Conductance Behavior of Manganese Soap Solutions in 1-Butanol and 3-Methyl-1-butanol

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The specific conductance of manganese soap solutions in 1-butanol and 3-methyl-1-butanol has been measured at temperatures in the range 35—50 °C. Manganese soaps form micellar aggregates and the CMC, which decreases with increase in chain length of the soaps of saturated fatty acids, was found to be independent of the nature of the solvent. Conductance behavior of soaps is given by the equation $\log \lambda_M = A + B \log C$ where A and B are constants and C is the concentration in mol/dm^3. Constant A increases with increase in temperature and chain length of the soap. Constant B is independent of temperature but varies with soap chain. Molecular conductance at infinite dilution, λ_∞, dissociation constant, K, activation energy of conductance, ΔE_λ, and heat of dissociation, $\Delta H°$, have been evaluated.

Measurement of the conductance of metal soaps involves no special problem except the application of external electrical forces. Since the mobility of the ion present as simple species resembles that of dissociated salts and differs markedly from that of aggregated ions, there is an abrupt change in specific conductance at CMC. Electrical conductance of various ionic agents has been reported.[1–4] The conductance of sodium and potassium soaps in ethanol, toluene, and pyridine was determined[5] and sodium oleate in ethanol was reported[6] to behave as simple electrolyte. Several workers[7–9] have studied the CMC of magnesium, calcium, barium, and strontium soap solutions and determined parameters such as K, λ_∞, and $\Delta H°$. From the conductance behavior[10] of magnesium soaps in lower aliphatic alcohols, it was confirmed that CMC is uneffected by change in temperature. An investigation of CMC of nickel, cobalt, and iron soaps has been made[11] by conductance measurement at different temperatures.

We have studied the conductance of manganese soaps (oleate, laurate, decanoate and octanoate) in 1-butanol and 3-methyl-1-butanol at different temperatures in order to a) determine the CMC of the soap solutions, b) confirm the effect of temperature, if any, on CMC, and c) determine dissociation constant, K, molecular conductance at infinite dilution, λ_∞ and heat of dissociation, $\Delta H°$.

Experimental

Materials. 1-Butanol, 3-methyl-1-butanol, manganese chloride, oleic acid, and octanoic, decanoic and lauric acids (Merck or B.D.H. reagent grade) were used. The fatty acids were purified by distillation under reduced pressure, the purity being confirmed by bp measurements.

Preparation of Soaps. Manganese soaps were prepared by the interaction of manganese chloride solution in a small quantity of distilled water with a hot solution of sodium soap, the latter being added drop-wise while the whole mass was continuously stirred at 50—55 °C. The precipitate was filtered and washed with hot water until the filtrate gave no reaction to manganese chloride. After initial drying in an air oven (100—105 °C) final drying was carried out under reduced pressure.

Apparatus and Procedure. All the measurements were carried out in a thermostat at constant temperature (±0.05 °C). A conductivity bridge (Phillips, PR 9500, India) and a dipping type conductivity cell were used for measuring the conductance of soap solutions. All data were obtained by concentration runs, solutions were diluted by adding the solvent in a desired proportion and the conductance was measured. The reproducibility of the results was verified by repeating the measurements.

Results and Discussion

Specific conductance, κ, of manganese soap solutions increases with increasing concentrations of soap solutions at different temperatures. The κ-C plots (Fig. 1) are characterised by an intersection of two straight lines at a definite concentration called CMC (Table 1). The values of CMC of soaps are unaffected by change in temperature but decrease with increasing chain length of the soap.

Molecular conductance, λ_M, obtained from the measured specific conductance of solutions decreases with increase in the concentration of the soap solutions. The plots (Fig. 2) of λ_M *vs.* $C^{1/2}$ are concave upward.

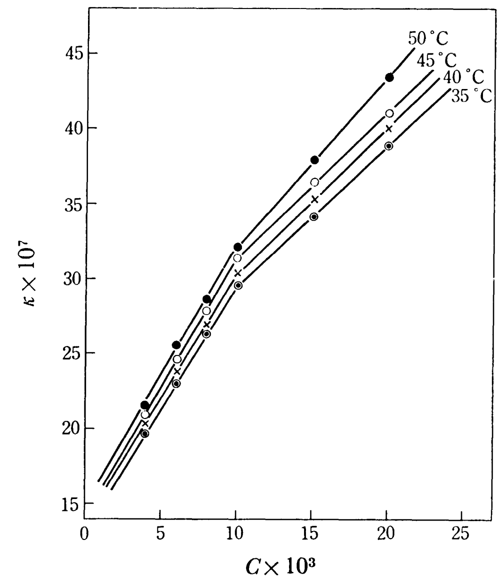

Fig. 1. Plot of specific conductivity, κ *vs.* concentration, C, of manganese oleate in 1-butanol at temperatures, 35—50 °C.

Table 1. Values of CMC and heat of dissociation, ΔH° in kcal of manganese soaps at all temperatures (35—50 °C)

Soap	1-Butanol		3-Methyl-butanol	
	CMC	ΔH°	CMC	ΔH°
Oleate	0.010 M	25.51	0.008 M	10.08
Laurate	0.007 M	27.51	0.007 M	13.29
Decanoate	0.008 M	30.25	0.008 M	39.42
Octanoate	0.009 M	33.04	0.009 M	43.54

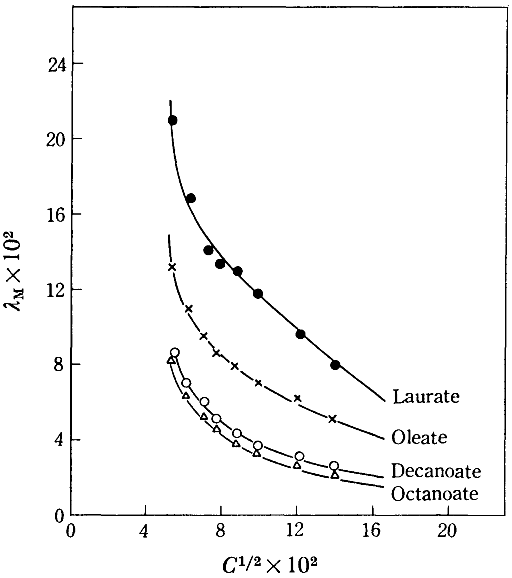

Fig. 2. Plot of molecular conductivity, λ_M, vs. square root of concentration, $C^{1/2}$, of manganese soaps in 3-methyl-1-butanol at 35 °C.

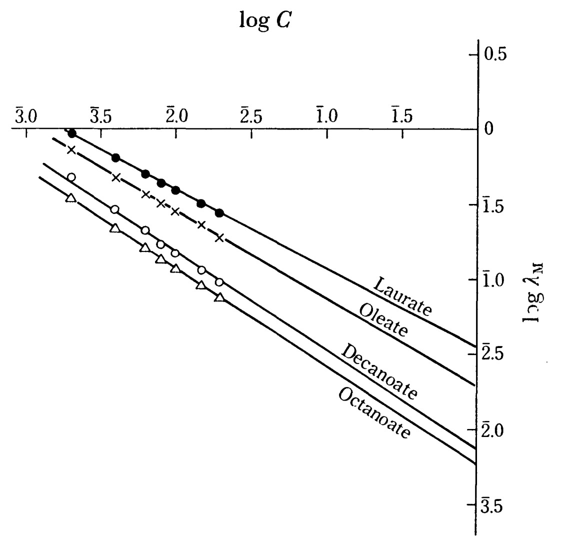

Fig. 3. Plot of $\log \lambda_M$ vs. $\log C$ of manganese soaps at 35 °C in 1-butanol.

This is due to the weak electrolyte behavior of the soaps.

The conductance behavior of manganese soap solutions at various temperatures (Fig. 3) is represented by

$$\log \lambda_M = A + B \log C, \quad (1)$$

where A and B are constants and C is the concentration in mol/dm³

The values of constants A and B have been found from the slopes and intercepts of the linear plots of $\log \lambda_M$ vs. $\log C$ (Table 2). It is seen that constant A in 1-butanol is higher than 3-methyl-1-butanol varying with soap at different temperatures in the order

laurate>oleate>decanoate>octanoate

Constant B (Table 3) is independent of temperature which supports the idea that CMC remains unaffected by temperature.

The molecular conductance temperature variation can be expressed by

$$\lambda_M = A e^{-\Delta E_\lambda / RT}, \quad (2)$$

where A and ΔE_λ are constants.

Constant ΔE_λ is of importance, since information can be obtained on the aggregation by measuring the activation energy of conductance. The plots of $\log \lambda_M$ vs. $1/T$ are straight lines in alcohols. The activation energy of conductance, ΔE_λ has been calculated from the slopes of linear plots. Table 4 indicates and appreciable difference in the values of ΔE_λ below an above CMC which supports the micellar behavior of manganese soaps in alcohols.

Dissociation Constant, Heat of Dissociation, and Molecular Conductance at Infinite Dilution. Manganese soap has been reported to behave as a weak electrolyte in dilute solutions,[13] the dissociation of soap can thus be derived as follows:

$$\underset{C(1-\alpha)}{(COOR)_2Mn} \rightleftharpoons \underset{C\alpha}{Mn^{2+}} + \underset{2C\alpha}{2RCOO^-}, \quad (3)$$

$$K = \frac{[Mn^{2+}][RCOO^-]^2}{[(COOR)_2Mn]} \quad (4)$$

$$= \frac{4C^2\alpha^3}{1-\alpha}. \quad (5)$$

The degree of dissociation, α, of soaps in solution is very small. Ionic concentration would be low and interionic effects can be neglected. On replacing $\alpha = \lambda_M/\lambda_\infty$ and rearranging, we obtain

$$C^2\lambda_M^2 = \frac{K\lambda_\infty^3}{4\lambda_M} - \frac{\lambda_\infty^2 K}{4}. \quad (6)$$

The plots of $C^2\lambda_M^2$ vs. $1/\lambda_M$ are linear below CMC and the equation fails above this concentration. The values of K and λ_∞ obtained from Eq. 6 at different temperatures are given in Tables 5 and 6.

The dissociation constant decreases with increase in temperature and decrease in dielectric constant of the solvent. In a medium of low dielectric constant, the electrostatic attractive forces between positive and negative ions are large, giving rise to diminished small dissociation.

The heat of dissociation, ΔH° has been calculated from the slopes of the plots of $\log K$ vs. $1/T$ and is given in Table 1. We see that the values of ΔH° decrease with increase in the chain length of soap.

Molecular conductance at infinite dilution, λ_∞ increases with increase in temperature which is due to the decrease in the viscosity of solvent. The rise in temperature causes increase in ionic mobility despite the fact that the addition of the soap increases the viscosity of the solvent.

Table 2. Values of A of manganese soaps at temperatures in the range 35—50 °C

Solvent	Temp °C	Constant A			
		Oleate	Laurate	Decanoate	Octanoate
1-Butanol	35	$\bar{2}.32$	$\bar{2}.58$	$\bar{3}.86$	$\bar{3}.80$
	40	$\bar{2}.34$	$\bar{2}.62$	$\bar{3}.88$	$\bar{3}.82$
	45	$\bar{2}.36$	$\bar{2}.66$	$\bar{3}.90$	$\bar{3}.86$
	50	$\bar{2}.38$	$\bar{2}.72$	$\bar{3}.90$	$\bar{3}.88$
3-Methyl-1-butanol	35	$\bar{3}.86$	$\bar{2}.00$	$\bar{3}.30$	$\bar{3}.24$
	40	$\bar{3}.90$	$\bar{2}.06$	$\bar{3}.36$	$\bar{3}.28$
	45	$\bar{3}.92$	$\bar{2}.08$	$\bar{3}.38$	$\bar{3}.30$
	50	$\bar{3}.98$	$\bar{2}.10$	$\bar{3}.40$	$\bar{3}.36$

Table 3. Values of B of manganese soaps at temperatures in the range 35—50 °C

Solvent	Temp °C	Constant B			
		Oleate	Laurate	Decanoate	Octanoate
1-Butanol	35	0.56	0.52	0.66	0.64
	40	0.56	0.52	0.66	0.64
	45	0.56	0.50	0.66	0.62
	50	0.56	0.50	0.66	0.62
3-Methyl-1-butanol	35	0.48	0.52	0.64	0.66
	40	0.48	0.50	0.62	0.64
	45	0.48	0.50	0.62	0.66
	50	0.50	0.50	0.62	0.62

Table 4. Range of activation energy of conductance, ΔE_λ for manganese soaps below and above CMC

Soap	ΔE_λ in kcal			
	1-Butanol		3-Methyl-1-butanol	
	below CMC	above CMC	below CMC	above CMC
Oleate	1.37—1.38	1.83—1.84	1.37—1.60	1.60—1.80
Laurate	1.37—1.84	2.30—3.21	0.60—1.37	1.37—2.06
Decanoate	0.92—1.37	1.83—1.84	0.91—0.92	1.37—2.06
Octanoate	0.91—0.92	1.83—2.29	1.14—1.60	1.83—2.00

Table 5. Values of dissociation constants, K, for manganese at temperatures in the range 35—50 °C

Solvent	Temp °C	$K \times 10^5$			
		Oleate	Laurate	Decanoate	Octanoate
1-Butanol	35	6.874	0.494	22.000	33.300
	40	3.852	0.326	7.960	13.140
	45	1.920	0.153	5.810	8.000
	50	0.968	0.074	1.280	2.489
3-Methyl-1-butanol	35	2.500	3.692	0.078	0.347
	40	3.212	3.241	0.032	0.154
	45	1.703	2.110	0.012	0.073
	50	1.279	1.341	0.004	0.016

Table 6. Values of molecular conductivity at infinite dilution, λ_∞, at temperatures in the range 35—50 °C

Solvent	Temp °C	λ_∞			
		Oleate	Laurate	Decanoate	Octanoate
1-Butanol	35	1.230	1.800	0.962	0.600
	40	1.477	2.158	1.487	0.818
	45	1.882	2.800	1.530	1.000
	50	2.932	3.454	2.500	1.501
3-Methyl-1-butanol	35	0.200	0.319	0.336	0.173
	40	0.208	0.330	0.444	0.233
	45	0.227	0.385	0.600	0.306
	50	0.250	0.457	0.925	0.500

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References

1) M. E. L. McBain, W. B. Dye, and S. A. Johnston, *J. Am. Chem. Soc.*, **61**, 3210 (1939).
2) A. Lottermoser, and F. Puschel, *Kolloid-Z.*, **63**, 175 (1933).
3) A. W. Ralston and C. W. Hoerr, *J. Am. Chem. Soc.*, **64**, 772 (1942).
4) H. F. Walton, E. N. Hiebert, and E. H. Sholtes, *J. Colloid Sci.*, **1**, 385 (1946).
5) S. S. Bhatnagar, and M. Prasad, *Kolloid-Z.*, **34**, 193 (1924).
6) W. A. Patrick, W. L. Hyden, and E. F. Milan, *J. Phys. Chem.*, **29**, 1004 (1925).
7) R. P. Varma, and K. Kumar, *Cellul. Chem. Technol.*, **9**, 23 (1975).
8) R. P. Varma, and P. Bahadur, *Cellul. Chem. Technol.*, **9**, 393 (1975).
9) R. P. Varma, and R. Dayal, *J. Am. Oil Chem. Soc.*, **53**, 39 (1976).
10) R. P. Varma, and K. Kumar, *Kolloid-Z. Z. Polym.*, in press.
11) R. P. Varma, H. K. Bhargava, and R. Dayal, *Roczniki Chemii. ann. Soc. Chim. Polonorum*, **50**, 307 (1976).
12) K. N. Mehrotra, and R. P. Varma, *J. Am. Oil Chem. Soc.*, **45**, 673
13) R. P. Varma, and P. Bahadur, *Cellul. Chem. Technol.*, **8**, 27 (1974).