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B. K. Tyagi^a; R. P. Varma^b; Anil Kumar^b

^a Department of Physics, The Principal of D. A. V. (P.G.) College, Muzaffarnagar, U.P., India ^b

Chemistry Department, D. A. V. (P.G.) College, Muzaffarnagar, U.P., India

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INVESTIGATIONS INTO THE PHYSICOCHEMICAL BEHAVIOUR OF COBALT(II)LAURATE

B. K. TYAGI¹, R. P. VARMA² and ANIL KUMAR^{2,*}

¹*Department of Physics and the Principal of D. A. V. (P.G.) College,
Muzaffarnagar (U.P.)-251 001, India*

²*Chemistry Department, D. A. V. (P.G.) College,
Muzaffarnagar (U.P.), India*

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The infrared results suggest that cobalt(II) laurate is ionic in character and the fatty acid exists as a dimer. The X-ray analysis reveals that the metal soap has a single layer structure. The absorption spectra of the solutions of cobalt(II) laurate in a mixture of 80% benzene and 20% methanol (V/V) are characterised by absorption maxima near 360 and 540 nm. The plots of various physical properties (Viz. conductivity, density and viscosity) versus soap concentration exhibit an intersection of two straight lines at a definite soap concentration, called the critical micelle concentration (CMC) of these soap solutions.

KEY WORDS: Transition metal soaps, viscometry, specific conductance.

1 INTRODUCTION

There is no gain-saying the industrial importance of the transition metal soaps. Research workers in the past have pursued studies on different aspects of these surface active agents. The perusal of literature^{1–16} however suggests that a thorough probe into the physicochemical behaviour of cobalt soaps is yet to be made. The present work thus embodies investigation into both solid state (IR, X-ray) as well as solution (colorimetry, conductometry, viscometry and density) behaviour of cobalt (II) laurate.

MATERIALS AND METHODS

Merck/BDH AR grade chemicals were used in the present study. Cobalt(II) laurate was prepared by direct metathesis of corresponding potassium soap with the required amount of aqueous solution of cobalt(II) nitrate at 55–60°C. The pink coloured precipitate was digested, filtered and washed, first with warm distilled water and subsequently with acetone. The initial drying in an air oven at 60–70°C was followed by drying under reduced pressure. The compound so obtained was recrystallised twice

*Address for correspondence: Dr. Anil Kumar Tyagi, 263/153, II Floor, Sadar Bazar, Muzaffarnagar (U.P.) -251 001, India.

from benzene and dried in vacuo for at least 48 h before use. The purity of the compound was tested by determining its m.p. (96.0°C) and by the elemental analysis.

The IR spectra of lauric acid and cobalt(II)laurate were recorded on a Perkin-Elmer 'Model 577' grating spectrophotometer in the region, $4000\text{--}400\text{ cm}^{-1}$ using potassium bromide disc method. The X-ray diffraction patterns for the metal soap were recorded using a Philips X-rays diffractometer 'PW 1730' and Cu-K_α radiation filtered through a monochromator (nickel-foil) over the range of diffraction angle, $2\theta = 3^\circ\text{--}60^\circ$. The XRD curves were recorded under the applied voltage of $30\text{KV--}15\ \mu\text{A}$, using scanning speed of 3° min^{-1} . The wavelength of radiation was taken as $1.542\ \text{\AA}$. The absorption measurements of the solutions of cobalt (II) laurate in a mixture of 80% benzene and 20% methanol (V/V) were carried out in the region of 340–940 nm with a Toshniwal visible spectrophotometer 'model CL 10A 3' having wavelength reproducibility of $\pm 1\text{ nm}$. A digital conductivity meter Toshniwal CL 01.10 A) and a dipping type conductivity cell with platinised electrodes were used for measuring the conductance of soap solutions. An Ostwald type viscometer was used for measuring the viscosity. The density measurements were made with the help of a pycnometer. The measurements were carried out at a constant temperature $40 \pm 0.05^\circ\text{C}$ in a thermostat.

RESULTS AND DISCUSSION

A number of peaks arising from the diffraction of X-rays by planes of metal ions (basal planes) have been observed over the range of $3^\circ\text{--}60^\circ$ in the diffraction patterns of cobalt(II)laurate. The interplanar spacings, d , have been calculated from the positions of peaks using well known Bragg's relationship. The long spacings or average interplanar spacings (i.e. the perpendicular separation of basal planes) for cobalt(II)laurate ($37.4\ \text{\AA}$) and cobalt(II)caprate ($32.5\ \text{\AA}$) are found to differ by $4.9\ \text{\AA}$. It is also observed that the values of long spacings are approximately equal to the calculated dimensions for corresponding anion (laurate: $37\ \text{\AA}$ and caprate: $32\ \text{\AA}$). The above facts suggest: (a) the CO_2^- ions are arranged in a plane (basal plane) equally spaced in the soap crystal with fully extended zig-zag chains of fatty acid radicals on both sides of each basal plane, and (b) the molecular axes are almost perpendicular to the basal plane. Cobalt(II)laurate thus has a single layer structure as proposed by Vold and Hattiangdi¹⁷ for disoaps.

The infrared spectrum of cobalt(II)laurate (metal soap) shows absorption bands at $2960, 2920, 2850, 1660\text{--}1540, 1460\text{--}1400, 1320\text{--}1310, 1110, 930, 720, 680, 450\text{ cm}^{-1}$. There are marked differences in the spectra of metal soap and fatty acid in some spectral regions. The characteristic vibrations of free acid ($2650, 1700, 1449, 950$ and 550 cm^{-1}) were found to be completely absent in the spectrum of cobalt dilaurate. The IR bands in the spectrum of lauric acid are associated with the carboxyl group of the acid molecule in dimeric state and confirm the existence of intermolecular hydrogen bonding between two molecules of lauric acid. The complete disappearance of the absorption band at 1700 cm^{-1} and appearance of two bands at $1660\text{--}1540$ and $1460\text{--}1400\text{ cm}^{-1}$, which may be assigned^{18–20} to $\nu_{\text{as}}\text{COO}^-$ and $\nu_{\text{s}}\text{COO}^-$ modes of carboxylate group of cobalt (II) laurate, indicate the ionic nature of this group in the soap. The band at 450 cm^{-1} observed in the spectrum of cobalt (II) laurate is assigned to the metal-to-oxygen (CO—O) bond.

The absorption spectra of the solutions of cobalt(II)laurate in 80/20 (V/V) benzene-methanol mixture are characterised by absorption maxima near 360 and 540 nm (Fig. 1). Under octahedral symmetry, the electronic configuration of CO^{2+} permits the following three spin allowed $d-d$ electronic transitions from the ground state, $4T_1(F)$: $4T_{1g}(F) \rightarrow 4T_{2g}$; $4T_{1g}(F) \rightarrow 4A_{2g}$; $4T_{1g}(F) \rightarrow 4T_{1g}(P)$. The appearance of absorption band near 540 nm is assigned to the third transition, viz. $4T_{1g}(F) \rightarrow 4T_{1g}(P)$. The first transition occurs at about 1200 nm but being beyond the range of our instrument could not be observed. Since the second transition is weaker than the third transition and is also closer by, the same could not be observed, too. The spectral measurements have also been carried out with cobalt(II)nitrate solutions. For salt solutions, only one absorption maximum at 510 nm is observed. It is thus evident that the behaviour of cobalt(II)laurate is quite different from that of cobalt salts. The plot of optical density, O.D. versus soap concentration (Fig. 2) is however found to be linear suggesting the applicability of Beer-Lambert's law to these soap solutions.

The increase in specific conductance, $k(\text{mho cm}^{-1})$ with increasing concentration, $C(\text{mol dm}^{-3})$ of the solutions of cobalt(II)laurate in 80/20 (V/V) benzene-methanol mixture at 40°C (Fig. 2) may be ascribed to the ionisation of the metal soap into metal cations, CO^{2+} and fatty acid anions, $\text{C}_{11}\text{H}_{23}\text{COO}^-$ (in dilute solutions). The intersection at $2.7 \times 10^{-2} \text{ M}$ observed in the $k-C$ plot (Fig. 2) refer to the critical micelle

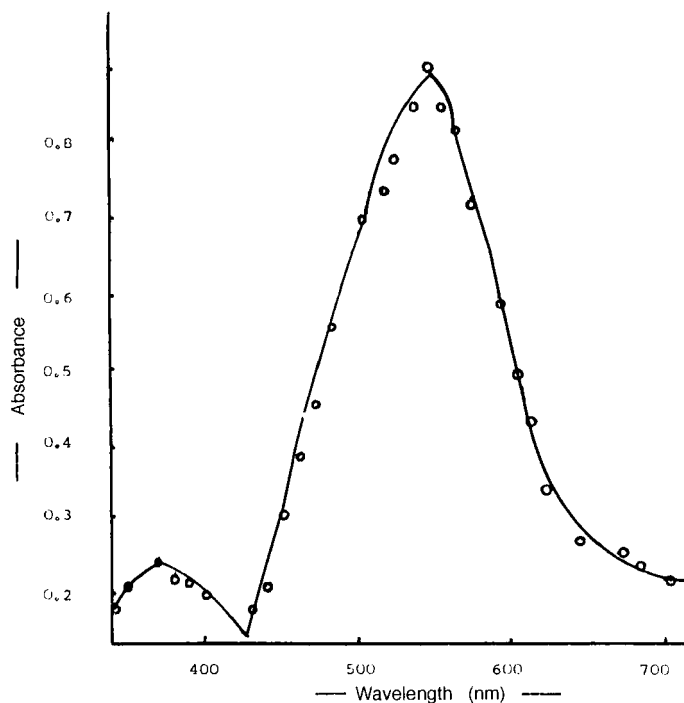


Figure 1 Absorbance versus wavelength of cobalt(II)laurate solutions.

concentration, CMC of the soap solutions (Tab. 1). The k - C plot (Fig. 2) when extrapolated to zero soap concentration gives the specific conductance for the solvent at 40°C (Tab. 1).

Since the molar conductance (mho cm^2), μ vs square root of soap concentration, $C^{1/2}$ plot is not found to be linear, the limiting molar conductance, μ_0 of these solutions can not be obtained by the usual method of extrapolation as the Debye-Huckel-Onsager's equation does not hold good for these solutions. Hence, the following expression²¹ can be derived.

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

The graphical value of limiting molar conductance, μ_0 (mho cm^2), recorded in Table 1, has been evaluated from $\mu^2 C^2$ vs $1/\mu$ plot. The degree of dissociation, α of dilute soap solutions (below the CMC), recorded in Table 1, is calculated by using $\alpha = \mu/\mu_0$ (employing graphical value of μ_0). The values of dissociation constant, K (Tab. 1) for the solutions below the CMC have been evaluated using the expression, $K = 4C^2 \cdot \alpha^3 / (1 - \alpha)$, derived from the dissociation equilibrium in Ostwald's manner. The values of both α and K (Tab. 1) for dilute soap solutions also support the view that cobalt (II) laurate behaves as a weak electrolyte.

The density, ρ ($\text{g} \cdot \text{cm}^{-3}$) of the soap solutions at 40°C is found to increase with increasing soap concentration, C (Fig. 2). The ρ - C plot (Fig. 2) is found to intersect at

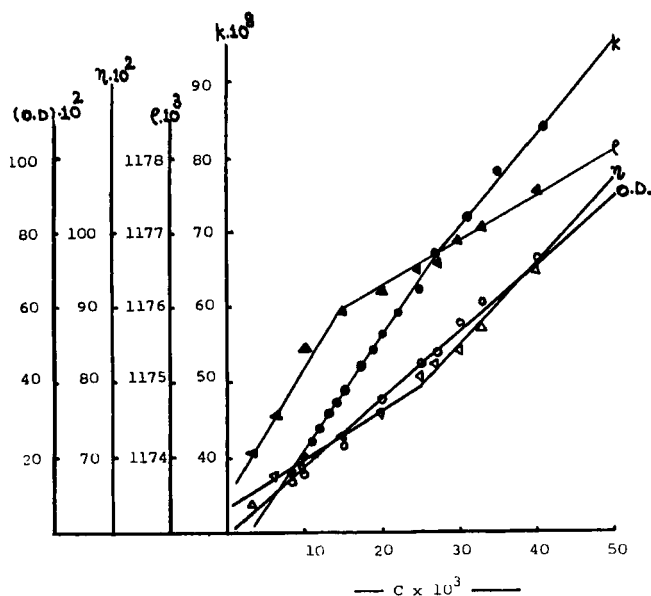


Figure 2 Plots of specific conductance, k (mho cm^{-1}), density, ρ ($\text{g} \cdot \text{cm}^{-3}$), viscosity, η (centipoise) and optical density, O.D. of cobalt(II)laurate in 80/20 (V/V) benzene-methanol at 40°C.

Table 1 Parameters from conductivity, density and viscosity measurements of the soap solutions in 80/20 (V/V) benzenemethanol at 40°C.

Parameters	Derived from	Values for cobalt(II)laurate in 80/20 (V/V) benzene-methanol
Critical micelle concentration CMC (mol dm ⁻³)	k vs C and η vs C	$(2.5-2.7) \times 10^{-2}$ M
Specific conductance for solvent, k_0 (mho cm ⁻¹)	k vs C	2.6×10^{-7}
Limiting molar conductance, μ_0 (mol cm ²)	$\mu^2 C^2$ vs $1/\mu$	103.40
Degree of dissociation, α below the CMC	μ/μ_0	0.24–0.43
Dissociation constant, K below the CMC	$4 C^2 \alpha^3 - \alpha$	$(3.7-4.5) \times 10^{-5}$
Density of solvent, ρ (g.cm ⁻³)	ρ vs C	1.1735
Constants of Roots equation	$(\rho - \rho_0)/C$ vs $C^{1/2}$	$A = 0.4$ $B = -2.0$
Viscosity of solvent, η_0 (c.p)	η vs C	0.635
Molar volume, \bar{V} (dm ³ mole ⁻¹)	η_{SP} vs C	4.9
Constants of Moulik's equation	$1/C$ vs $1/\log(\eta/\eta_0)$	5.0
	$(\eta/\eta_0)^2$ vs C^2	$M = 1.1$ $K = 1.2 \times 10^3$
Constants of Jones-Dole's equation	$\eta_{SP}/C^{1/2}$ vs $C^{1/2}$	$A = 0.20$ and $B = 7.8$ (below CMC)
		$B = 0.64$ and $B = 16.8$ (above CMC)

1.5×10^{-2} M. The plot $(\rho-C)$ upon extrapolating to zero soap concentration gives the density (Tab. 1) for the solvent, ρ_0 (g·cm⁻³). The density data have been explained in terms of Roots equation²². For dilute soap solutions (below the CMC), the values of constants A and B evaluated from the plot of $(\rho - \rho_0)/C$ vs $C^{1/2}$ (Tab. 1) signify that the soap molecules do not show appreciable aggregation below the CMC (pre-micellar region).

The plots of both viscosity, η (Centipoise) vs. Soap concentration, C (Fig. 2) and the specific viscosity, η_{SP} vs C (Einstein equation²³) are also found to intersect at 2.5×10^{-2} M. The extrapolated value of viscosity to zero concentration, η_0 (η - C plot) is recorded in Table 1. The viscosity results have been interpreted on the basis of the well known equations²³⁻²⁶. The values of molar volume, \bar{V} (dm³ mol⁻¹) evaluated from the plot of η_{SP} vs C (Einstein²³-type plot) and $1/C$ vs. $1/\log(\eta/\eta_0)$ [Vand²⁴-type plot], recorded in Table 1, are found to be consistent showing the applicability of the equations to the soap solutions in Pre-micellar region. The interaction coefficient, ϕ calculated from the intercept of $1/C$ vs $1/\log(\eta/\eta_0)$ plot is 6.0. The plots of $(\eta/\eta_0)^2$ vs C^2 (Moulik²⁵-type plot) for dilute soap solutions are linear indicating that the equation of Moulik²⁵ holds good in the pre-micellar region. Moulik's constants (M , K), recorded in Table 1, have been evaluated from intercept and slope of (η/η_0) vs C^2 plot. For soap solutions, the constants of Jones-Dole's equation²⁶ (A and B) evaluated from intercept and slope of $\eta_{SP}/C^{1/2}$ vs $C^{1/2}$ plot are found to accord with $B > A$ (Tab. 1). The above facts confirm that the aggregation of soap molecules begin only at a definite soap concentration, known as the critical micelle concentration (CMC).

The present investigation thus signifies facts that might be useful in ascertaining the applied worth of the metal soap. The IR spectrum supports the ionic character in

cobalt(II)laurate. The spectrophotometric measurement of these solutions corroborate the octahedral symmetry for cobalt soap. The X-ray analysis ascribes a single layer structure to the metal soap. The physical methods, viz., conductivity, density and viscosity, have also proved useful in examining the solution behaviour of this compound.

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