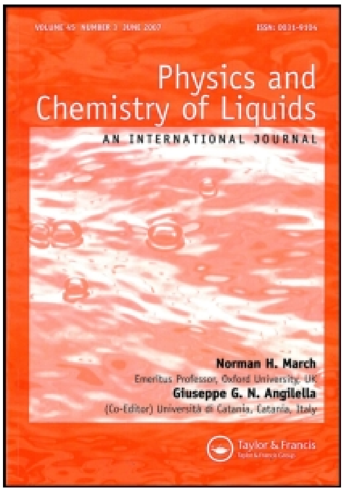

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CONDUCTIVITY, MOLAR VOLUME AND RHEOLOGY OF URANYL SOAP

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The apparent molar volume, ϕ_v (cm^3 mol^{-1}) and fluidity, ϕ (P^{-1} or rheo) for the solutions of uranyl stearate in mixtures of DMF-benzene, DMSO-benzene and MeOH-benzene (50%V/V) at 40°C have been evaluated from the data of density, ρ (g cm^{-3}) and viscosity, $\eta(P)$, respectively. The limiting apparent molar volume, ϕ_v^0 (cm^3 mol^{-1}) has been calculated by using Masson's equation. The intrinsic viscosity $[n]$, having units of a reciprocal concentration (dm^3 mol^{-1}), is computed by extrapolating a plot of η_{Sp}/C (the relative increase in viscosity per unit concentration) against soap concentration to infinite dilution. The CMC$_S$ for the soap solutions as determined by the plots of specific conductivity, k (mho cm^{-1}) versus concentration, C (mol dm^{-3}) are found to be consistent with those determined by $\rho - C$ and $\eta - C$ plots.

KEY WORDS: Uranyl soap, critical micelle concentration, density, molar volume, viscosity, fluidity, rheology.

INTRODUCTION

While major developments have taken place in the study of alkali, alkaline earth and transition metal soaps, the studies on actinide soaps have remained almost untouched with the result that only a few references$^{1-5}$ are available in this relatively unexplored field. The physicochemical characteristics and structure of these soaps depend on the method and conditions of preparation. The information about the structure and properties of these soaps is of great significance for their use in industries under varying conditions. The present investigation endeavours to look into the electrolytic structure of uranyl (II) stearate by employing conductance method while it probes into the bulk behavioural aspects like molar volume and rheology (viscosity/fluidity) by using density and viscosity measurements.

EXPERIMENTAL

Merck/BDH reagent grade chemicals were used. Stearic acid was purified by distillation under reduced pressure. The m.p. of the purified acid was 128°C. Uranyl (II) stearate was prepared by the direct metathesis of potassium stearate with uranyl nitrate at 50–55°C under vigorous stirring. The precipitated soap was digested, filtered, washed with distilled water-ether and dried. The metal soap thus obtained was crystallised twice from benzene-dimethylformamide and dried under vacuum for atleast 48 h before use. The purity was checked up by the elemental analysis and determining the m.p. (118°C).

The conductivity measurements of the solutions of uranyl (II) stearate in mixtures of DMF-benzene, DMSO-benzene and MeOH-benzene (50%V/V) were made with a Toshniwal digital conductivity meter "Model CL 01.10A" using dipping type conductivity cell with platinised electrodes. The density measurements (± 0.0001) were made with the help of pyknometer. Ostwald's type viscometer was used for measuring viscosity (± 0.002) of the solutions. The measurements were carried out at a constant temperature (40 ± 0.05°C) in a thermostat.

RESULTS AND DISCUSSION

Conductivity

The increase in the specific conductance, k(mho cm^{-1}) of the solutions of uranyl (II) stearate in mixtures of methanol-benzene, dimethylformamide-benzene and dimethylsulphoxide-benzene (50%V/V) with increasing soap concentration, C (mol dm^{-3}) at 40°C (Fig. 1) may be ascribed to the ionisation of the metal soap into uranyl ions, UO_2^{++} and fatty acid anions, $C_{17}H_{35}COO^-$ (in dilute solutions) and to the formation of the micelles (in concentrated solutions). The values of critical micelle concentration, CMC of these solutions at 40°C (Table 1) have been determined by the k-C plots (Fig. 1).

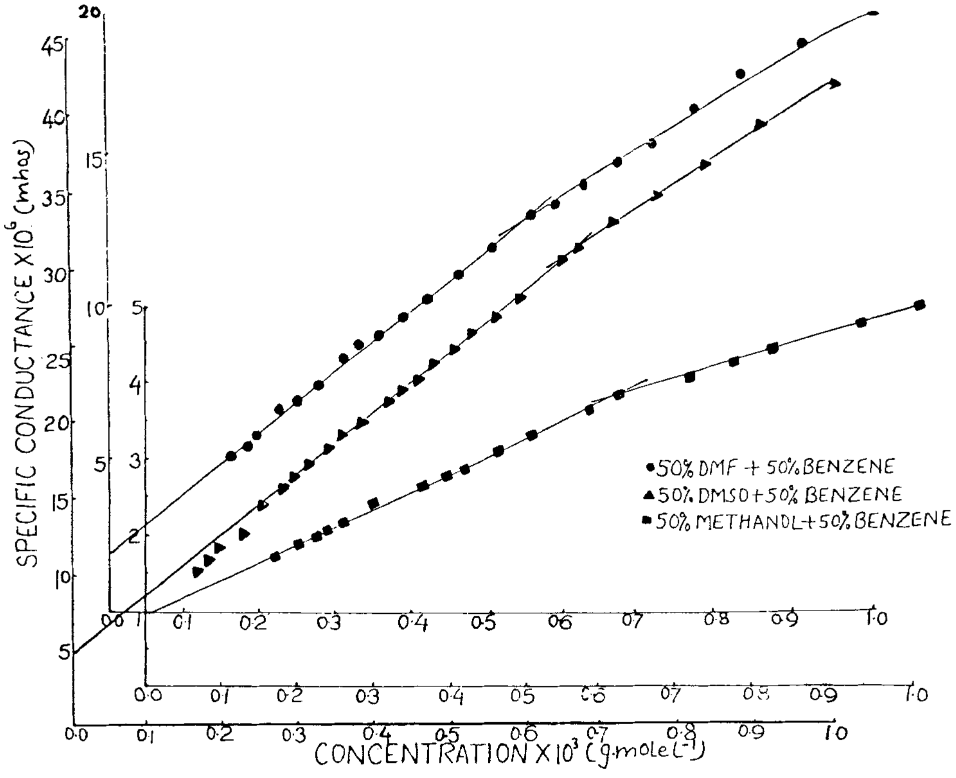

Figure 1 Specific conductance vs Concentration.

Table 1 Parameters from density and viscosity measurements of the solutions of uranyl stearate in mixtures of dimethylformamide-benzene, dimethylsulphoxide-benzene and methanol-benzene (50%V/V) at 40°C.

Parameters	*Derived from*	*MeOH-Benzene*	*DMF-Benzene*	*DMSO-Benzene*
Critical micelle concentration, CMC (mol dm^{-3})	k vs C, ρ vs C and η vs C	6.67×10^{-4}	5.55×10^{-4}	6.67×10^{-4}
density of solvent, ρ_0(g·cm^{-3})	ρ vs C	0.8403	0.9082	0.9400
Constants of Roots equation (A, B)	$(\rho - \rho_0)/C$ vs $C^{1/2}$	$A = 4.98 \times 10^{-4}$ $B = -1.66 \times 10^{-3}$	$A = 4.66 \times 10^{-4}$ $B = -6.67 \times 10^{-3}$	$A = 12.50 \times 10^{-4}$ $B = -25.00 \times 10^{-3}$
Limiting apparent molar volume, ϕ_v^0(cm^3 mol^{-1})	ϕ_v vs $C^{1/2}$	-50×10^2	-46×10^2	-124×10^2
Constant, S_v	ϕ_v vs $C^{1/2}$	20	80	240
Viscosity of solvent, $\eta_0(P)$	η vs C	0.567	0.610	0.728
Molar volume, Vm (dm^3 mol^{-1})	η_{Sp} vs C	29.3	39.6	164.5
Moulik's constants (M, K)	$(\eta/\eta_0)^2$ vs C^2	$M = 1.006$ $K = 58 \times 10^4$	$M = 1.006$ $K = 6.1 \times 10^4$	$M = 1.024$ $K = 43.3 \times 10^4$
Interaction coefficient, θ	$1/C$ vs $1/\log(\eta/\eta_0)$	5.0×10^2	6.0×10^2	7.5×10^2
Relative viscosity, ηr	η/η_0	1.002–1.044	1.003–1.052	1.015–1.205
Specific viscosity, η_{Sp}	$\eta r - 1$	0.002–0.044	0.003–0.052	0.015–0.205
Intrinsic viscosity, $[\eta]$ (dm^3 mol^{-1})	η_{Sp}/C vs C	20	31	148
Fluidity, ϕ (P^{-1} or rhe)	$1/\eta$	1.689 – 1.761	1.558–1.634	1.140–1.353

The concave nature of the plots of molar conductance, μ (mho cm^2/g-eq) vs. square root of soap concentration, $C^{1/2}$ suggests that the soap behaves as a weak electrolyte in these solutions and the limiting molar conductance, μ_0 cannot be obtained by the extrapolation of $\mu - C^{1/2}/$ plots. The following expression[6] can, therefore, be derived:

$$\mu^2 C^2 = \frac{K\mu_0^3}{4\mu} - \frac{\mu_0^2 K}{4}$$

The graphical values of K (3.5×10^{-8}, 1.1×10^{-6}, 2.0×10^{-7}) and μ_0 (27.6, 39.0, 140.0) for the soap solutions in MeOH-benzene, DMF-benzene and DMSO-benzene (50%V/V), respectively, have been obtained from slope and intercept of the linear plots of $\mu^2 C^2$ vs. $1/\mu$ below the CMC. The values of dissociation constant, K for different soap concentrations (below and above the CMC) are also evaluated (Fig. 2) by using the expression[6]; $K = 4C^2\alpha^3/1 - \alpha$. The values of degree of dissociation, α (Fig. 3) required to evaluate the dissociation constant ($K = 4C^2\alpha^3/1 - \alpha$) have been computed employing the expression: $\alpha = \mu/\mu_0$. The graphical values of μ_0 have been used for this purpose. The values of both these parameters (α, K) also suggest that uranyl (II) stearate behaves as a weak electrolyte in these solvent mixtures. The drift in the values of K (Fig. 2) however suggests that the degree of dissociation, α can not be assumed to be equal to the conductance ratio, μ/μ_0, as the activity coefficients, in this case, may not be exactly equal to unity. The value of true dissociation constant, K' can then be expressed

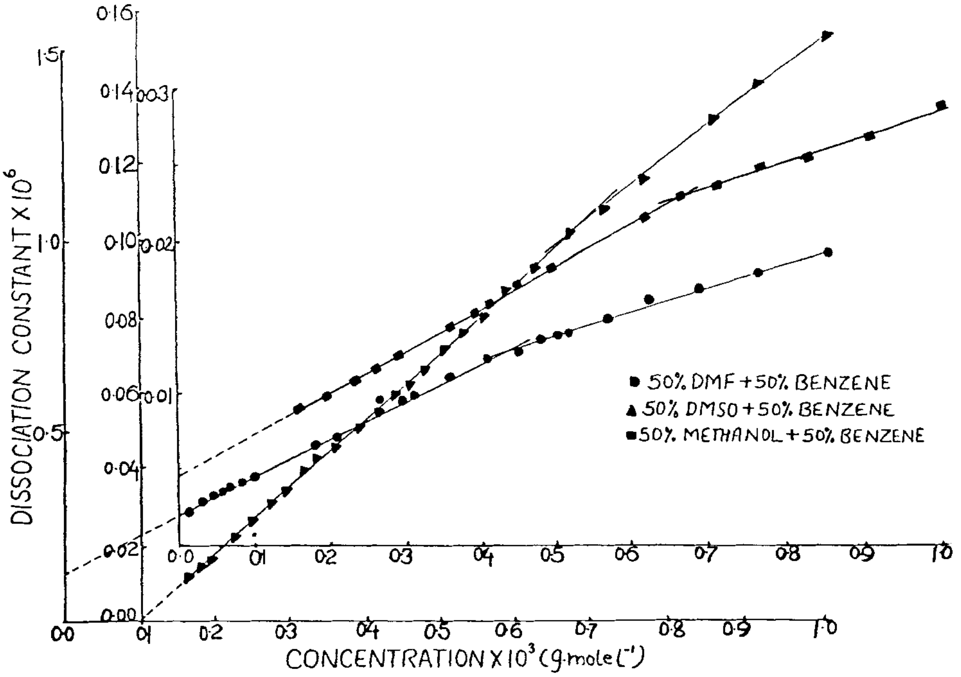

Figure 2 Dissociation constant vs Concentration.

as : $K' = (4C^2\alpha^3/1 - \alpha)(f_+f_-^2/f_{soap})$, where f_+, f_- and f_{soap} represent activity coefficients of cation, anion and soap, respectively. Since the activity coefficient of the non-ionised molecules of soap i.e. f_{soap} may be taken as unity, the Debye-Huckel's limiting law enables us to obtain: $\log K = \log K' + A\sqrt{C\alpha}$, where A is a constant for the solvent at the specified temperature. The plots of $\log K$ vs $\sqrt{C\alpha}$ for the soap solutions (below the CMC) are found to be linear and the values of true equilibrium or dissociation constant (1.6×10^{-8}, 1.8×10^{-7}, 2.0×10^{-8}) for MeOH-benzene, DMF-benzene and DMSO-benzene, respectively, are obtained from the intercept of these plots. The data again support the conclusion that the metal soap behaves as a weak electrolyte in these solutions. Consequently, it may be stated that the conductivity results can be explained on the basis of Ostwald's formula and Debye-Huckel's theory of weak electrolyte.

Molar volume

The density ($g\,cm^{-3}$) of uranyl (II) stearate in mixtures of MeOH-benzene, DMF-benzene, and DMSO-benzene (50%V/V) at 40°C (Fig. 4) is found to increase with increasing soap concentration, C(mol dm^{-3}). The $\rho - C$ plots (Fig. 4) are characterised by an intersection of two straight lines at a critical concentration, also called the critical micelle concentration, CMC (Table 1). The graphical values of density for the solvent, ρ_0 (Table 1) are obtained by extrapolating the $\rho - C$ plots (Fig. 4) to zero soap

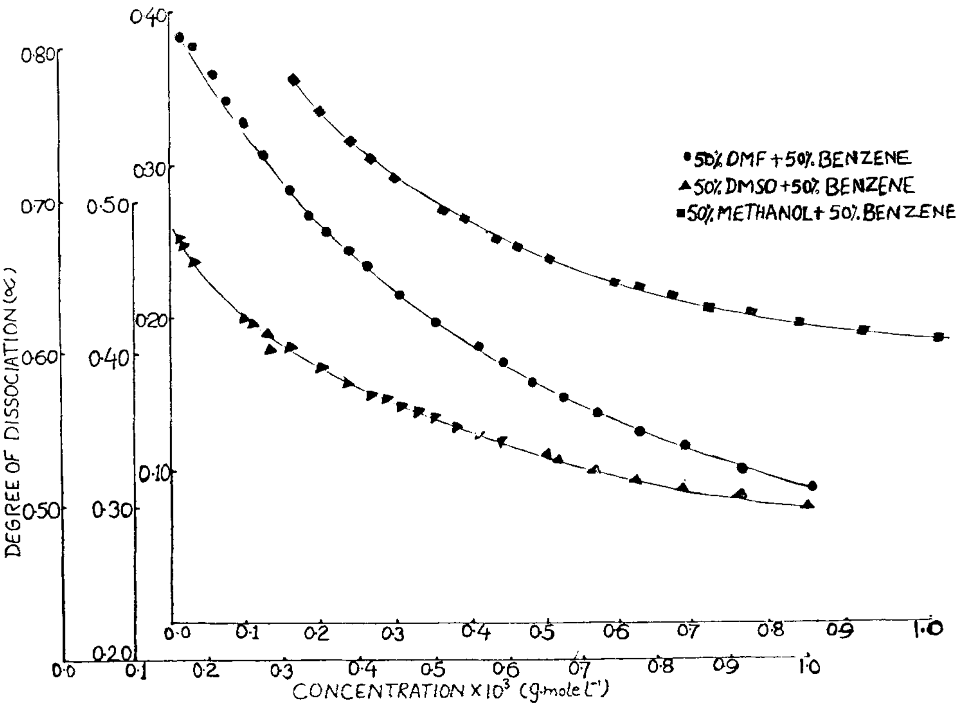

Figure 3 Degree of dissociation vs Concentration.

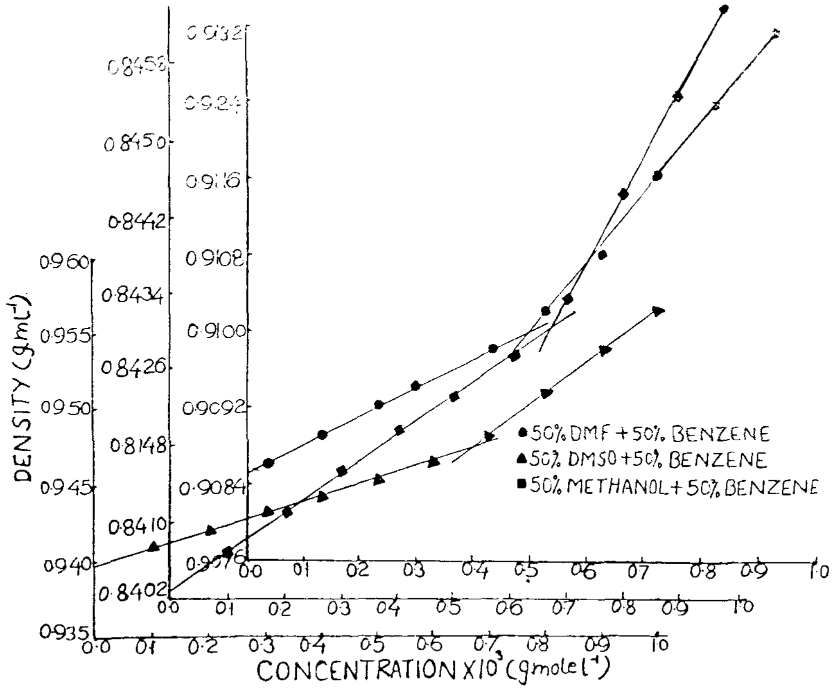

Figure 4 Density vs Concentration.

concentration. The equation by W. C. Roots[7] has been applied to dilute soap solutions (Fig. 5) below the CMC to evaluate the Roots constants[7] (A and B). The order: $A > B$ (Table 1) suggests that the solute-solvent inter-actions predominate in dilute solutions of uranyl soap and that the micellization only begins at the CMC.

The density data (Fig. 4) are used to evaluate the apparent molar volume, ϕ_v (cm^3 mol^{-1}) by employing equation[8]:

$$\phi_v = \frac{M}{\rho} - \frac{10^3(\rho - \rho_0)}{C\rho\rho_0}$$

where M, ρ, ρ_0 and C represent the molecular weight of the metal soap, density of the solution, density of solvent and concentration of the solution, respectively. It is obvious (Fig. 6) that with increasing metal soap concentration, ϕ_v below the CMC increases ($-\phi_v$ decreases) while the same decreases ($-\phi_v$ increases) above the CMC. The limiting apparent molar volume, ϕ_v^0 (cm^3 mol^{-1}) has been obtained by extrapolating the linear plot of ϕ_v vs $C^{1/2}$ (Fig. 6) for dilute soap solutions (below the CMC) according to Masson's equation[9]: $\phi_v = \phi_v^0 + S_v C^{1/2}$. The limiting apparent molar volume, ϕ_v^0 and the experimental limiting slope, S_v (Table 1) are measures of solute-solvent and ion-ion interactions, respectively. The positive values of S_v suggest strong ion-ion interactions leading to a fair chance of micellisation in these solutions.

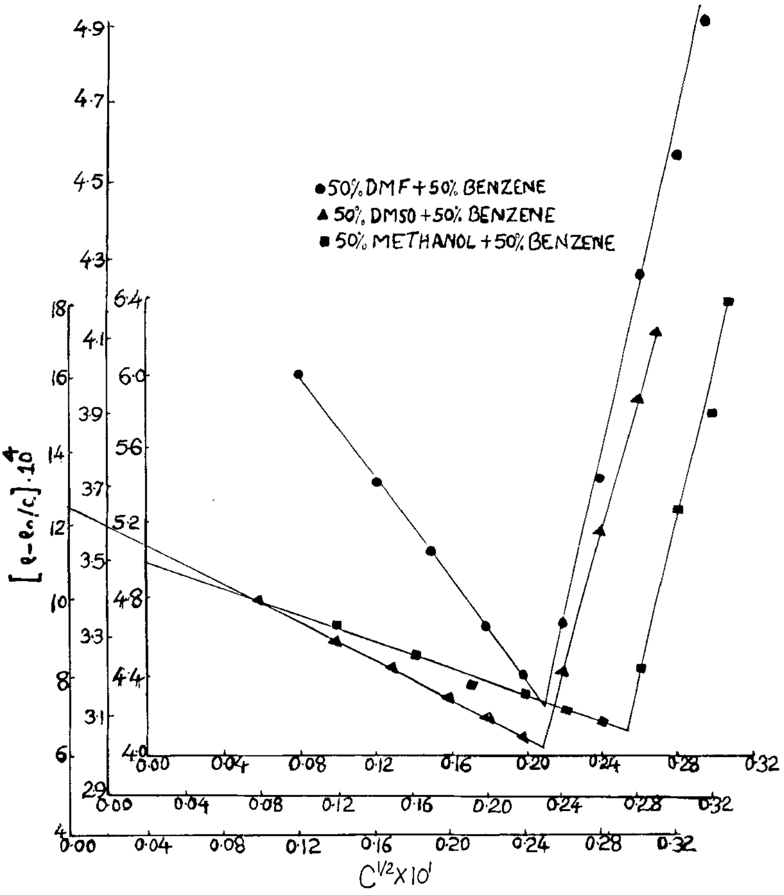

Figure 5 $(\rho - \rho_0)/C$ vs $C^{1/2}$.

The apparent molar volume, like any other partial molar quantity, expresses the change in an extensive thermodynamic property per mole of a component added. The solution volume changes as the component is added. The partial molar volumes of ionic solute usually are smaller than expected. In some cases, it is actually negative in dilute solution. This means that when a small amount of solid is added to a polar solvent, the volume of the solution is smaller than the volume of the solvent. The reason is the phenomenon of electrostriction in which smaller cation (UO_2^{++} ion), with its strong electric field, packs polar solvent molecules around itself in a smaller volume than they occupy in the bulk solvent.

Rheology

The viscosity, η and fluidity, ϕ (reciprocal of viscosity) are considered to be the important rheological parameters. A major characteristic of liquids is their ability to flow. Highly viscous liquids flow only very slowly because their large molecules get

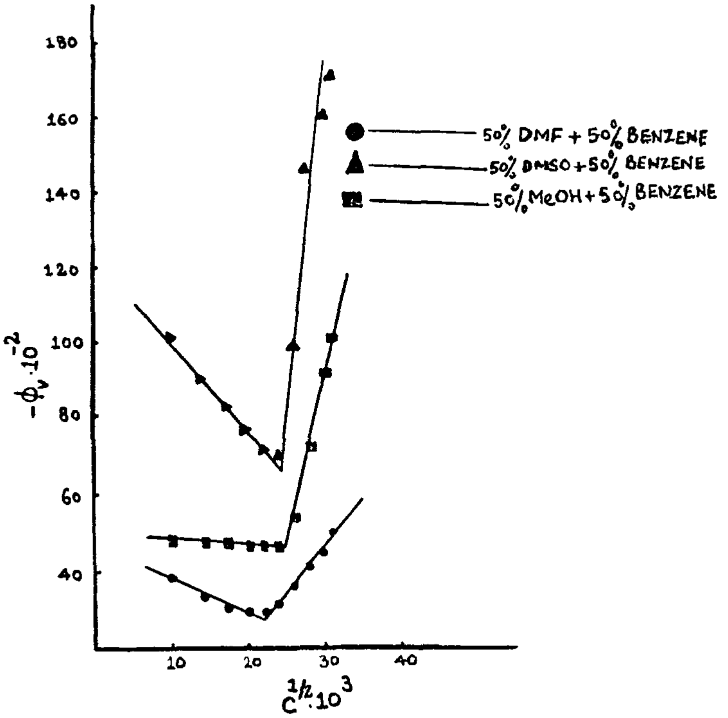

Figure 6 Apparent molar volume, ϕ_v (cm^3 mol^{-1}) vs Square root of concentration, $C^{1/2}$.

entangled. Mobile liquids have low viscosities. When ionic crystal has dissolved, the solution consists of a distribution of ions supported by the solvent (electrolyte solution). In dilute uranyl soap solutions, the cations UO_2^{++} and anions, $C_{17}H_{35}COO^-$ are so far apart that they have insignificant interactions, but as the concentration increases anions tend to congregate in the vicinity of the cations, and vice-versa. The plots of fluidity, ϕ (P^{-1} or rhe) of uranyl soap solutions as a function of soap concentration, C (mol dm^{-3}) manifest the cited fact i.e. the fluidity (Table 1) decreases (viscosity increases) with increasing soap concentration owing to the formation of large entities (micelles) at higher concentration of the soap solutions.

The plots (Fig. 7) of viscosity, $\eta(P)$ vs soap concentration ($\eta - C$) are characterised by an intersection of two straight lines at the CMC (Table 1). The viscosity for the solvent mixtures, $\eta_0(P)$ are evaluated (Table 1) by extrapolating $\eta - C$ plots (Fig. 7) to zero soap concentration. The viscosity data have been interpreted on the basis of the well known equations[10-13] proposed by Einstein[10], Moulik[11], Vand[12] and Jones-Dole[13]. Einstein-type-plots (η_{Sp} vs C) are used to evaluate molar volume, Vm (dm^3 mol^{-1}). The interaction coefficient, θ (Table 1) has also been calculated by employing Vand-type-plot [$1/C$ vs. $1/\log(\eta/\eta_0)$]. The values for Moulik's constants (M and K) evaluated from $(\eta/\eta_0)^2$ vs. C^2 plots follow the order: $K > M$ (Table 1) indicating the predominance of ion-ion interactions (good probability of micellization). The constants A and B from Jones-Dole equation[13] have been evaluated by employing plots of $\eta_{Sp}/C^{1/2}$ vs $C^{1/2}$. For

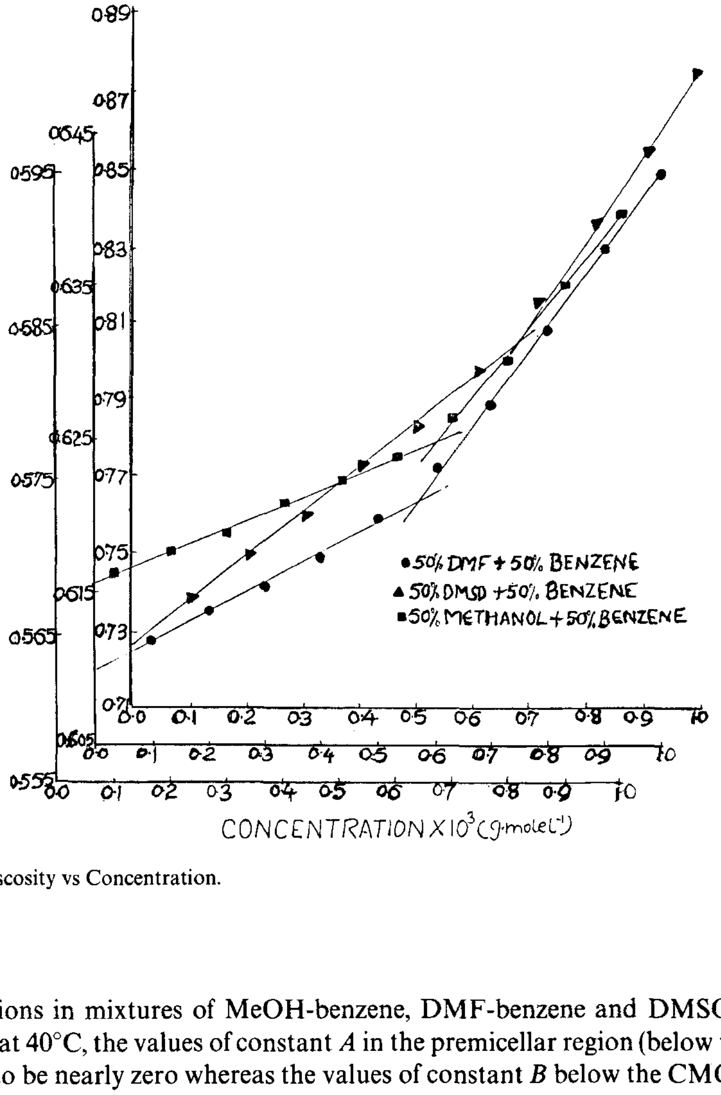

Figure 7 Viscosity vs Concentration.

soap solutions in mixtures of MeOH-benzene, DMF-benzene and DMSO-benzene (50%V/V) at 40°C, the values of constant A in the premicellar region (below the CMC) are found to be nearly zero whereas the values of constant B below the CMC are 27.5, 31.8 and 162.1, respectively. However, for post micellar region (above the CMC) the values of A (2.5, 1.7 and 1.8) and B (144.6, 101.8 and 412.6), i.e. $B > A$, suggest that the soap molecules do not aggregate appreciably in the premicellar region. The values of constant B (soap-solvent interaction) are thus found to differ widely below and above the CMCs. This may be attributed to the fact that the aggregation of the soap molecules boosts up the electrokinetic forces causing more intake of the solvent resulting in the increasing viscosity of the system.

The significance of the parameters like relative viscosity, η_{rel}, specific viscosity, η_{Sp} and intrinsic viscosity, η has already been discussed in the earlier communication[14] while their values are recorded in Table 1. The present investigation thus succeeds in probing into the electrical, micellar and bulk behaviour (molar volume, rheology) of uranyl (II) stearate solutions in organic media.

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