

# Studies on the Behaviour of Cobalt and Calcium Soaps. Part VII. Viscosity and Surface Tension Studies in Benzene and Carbon Tetrachloride

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Viscosities and surface tensions of cobalt and calcium oleates in benzene and carbon tetrachloride solutions are determined at different temperatures (35–50°). The soaps form micellar aggregates and the critical micelle concentrations are found independent of temperature. The equations of Vand and Moulik are applicable only above CMC. The effects of temperature and concentration of soap on the fluidity of soap solutions are discussed in the light of Arrhenius and Eyring equations and activation parameters of viscous flow,  $\Delta H^*$ ,  $\Delta S^*$  and  $\Delta G^*$  have been calculated. The surface tensions of cobalt and calcium soap solutions are explained on the basis of Langmuir's expression:  $\gamma/\gamma_0 = 1 - X \ln C/Y$  which is used to calculate the surface area covered by the soap micelle formed from 1 mol of the soap at different temperature (35–50°).

**V**ISCOSITY and surface tension of dilute colloidal solutions may indirectly give information about the nature of the dispersed phase. A number of studies have been made on viscosity<sup>1-3</sup> and surface tension<sup>4,5</sup> of solutions of surface active agents to evaluate the critical micelle concentration (CMC). In continuation of our earlier studies<sup>6-8</sup> on the behaviour of cobalt and calcium soaps in organic solvents, this communication deals with the viscosity and surface tension measurements of these soaps in benzene and carbon tetrachloride. The object of this study is to (a) determine the micellar aggregation and effect of temperature (b) test the applicability of viscosity equations (c) calculate the activation parameters of viscous flow and (d) investigate the surface behaviour of soap solutions.

## Experimental

E. Merck or BDH reagent grade cobalt sulphate, calcium acetate, oleic acid, benzene and carbon tetrachloride were used. The fatty acid was purified by distillation under reduced pressure. The b.p. of the solvents, purified by standard methods<sup>9</sup> were benzene 80° and carbon tetrachloride 76.5°.

The corresponding metal soaps were prepared by adding a hot solution of sodium soap to an aqueous solution of metal salt, the former being added dropwise with stirring at 50–5°. The precipitate was filtered off and washed with hot water. After initial drying in air oven (100–5°), final drying was carried out under reduced pressure. The soaps were analysed and the percentage of the respective metal were cobalt, 9.43 (calcd. 9.48) and calcium, 6.62 (calcd. 6.65).

The viscosity, surface tension and density of soap solutions were determined by means of Ostwald viscometer, stalagmometer and dilatometer respectively at different temperatures in a thermostat ( $\pm .05^\circ$ ). The accuracy of the results was checked by determining the

viscosity and surface tension of a known liquid (benzene) and was found to be 0.3% and 0.5% respectively.

## Results and Discussion

**Viscosity:** The plots (Fig. 1) of viscosity,  $\eta$  (millipoise) vs concentration of soap solution,  $C$  (moles litre<sup>-1</sup>) are characterised by an intersection of two straight lines at a concentration 0.005 and 0.008  $M$  for cobalt oleate and 0.004 and 0.010  $M$  for calcium oleate in benzene and carbon tetrachloride respectively indicating CMC of the soaps which is found to be independent of temperature. The viscosity data show that at equal concentrations cobalt oleate impart greater viscosity as compared to calcium oleate.

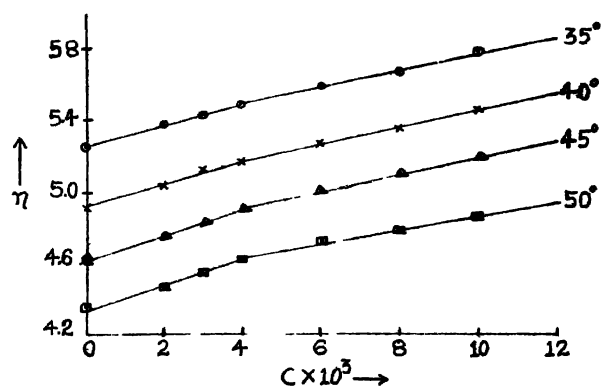


Fig. 1. Plot of viscosity vs concentration (moles litre<sup>-1</sup>) of calcium oleate in benzene at temperatures 35–50°.

The viscosity of soap solutions has been satisfactorily represented in the concentration range above CMC by the following<sup>10,11</sup> equations:

$$\text{Vand: } 1/C = (0.921/\bar{V})^{-1} .1/\log(\eta/\eta_0) + Q\bar{V} \dots (i)$$

TABLE 1—VISCOSITY PARAMETERS FOR COBALT AND CALCIUM SOAPS AT 35–50°

Temp. (°C)	Tested Conc. limit (moles litre <sup>-1</sup> )	Valid zones (mole litre <sup>-1</sup> )	V	-Q	M	K <sup>1</sup> × 10 <sup>-3</sup>
<b>BENZENE</b>						
<b>Cobalt oleate</b>						
35	.002–.015	.008–.015	18.87	6.89	1.340	13.00
40	.002–.015	.008–.015	22.08	6.74	1.430	12.50
45	.002–.015	.006–.015	28.52	6.66	1.490	13.00
50	.002–.015	.006–.015	38.64	6.60	1.560	13.00
<b>Calcium oleate</b>						
35	.002–.01	.004–.01	4.49	6.91	1.080	12.50
40	.002–.01	.004–.01	5.75	6.96	1.105	12.50
45	.002–.01	.004–.01	6.67	8.25	1.115	13.50
50	.002–.01	.004–.01	7.36	8.83	1.125	13.00
<b>CARBON TETRACHLORIDE</b>						
<b>Cobalt oleate</b>						
35	.002–.015	.006–.015	4.70	13.84	1.104	4.60
40	.002–.015	.006–.015	4.24	12.98	1.097	4.35
45	.002–.015	.006–.015	3.87	12.93	1.089	4.15
50	.002–.015	.006–.015	3.41	11.74	1.080	4.10
<b>Calcium oleate</b>						
35	.002–.02	.010–.02	4.60	21.73	1.100	1.40
40	.002–.02	.010–.02	4.14	23.53	1.090	1.35
45	.002–.02	.008–.02	3.13	23.95	1.084	1.28
50	.002–.02	.008–.02	1.93	25.85	1.054	1.25

where Q,  $\bar{V}$  and C are the interaction coefficient, molar volume (in litre mole<sup>-1</sup>) and concentrations of the solute respectively.

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

The applicability of the viscosity equation (i) and (ii) has been tested from the plots of  $1/C$  vs  $1/\log(\eta/\eta_0)$  (Fig. 2) and  $(\eta/\eta_0)^2$  vs  $C^2$  (Fig. 3). These equations are found valid in the concentration range above CMC. The viscosity parameters  $\bar{V}$ , Q, M and  $K^1$  have been calculated from the slopes and intercepts of the plots and are given in Table 1.

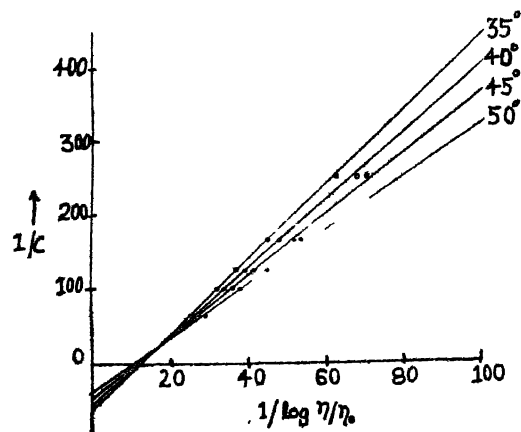


Fig. 2. Plot of  $1/C$  (moles litre<sup>-1</sup>) vs  $1/\log(\eta/\eta_0)$  of cobalt oleate in carbon tetrachloride at temperatures 35–50°.

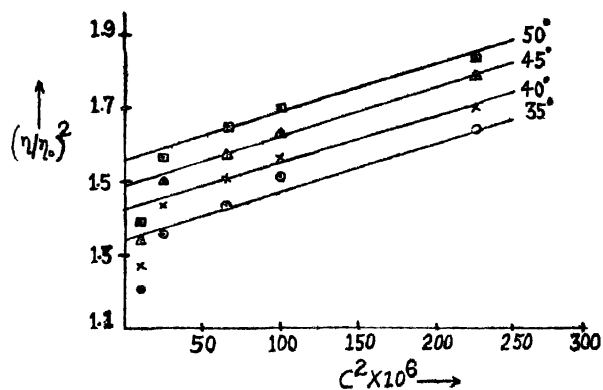


Fig. 3. Plot of  $(\eta/\eta_0)^2$  vs  $C^2$  (moles litre<sup>-1</sup>) of cobalt oleate in benzene at temperatures 35–50°.

Molar volume,  $\bar{V}$  increases with increasing temperature in benzene and decreases in carbon tetrachloride. It is observed (Table 1) that the value of -Q shows an increase with increasing temperature for calcium oleate but shows the reverse behaviour for cobalt oleate. A comparison of these parameters indicates that cobalt soap shows higher molar volume and lower interaction coefficient than the corresponding values of calcium soap. The  $\bar{V}$  values in benzene are found higher than carbon tetrachloride while -Q shows the reverse trend.

The values of M and  $K^1$  increase with increasing temperature in benzene while in carbon tetrachloride M decreases with increasing temperature and  $K^1$

remains almost constant. These parameters for cobalt soaps are higher than calcium soaps.

The plots of logarithm of viscosity  $\log \eta$  vs reciprocal of absolute temperature,  $1/T$  are straight lines showing the validity of Arrhenius equation :

$$1/\eta = A \exp (E_\phi/RT) \quad \dots \text{(iii)}$$

where  $A$  and  $E_\phi$  are the Arrhenius coefficient and activation energy of viscous flow respectively. The activation energy of viscous flow,  $E_\phi (= \Delta H^*$  in Table 2) has been calculated from the slopes of the linear plots. The values of  $-\Delta H^*$  vs  $C$  show a change at CMC and rate of change becomes slow but increases rapidly at higher concentration.  $\Delta H^*$  measures energy barrier to fluid motion and the increase in these parameters with concentration indicates less fluidity and thus confirms micellar aggregation.

The temperature dependence of  $1/\eta$  (fluidity) has also been evaluated according to the theory of absolute reaction rates in terms of Eyring's equation<sup>12</sup> :

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

Where  $V$  is the molar volume of the solvents,  $R$  is gas constant,  $T$  is the absolute temperature and  $\eta$  is the viscosity in poise.  $N$  and  $h$  are Avogadro number and Planck's constant respectively.  $\Delta S^*$  and  $\Delta G^*$  are activation entropy and free energy of viscous flow respectively. The free energy of viscous flow,  $\Delta G^*$  is then calculated at 35° from Gibb's equation.

The variation of entropy of activation,  $\Delta S^*$  (Table 2) is similar to the behaviour of  $\Delta H^*$ . The rate of flow in fluid process is controlled by the free energy of viscous flow,  $\Delta G^*$ . The plot of  $\Delta G^*$  vs  $C$  is found

aggregates in solutions. The slopes of  $\Delta G^* - C$  plots are  $-22.0$  and  $-7.0$  for cobalt and  $-24.0$  and  $-16.0$  for calcium oleates in benzene and carbon tetrachloride respectively.

**Surface tension :** Surface tension  $\gamma$  (dynes  $\text{cm}^{-1}$ ) of the soap solution decreases with increase in temperature and soap concentration. This is due to the tendency of aggregate formation with increase in soap concentration. The decrease in benzene is found to be more pronounced in presence of cobalt soap than corresponding concentrations of calcium soap. The effect of these soaps on carbon tetrachloride solutions is opposite to the effects on benzene. The plots of  $\gamma$  vs  $C$  show a rapid fall upto CMC and then decrease very slowly with the addition of higher concentrations of soap.

Surface tension data have been interpreted by the following<sup>14</sup> equation :

$$\gamma/\gamma_0 = 1 - \frac{KT n_1}{\gamma_0} \ln \left( 1 + \frac{n_2}{k} \right) \quad \dots \text{(v)}$$

where  $n_1$  is the number of exposed solvent sites per  $\text{cm}^2$  of its surface,  $n_2$  is the concentration of the substrate molecule  $\text{cm}^{-3}$  in bulk,  $K$  is a constant for the solvent and the others terms have their usual significance.

$$\text{on substituting } \frac{KT n_1}{\gamma_0} = X \text{ and } \frac{n_2}{K} = C/Y$$

one obtains

$$\gamma/\gamma_0 = 1 - X \ln (1 + C/Y) \quad \dots \text{(vi)}$$

where  $X$  and  $Y$  are constants. On applying the condition  $C/Y \gg 1$  the following approximate expres-

TABLE 2—ACTIVATION PARAMETERS FOR FLUIDITY OF COBALT AND CALCIUM OLEATES

Conc. of soap in $M$	Benzene			Conc. of soap in $M$	Carbon tetrachloride		
	$-\Delta H^*$ k,J mole <sup>-1</sup>	$-\Delta S^*$ JK <sup>-1</sup> mole <sup>-1</sup>	$\Delta G^*$ k,J mole <sup>-1</sup>		$-\Delta H^*$ k,J mole <sup>-1</sup>	$-\Delta S^*$ JK <sup>-1</sup> mole <sup>-1</sup>	$\Delta G^*$ k,J mole <sup>-1</sup>
COBALT							
.002	6.32	60.76	12.39	.002	7.47	68.25	13.55
.003	6.51	61.83	12.53	.004	7.56	68.70	13.59
.005	6.70	62.58	12.57	.006	7.66	69.13	13.63
.008	6.89	63.64	12.71	.008	7.76	69.53	13.66
.010	7.28	65.13	12.78	.010	7.85	69.92	13.69
.015	7.85	67.29	12.87	.015	8.04	70.72	13.74
CALCIUM							
.002	8.81	68.55	12.31	.002	7.66	68.89	13.56
.003	9.00	69.24	12.32	.004	7.85	69.56	13.57
.004	9.19	69.93	12.34	.008	8.23	70.96	13.62
.006	9.38	70.72	12.40	.010	8.62	72.30	13.65
.008	9.58	71.47	12.44	.015	8.81	73.00	13.68
.010	9.77	72.23	12.48	.020	9.00	73.69	13.70

to be linear and shows the presence of aggregated molecules in the solvent. It has been observed earlier<sup>18</sup> that solute-solvent interaction occurs if the variation of  $\Delta G^*$  with the solute concentration is non linear. Here the linear plots confirm that no solute-solvent interaction occurs but the soap forms micellar

sion, which Langmuir<sup>15</sup> showed to apply at high solute concentration and in condition of surface saturation, was obtained

$$\gamma/\gamma_0 = 1 - X \ln C/Y \quad \dots \text{(vii)}$$

The plots of  $\gamma$  vs  $\log C$  are linear which shows the

applicability of the above equation. Constant X and Y have been calculated from the slopes and intercepts of these linear plots at different temperatures (Fig. 4) and the results are given in Table 3.

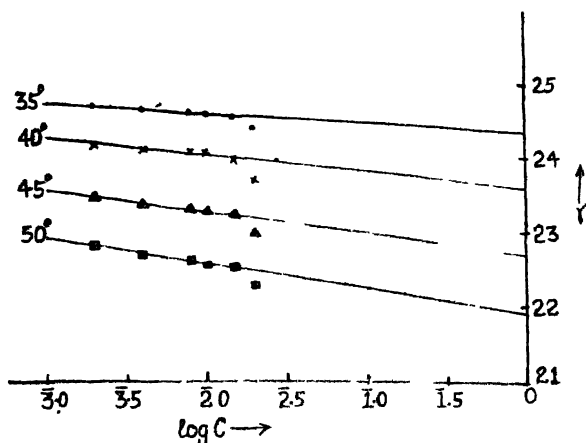


Fig. 4. Plot of  $\gamma$  (dynes  $\text{cm}^{-1}$ ) vs  $\log C$  (moles  $\text{litre}^{-1}$ ) of calcium oleate in carbon tetrachloride at temperatures 35-50°.

TABLE 3—VALUES OF X, AREA,  $A \times 10^{-10}$  IN  $\text{cm}^2$ , AND Y OF COBALT AND CALCIUM OLEATES AT DIFFERENT TEMPERATURES (35-50°).

Temp. in °C	$X \cdot 10^3$		$A \cdot 10^{-10}$		$Y \cdot 10^4$	
	Cobalt	Calcium	Cobalt	Calcium	Cobalt	Calcium
BENZENE						
35	8.2	17.6	11.79	5.49	4.4	2.8
40	6.8	20.8	14.98	4.89	4.8	3.1
45	6.6	23.0	16.24	4.68	4.9	3.8
50	5.0	25.6	22.49	4.42	6.3	4.2
CARBON TETRACHLORIDE						
35	11.1	3.3	7.86	31.37	6.3	6.4
40	10.2	4.0	9.59	26.64	5.8	6.0
45	8.2	5.5	13.53	20.30	2.8	4.6
50	6.7	6.6	17.42	17.67	0.9	3.7

The constant X of cobalt soap decreases and calcium soap increases with increasing temperature. A comparison of the results shows that X for cobalt soap is higher than for calcium soap. This indicates that higher increase in number of exposed solvent site per  $\text{cm}^2$  of the surface occurs in presence of the cobalt soap.

The constant Y of soap solutions increases with increase in temperature in benzene. This increase may be due to increase in substrate molecule per ml in the bulk. However, in carbon tetrachloride the value of Y decreases with increasing temperature. On differen-

tiating equation (vii) :

$$\frac{d\gamma}{d \ln C} = -X \gamma_0 \quad \dots \text{(viii)}$$

and by substituting in Gibb's adsorption equation the adsorption excess ( $\Gamma$ ) i. e. the excess concentration of solute per unit area of surface is found to be

$$\Gamma = -\frac{C}{RT} \cdot \frac{d\gamma}{d \ln C} = \frac{X \gamma_0}{RT} \quad \dots \text{(ix)}$$

Therefore the surface area A covered by soap micelles formed by one mole of the soap:

$$A = \frac{1}{\Gamma} = \frac{RT}{X \gamma_0}$$

The surface area, A occupied by the micelle formed by 1 mole of the soap has been calculated and is given in Table 3. The value of A for calcium soap in both the solvents decreases with increasing temperature. However, for cobalt soap the value of A increases with increasing temperature. The surface area occupied by the micelle formed by 1 mole of cobalt soap is higher in benzene but lower in carbon tetrachloride.

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