Conductometric and Spectrophotometric Investigations on Manganese(II) Decanoate in Organic Solvents

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The specific conductance of manganese(II) decanoate in DMF and 1-butanol was measured with a view to determine the critical micelle concentration (CMC), degree of dissociation, and dissociation constant. It was found that the soap behaves as a simple electrolyte and is ionic in nature. The CMC was found to be independent of the dielectric constant of the solvent. The ionic character of manganese(II) decanoate was also confirmed by spectrophotometric measurements.

The study of transition metal soaps is becoming increasingly important in technological and academic fields. The physico-chemical characteristics and structure of metal soaps are controlled by the method and conditions of their preparation, and so the studies of soaps are of great significance for their uses in various industries under different conditions. The methods of preparation[1–7] and structural characteristics[8–13] of transition metal soaps were investigated. Varma et al.[14,15] determined the critical micelle concentration (CMC) of nickel, cobalt, and iron soaps at different temperatures conductometrically. Fogg and Pink[16] carried out the electrical conductance and dielectric constant measurements for zinc, manganese, and copper soaps in 2-methyl-1-propanol and benzaldehyde. The IR spectra of the cobalt soaps, cobalt complexes, and copper soaps were investigated by Chuev and and Shchennikova,[17] Kambe,[18] and Kuroda,[19] respectively. Zul'fugarly et al.[20] studied the IR spectra of nickel, copper, and manganese naphthenates. The absorption spectra of nickel and chromium soaps in different solvents were studied by Malik and Ahmad.[21,22] Tsuchida et al.[23] carried out the spectrochemical studies of the microscopic crystals of copper(II) alkanoates to establish the structure in solid state as well as in solutions.

The present work deals with the characteristics and structure of the solutions of manganese(II) decanoate in DMF and 1-butanol using IR, spectrophotometric and conductometric techniques.

Experimental

Preparation of Soap. Manganese(II) decanoate was prepared by adding a hot solution of potassium decanoate dropwise to an aquoous solution of manganese(II) acetate while the whole mass was continuously stirred at 50—55 °C. The precipitated soap was washed with hot water and acetone to remove the excess of metal ions and unchanged potassium decanoate. After initial drying in an air oven at 60—65 °C the final drying was carried out under reduced pressure. The soap was purified by recrystallization with methanol. The purity of the soap was checked by elemental analysis, IR spectra and by determination of its melting point, 85 °C. The reproducibility of the results was checked by preparing two samples of the soap under similar conditions.

Measurements. (A) Infrared Absorption Spectra: The IR absorption spectra of decanoic acid, potassium decanoate, and manganese(II) decanoate were recorded with a Perkin-Elmer Model 577 Grating Spectrophotometer in a region of 4000—400 $\mathrm{cm^{-1}}$ using a potassium bromide disc method.

(B) Spectrophotometry: The absorption measurements of the solutions of manganese(II) decanoate in DMF and 1-butanol were carried out in the region of 350—940 nm with a Digital Toshniwal Visible Spectrophotometer (Model CL 10 A 3) having wavelength reproducibility of ±1 nm.

(C) Conductance: The conductance of the solutions was measured with a Toshniwal Digital Conductivity Meter (Model CL 01, 10 A) and a dipping type conductivity cell (cell constant: 0.90) with platinized electrodes at a constant temperature, (40±0.05 °C). The specific conductance and molecular conductance are expressed in $\mathrm{S\,cm^{-1}}$ and in $\mathrm{S\,cm^2\,g\text{-}mol^{-1}}$, respectively.

Results and Discussinn

(A) Infrared Absorption Spectra. The IR spectrum of manganese(II) decanoate was compared with those of potassium decanoate and decanoic acid (Table 1). The absence of water of crystallization in potassium and manganese(II) decanoate was confirmed by the absence of a band near 3500 $\mathrm{cm^{-1}}$ in their spectra. The absorption maxima, characteristic of the aliphatic portion of the fatty acid molecules, remained unchanged on the formation of the soap from the corresponding acid. The absorption bands near 2660, 1680, 930, 690, and 550 $\mathrm{cm^{-1}}$, observed in the spectrum of fatty acid, are associated with the carboxylic group of the acid molecule. The absorption band near 1680 $\mathrm{cm^{-1}}$ revealed that the fatty acids possess dimeric structure with hydrogen bonding between the two molecules of the fatty acid. These characteristic vibrations of the fatty acid were found to be completely absent in the spectra of the potassium and manganese soaps. In general, carboxylic acids on formation of metal soaps showed two important bands, one due to the asymmetric stretching vibration and the other due to the symmetric vibration of the carboxylate ion. These vibrations were observed near 1550 and 1430 $\mathrm{cm^{-1}}$ in the spectra of potassium and

Table 1. Infrared Absorption Frequencies (cm^{-1}) Together with Their Assignments[a)]

S.No.	Absorption	Decanoic acid	Potassium decanoate	Manganese (II) decanoate
1.	CH_3, C-H asymmetric stretching	2960 W	2940 W	2960 W
2.	CH_2, C-H asymmetric stretching	2920 S	2910 S	2920 S
3.	CH_2, C-H symmetric stretching	2855 S	2840 S	2850 S
4.	OH, stretching	2660 VS	—	—
5.	C=O, stretching	1680 VS	—	—
6.	COO^-, C-O asymmetric stretching	—	1550 VS	1550 S
7.	CH_2, deformation	1470 M	1460 M	1460 M
8.	COO^-, C-O symmetric stretching	—	1430 W	1430 VS
9.	CH_2, (adjacent to COOH group) deformation	1400 VS	—	1420 S
10.	CH_3, symmetric deformation	1350 W	1330 W	1330 S
11.	Progressive bands (CH_2 twisting and wagging)	1270—1220 W	1300—1200 W	1280—1210 VS
12.	CH_3 rocking	1110 W	1110 VW	1100 W
13.	OH, out-of-plane deformation	930 VS	—	—
14.	CH_2 rocking	720 VS	720 VS	730 S
15.	COOH bending mode	690 M	—	—
16.	COOH wagging mode	550 M	—	—
17.	Mn-O bond	—	—	480 VS

a) Key to abbreviation, VW=very weak, VS=very strong, S=strong, M=medium, W=weak.

manganese soaps.

The appearance of two absorption bands in the spectra of potassium and manganese soaps, instead of one band observed near 1680 cm^{-1} in the spectrum of fatty acid, indicates that the two C-O bonds of the carboxyl group of the soap molecules are identical and the resonance character of the ionized carboxyl group is retained in the soap. The results show that manganese(II) decanoate is ionic in nature and metal-to-oxygen bond of the soap has ionic character.

(B) Spectrophotometry. The solutions of manganese(II) decanoate in DMF and 1-butanol exhibit well defined absorption maxima at 370 nm (27027 cm^{-1}) and 490 nm (20408 cm^{-1}). The absorption studies were also carried out with the solutions of manganese(II) acetate in DMF and 1-butanol and it was observed that the absorption maxima for manganese(II) acetate solution also occur at the same wavelengths (370 and 490 nm). This shows that the behavior of manganese(II) decanoate in DMF and 1-butanol is similar to manganese(II) acetate.

Mn(II) possesses d^5 electronic configuration and the same type of energy level diagram could be applied whether the metal ion is surrounded by tetrahedral or octahedral environments. The two observed bands correspond to ${}^6A_{1g}\rightarrow{}^4A_{1g}(G)$, ${}^4E_g(G)$ (this pair of transition is degenerated in octahedral geometry) and ${}^6A_{1g}\rightarrow{}^4E_g(D)$ transitions whose energies correspond to $10B+5C$ and $17B+5C$, respectively.[24)] A variation in these band energies provides a simple measure of their nephelauxetic ratio, β.[25)] Thus these transitions have been used to calculate the values of various parameters (Table 2). Racah interelectronic repulsion parameters, B and C were calculated from the observed maxima. The crystal field splitting energy parameter, D_q, nephelauxetic ratio, β, and percentage covalency, δ, were evaluated by using the relationships:

$$\frac{D_q}{B}=1.1, \tag{1}$$

$$\beta=\frac{B}{B_o}, \tag{2}$$

$$\delta=\left(\frac{1-\beta}{\beta}\right)\times 100, \tag{3}$$

where B_o is the value of the interelectronic repulsion parameter for free manganese(II) ion and is equal to 960 cm^{-1}. The value of δ may be positive or negative for covalent and ionic bonding, respectively. Henrie and Choppin[26)] suggested another bonding parameter, b, given by the relationship:

$$b^{1/2}=\left(\frac{1-\beta}{2}\right)^{1/2}. \tag{4}$$

The value of nephelauxetic ratio, β, for manganese(II) decanoate is slightly less than unity and so the metal-to-oxygen bonding in the soap has very small covalent

Table 2. Electronic Spectral Bands, Their Assignments and Various Parameters of Manganese(II) Decanoate

Transitions		Racah Parameters		D_q	Nephelauxetic ratio	Bonding parameter	Percentage covalency
ν_2	ν_3	B	C		β	$b^{1/2}$	δ
27027 cm^{-1} (370 nm)	20408 cm^{-1} (490 nm)	945.5	2190.6	1040	0.9849	0.086	1.53

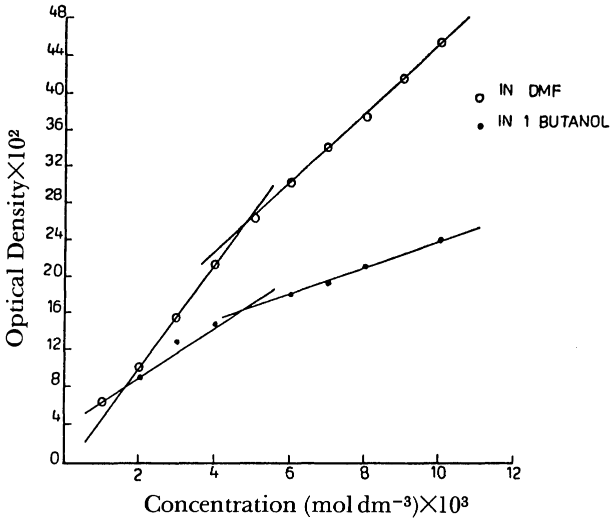

Fig. 1. Optical density vs. concentration of manganese(II) decanoate in DMF and 1-butanol.

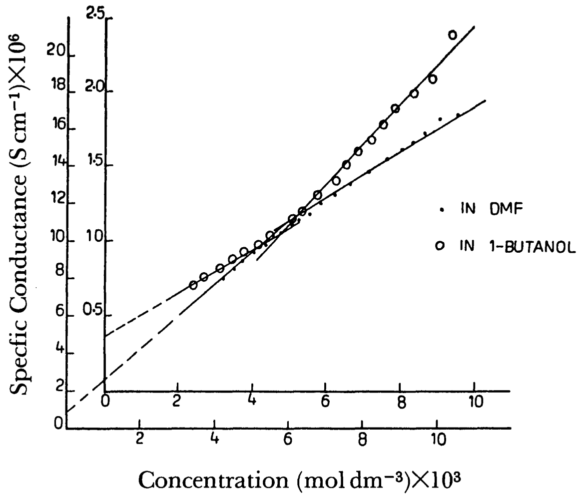

Fig. 2. Plots of specific conductance vs. concentration of manganese(II) decanoate in organic solvents at 40±0.05 °C.

character and this soap is almost ionic in nature. The small value of δ again confirms that the bonding is ionic in nature.

The plots of the optical density vs. soap concentration (Fig. 1) are characterized by an intersection of two straight lines at a concentration which corresponds to the CMC of manganese(II) decanoate in DMF and 1-butanol (0.0048—0.0047 mol dm^{-3}). The plots are linear below the CMC which proves the validity of Beer-Lambert's law in dilute solutions of the soap. It is evident that the spectrophotometric method can be used for the estimation of manganese content at λ_{max} in dilute soap solutions in organic solvents.

(C) Conductance. The molecular conductance, μ, of the solutions of soap involves the effects of both the simple ions and the micelles and so the specific conductance, κ, is plotted against the soap concentration, C, (Fig. 2) to determine the CMC. The specific conductance of the solutions of manganese(II) decanoate in DMF and 1-butanol increases with increasing soap concentration (Tables 3 and 4) which may be due to the ionization of manganese(II) decanoate into simple metal cations Mn^{2+} and fatty acid anions $C_9H_{19}COO^-$ in dilute solutions and due to the formation of micelles at higher soap concentrations. The plots of specific conductance vs. soap concentration are char-

Table 3. Conductance Measurements of Manganese(II) Decanoate in DMF at 40.0±0.05 °C

S. No.	Concentration $C\times10^3$	Specific conductance $\kappa\times10^6$	Molar conductance μ	Degree of dissociation α_1	Degree of dissociation α_2	Dissociation constant $K_1\times10^3$	Dissociation constant $K_2\times10^4$
	mol dm^{-3}	S cm^{-1}	S cm^2 g-mol^{-1}				
1.	10.0	17.3	1.73	0.48	0.54	4.5	1.42
2.	9.5	16.8	1.76	0.49	0.55	4.4	1.38
3.	9.0	16.3	1.81	0.50	0.57	4.6	1.39
4.	8.6	15.8	1.83	0.51	0.58	4.5	1.34
5.	8.3	15.3	1.84	0.51	0.58	4.4	1.28
6.	8.0	14.9	1.86	0.52	0.59	4.4	1.24
7.	7.6	14.5	1.90	0.53	0.60	4.5	1.23
8.	7.1	13.7	1.92	0.54	0.61	4.3	1.13
9.	6.6	13.1	1.98	0.55	0.62	4.5	1.12
10.	6.2	12.5	2.01	0.56	0.63	4.4	1.07
11.	5.8	12.0	2.06	0.57	0.65	4.5	1.04
12.	5.5	11.5	2.09	0.58	0.66	4.4	1.01
13.	5.2	11.1	2.13	0.59	0.67	4.5	0.99
14.	5.0	10.8	2.16	0.60	0.68	4.5	0.99
15.	4.7	10.4	2.21	0.62	0.70	4.6	0.98
16.	4.3	9.9	2.30	0.64	0.73	4.9	1.02
17.	4.0	9.4	2.35	0.66	0.74	5.0	1.00
18.	3.7	8.9	2.40	0.67	0.76	5.0	0.97
19.	3.4	8.5	2.50	0.69	0.79	5.4	1.06
20.	3.2	8.0	2.50	0.70	0.79	5.1	0.94

Table 4. Conductance Measurements of Manganese(II) Decanoate in 1-Butanol at 40.0±0.05 °C

S. No.	Concentration $C\times10^3$ mol dm^{-3}	Specific conductance $\kappa\times10^6$ S cm^{-1}	Molar conductance μ S cm^2 g-mol^{-1}	Degree of dissociation α_1	Degree of dissociation α_2	Dissociation constant $K_1\times10^3$	Dissociation constant $K_2\times10^5$
1.	10.0	2.68	0.268	0.55	0.74	6.7	62.3
2.	9.3	2.38	0.255	0.53	0.70	5.5	39.5
3.	8.8	2.19	0.248	0.51	0.68	4.6	30.4
4.	8.3	2.03	0.244	0.50	0.67	4.1	25.1
5.	7.8	1.92	0.246	0.51	0.68	4.1	23.9
6.	7.5	1.81	0.241	0.50	0.66	3.7	19.0
7.	7.1	1.72	0.242	0.50	0.67	3.5	18.3
8.	6.8	1.62	0.238	0.49	0.66	3.2	15.6
9.	6.5	1.56	0.240	0.50	0.66	3.2	14.2
10.	6.2	1.49	0.240	0.50	0.66	3.1	13.0
11.	5.7	1.37	0.240	0.50	0.66	2.8	10.9
12.	5.3	1.26	0.237	0.49	0.65	2.4	8.8
13.	5.0	1.19	0.238	0.49	0.66	2.3	8.4
14.	4.6	1.13	0.245	0.51	0.68	2.4	8.3
15.	4.4	1.07	0.243	0.50	0.67	2.2	7.0
16.	4.1	1.02	0.243	0.51	0.68	2.1	6.6
17.	3.9	0.98	0.251	0.52	0.69	2.1	6.4
18.	3.7	0.94	0.254	0.52	0.70	2.1	6.2
19.	2.8	0.78	0.278	0.57	0.77	2.2	6.2
20.	2.4	0.71	0.295	0.60	0.82	2.3	7.0

acterized by an intersection of two straight lines at a definite soap concentration indicating the beginning of the formation of ionic micelles at this soap concentration. The values of the CMC are almost the same (0.0048—0.0047 mol dm^{-3}) for the solvents studied.

The molecular conductance, μ, of the solutions of manganese(II) decanoate decreases with the increasing soap concentration. The plots of μ vs. $C^{1/2}$ indicate that Debye-Huckel-Onsagar's equation is not applicable to these soap solutions and the limiting molecular conductance can not be determined by the usual extrapolation method.

An expression for the dissociation of manganese(II) decanoate can be developed in Ostwald's manner. If C is the concentration (mol dm^{-3}) and α is the degree of dissociation of manganese(II) decanoate, the equivalent concentrations of different species can be written as:

$$\begin{array}{ccc} (C_9H_{19}COO)_2Mn \rightleftarrows & Mn(C_9H_{19}COO)^+ + & C_9H_{19}COO^-, \\ C(1-\alpha_1) & C\alpha_1 & C\alpha_1 \end{array}$$

$$\begin{array}{ccc} (C_9H_{19}COO)_2Mn \rightleftarrows & Mn^{2+} + & 2\,C_9H_{19}COO^-. \\ C(1-\alpha_2) & C\alpha_2 & C\alpha_2 \end{array}$$

The dissociation constants, K_1 and K_2, may be expressed as

$$K_1=\frac{C\alpha_1^2}{1-\alpha_1}, \tag{5}$$

$$K_2=\frac{4C^2\alpha_2^3}{1-\alpha_2}. \tag{6}$$

Since the degree of dissociation of manganese(II) decanoate is small, ionic concentrations will be low and so the interionic effects are almost negligible. Therefore, the dilute solutions of soap do not deviate appreciably from ideal behavior and the activities of ions can be taken as almost equal to the concentrations and the degree of dissociation may be replaced by conductance ratio, (μ/μ_o). On substituting the value of α and rearranging, Eqs. 5 and 6 can be expressed as:

$$\mu C=\frac{K_1\mu_o^2}{\mu}-K_1\mu_o, \tag{7}$$

$$\mu^2C^2=\frac{K_2\mu_o^3}{4\mu}-\frac{\mu_o^2K_2}{4}. \tag{8}$$

The values of the dissociation constants, K_1 and K_2, and limiting molecular conductance, μ_o, have been obtained from the slope and the intercept of the linear plots of μC vs. $1/\mu$ and μ^2C^2 vs. $1/\mu$, respectively.

The values of the degree of dissociation, α_1 and α_2, lie between 0.48 to 0.70 and 0.54 to 0.79 in DMF and 0.49 to 0.60 and 0.65 to 0.82 in 1-butanol, respectively. The results show that the soap behaves as a simple electrolyte in these solutions.

The values of the dissociation constants, K_1 and K_2, obtained from the plots of μC vs. $1/\mu$ and μ^2C^2 vs. $1/\mu$ are 4.2×10^{-3} and 1.1×10^{-4} for solutions in DMF and 2.1×10^{-3} and 7.1×10^{-5} for solutions in 1-butanol, respectively. The higher values of dissociation constants in DMF than 1-butanol are due to the high dielectric constant of DMF. The values of the dissociation constants remain almost constant below the CMC and then change at higher soap concentrations due to the failure of Debye-Huckel's activity equations at higher soap concentrations. The plots of dissociation constant vs. soap concentration show a break at the CMC. The values of the CMC obtained from spectroscopic measurements are in agreement with that obtained from conductance measurements.

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