Conductometric Investigations of Zirconyl Soaps in a Xylene–Methanol Mixture

K.N. Mehrotra* and M. Anis

Department of Chemistry, Institute of Basic Sciences, Agra-282 002, India

ABSTRACT: Conductometric measurements of solutions of zirconyl soaps in xylene–methanol (4:1, vol/vol) mixture were carried out at 30–50°C, and the results were used to determine the degree of ionization, ionization constant, and various thermodynamic parameters for both ionization and association processes. The results show that the soaps behave as weak electrolytes in dilute solutions, and the concentrations at which aggregation commences increased with increasing temperature and decreasing chainlength of the soap molecules.
JAOCS 74, 775–779 (1997).

KEY WORDS: Aggregation concentration, association process, degree of ionization, ionization constant, ionization process, specific conductance, thermodynamic parameters, zirconyl soaps.

Metallic soaps are increasingly important in technological as well as academic fields. Metal soaps possess both lyophilic and lyophobic moieties in the same molecule, which lends them unique characteristics and makes them useful for many industries. However, applications of metal soaps are based on empirical knowledge, and the selection of a soap for a specific purpose is mainly governed by economic factors. Kapoor and Mehrotra (1) prepared tetracarboxylates of zirconium by the reaction of zirconium chloride with fatty acids in refluxing benzene. Brainina *et al.* (2) and Prozorovskaya *et al.* (3) prepared tetracarboxylates of zirconium by ligand exchange reactions. Miyazaki *et al.* (4) prepared zirconium stearate by adjusting the pH of monohydrate zirconium sulfate to 2.8 with aqueous sodium carbonate and then mixing with sodium stearate under constant stirring at 70°C. Anhydrous zirconium carboxylates were also synthesized (5) by the reaction of zirconium hydride with carboxylic acid. Hirosawa (6) used zirconium soaps (palmitate and stearate) as waterproofing agents. Krystufek *et al.* (7) reported that hydrophobization agents that contained zirconium oxysoaps facilitated hydrophobization of textile substrates. Fukuda *et al.* (8) prepared polyurethane prepolymer with storage stability by mixing isocyanate-terminated urethane prepolymer and zirconium octanoate.

The present work deals with determination of the degree of ionization, the ionization constant, and various thermodynamic parameters for the ionization and association process for zirconyl soaps in xylene–methanol mixture (4:1, vol/vol) from conductivity measurements at different temperatures.

EXPERIMENTAL PROCEDURES

All chemicals were analytical reagent grade. Zirconyl soaps (caproate, caprylate, caprate, and laurate) were prepared by direct metathesis of the corresponding potassium soap with the required amount of aqueous solution of zirconium oxychloride. The soaps were purified by recrystallization from a benzene–methanol mixture, and purity of the soaps was checked by their melting points (caproate: 137.0; caprylate: 146.0; caprate: 158.0; and laurate: 167.0°C), elemental analysis, and infrared spectra.

The conductance measurements of the solutions of zirconyl soaps were carried out with a digital conductivity meter (Model CL 01-10A) (Toshniwal Instruments Pvt. Ltd., Bombay, India) and a dipping-type conductivity cell with platinized electrodes at different temperatures (30, 40, and 50 ± 0.05°C).

RESULTS AND DISCUSSION

The specific conductance (k) of the solutions of zirconyl soaps in xylene–methanol mixture (4:1, vol/vol) increases with increasing temperature (Fig. 1), increasing soap concentration, and decreasing chainlength of the soap molecules (Fig. 2). The increase in specific conductance with soap concentration may be due to ionization of the zirconyl soaps into zirconyl cations, ZrO^{2+}, and fatty acid anions, $RCOO^-$ (where R is C_5H_{11}, C_7H_{15}, C_9H_{19}, and $C_{11}H_{23}$ for caproate, caprylate, caprate, and laurate, respectively) and to the aggregation of anions at higher soap concentrations. The plots of specific conductance vs. soap concentration (Figs. 1 and 2) are characterized by an intersection of two straight lines at a definite soap concentration, which corresponds to the concentration of zirconyl soap at which aggregation begins.

The results show that the values of the concentration at which aggregation commences increase with increasing temperature (Table 1), which is in agreement with the results re-

---

*To whom correspondence should be addressed at Department of Chemistry, Institute of Basic Sciences, Khandari Road, Agra-282002, India.

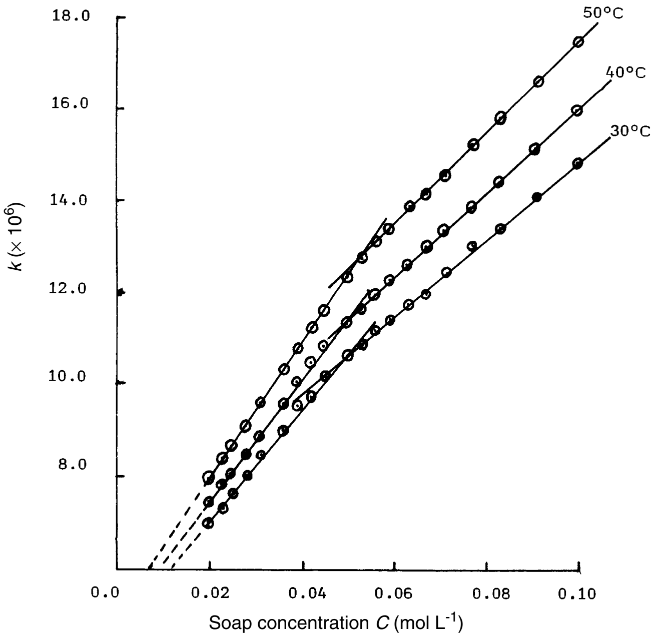

FIG. 1. Variation of specific conductance k vs. concentration C of zirconyl soap (caproate).

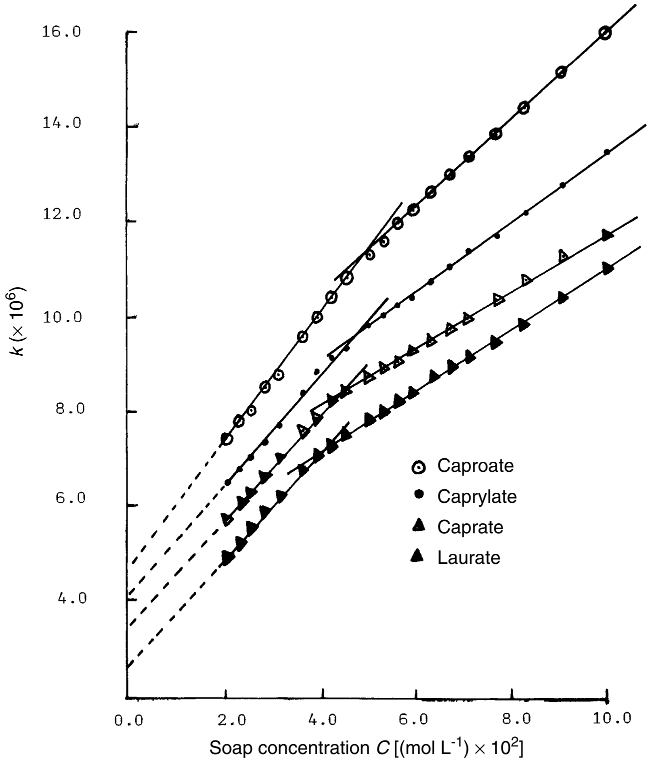

FIG. 2. Variation specific conductance k vs. zirconyl soap concentration C at 40 ± 0.05°C.

ported for aqueous solutions of alkali metal carboxylates. Aggregation occurs when the energy released as a result of association of hydrocarbon chains of the monomer is sufficient to overcome the electrical repulsion between the ionic head groups and to balance the decrease in entropy that accompanies the aggregation. The values of the concentration at which aggregation commences increase with increasing temperature as the kinetic energy of the monomers increases with increasing temperature. The values of the concentration at which aggregation commences decrease with increasing chainlength of the soap molecules (Table 1). The molar conductance μ of the solutions of zirconyl soaps decreases with increasing soap concentration, which may be due to the combined effects of ionic atmosphere, solvation of ions, and decrease of mobility and ionization with the formation of aggregates. However, the limiting molar conductance μ_0 cannot be obtained from the plots of molar conductance μ vs. the square root of the soap concentration, $C^{1/2}$ (which are concave upward with increasing slopes), indicating that the Debye-Hückel-Onsager equation is not applicable to these soap solutions. An expression for the ionization of zirconyl soaps may be obtained in Ostwald's manner. If C is the concentration in mol L^{-1} and α is the degree of ionization of zirconyl soaps, the equivalent concentrations of different species may be represented as:

TABLE 1
Aggregation Concentration and Thermodynamic Parameters of Zirconyl Soaps[a]

Soap	Temp. (°C)	Aggregation concentration ($X_A \times 10^2$), (mol L^{-1})	$-\ln X_A$	μ_0	$K \times 10^4$	log K
Caproate	30	4.85	5.463	0.630	5.421	−3.27
	40	5.00	5.422	0.851	2.320	−3.64
	50	5.20	5.377	1.111	1.167	−3.93
Caprylate	30	4.40	5.562	0.467	9.078	−3.04
	40	4.65	5.494	0.627	4.487	−3.35
	50	4.90	5.436	0.811	2.250	−3.65
Caprate	30	4.20	5.608	0.355	14.330	−2.84
	40	4.40	5.549	0.469	7.638	−3.12
	50	4.70	5.478	0.645	3.664	−3.44
Laurate	30	3.80	5.708	0.295	21.978	−2.66
	40	4.10	5.619	0.391	11.350	−2.94
	50	4.30	5.567	0.511	6.281	−3.20

[a] As found in a mixture of xylene-methanol at different temperatures.

$$\mathrm{ZrO(RCOO)_2} \rightleftharpoons \mathrm{ZrO^{2+}} + 2\,\mathrm{RCOO^-}$$

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

where R is C_5H_{11}, C_7H_{15}, C_9H_{19}, and $C_{11}H_{23}$ for caproate, caprylate, caprate, and laurate, respectively. The ionization constant K can be expressed as:

$$K = \frac{[\mathrm{ZrO^{2+}}][\mathrm{RCOO^-}]^2}{[\mathrm{ZrO(RCOO)_2}]}$$

$$K = \frac{(C\alpha)\,(2C\alpha)^2}{C(1-\alpha)} = \frac{4C^2\alpha^3}{1-\alpha} \qquad [1]$$

Interionic effects in dilute solutions may be regarded as negligible. By assuming α is equal to the conductance ratio (μ/μ_o), after rearranging, Equation 1 can be expressed as:

$$\mu^2C^2 = (K\mu_0^3/4\mu) - K\mu_0^2/4 \qquad [2]$$

where μ and μ_0 are the molar conductances at finite and infinite dilution, respectively.

The values of K and μ_0 were obtained from the slope ($K\mu_0^3/4$) and intercept ($-K\,\mu_0^2/4$) of the plots of μ^2C^2 vs. $1/\mu$ for dilute soap solutions and are recorded in Table 1. The results show that the limiting molar conductance μ_0 increases while the ionization constant K decreases with increasing temperature and decreasing chainlength of the soap molecules (Table 1). The decrease in the values of K with increasing temperature indicates the exothermic nature of ionization of soaps in the xylene–methanol (4:1, vol/vol) mixture.

The degree of ionization ($\alpha = \mu/\mu_0$) decreases with increasing temperature and remained nearly constant with increasing soap concentration for dilute solutions, as expected for weak electrolytes, but showed a small increase above the aggregation concentration (Fig. 3). The plots show a break at a definite soap concentration, the concentration at which aggregation begins. The increase in ionization constant K at higher soap concentrations may be due to the fact that the degree of ionization α cannot be assumed as equal to the conductance ratio μ/μ_0 because the activity coefficients may not be exactly equal to unity at higher soap concentrations. The results show that the soaps behave as weak electrolytes in dilute solutions.

The relation between the ionization constant K and the heat of ionization H_I^0 can be written as:

$$\frac{\delta \ln K}{\delta T} = \frac{\Delta H_I^0}{RT^2}$$

$$\text{or } \log K = -\frac{\Delta H_I^0}{2.303\,RT} + \text{constant} \qquad [3]$$

The values of the heat of ionization ΔH_I^0 were obtained from the slope of the plots of log K vs. $1/T$ (Fig. 4) and are recorded in Table 2. The heat of ionization for zirconyl soap is negative, indicating that the ionization of zirconyl soap is exothermic in nature. The results show that the heat of ionization increases (becomes less negative) with an increase in the chainlength of the soap (Table 2).

The changes in free energy ΔG_I^0 and entropy S_I^0 per mole for the ionization process were evaluated by using these relationships:

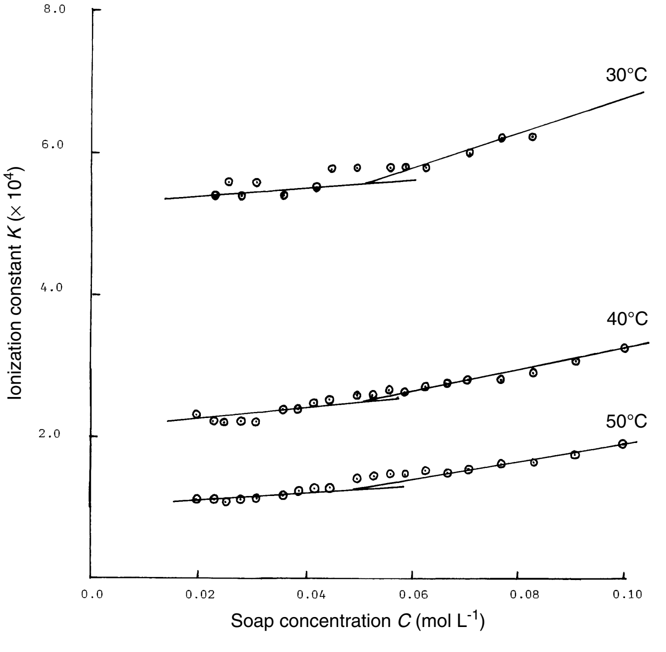

FIG. 3. Variation of ionization constant K vs. concentration C of zirconyl soap (caproate).

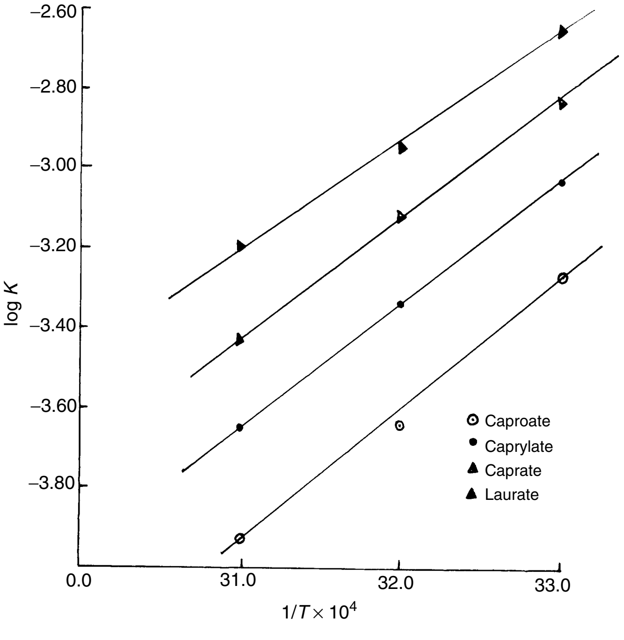

FIG. 4. Logarithm of ionization constant, log K, vs. reciprocal of absolute temperature, T^{-1}.

TABLE 2
Thermodynamic Parameters for the Ionization Process

	ΔG_I (kcal mol^{-1})			$-\Delta S_I \times 10^2$ (kcal K^{-1} mol^{-1})			$-\Delta H_I$
Soap	30°C	40°C	50°C	30°C	40°C	50°C	(kcal mol^{-1})
Caproate	45.12	51.86	57.92	17.46	19.05	20.34	7.77
Caprylate	42.02	47.78	53.72	16.23	17.55	18.85	7.15
Caprate	39.28	44.48	50.60	15.29	16.45	17.85	7.06
Laurate	38.10	42.03	47.15	14.62	15.41	16.52	6.20

TABLE 3
Thermodynamic Parameters for the Association Process

	$-\Delta G_A$ (kcal mol^{-1})			$\Delta S_A \times 10^2$ (kcal K^{-1} mol^{-1})			ΔH_A
Soap	30°C	40°C	50°C	30°C	40°C	50°C	(kcal mol^{-1})
Caproate	6.55	6.72	6.88	2.75	2.72	2.68	1.78
Caprylate	6.67	6.81	6.95	2.96	2.91	2.86	2.30
Caprate	6.73	6.88	7.01	3.08	3.03	2.98	2.61
Laurate	6.85	6.96	7.12	3.16	3.10	3.05	2.73

$$\Delta G_I^0 = -RT \ln K_I \qquad [4]$$

$$\text{and } \Delta S_I^0 = \frac{[\Delta H_I^0 - \Delta G_I^0]}{T} \qquad [5]$$

For the association process, when the counter ions are bound to the aggregate, the standard free energy of association (per mole of monomer), ΔG_A^0, for the phase separation model (9,10) is given by the relationship

$$\Delta G_A^0 = 2\,RT \ln X_A \qquad [6]$$

where X_A is the aggregation concentration, expressed as a mole fraction and defined as $X_A = n_s/(n_s + n_0)$.

Because the number of moles of free surfactant, n_s, is small compared with the number of moles of solvent, n_0, the above expression can be written as $X_A = n_s/n_0$.

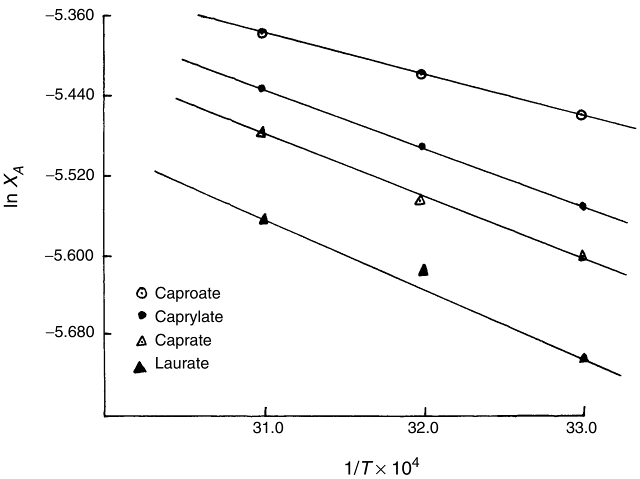

FIG. 5. Logarithm of aggregation concentration ln X_A vs. reciprocal of absolute temperature T^{-1}.

The standard enthalpy change of association per mole of monomer for the phase separation model (9,10), H_A^0, is given by the relationship:

$$\frac{\delta(\ln X_A)}{\delta T} = \frac{\Delta H_A^0}{2\,RT^2}$$

$$\text{or } \ln X_A = -\frac{-\Delta H_A^0}{2\,RT} + \text{constant} \qquad [7]$$

The values of ΔH_A^0 were obtained from plots of ln X_A vs. 1/T (Fig. 5) and are recorded in Table 3. The positive values of ΔH_A^0 indicate that the association for zirconyl soaps in a mixture of xylene–methanol (4:1, vol/vol) is endothermic.

The positive values of ΔS_A and negative values of ΔG_A for the association process, and the negative values of ΔS_I and positive values of ΔG_I for the ionization process indicate that association is favored over ionization. The values of ΔS_I and ΔS_A increase while those of ΔG_I and ΔG_A decrease with increasing chainlength of the soap molecules. The increase in ΔG_I and the decrease in ΔG_A with increasing temperature indicate that the association is favored over ionization.

We therefore conclude that the thermodynamics of ionization and association can be satisfactorily explained in light of the phase separation model on the basis of conductivity measurements.

REFERENCES

1. Kapoor, R.N., and R.C. Mehrotra, Reactions of Zirconium Tetrachloride and Isopropoxide with Fatty Acids, *J. Chem Soc.*: 422–426 (1959); *Chem. Abstr. 53*:9043a (1959).

2. Brainina, E.M., R.Kh. Freidlina, and A.V. Nesmeyanov, A New Method of Preparation of Tetraacyloxy Derivatives of Zirconium, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*:608–12, (1961); *Chem. Abstr. 55*:22109f (1961).
3. Prozorovskaya, Z.N., L.N. Komissarova, and V.I. Spitsyn, Zirconium and Hafnium Butyrates, *Zh. Neorg. Khim. 13*:706–711 1968.
4. Miyazaki, H., T. Usui, K. Nakamura, and Y. Orgino, Zirconium Stearate Soap, *Jpn. Kokai Tokkyo Koho 8007,221* (Cl. C07C5/41) Jan. 19, 1980, Appl. 78/78, 360 June 28 (1978), pp. 3.
5. Wailes, P.C., and H. Weigold, Hydrido Complexes of Zirconium I. Preparation, *J. Organometal Chem. 24*:413–417 (1970).
6. Hirosawa, S., Water Proofing Agents for Cement Products, Japanese Patent, 7241408 (1974); *Chem. Abstr. 80***:**30208t (1974).
7. Krystufek, J., J. Kopal, and O. Walter, Preparing Textile Substrates for Emery Sheets, Czech. CS199, 139 (Cl. D06C29/00) June 15 (1982); Appl. 78/257, May 19 (1978); pp. 7.
8. Fukuda, K., Y. Sasaki, M. Sekine, and T. Sugita, Polyurethane Prepolymer with Storage Stability, *Jpn. Kokai Tokkyo Koho JP 6169824* [86 69824] (Cl C08 G18/08) Apr. 10 (1986); Appl. 84/161, 528, Aug. 2 (1984); pp. 4.
9. Barry, B.W., and G.F.J. Russell, Prediction of Micellar Molecular Weights and Thermodynamics of Micellization of Mixture of Alkyltrimethyl Ammonium Salts, *J. Colloid Interface Sci. 40*:174–194 (1972).
10. Robins, D.C., and I.L. Thomas, Effect of Counterions on Micellar Properties of 2-(Dodecylamino) Ethanal Salts. I. Surface Tension and Electrical Conductance Studies, *Ibid. 26*:407–414 (1968).

[Received October 28, 1996; accepted April 3, 1997]