanoate, hexanoate, octanoate, and decanoate were 89, 95, 102, and 105 °C, respectively. The results of elemental analysis were in close agreement with the calculated values (Table I).

The solutions of samarium soaps were prepared by dissolving a known mass of soap in the required volume of solvent. In this way, a number of solutions containing different concentrations of samarium soaps in benzene–methanol mixtures were prepared and kept at a constant temperature for about 1 h in a thermostat. A multifrequency ultrasonic interferometer (M-83, Mittal Enterprises, New Delhi), operating at a frequency of 4 MHz, was used to measure the ultrasonic speed of samarium soap solutions at a constant temperature of 40 ± 0.05 °C. The maximum uncertainty of speed results was ±0.2%. The densities of solvent and samarium soap solutions were measured by an Ostwald pycnometer. The capacity of the pycnometer was 12 mL.

Table I. Analytical Data of Samarium Soaps (mass %)

	C		H	
soap	found	calcd	found	calcd
samarium pentanoate	13.27	13.22	1.97	1.98
samarium hexanoate	14.51	14.52	2.22	2.22
samarium octanoate	16.51	16.55	2.58	2.59
samarium decanoate	18.10	18.07	2.86	2.86

Calculations

The various acoustic parameters, viz., adiabatic compressibility (β), intermolecular free length (L_f), specific acoustic impedance (Z), apparent molal compressibility (ϕ_k), apparent molal volume (ϕ_v), molar sound speed (R), and solvation number (S_n), have been evaluated by using the following relationships:

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

$$L_f = K(\beta)^{1/2} \tag{2}$$

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

$$\phi_k = (1000/C\rho_o)(\rho_o\beta - \beta_o\rho) + \beta_o M/\rho_o \tag{4}$$

$$\phi_v = (1000/C\rho_o)(\rho_o - \rho) + M/\rho_o \tag{5}$$

$$R = (M/\rho)v^{1/3} \tag{6}$$

$$M = \frac{n_o M_o + nM}{n_o + n}$$

$$S_n = (n_o/n)[1 - V\beta/(n_o V_o \beta_o)] \tag{7}$$

where ρ_o, ρ; β_o, β; V_o, V; n_o, n; and M_o, M are the density, adiabatic compressibility, molar volume, number of moles, and molecular weight of solvent and soap solution, respectively, and v, K, and C are the ultrasonic speed of solution, Jacobson's constant, and concentration of soap solution (mol dm^{-3}), respectively.

Results and Discussion

The ultrasonic speed for the solutions of samarium soaps increases with increasing concentration and chain length of the soap (Tables II and III). The variation of the ultrasonic speed with concentration depends upon the concentration derivatives of density, ρ, and compressibility, β, and can be expressed as

$$\frac{dv}{dC} = -\frac{v}{2}\left[\frac{\delta\rho/\delta C}{\rho} + \frac{\delta\beta/\delta C}{\beta}\right] \tag{8}$$

The results (Tables II and III) indicate that the density increases whereas adiabatic compressibility decreases with

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Table II. Ultrasonic Speed v, Density ρ, Adiabatic Compressibility β, Intermolecular Free Length L_f, Specific Acoustic Impedance Z, Apparent Molal Compressibility ϕ_k, Apparent Molar Volume ϕ_v, Molar Sound Velocity R, and Solvation Number S_n for Various Concentrations C of Samarium Pentanoate in 60 vol % Benzene + 40 vol % Methanol at 40 ± 0.05 °C

C/(mol dm^{-3})	ρ/(kg m^{-3})	$10^{-3}v$/(m s^{-1})	$10^9\beta$/(m^2 N^{-1})	$10L_f$/m	10^2Z/(kg m^2 s^{-1})	$-10^6\phi_k$/(m^2 N^{-1})	$10^3\phi_v$/(m^3 mol^{-1})	R/(m s^{-1})	S_n
0.01	0.8307	1.133	9.378	6.217	9.412	1.995	462.37	29.66	41.5
0.02	0.8311	1.153	9.051	6.108	9.583	2.398	480.44	29.96	48.6
0.03	0.8316	1.172	8.754	6.001	9.746	2.429	482.45	30.25	49.2
0.04	0.8324	1.190	8.483	5.913	9.906	2.391	474.42	30.48	48.5
0.05	0.8340	1.206	8.244	5.829	10.058	2.323	450.32	30.75	46.9
0.06	0.8362	1.224	7.982	5.736	10.235	2.327	422.21	30.96	46.5
0.07	0.8382	1.238	7.784	5.664	10.377	2.235	405.57	31.14	44.7
0.08	0.8404	1.250	7.615	5.603	10.505	2.133	390.08	31.31	42.7
0.09	0.8424	1.264	7.430	5.534	10.648	2.096	380.71	31.50	41.5
0.10	0.8442	1.277	7.264	5.472	10.784	1.997	375.63	31.69	40.1

Table III. Ultrasonic Speed v, Density ρ, Adiabatic Compressibility β, Intermolecular Free Length L_f, Specific Acoustic Impedance Z, Apparent Molal Compressibility ϕ_k, Apparent Molal Volume ϕ_v, Molar Sound Velocity R, and Solvation Number S_n for Various Concentrations C of Samarium Hexanoate in 60 vol % Benzene + 40 vol % Methanol at 40 ± 0.05 °C

C/(mol dm^{-3})	ρ/(kg m^{-3})	$10^{-3}v$(m s^{-1})	$10^9\beta$/(m^2 N^{-1})	$10L_f$/m	10^2Z/(kg m^{-2} s^{-1})	$-10^6\phi_k$/(m^2 N^{-1})	$10^3\phi_v$(m^3 mol^{-1})	R/(m s^{-1})	S_n
0.01	0.8310	1.140	9.260	6.178	9.473	3.210	476.93	29.72	61.6
0.02	0.8318	1.163	8.888	6.053	9.674	3.248	488.98	30.05	62.5
0.03	0.8326	1.186	8.539	5.932	9.875	3.184	492.92	30.38	61.5
0.04	0.8344	1.208	8.213	5.818	10.080	3.124	464.88	30.66	60.0
0.05	0.8364	1.230	7.903	5.707	10.288	3.060	443.19	30.93	58.4
0.06	0.8388	1.252	7.606	5.599	10.502	3.004	420.70	31.19	57.2
0.07	0.8406	1.267	7.411	5.527	10.650	2.808	414.97	31.40	53.8
0.08	0.8428	1.285	7.186	5.442	10.830	2.704	404.64	31.63	51.8
0.09	0.8448	1.300	7.004	5.373	10.982	2.573	399.28	31.84	49.5
0.10	0.8470	1.317	6.807	5.297	11.155	2.486	392.59	32.06	47.9

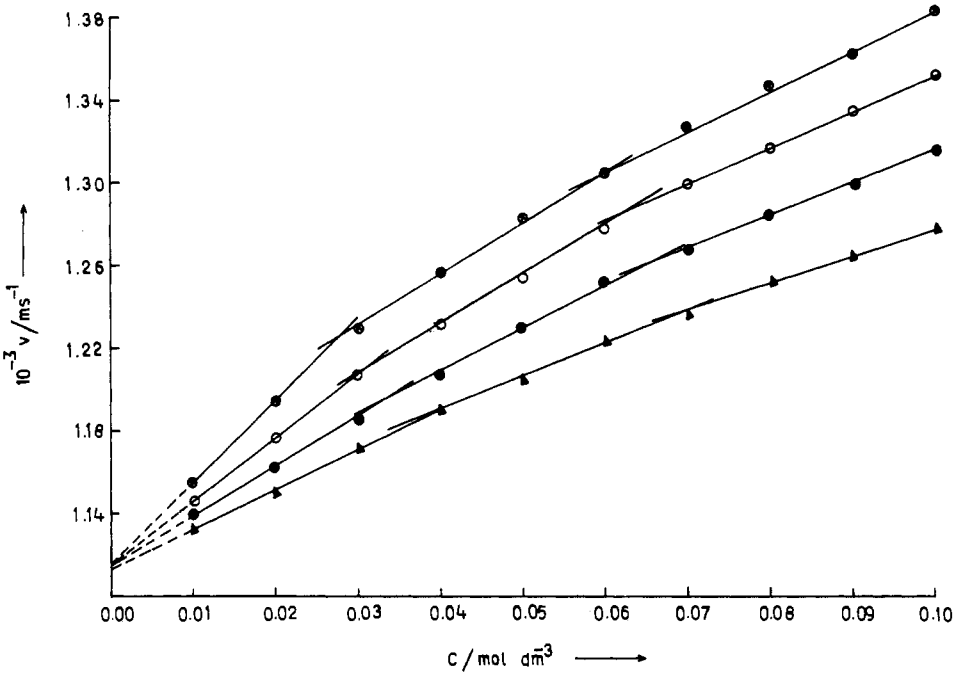

Figure 1. Ultrasonic speed v as a function of concentration C for various samarium soaps: pentanoate, hexanoate, octanoate, and decanoate.

increasing soap concentration. Therefore, the concentration derivative of density, $d\rho/dC$, is positive while the concentration derivative of compressibility, $d\beta/dC$, is negative. Since the quantity $d\beta/dC$ predominates over $d\rho/dC$ for soap solutions, the concentration derivative of speed, dv/dC, will be positive and so the speed increases with increasing soap concentration. The variation in ultrasonic speed, v, with soap concentration, C, follows the relationship

$$v = v_0 + GC \tag{9}$$

where v_0 is the ultrasonic speed in pure solvent and G is Garnsey's constant (*13*). Both ultrasonic speed v and adiabatic compressibility β, when plotted as a function of soap concentration C, show breaks at definite soap concentrations which correspond to the critical micellar concentrations I and II of samarium soaps (Figure 1). The values of the critical micellar concentration are constant with previous results obtained from conductivity (*10*) and viscosity measurements. The plots of ultrasonic speed (Figure 1) and adiabatic compressibility against concentration when extrapolated to zero soap concentration give values in accordance with the experimental values (Table IV), indicating that the soap molecules do not aggregate to an appreciable extent below the critical micellar concentration. The slopes of the plots of ultrasonic speed against concentration have been used to determine the values of Garnsey's constant, G, which increases with increasing chain length of the soap molecule.

Table IV. Values of Critical Micellar Concentrations I and II, Extrapolated and Experimental Values of Pure Solvent v_o, Garnsey's Constant G, Constants A and B (Equation 10), Limiting Apparent Molal Compressibility $\phi_k°$, and Limiting Apparent Molal Volume $\phi_v°$ for Samarium Soaps in 60 vol % Benzene and 40 vol % Methanol at 40 ± 0.05 °C

compound	cmc/(mol dm^{-3}) I	cmc/(mol dm^{-3}) II	$10^{-3}v_o{}^a$/(m s^{-1})	$10^{-3}v_o{}^b$/(m s^{-1})	$10^{-3}G$/(m^2 mol^{-1} s^{-1})	-10^9A/(m^3 N^{-1} mol^{-1})	-10^9B/(m^2 N^{-1})	$-10^6\phi_k°$/(m^2 N^{-1})	$10^3\phi_v$/(m^3 mol^{-1})
samarium pentanoate	0.038	0.069	1.114	1.119	2.18	13.3	62.2	1.40	430
samarium hexanoate	0.033	0.065	1.116	1.119	2.50	36.3	75.8	3.20	458
samarium octanoate	0.030	0.063	1.116	1.119	3.43	43.0	100.0	4.20	496
samarium decanoate	0.028	0.060	1.116	1.119	4.00	63.0	150.0	6.20	528

[a] Extrapolated. [b] Experimental.

Table V. Values of Limiting Apparent Molal Compressibility $\phi_k°$ (Equation 11), Constant S_k (Equation 11), and Solvation Number S_n (Equation 7)

electrolyte	$-\phi_k° \times 10^8$/(m^2 N^{-1})	$S_k \times 10^8$/(m^3 N^{-1} mol^{-1})	S_n	temp/°C	ref
samarium pentanoate	0.014	0.40	40–49	40	Talbe IV
samarium hexanoate	0.032	0.30	50–63	40	Table IV
samarium octanoate	0.042	0.20	54–81	40	Table IV
samarium decanoate	0.062	1.00	60–104	40	Table IV
barium butyrate	0.021	0.03	8.5–16.1	40	19
strontium butyrate	0.026	0.07	8.2–23.7	40	19
calcium dodecanoate	0.860			40	16
calcium decanoate	0.790			40	16
lanthanum decanoate	1.420		40.5–48.9	40	8
lanthanum dodecanoate	2.100		59.5–63.8	40	8
cobalt acetate		0.01	28.5	25	17
strontium nitrate		0.02		30	18
barium chloride		0.03		25	14
strontium carbonate		0.05		25	14
barium bromide			15.4		17

The adiabatic compressibility β of these soap solutions is found to obey Bachem's relationship (*14*):

$$\beta = \beta^o + AC + BC^{3/2} \quad (10)$$

where A and B are constants. The values of constants A and B (Table IV) have been obtained from the intercept and the slope of the plots of $\beta - \beta_o/C$ against $C^{1/2}$. The adiabatic compressibility of dilute solutions of samarium soaps decreases with increasing concentration and chain length of the soap. The conductance results show that the samarium soaps behave as weak electrolytes in nonaqueous solvent and ionize into simple metal ions Sm^{3+} and fatty acid anions $RCOO^-$ (where R is C_4H_9, C_5H_{11}, C_7H_{15}, and C_9H_{19} for pentanoate, hexanoate, octanoate, and decanoate, respectively). The decrease in adiabatic compressibility might be due to the fact that the ions in solutions are surrounded by a layer of solvent molecules firmly bound and oriented toward ions. The orientation of the solvent molecules around the ions may be due to the influence of the electrostatic field of ions and results in internal pressure and in lowering of the compressibility of the solutions, i.e., the solutions become harder to compress (*15*).

The apparent molal properties are found to be dependent on the concentration of the solutions. The apparent molal compressibility ϕ_k can be expressed by eq 4.

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

$$\phi_k = \phi_k° + S_kC^{1/2} \quad (11)$$

where $\phi_k°$ is the limiting apparent molal compressibility and S_k is a constant. The values of $\phi_k°$ and S_k have been evaluated (Table V) from the intercept and slope of the linear parts of the plots of ϕ_k against $C^{1/2}$ (Figure 2) at lower concentrations and compared with the results of different electrolytes (*8, 14, 16–19*). The positive values of S_k signify a considerable soap–solvent interaction in dilute soap solutions. The value of $\phi_k°$ are found to increase with the increase in the chain length of the soap molecule.

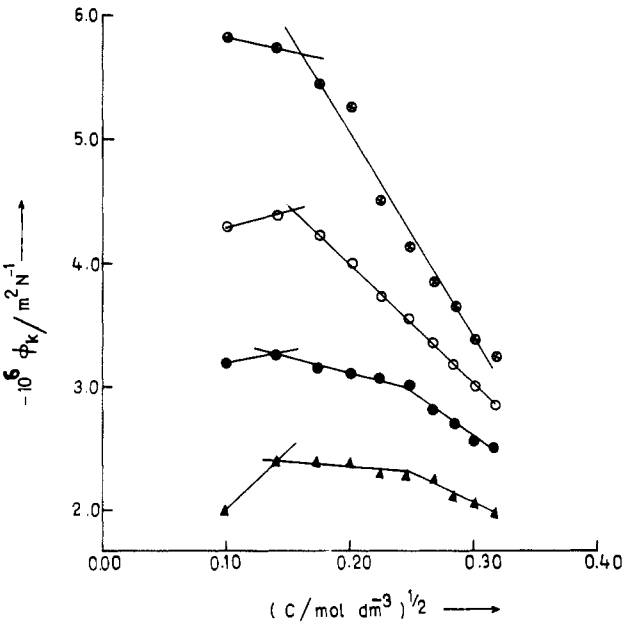

Figure 2. Apparent molal compressibility ϕ_k as a function of the square root of concentration $C^{1/2}$ for various samarium soaps: pentanoate, hexanoate, octanoate, and decanoate.

The apparent molal volume, ϕ_v, is related to the molar concentration of soap C by eq 5. The plots of ϕ_v against $C^{1/2}$ are characterized by a break at a definite soap concentration. The values of the limiting apparent molal volume, $\phi_v°$, have been obtained from the intercept of the plots and are found to increase with the increase in the chain length of the soap molecule (Table IV). Pasynskii (*20*) defined the solvation number (eq 7) as the number of solvent molecules present in the primary solvation sheath.

The values of ϕ_k, ϕ_v, and S_n for the solutions of samarium soaps increase for dilute solutions but decrease linearly above 0.03 M soap concentration. The decrease in the values at higher soap concentration may be explained on the basis of close packing of ionic head groups in the micelles, resulting

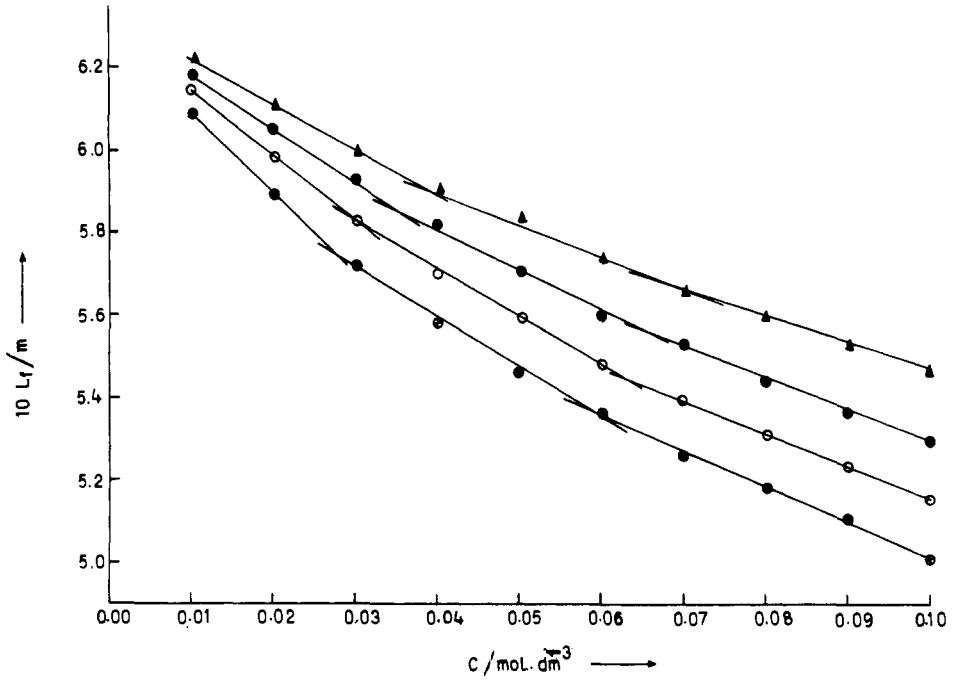

Figure 3. Intermolecular free length L_f as a function of concentration C for various samarium soaps: pentanoate, hexanoate, octanoate, and decanoate.

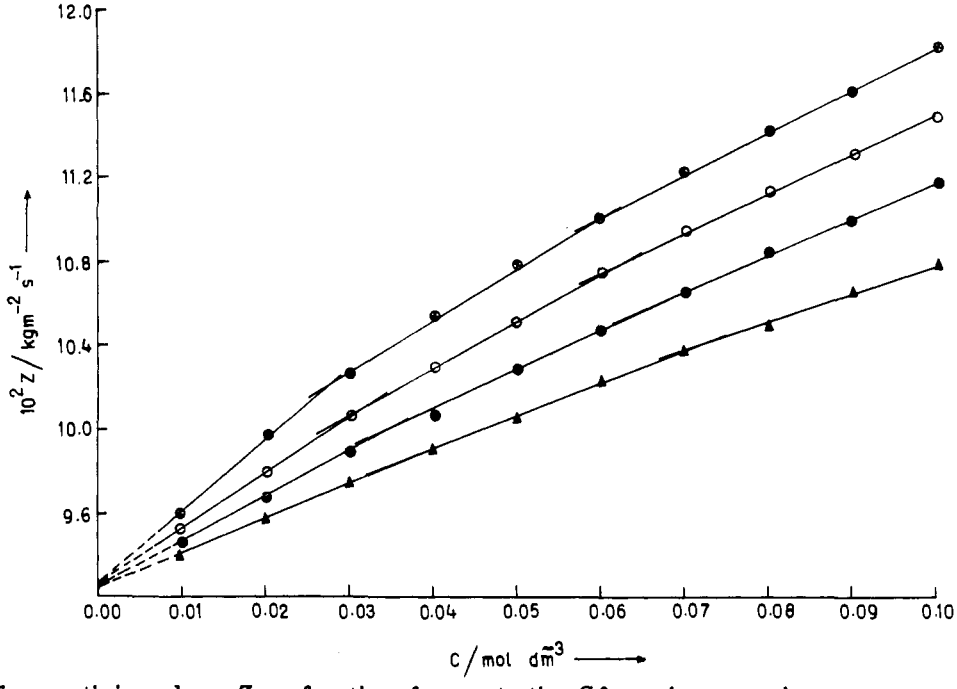

Figure 4. Specific acoustic impedance Z as a function of concentration C for various samarium soaps: pentanoate, hexanoate, octanoate, and decanoate.

in an increase in ionic repulsion and, finally, internal pressure. The higher values of the solvation number are in good agreement with other hydration numbers in the literature (*8*, *17*, *20*).

The intermolecular free length, L_f, is the predominant factor determining the ultrasonic speed in solutions and is related to the compressibility by the relationship $K(\beta)^{1/2}$ where K is the temperature-dependent Jacobson's constant (*21*). The values of L_f decrease with increasing concentration and chain length of the soap (Tables II and III). The decrease in the values of L_f with increasing ultrasonic speed indicates that there is a significant soap–solvent interaction (*22*) due to which the structural arrangement is considerably affected.

The specific acoustic impedance (*23*), Z, is the product of ultrasonic speed and density of the other medium (eq 3). The decrease in the values of L_f and increase in the values of Z with an increase in the soap concentration as well as with the chain length of the soap (Tables II and III) can be explained on the basis of a hydrophobic interaction between soap and solvent molecules, which increases with the intermolecular distance, leaving relatively wider gaps between the molecules and thus becoming the main cause of impediment to the propagation of ultrasound waves. All the plots show breaks (Figures 3 and 4), indicating the cmcs which are in accordance with the values obtained from other parameters. The molar sound speed, R, has been calculated by eq 6. The values of

the molar sound velocity show a regular increase with an increase in the concentration and chain length of the soap.

The ultrasound speed results show that there is a significant interaction between the soap–solvent molecules in dilute solutions and the soap molecules do not aggregate in dilute solutions. The values of the cmc for samarium soaps are in agreement with the values obtained from other physical properties.

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Registry No. Benzene, 71-43-2; methanol, 67-56-1; samarium pentanoate, 34283-42-6; samarium hexanoate, 42181-48-6; samarium octanoate, 124392-03-6; samarium decanoate, 124559-49-5.