Studies on Conductivity of the System: Barium Soap-Water and Propanol-1

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Abstract

The conductivity behavior of barium soap solutions in water-propanol-1 mixtures is exhibted by an equation:

$$\log \mu = A + B \log C$$

where A and B are constants, C is concentration of barium soap in q, moles/litre and μ is molecular conductivity.

The values of the constant B are independent of the chain length of the soap below 50% propanol-1 concentration whereas above 50%, the values increase with the increase in the number of carbon atoms in the soap. The values of constant A also show a transition at 50% propanol-1 concentration.

The results confirm that the change in the behavior takes place at about 50% propanol-1 concentration.

Introduction

THE CONDUCTIVITY OF AQUEOUS SOAP solutions has been extensively studied but the effect of organic additives has not been much investigated. A number of workers (1–4) have investigated soap solutions which bridge the transition from aqueous to nonaqueous solutions. It has been first pointed out by Laing (5) that the soaps dissolve in alcohols as simple electrolytes rather than as colloidal electrolytes. Bhatnagar and Prasad (6) have determined the specific and equivalent conductivities of sodium and potassium soaps in alcohols, toluene, and pyridine. The effect of the concentration of o-cresol on the conductivity of soap solutions has been studied by Angelescu (7) and by Angelescu and Woinarosky (8). The effect of propanol-1, propanol-2 and of propionic acid on the conductivity of aqueous soap solutions has been studied by Flockhart and Ubbelohde (9) and it has been suggested that these additives lower the c.m.c. when added in small amounts and thus favour micelle formation. The conductance of lithium and cesium soaps in various polar solvents has been investigated by Little and Singleterry (10); the conductivity of sodium soap solutions in the presence of varying amounts of different alcohols has been studied by Bose et al. (11–13). The effect of various organic additives on the conductivity of the system: water-0.2M lithium laurate and butanol-1 has been investigated by Mehrotra and Bhargava (14).

A systematic study of the molecular conductivity of barium soaps in water-propanol-1 mixtures of varying composition has been undertaken to find out the nature of the micelles formed in mixed solvents under different conditions.

Experimental Procedures

Materials

Merck reagent grade propanol-1, caprylic, capric, and lauric acids were used and purified by distilling under reduced pressure. Purity of reagents was confirmed by the determination of their melting and boiling points.

Preparation of Soaps

Sodium soaps were prepared by refluxing equivalent amounts of fatty acids and sodium hydroxide in alcohol for 10–12 hr on a water bath. The soaps were purified by recrystallization from alcohol and then dried in vacuum.

The barium soaps were prepared by direct metathesis of the corresponding sodium soap with the required amount of barium hydroxide solution at 50–55C. The precipitated barium soaps were washed with distilled water and then with alcohol to remove the free precipitant and acid, respectively. After initial drying in an air oven at 100–105C, the final drying was carried out under reduced pressure.

Preparation of Solutions

A calculated amount of the soap was weighed in a standard flask; the solution was produced by adding required amounts of propanol-1 and conductivity water. In this way a number of solutions of 10–80% propanol-1 containing different soap concentrations (0.001–0.105M) were prepared.

Conductivity Determinations

A. Kohlrausch Universal Bridge (W. G. Pye & Co., Ltd., Cambridge, England) was used for measuring the conductance of the soap solutions. All measurements were made in a thermostat at constant temperature (±0.05C). A dipping type conductivity cell with platinized platinum electrodes was used. The cell constant was determined with 0.10N and 0.01N solutions of purified potassium chloride.

The reproducibility of the measurements was examined by repeating the measurements several times. The reproducibility of resistance readings was 0.1%. The results given in the figures are molecular conductivities at 40C.

Results and Discussion

The plots (Fig. 1) of molecular conductivity against volume percentage of propanol-1 show that the conductivity decreases linearly as the volume percentage of propanol-1 in the system increases from 20% to 70%. The plots show a slight deviation from the linear decrease above 70% propanol-1 concentration and this may be due to the change in the viscosity behavior of soap solutions above 70% propanol-1 concentration. The viscosity of the soap solutions increases as the volume percentage of propanol-1 increases from 20% to 70% and then decreases with further increase in propanol-1 concentration in the system. The viscosity results show a change in behavior at 70% propanol-1 concentration (15). The molecular conductivity of the soap solutions in water-propanol-1 mixtures decreases as the concentration of the soap in the system increases.

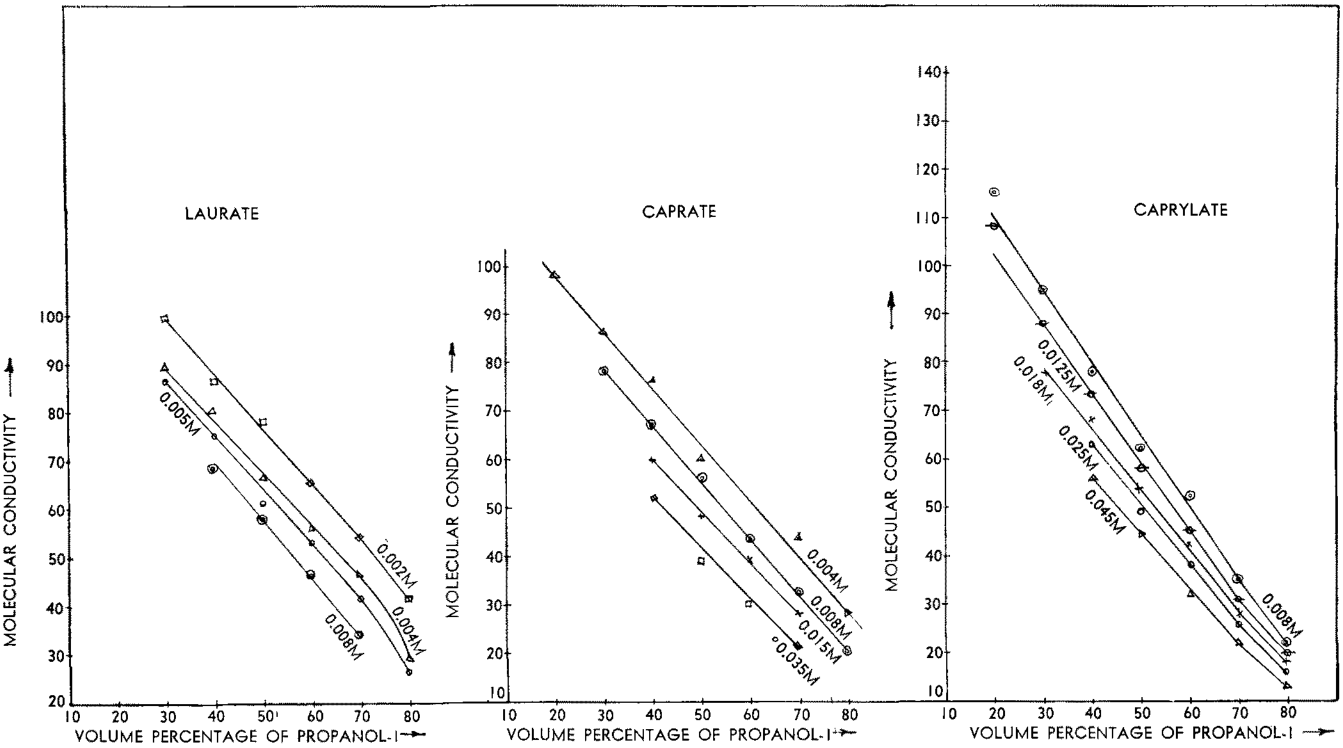

Fig. 1.

The plots of molecular conductivity, μ, against the square root of concentration (in M), $C^{1/2}$, are concave upwards (Fig. 3). This may be due to the fact that the factor, (μ/μ_0), steadily decreases the slope on μ-$C^{1/2}$ plot as the concentration increases and therefore gives a curve which is concave upwards. It has been suggested that association takes place in soap solutions and the degree of association decreases as the volume percentage of propanol-1 in the system increases.

It may be pointed out that the plots of $\log\mu$ against log C for soap solutions are linear for all compositions of water-propanol-1 mixtures (Fig. 2). The behavior of the soap solutions may be exhibited by equation

$$\log\mu = A + B \log C \qquad [1]$$

where A and B are constants.

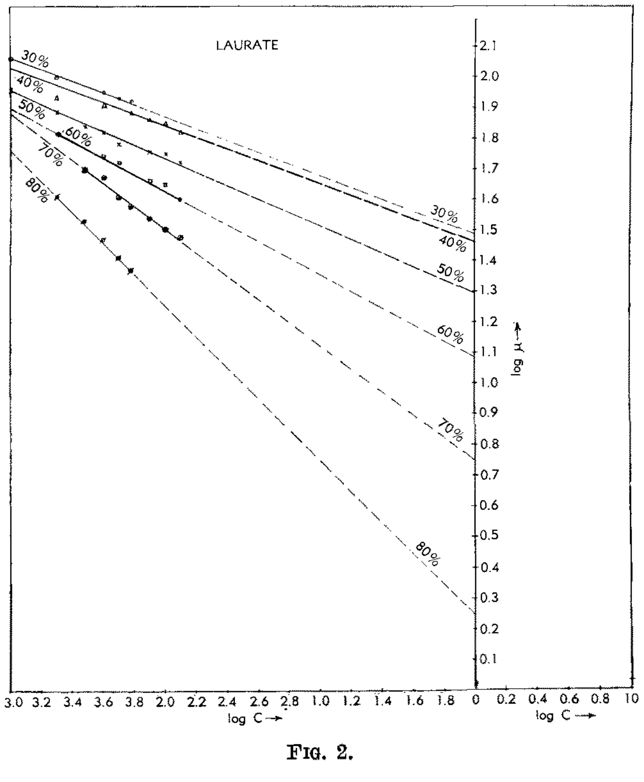

Fig. 2.

The values of $\log\mu$ for zero values of log C (i.e., for C = 1) have been found by extrapolation. The values of molecular conductivity of solutions of 1M (i.e. $\mu_{c=1}$) in water-propanol-1 mixtures of various compositions have been calculated and are given in Table I. It may be pointed out that it is not possible to prepare soap solutions of such high concentrations (1M) in water-propanol-1 mixtures. It has been observed that $\mu_{c=1}$ decreases with the increase in the volume percentage of propanol-1 in the system (Table I). The differences in the successive values of $\mu_{c=1}$ (for 10% increase in propanol-1 concentration) suggest that a change in behavior occurs above 50% propanol-1 concentration and this may be due to the change in the nature of the solvent. A similar change in specific conductivity values of water-propanol-1 mixtures (without soap) of varying composition has also been observed above 50% propanol-1 concentration. The change above 50% propanol-1 concentration (by volume) may be due to the big difference in molar volumes of water and propanol-1.

TABLE I

Extrapolated values of $\mu_{c=1}$

Temperature 40C

Volume % of propanol-1	Name of the soap		
	Laurate	Caprate	Caprylate
20	......	42.7	52.5
30	30.9	35.5	37.2
40	28.9	28.9	33.1
50	19.5	19.5	23.4
60	11.7	11.8	15.9
70	5.6	7.6	9.3
80	1.7	2.4	5.2

TABLE II
Values of constant B
Temperature 40C

Volume % of propanol-1	Name of the soap		
	Laurate	Caprate	Caprylate
20	.....	0.16	0.17
30	0.17	0.17	0.20
40	0.20	0.17	0.17
50	0.21	0.20	0.20
60	0.27	0.30	0.23
70	0.40	0.30	0.27
80	0.50	0.43	0.30

It may also be pointed out that the values for caprylate are higher than the corresponding values for caprate and laurate, this may be due to the greater tendency of aggregates to form in laurate and caprate than in caprylate.

The values of constant B (i.e., the slopes of the plots (Fig. 2) for all the soaps vary between 0.16 to 0.21 for systems containing propanol-1 below 50%, whereas the values of the slopes are between 0.23–0.50 for systems containing higher volume concentrations of propanol-1. Constant B in Eq. 1 is independent of the chain length of the soap below 50% propanol-1 concentration whereas it increases with the increase in the number of carbon atoms in the soap in presence of higher concentrations of propanol-1. This confirms that the change in behavior takes place at about 50% propanol-1 concentration. It has been suggested that hydrophilic oleomicelles, according to the classification of micelles by Schulman and Riley (16), are formed at lower concentrations of propanol-1 in the system, whereas the soap behaves as weak electrolyte in water-propanol-1 mixtures of lower dielectric constant containing higher percentages of propanol-1.

Comparison of the results shows that the molecular conductivity of soap solutions at different concentrations in water-propanol-1 mixtures are higher for caprylate than corresponding values of caprate and laurate; the difference in value is much higher at lower concentrations of propanol-1 (up to 50%) than in the presence of higher percentages of propanol-1 in the system. Also the molecular conductivity of the soap solutions does not show a linear increase with the rise of temperature even for a (45–55C) range.

ACKNOWLEDGMENTS

R. C. Kapoor, Head of the Chemistry Department, Jodhpur University, gave valuable criticism throughout the investigation. R. P. Varma is grateful to C.S.I.R., New Delhi, for the research fellowship award.

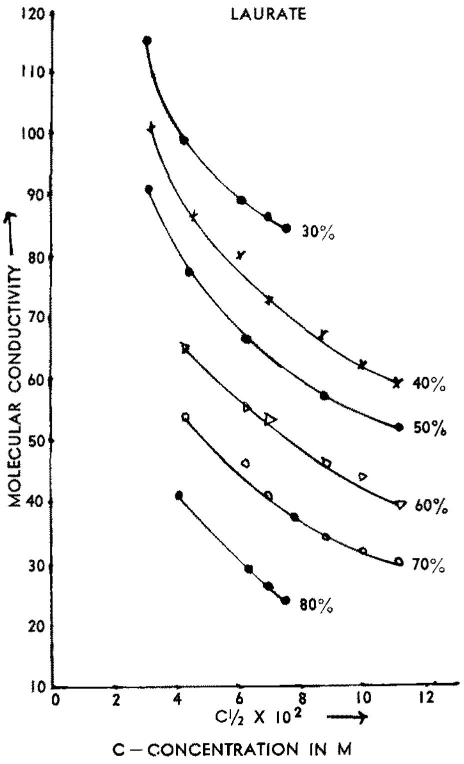

FIG. 3.

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[Received April 12, 1968]