Viscosity of Magnesium Soap Solutions in n-Propanol and Butanol

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ABSTRACT AND SUMMARY

The critical micelle concentration (CMC) of magnesium soaps in n-propanol and butanol have been determined by viscosity measurements. The equations of Vand and Moulik are applicable only above CMC. The parameters of equations may be used to calculate the viscosity of soap solutions in the concentration range in which the equations hold good. The temperature effect on viscous flow follows Arrhenius' equation. The effect of soap concentration on fluidity of soap solutions has been discussed in the light of Eyring's equation and the activation parameters of viscous flow, ΔH*, ΔS*, and ΔG* with respect to the solvent have been calculated.

INTRODUCTION

In continuation of our earlier work (1,2) this communication deals with the viscosity studies of magnesium soaps (valerate, caproate, and caprylate) in n-propanol and butanol at different temperatures. The object of this study is (a) to determine critical micelle concentration (CMC), study the effect of temperature on micellar aggregation, and compare the results obtained from conductivity measurements (3); (b) to test the applicability of viscosity equations; and (c) to calculate the activation parameters of viscous flow.

EXPERIMENTAL PROCEDURES

The chemicals were purified and the soaps were prepared by the method described in a previous communication (1). An Ostwald Viscometer was used to determine the viscosity of soap solutions in a thermostatically controlled (± 0.05 C) bath. The densities were measured with a dilatometer constructed of pyrex glass having a reservoir volume of 15 ml. The measuring section was constructed of precisely bored graduated capillaries. The dilatometer was calibrated with conductivity water and the accuracy of measurements was checked against some test solutions of known density at different temperatures. The density data obtained agreed with literature values within ± 0.001 to 0.003%.

TABLE I

Viscosity of Magnesium Valerate Solutions in Alcohols at 35-50 C

Conc. of soap in moles litre^{-1}	Viscosity in millipoise at ° C 35 C	40 C	45 C	50 C
n-propanol				
0.003	16.22	14.09	11.97	9.84
.005	16.28	14.14	12.05	9.86
.010	16.39	14.22	12.18	9.96
.020	16.45	14.32	12.26	10.03
.030	16.55	14.39	12.32	10.08
.040	16.64	14.47	12.38	10.14
.050	16.70	14.59	12.45	10.20
n-butanol				
.003	20.78	17.94	14.80	12.05
.005	20.84	18.03	14.95	12.09
.010	20.93	18.18	15.16	12.15
.020	21.07	18.27	15.24	12.23
.030	21.14	18.35	15.32	12.29
.040	21.22	18.51	15.41	12.34
.050	21.29	18.65	15.52	12.41

RESULTS AND DISCUSSION

The viscosity, η of soap solutions (Table I), increases with increasing soap concentration at different temperatures. This increase in viscosity is due to the increasing tendency to form aggregates at higher concentrations. A plot (Fig. 1) of viscosity vs. soap concentration gives an intersection of two straight lines at a concentration 0.01, 0.01, and 0.005 M indicating the formation of micelle (4-7) for valerate, caproate, and caprylate respectively. It is observed that CMC of soaps are independent of the temperature and nature of the solvent (3).

The extrapolated values of viscosity for zero soap concentration in alcohols (Table II) are in agreement with the corresponding experimental values at various temperatures and are independent of chain length of the soaps. This confirms that the soap molecules do not aggregate to an appreciable extent below CMC whereas there is a marked change in aggregation at the CMC.

It also must be pointed out that the viscosity of soap solutions increases with increasing chain length of soap. This may be due to an increase in the size of the micelles with an increasing number of carbon atoms in the soap. The values of viscosity of soap solutions in n-butanol are higher than the corresponding values obtained in n-propanol.

The viscosity of magnesium soap solutions has been satisfactorily represented by the following (8,9) equations:

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

Where Q and $\bar{V}$ are the interaction coefficient and molar volume of the solute in litre mole^{-1}, C is the concentration of solute in mole litre^{-1} and η_0 is the viscosity of the solvent.

$$\text{Moulik:}\ (\eta/\eta_0)^2 = M + K^1C^2 \qquad \text{(ii)}$$

FIG. 1. Plots of viscosity vs. concentration of magnesium caproate solutions in n-butanol.

TABLE II

Extrapolated and Experimental Values of Viscosity of Magnesium Soap Solutions for Zero Soap Concentration at 35-50 C

Temperature in °C	Viscosity in millipoise			
	Extrapolated			
	Caprylate	Caproate	Valerate	Experimental
n-Propanol				
35	16.10	16.20	16.15	16.180
40	13.95	14.00	14.00	14.050
45	11.95	11.95	11.90	11.930
50	9.80	9.80	9.80	9.811
n-Butanol'				
35	20.65	20.70	20.70	20.710
40	17.80	17.85	17.75	17.810
45	14.95	14.90	14.90	14.900
50	12.00	12.05	12.00	11.960

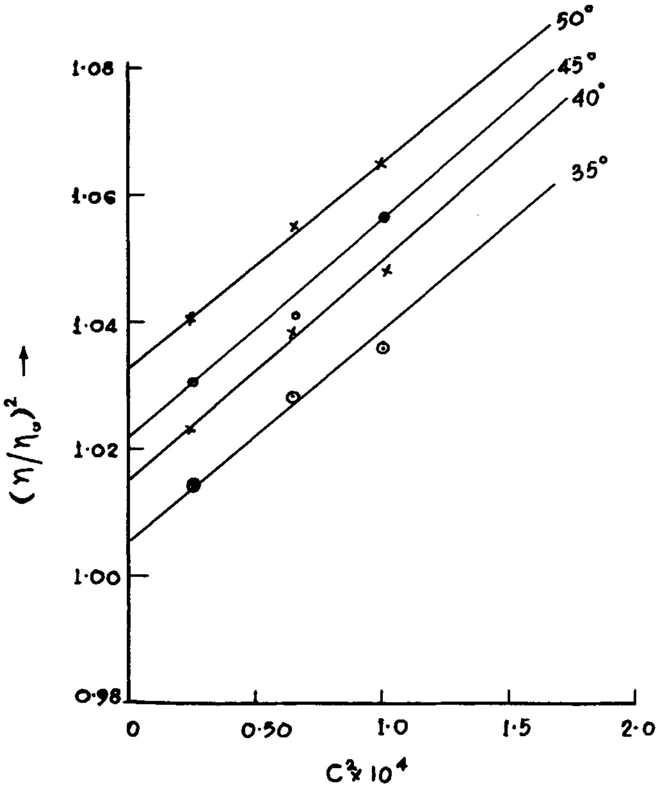

FIG. 2. Plot of $(\eta/\eta_0)^2$ vs. C^2 of magnesium caprylate in n-propanol at 35-50 C.

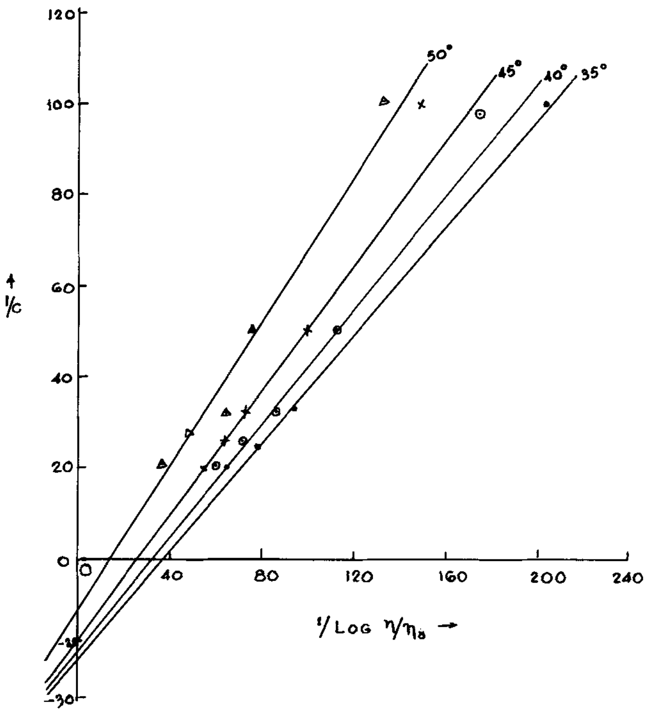

FIG. 3. Plot of $1/C$ vs. $1/\log \eta/\eta_0$ of magnesium caproate in n-propanol.

Where M and K^1 are constants.

The procedure for testing the Vand and Moulik equations by plotting (Figs. 2 and 3) $1/C$ vs. $1/\log(\eta/\eta_0)$ and $(\eta/\eta_0)^2$ vs. C^2 has been applied. The equations hold good for the data only in the limited range of concentrations (Tables III and IV) above CMC.

The values of $\bar{V}$ (Tables III and IV) increase with an increase in temperature in alcohols. It has been observed that the values of $\bar{V}$ of caprylate are much higher than the corresponding values of lower soaps. Comparison of the data shows that $\bar{V}$ increases with increasing chain length of soap.

It has been observed that the values of interaction coefficient, Q (Tables III and IV) show an increase with increasing temperature in n-propanol and butanol. These values also increase in n-butanol with increasing chain length of soap.

The values of M and K^1 have been calculated in order to compare the applicability of both the equations and are

TABLE III

Viscosity Parameters for Magnesium Soap Solutions in n-Propanol at 35-50 C

Temperature in °C	Tested conc. limit (moles/litre)	Valid Zones (moles/litre)	$\bar{V}$	Q	M	K^1
Magnesium valerate						
35	0.003 - .05	0.01 - .05	0.41	-30.16	1.026	20
40	.003 - .05	.02 - .05	.46	-20.49	1.033	18
45	.003 - .05	.02 - .05	.47	-4.30	1.045	20
50	.003 - .05	.02 - .05	.48	-3.18	1.054	20
Magnesium caproate						
35	.003 - .05	.01 - .05	.46	-46.82	1.027	18
40	.003 - .05	.01 - .05	.47	-42.45	1.034	17
45	.003 - .05	.02 - .05	.48	-37.10	1.047	24
50	.003 - .05	.01 - .05	.49	-22.45	1.056	25
Magnesium caprylate						
35	.003 - .02	.005 - .01	1.01	-52.31	1.005	340
40	.003 - .02	.005 - .01	1.11	-25.33	1.004	360
45	.003 - .02	.005 - .02	1.27	-17.31	1.020	340
50	.003 - .02	.005 - .02	1.40	-2.86	1.030	320

TABLE IV

Viscosity Parameters for Magnesium Soap Solutions in n-Butanol at 35-50 C

Temperature in °C	Tested conc. limit (moles/litre)	Valid Zones (moles/litre)	$\bar{V}$	Q	M	K^1
Magnesium valerate						
35	0.003 - .05	0.02 - .05	0.14	-253.30	1.030	13
40	.003 - .05	.01 - .05	.20	-144.70	1.037	15
45	.003 - .05	.01 - .05	.28	-101.40	1.048	16
50	.003 - .05	.01 - .05	.30	-83.52	1.058	14
Magnesium caproate						
35	.003 - .05	.02 - .05	.21	-130.3	1.038	17
40	.003 - .05	.02 - .05	.23	-91.20	1.051	14
45	.003 - .05	.01 - .05	.25	-71.08	1.056	14
50	.003 - .05	.01 - .05	.26	-58.16	1.059	14
Magnesium caprylate						
35	..003 - .02	.005 - .01	1.38	-44.87	1.008	260
40	.003 - .02	.005 - .01	1.57	-36.41	1.010	290
45	.003 - .02	.005 - .02	1.84	-27.69	1.023	280
50	.003 - .02	.005 - .02	2.49	-17.29	1.032	290

TABLE V

Activation Parameters for Fluidity of Magnesium Valerate in Alcohols

	n-propanol			n-butanol		
Conc. of soap in moles litre^{-1}	ΔH* in k cal mole^{-1}	ΔS* in cal deg^{-1}mole	ΔG* in k cal mole^{-1}	ΔH* in k cal mole^{-1}	ΔS* in cal deg^{-1}mole^{-1}	ΔG* in k cal mole^{-1}
0.003	6.75	8.79	3.506	7.74	12.85	3.783
.005	6.78	9.54	3.508	8.06	13.89	3.784
.010	6.81	10.78	3.509	8.29	14.63	3.785
.020	6.91	11.02	3.515	8.41	15.00	3.789
.030	7.14	11.78	3.520	8.52	15.35	3.794
.040	7.60	13.24	3.522	8.98	16.84	3.795
.050	8.06	14.72	3.524	9.12	17.28	3.799

recorded in Tables III and IV. It has been observed that the values of M increase with increasing temperature and chain length of the solvent used. The values of K^1 do not show any definite trend in variation with temperature. It is of interest to note that the values of K^1 for caprylate are exceptionally higher than other systems.

It may be mentioned that Vand's equation contains perfectly defined parameters, $\bar{V}$ and the interaction coefficient, Q is only approximately obtained (10). It appears that most probably Q is a specific property of a solute and not the general property (11). The parameters M and K^1 of Moulik's equation are not yet defined.

The plots of logarithm of viscosity, log η vs. reciprocal of absolute temperature, 1/T are straight lines showing the validity of Arrhenius' equation:

$$\frac{1}{\eta} = A\, e^{E\phi/RT} \qquad \text{(iii)}$$

Where A and $E\phi$ are the Arrhenius coefficient and activation energy of viscous flow.

The activation energy of viscous flow, $E\phi$(= ΔH* in Table V) has been calculated from the slopes of linear plots. The interpretation of viscous flow according to the theory of absolute reaction rates has also been presented by Eyring and coworkers (12). The temperature dependence of $1/\eta$ has been evaluated in terms of Eyring's equation,

$$\frac{1}{\eta} = \left(\frac{V}{hN}\right) \exp\left(-\Delta H^*/RT\right) \exp\left(\frac{\Delta S^*}{R}\right) \qquad \text{(iv)}$$

Where h and N are planck's constant and Avogadro number respectively, V is the molar volume of the solvent, R is gas constant in cals. deg^{-1}mole^{-1}, T is the absolute temperature, and η is the viscosity in poise. ΔH*, ΔS*, and ΔG* are activation energy, entropy, and free energy of viscous flow respectively. ΔG* is calculated from Gibbs' equation at 35 C.

Table V indicates that ΔH* and ΔS* increase with increasing concentration of soap. It is observed that the plots of these parameters vs. concentration of soap show a change at CMC and the rate of change becomes slow but increases rapidly at higher concentrations. Since ΔG* controls the flow rate which is governed by the slowest step in the fluid process, the data suggest that below CMC there is essentially no new process other than the flow of pure solvent. It is considered that nonlinearity of ΔG* with the concentration with an added solute becomes indicative of the formation of solute-solvent aggregate (13) as the principal kinetic entity.

The plots of ΔG* vs. C show a linear increase above CMC, which indicate that there is no solvent-solute aggregation but confirm the micellar aggregation of soap in alcohols. The slopes of linear plots of ΔG* vs. C are 0.35, 0.37, and 1.2 k cals. mole^{-1}litre^{-1} in n-propanol and 0.36, 0.35, and 0.80 k cals. mole^{-2}litre^{-1} in n-butanol for valerate, caproate, and caprylate respectively.

ACKNOWLEDGMENT

K.N. Mehrotra gave advice, and authorities at D.A.V. College, Muzaffarnagar, India provided facilities.

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[Received October 26, 1976]