Studies on Viscosity of Calcium Soaps in Aqueous Methanol

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ABSTRACT

Viscosity measurements of calcium soaps show that two kinds of micelles are formed in aqueous methanol mixtures. The change in the nature of micelles from hydrophilic oleomicelles to lipophilic hydromicelles occurs in solvents containing 40-50% (v/v) of methanol. The equations of Vand and Moulik are applicable only above the critical micelle concentration of the soaps. The parameters of the equations have been evaluated. These may be used to calculate the viscosity of soap solutions in the concentration range in which the equations hold good.

INTRODUCTION

In a previous communication (1), conductivity measurements of calcium soap solutions in aqueous methanol have been used to determine the critical micelle concentrations of the soaps. In the present work, the viscosity of calcium soaps in mixed solvents has been determined to study the micelle formation under different conditions and confirm the results obtained from conductivity measurements (1).

EXPERIMENTAL PROCEDURES

The chemicals were purified, and the soaps were prepared by the method described in the previous communication (1). An Ostwald viscometer was used to determine the viscosity of soap solutions in a constant temperature (40 ± 0.05 C) bath. The densities were measured with an accuracy of ± 0.0001 with a pyknometer.

RESULTS AND DISCUSSION

The viscosity of soap solutions increases with increasing soap concentration due to the increasing tendency of the solutions to form micellar aggregates at higher concentrations. The plots (Figs. 1 and 2) of viscosity vs soap concentration indicate that a point is reached at which a discontinuity occurs and the viscosity increases at a slower rate. The concentrations at the inflection point are 0.012 and 0.010 M, indicating probable formation of micelle for valerate and caproate, respectively at all concentrations of methanol (v/v). However, the plots (Fig. 3) for caprylate solutions are linear.

It also must be pointed out that the viscosity of the soap solutions increases with an increase in the chain length of the soap. This may be due to an increase in the size of the micelles with increasing number of carbon atoms in the soap. The viscosities of solutions of various soaps' molecular concentration are in the following order:

caprylate > caproate > valerate.

The extrapolated values of viscosity for zero soap concentration for all compositions of water-methanol mixtures (Table I) show an increase with increasing concentration of methanol (up to 40%) and then a decrease. It also has been observed that the extrapolated values are in agreement with the corresponding experimental viscosity values of the solvent mixture and are independent of the chain length of the soap.

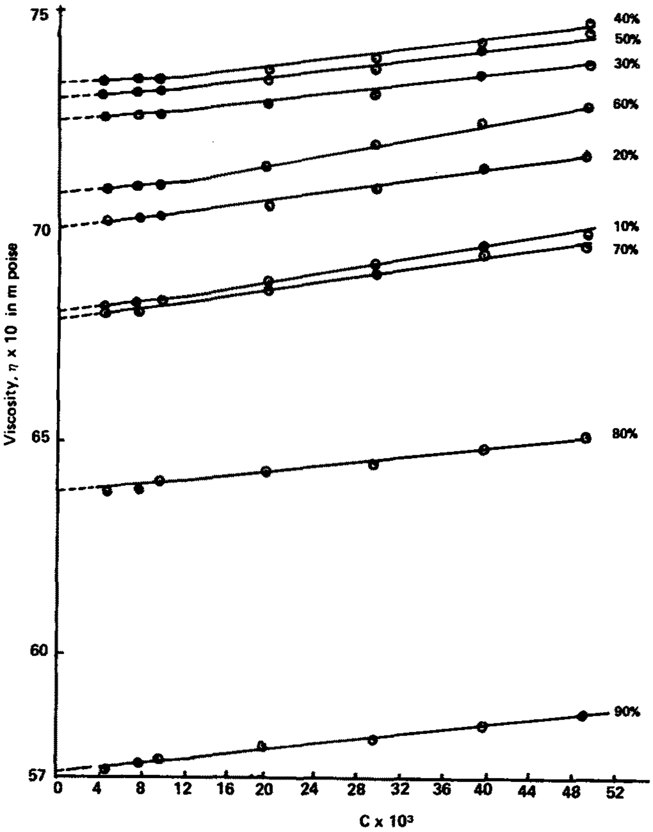

FIG. 1. Plots of viscosity in millipoise vs concentration in moles/liter of calcium valerate.

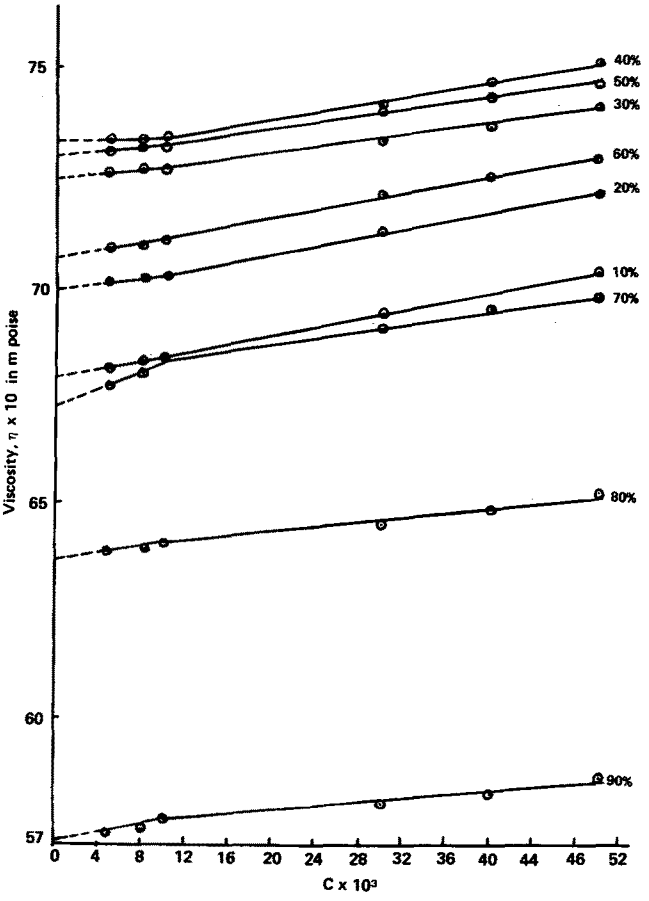

FIG. 2. Plots of viscosity in millipoise vs concentration in moles/liter of calcium caproate.

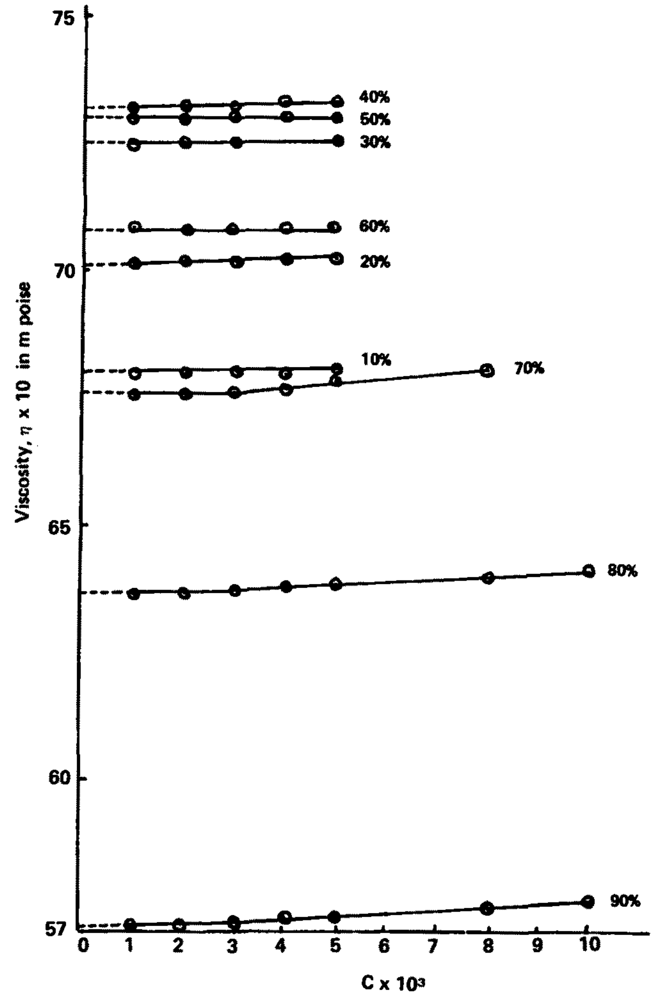

FIG. 3. Plots of viscosity in millipoise vs concentration in moles/liter of calcium caprylate.

It has been observed that the viscosity of the soap solutions in methanol increases linearly up to 40% (v/v) of methanol and then decreases. It has been suggested that hydrophilic oleomicelles are formed at concentrations of methanol lower than 40%, whereas lipophilic hydromicelles are produced at higher concentrations of methanol (2). A change in the behavior of calcium soaps in solutions containing 40% and 50% methanol also has been observed by conductivity studies (1).

It may be pointed out that the viscosity of calcium soap solutions in water-methanol mixtures were represented satisfactorily in the wide range of concentration by the following (3-4) equations:

$$\text{Vand: } 1/C = (0.921/\bar{V})^{-1} \cdot 1/\log \eta/\eta_0 + Q\bar{V}, \qquad \text{(I)}$$

where Q and $\bar{V}$ are the interaction coefficient and molar volume of the solute in liter mole^{-1} and C is the concentration of the solute in moles liter^{-1}.

$$\text{Moulik: } (\eta/\eta_0)^2 = M + K'C^2, \qquad \text{(II)}$$

where M and K′ are constants.

The plots of $1/C$ vs $1/\log \eta/\eta_0$ and $(\eta/\eta_0)^2$ vs C^2 were found to be linear for the data only for a limited range of concentration (Table II). The table reveals that the equations are valid only in the concentration range above the cmc (cmc for calcium valerate and calcium caproate are 0.012 M and 0.010 M, respectively). It should be pointed out that these equations did not represent behavior of the solutions of caprylate in lower concentrations of methanol because of lower solubility of soap.

The values of molar volume ($\bar{V}$) have been calculated from the slopes ($\bar{V}/0.921$) of the plot of $1/c$ vs $1/\log \eta/\eta_0$, and the results are given in Table II. The values of $\bar{V}$ do not remain constant with an increase in methanol concentration, but the sudden increase in the values for solutions containing 50% methanol suggests that a change in behavior occurs at this alcohol concentration. The values of $\bar{V}$ recorded in Table II show the order:

caprylate > caproate > valerate

This may be due to the greater tendency of aggregates to form in caproate than in valerate. The interaction coefficients Q, have been calculated from the intercept ($=Q\bar{V}$) and are given in Table II. The values show a change at ca. 50% concentration of methanol which again supports the result of $\bar{V}$.

To compare the applicability of both equations, the constants K′, and M have been calculated from the slopes and intercepts of the plots of the $(\eta/\eta_0)^2$ vs C^2, and the results are summarized in Table II. It has been observed that the values of M and K′ also show a change at ca. 50% methanol concentration.

Both the equations reveal that a change in the nature of micelles takes place at ca. 50% methanol concentration, which is in close agreement with the results obtained in conductivity measurements (1). Although Vand's equation contains perfectly defined parameter $\bar{V}$, the interaction coefficient Q is only ca. obtained (5). It appears that most probably Q is a specific property of a solute and is not a general property (6). It also should be mentioned that parameters M and K′ of equation (II) are not yet defined.

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TABLE I

Extrapolated and Experimental Values of Viscosity of Calcium Caprylate, Caproate, and Valerate Solutions for Zero Soap Concentration at 40 C in Different Mixtures of Water and Methanol

Volume percent of methanol	Viscosity (m poise)			
	Extrapolated			
	Caprylate	Caproate	Valerate	Experimental
10	6.80	6.79	6.80	6.794
20	7.01	6.99	6.99	7.011
30	7.25	7.25	7.24	7.249
40	7.32	7.34	7.33	7.323
50	7.30	7.29	7.29	7.297
60	7.08	7.06	7.07	7.081
70	6.76	6.72	6.77	6.753
80	6.36	6.37	6.38	6.365
90	5.71	5.70	5.72	5.714

TABLE II

Parameters for Calcium Valerate, Caproate, and Caprylate Solutions[a]

Volume percent of methanol	Tested concentration limit (moles/liter)	Valid zones (moles/liter)	$\bar{V}$	Q	M	K′
		Calcium valerate				
10	0.005-0.05	0.03-0.05	0.19	15.51	14	1.021
20	0.005-0.05	0.03-0.05	0.14	28.96	14	1.001
30	0.005-0.05	0.02-0.05	0.06	170.60	14	1.002
40	0.005-0.05	0.02-0.05	0.06	186.10	15	1.002
50	0.005-0.05	0.02-0.05	0.10	78.96	15	1.007
60	0.005-0.05	0.03-0.05	0.16	38.42	15	1.016
70	0.005-0.05	0.02-0.03	0.21	23.60	15	1.028
80	0.005-0.05	0.02-0.03	0.16	19.16	13	1.013
90	0.005-0.05	0.02-0.03	0.17	12.06	13	1.015
		Calcium caproate				
10	0.005-0.05	0.03-0.05	0.22	13.57	19	1.002
20	0.005-0.05	0.02-0.05	0.18	16.29	17	1.013
30	0.005-0.05	0.03-0.05	0.12	50.12	15	1.008
40	0.005-0.05	0.02-0.05	0.12	58.46	20	1.008
50	0.005-0.05	0.03-0.05	0.17	6.03	10	1.022
60	0.005-0.05	0.02-0.05	0.18	0.00	13	1.023
70	0.005-0.05	0.02-0.05	0.28	0.00	13	1.032
80	0.005-0.05	0.02-0.05	0.18	0.00	13	1.015
90	0.005-0.05	0.03-0.05	0.18	0.00	13	1.018
		Calcium caprylate				
70	0.003-0.01	0.004-0.01	0.46	0.00	200	1.005
80	0.003-0.01	0.004-0.01	0.28	0.00	100	1.003
90	0.003-0.01	0.004-0.01	0.32	0.00	150	1.004

[a]See text for definitions of $\bar{V}$, Q, M, and K′.

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