Studies on the Physical Properties of the System: Barium Caproate-Water and Propanol-1.

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Abstract

The critical micelle concentration of barium caproate has been determined by studying the density and viscosity of the soap solutions in water-propanol-1 mixtures of varying composition. Studies on solubility, density, viscosity and molecular conductivity confirm that the change in the nature of the micelles occurs between 50% and 60% propanol-1 concentrations.

Introduction

In previous communications (1–3), the conductivity, molar refraction and surface tension of barium soap solutions in mixed solvents have been investigated. In the present work, the physical properties (solubility, density, viscosity and conductivity) of the system: Barium caproate—water and propanol-1 have been studied to determine whether or not the micellar aggregates are formed in these soap solutions. This work has been initiated to determine the critical micelle concentration and to investigate the nature of the soap micelles formed in mixed solvents under different conditions.

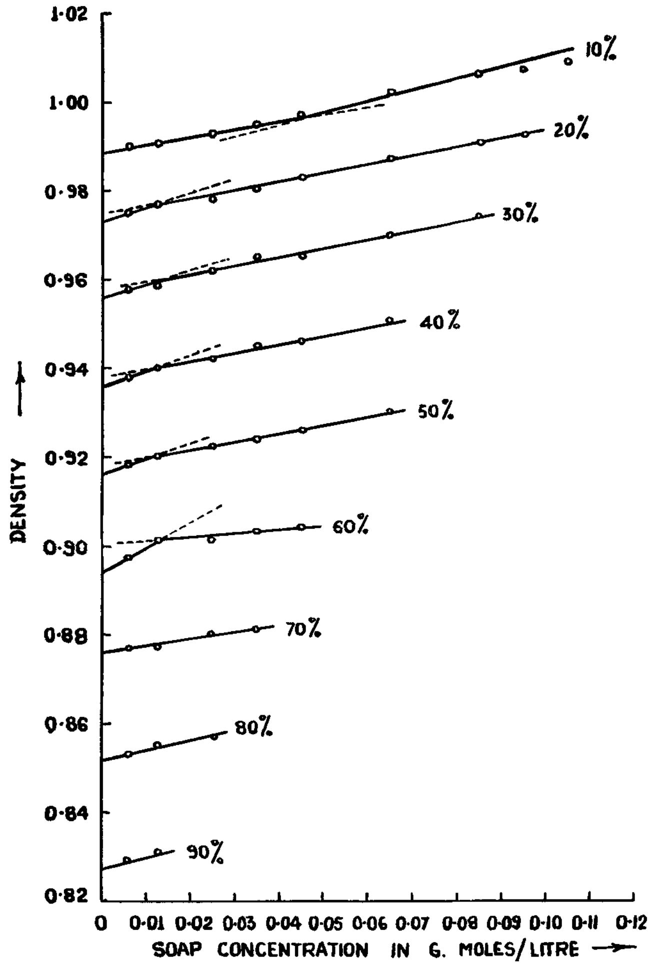

FIG. 1. Variation of Density With Soap Concentration.

Experimental Procedures

Preparation of Soap Solutions

Merck reagent grade propanol-1 and caproic acid were used after distilling under reduced pressure.

Sodium caproate was prepared by refluxing equivalent amounts of caproic acid and sodium hydroxide in alcohol for 10–12 hr on a water bath. The soap was purified by recrystallization from alcohol and then dried in vacuum.

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

A calculated amount of barium caproate was weighed in a standard flask and the solution was brought up to the mark by adding the required amounts of conductivity water and propanol-1. In this way a number of solutions of different concentrations of barium caproate in 10% to 90% propanol-1 (v/v) were prepared.

Apparatus

All measurements were made in a thermostat at constant temperature (40 $\pm$ 0.05 C). The density and viscosity of the soap solutions were measured by means of pyknometer and viscometer, respectively. A Kohlrausch universal bridge (W. G. Pye & Co., Ltd., Cambridge, England) and a dipping type conductivity cell with platinized electrodes were used for measuring the conductance of the soap solutions.

The reproducibility of the measurements was examined by repeating the measurements several times. The volume of the pyknometer was about 15 ml which allowed an accuracy of about one unit in the fourth place of the decimal of the density data. The reproducibility of the viscosity and resistance results was 0.3% and 0.1%, respectively.

Results and Discussion

Solubility

The solubility of caproate in water—propanol-1 mixtures of varying composition decreases with the increase in propanol-1 concentration in the system (Table I). The solubility shows a large decrease between 50% and 60% propanol-1 concentrations than between 20–30%, 30–40%, 40–50%, 60–70% and 70–80% propanol-1 concentrations. The larger decrease in solubility between 50% and 60% propanol-1 may be due to the change in the nature of the solvent. The decrease in solubility with the increase in volume per cent of propanol-1 may be due to the fact that mixed films of soap and alcohol are formed and that the alcohol takes the same position as the soap molecule in the palisade layer of the soap micelle. Therefore, the amount of soap required for the saturation of the palisade layer decreases with the increase in alcohol concentration in the system.

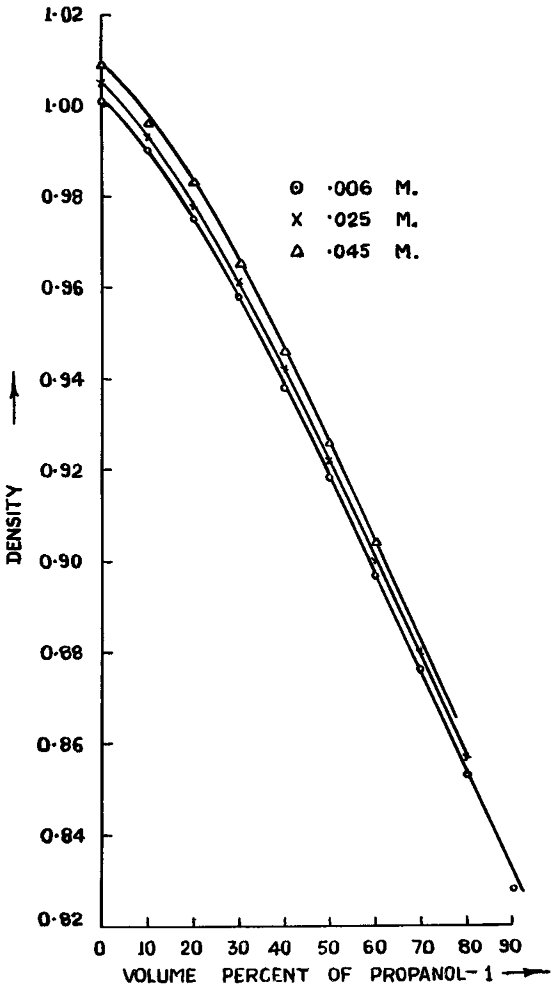

FIG. 2. Variation of Density With Solvent Composition.

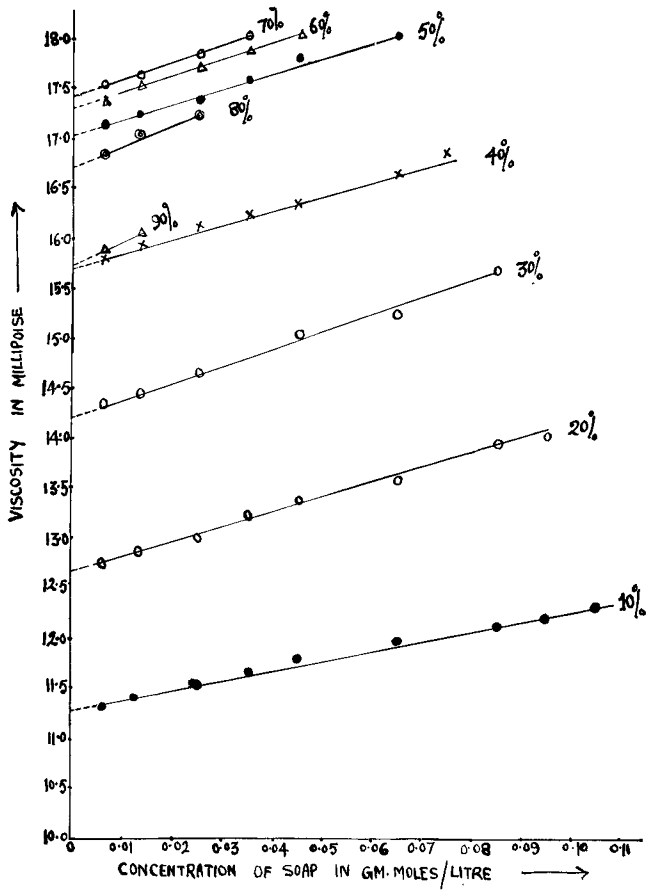

FIG. 3. Variation of Viscosity With Soap Concentration.

Density

The density, ρ, of caproate solutions in water—propanol-1 mixtures of varying composition increases with the increase in soap concentration. The variation in density with soap concentration for solutions containing propanol-1 below 60% is characterised by an intersection of two straight lines at a definite soap concentration which is independent of the solvent composition between 20% to 60% propanol-1 concentrations (Fig. 1). The point of intersection corresponds to the critical micelle concentration (CMC) at which there is a sudden change in the aggregation of the soap molecules. The CMC value for caproate in presence of 10% propanol-1 is much higher than the CMC (0.0125 M) for 20% to 60% propanol-1 systems. It is suggested that the alcohol is incor-

TABLE I

Solubility and Extrapolated Values of Density and Viscosity for Barium Caproate in Water-Propanol-1 Mixtures

Temperature 40 C

Volume % of propanol-1	Solubility in g moles/liter	Density: Extrapolated value	Density: For solvent mixture without soap	Viscosity (in millipoise): Extrapolated value	Viscosity (in millipoise): For solvent mixture without soap
10	0.105	0.989	0.984	11.3	11.33
20	0.095	0.972	0.970	12.7	12.55
30	0.085	0.956	0.953	14.2	14.21
40	0.075	0.935	0.934	15.7	15.34
50	0.065	0.915	0.913	17.0	16.81
60	0.045	0.893	0.893	17.3	17.18
70	0.035	0.873	0.871	17.4	17.30
80	0.025	0.850	0.846	16.7	16.35
90	0.012	0.825	0.827	15.7	15.48

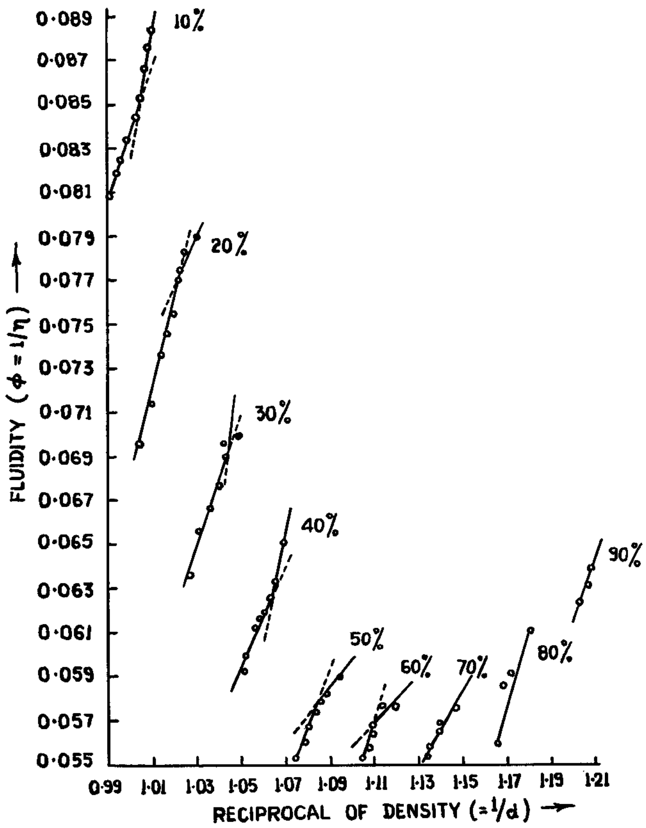

FIG. 4. Fluidity, ($\phi = 1/\eta$), Against Reciprocal of Density, 1/d.

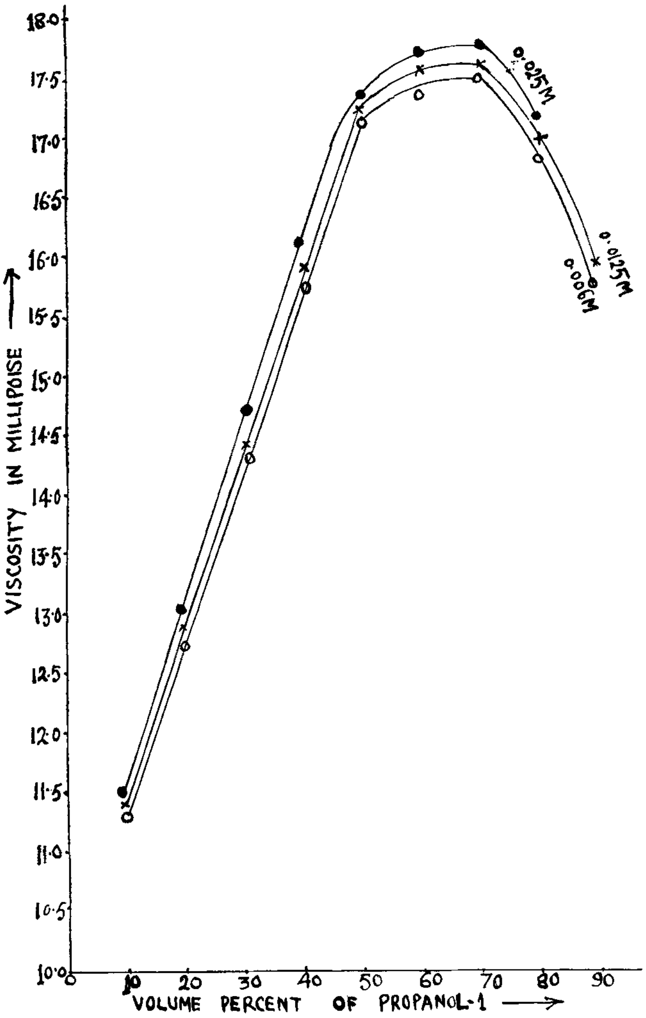

FIG. 5. Variation of Viscosity With Solvent Composition.

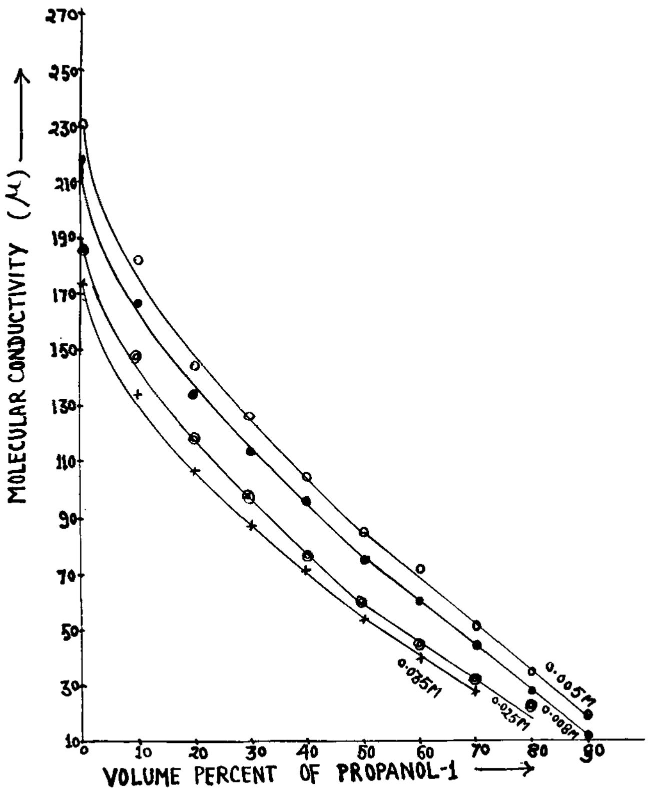

FIG. 6. Variation of Molecular Conductivity With Solvent Composition.

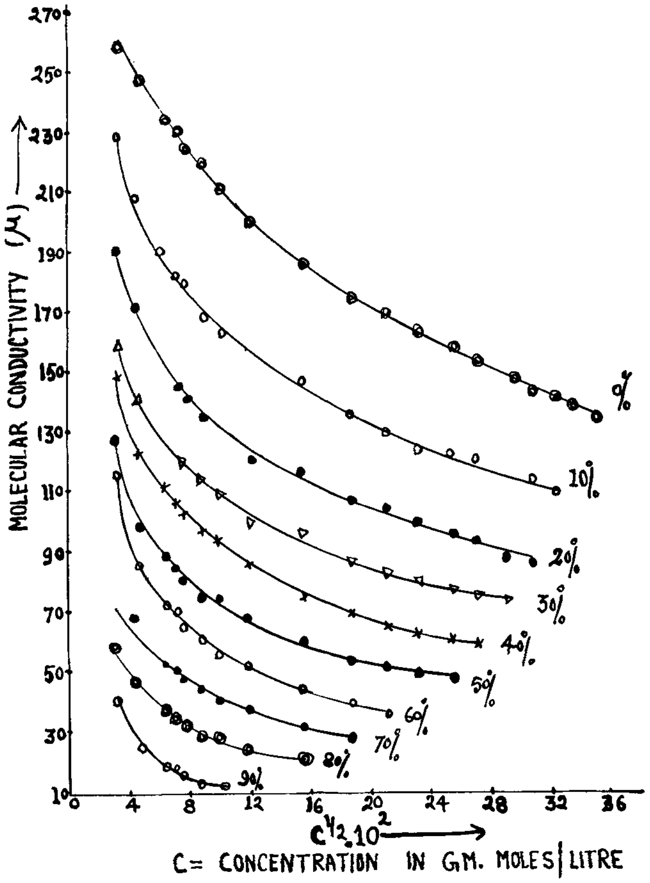

FIG. 7. Variation of Molecular Conductivity With The Square Root of Soap Concentration.

porated in the soap micelles and so the rapid aggregation starts at a much lower soap concentration in presence of higher concentrations of propanol-1.

It may be pointed out that the plots of density against soap concentration for solutions containing propanol-1 above 60% are linear whereas the plots for solutions containing propanol-1 below 60% are characterized by an intersection of two straight lines. This difference may be due to the change in the nature of the solvent. It has been suggested that hydrophilic oleomicelles [according to the classification of the micelles by Schulman and Riley (4)] are formed in presence of lower concentrations of propanol-1 and the change in the nature of the micelles takes place as the amounts of water and propanol-1 are varied in the system.

The plots of density, ρ, against soap concentration, C, are extrapolated to zero soap concentration and the extrapolated values for different compositions of the solvent mixture are summarized in Table I. The extrapolated values of density, ρ_0, are in agreement with the densities of the solvent mixture and are also independent of the chain length of the soap. Therefore the soap molecules do not show appreciable aggregation below CMC, whereas at this definite concentration there is a marked change in the aggregation of the soap molecules.

The density of caproate solutions and of the solvent mixture at first decreases nonlinearly as the volume per cent of propanol-1 increases to 50% and then decreases linearly with further increase in propanol-1 concentration (Fig. 2). This may be due to the change in the nature of the solvent as the amounts of water and propanol-1 are varied in the system.

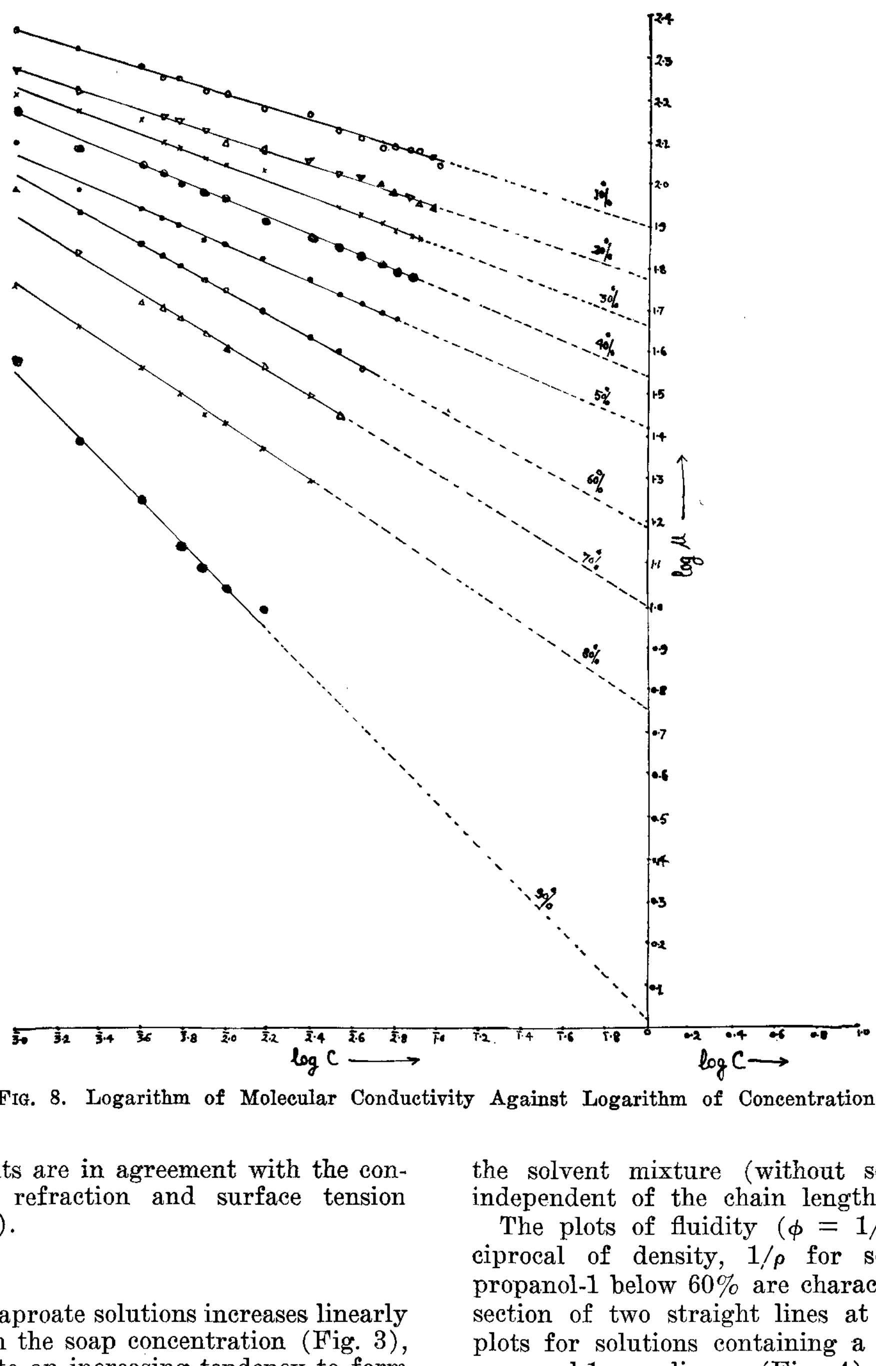

FIG. 8. Logarithm of Molecular Conductivity Against Logarithm of Concentration.

The density results are in agreement with the conclusions of molar refraction and surface tension measurements (2,3).

Viscosity

The viscosity of caproate solutions increases linearly with the increase in the soap concentration (Fig. 3), which may be due to an increasing tendency to form aggregates with increasing soap concentration. The plots of viscosity, η, against soap concentration (g moles/liter), C, are extrapolated to zero soap concentration and the results for various compositions of solvent mixtures are given in Table I. The extrapolated values of viscosity, η_0, are in agreement with the corresponding experimental viscosity values of the solvent mixture (without soap) and are also independent of the chain length of the soap.

TABLE II

Values of Constant B and $\mu_{c=1}$

Volume % of propanol-1	Values of constant B	Values of $\mu_{c=1}$
10	0.15	79.4
20	0.17	60.3
30	0.18	47.9
40	0.20	34.7
50	0.20	26.3
60	0.27	15.4
70	0.30	10.0
80	0.33	5.8
90	0.50	1.0

The plots of fluidity ($\phi = 1/\eta$), against the reciprocal of density, $1/\rho$ for solutions containing propanol-1 below 60% are characterized by an intersection of two straight lines at CMC, whereas the plots for solutions containing a higher per cent of propanol-1 are linear (Fig. 4). A similar change in the behavior has also been observed in the density results. The CMC values are in complete agreement with those obtained from density measurements.

The viscosity of the soap solutions and of the solvent mixture at first increases linearly as the volume per cent of propanol-1 increases to 50%, then increases slowly (between 50–70% propanol-1 concentrations), and finally decreases with the increase in propanol-1 concentration (Fig. 5). The increase in viscosity below 70% propanol-1 concentration may be due to the increase in the size of the micelles, because the alcohol is also incorporated in the micelles. The decrease in viscosity above 70% propanol-1 concentration may be due to the decrease in the degree of aggregation with the increase in propanol-1 concentration.

The viscosity results are in agreement with the results of the density measurements.

Molecular Conductivity

The molecular conductivity, μ, of caproate solutions in water—propanol-1 mixtures of varying compositions decreases as the volume per cent of propanol-1 in the system increases. The decrease in conductivity may be due to the combined effects of the change in dielectric constant, hydration, degree of aggregation and viscosity with the change in the composition of the solvent mixture.

The plots of molecular conductivity, μ, against volume per cent of propanol-1 show a change at 50% propanol-1 concentration (Fig. 6). The density and viscosity results also exhibit a change in the behavior at 50% propanol-1 concentration.

The molecular conductivity, μ, of caproate solutions in water—propanol-1 mixtures decreases with the increase in soap concentration. The plots of molecular conductivity, μ, against the square root of soap concentration (g moles/liter), $C^{1/2}$, are concave upwards (Fig. 7), and in this respect the behavior of the caproate system is similar to those of caprylate, caprate and laurate systems (1). The plots of log μ against log C are linear for all compositions of the solvent mixture and the conductivity behavior may be exhibited by an empirical equation:

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

where μ is molecular conductivity, A and B are constants and C is the concentration (in g moles/liter) of the soap solution.

The values of the constant B, i.e., the slopes of the plots of log μ against log C (Fig. 8) vary between 0.15 and 0.20 for systems containing propanol-1 below 50%, whereas the values of B range from 0.27 to 0.50 for systems containing higher concentrations of propanol-1 (Table II). This difference in behavior confirms that the change in the nature of the micelles occurs between 50% and 60% propanol-1 concentrations.

The values of log μ for zero values of log C (i.e., C = 1) are obtained by extrapolating the plots (Fig. 8) and the calculated molecular conductivities of caproate solutions of 1 g mole/liter concentration (i.e., $\mu_{c=1}$) and are given in Table II. The values of $\mu_{c=1}$ decrease with the increase in the volume per cent of propanol-1. The differences in the successive values of $\mu_{c=1}$ (for 10% increase in propanol-1 concentration) show that the change in the nature of the micelles takes place between 50% and 60% propanol-1 concentrations.

The molecular conductivity of caproate solution is higher than the corresponding values of higher soaps, which may be due to the increasing tendency to form aggregates with the increase in the chain length of the soap.

The results are in complete agreement with those of the studies of other physical properties (2,3).

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