



Molar volume and rheology of samarium alkanoates in mixed solvent

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Abstract: The apparent molar volume, ϕ_v , and fluidity, ϕ for the solution of samarium alkanoates (pentanoate and hexanoate) in the mixture of benzene-methanol (6:4 v/v) at $40 \pm 0.05^\circ\text{C}$ have been evaluated from the data of density, ρ and viscosity, η , respectively. The limiting apparent molar volume, ϕ_v° has been calculated by Masson's equation. The results show that there is a significant interaction between solute-solvent molecules.

Key words: Samarium alkanoates, solute-solvent interaction, molar volume, fluidity, rheology.

I. Introduction

Surfactants are surface active agents usually organic compounds, characterized by the possession of both polar and non-polar regions in the same molecule. This dual nature is responsible for the phenomenon of surface activity, and micellization and solubilization. The dual nature of a surfactant is typified by metal alkanoates, can be called association colloids, indicating their tendency to associate in solution, forming particles of colloidal dimensions. Rheology deals with the deformation and flow of nature of matter as a result of the exertion of mechanical forces. The results of rheological behavior provide a mathematical description of the viscous and elastic behavior of matter. Metal alkanoates have found extensive application in various industries. Wu et al¹ and Kanai² developed new technologies to synthesize metal alkanoates. The thermal properties and solution aggregation behavior of lanthanide alkanoates has been reviewed by Binnemans and Görller-walrand³. Workers have used ultrasonic⁴⁻⁸ measurements of metal alkanoates for the determination of ion-solvent interaction in organic solvents. Viscometric⁸⁻⁹ and conductometric¹⁰⁻¹⁵ measurements of lanthanide and transition metal alkanoates have been determined in different organic solvents. The focus of this experiment were to look in to the bulk behavioral aspects like apparent molar volume and rheology (viscosity/ fluidity) samarium alkanoates (pentanoate and hexanoate) by using density and viscosity measurements in a mixture of benzene and methanol (6:4 v/v) at $40 \pm 0.05^\circ\text{C}$.

II. Experimental

All chemicals used were of BDH/AR grade. Solvents benzene and methanol were purified by distillation under reduced pressure. Samarium alkanoates (pentanoate and hexanoate) were synthesized by direct metathesis of corresponding potassium alkanoates as mentioned in our earlier publication⁴. The purity was checked by their melting points (pentanoate -89°C and hexanoate -95°C) and absence of hydroxylic group was confirmed by IR spectra. The reproducibility of the results was checked by preparing two samples of the same alkanoates under similar conditions. The solutions of samarium alkanoates (pentanoate and hexanoate) were prepared by dissolving a known amount of solute in a benzene-methanol mixture (7:3 v/v) and were kept for 2 hr in a thermostat at $40 \pm 0.05^\circ\text{C}$. The samarium alkanoates (pentanoate and hexanoate) do not possess high solubility in pure solvents thus measurements were conducted in benzene - methanol mixture. Densities of the solvent and solution were measured by pycnometer. The Pycnometer was calibrated with distilled water and buoyancy corrections were applied. Ostwald type viscometer was used for measuring viscosity (± 0.002) of the solutions.

III. Results and Discussion

(A) Apparent Molar volume

The density, ρ of samarium alkanoates (pentanoate and hexanoate) in the mixture of benzene-methanol (6:4 v/v) at $40 \pm 0.05^\circ\text{C}$ (Fig.1) is found to increase with increasing solute concentration, C as well as increasing in chain length. The plot ρ - C (Fig.1) is characterized by an intersection of two straight lines at a critical concentration, CMC (Table 1). The plots of density vs. concentration below CMC have been extrapolated to zero surfactant concentration; the extrapolated values of density, ρ_0 for these alkanoates are in agreement with the experimental value of density of solvent mixture. The equation by W.C. Roots¹⁶ has been applied to dilute alkanoates solutions below CMC to evaluate the Roots constants¹⁶ (A and B). The order: $A > B$ was found, suggest that the

solute-solvent interactions predominate in dilute solutions of samarium alkanoates and micellization only begins at the CMC.

The density data (Fig.1) are used to evaluate the apparent molar volume, ϕ_v by employing equation¹⁷

$$\phi_v = \frac{M}{\rho} - \frac{10^3(\rho - \rho_0)}{C\rho\rho_0} \quad (1)$$

Where M , ρ , ρ_0 and C represent the molecular weight of the metal alkanoates, density of solution, density of solvent and concentration of the solution, respectively. It is obvious that increasing surfactant concentration, and chain length apparent molar volume ϕ_v increases ($-\phi_v$ decreases) below the CMC and the same decreases ($-\phi_v$ increases) above the CMC. The limiting apparent molar volume, ϕ_v^0 has been obtained by extrapolating the linear plot of ϕ_v vs. $C^{1/2}$ and found to be increase with increase in chain length (Table 1) for dilute alkanoates solutions (below the CMC) according to Masson's equation¹⁸ ($\phi_v = \phi_v^0 + S_v C^{1/2}$). The limiting apparent molar volume, ϕ_v^0 and the experimental limiting slopes, S_v (Table. I) are measures of solute- solvent and ion-ion interactions, respectively. The positive values of S_v indicates strong ion- ion interactions leading to a fair chance of micellization in these alkanoates solutions. The apparent molar volume, like any other partial molar quantity, expresses the change in an extensive thermodynamic property per mole of a 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 (Sm^{3+} ion), with its strong electric field, packs polar solvent molecules around itself in a smaller volume than they occupy in the bulk solvent.

(B) Rheology

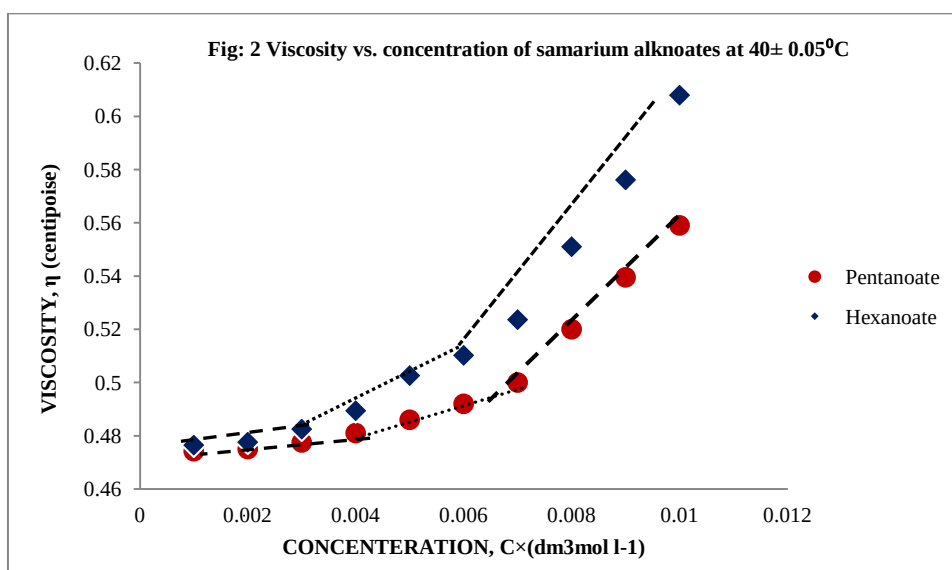
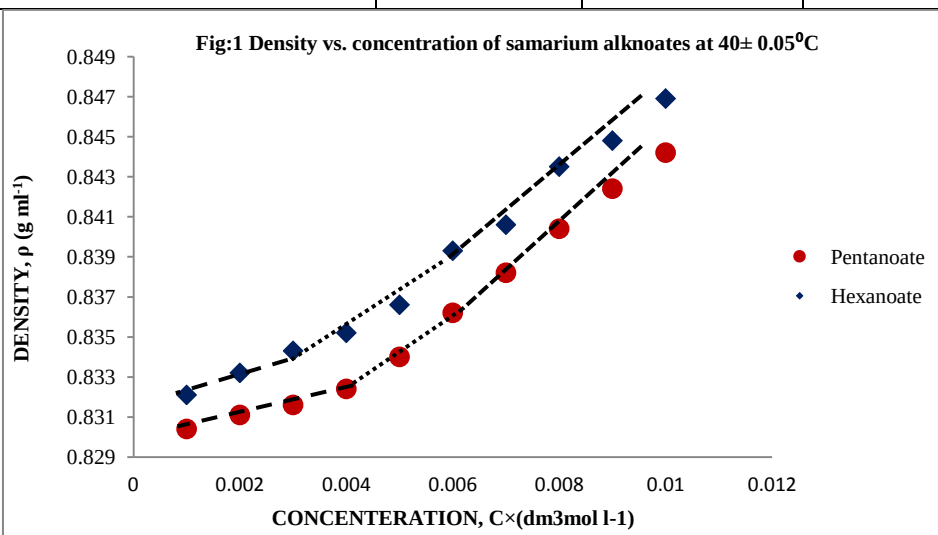
The viscosity, η and fluidity, Φ (reciprocal of viscosity) are considered to be the important rheological parameters. A major characteristic of liquid is their ability to flow. Highly viscous liquids flow only very slowly because their large molecules get emerged. Mobile liquids have low viscosities. When ionic crystal has dissolved, the solution consist of a distribution ions supported by the solvent (electrolyte solution). In dilute alkanoates solutions, the cations Sm^{3+} ion, and anions, RCOO^- 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 samarium alkanoates (pentanoate and hexanoate) solutions as a function of solute concentration, C manifest the cited fact i.e. the fluidity (Table 1) decreases (viscosity increases) with increasing alkanoates concentration and chain length owing to the formation of large entities (micelles) at higher concentration of surfactant solutions.

The plots (Fig. 2) of viscosity vs. alkanoates concentration, ($\eta - C$) are characterized by an intersection of two straight lines at CMC (Table 1). The viscosity for solvent mixture, η_0 are evaluated (Table 1) by extrapolating $\eta - C$ plots (Fig. 2) to zero surfactant concentration. The viscosity data have been interpreted on the basis of following well known equations¹⁹⁻²² proposed by Einstein¹⁹, Moulik²⁰, Vand²¹ and Jones-Dole²². Einstein type plots $\eta_{sp} - C$ are used to evaluate molar volume, V_m ($\text{dm}^3 \text{mol}^{-1}$). The interaction coefficient, θ (Table 1) has also been by employing Vand type plots [$1/C$ vs $1 / \log (\eta / \eta_0)$]. The values of interaction coefficient, θ were found to be negative and independent of chain length. 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 values of M were found to be almost independent of chain length. The constants A and B from Jones- Dole's equation have been evaluated by employing plots of $\eta_{sp}/\sqrt{C}$ vs. $\sqrt{C}$. For samarium alkanoates (pentanoate and hexanoate) solutions in mixtures of benzene-methanol (7:3 v/v) at 40°C, the values of constant B (solute-solvent interaction) was found (Table 1) to be larger than the values of constant A (solute-solute interaction), suggest that the solute molecules do not aggregate appreciably in the premicellar region (below the CMC). This may be attributed to the fact that the aggregation of alkanoates molecules boots up the electrokinetic forces causing more intake of the solvent resulting in the increasing viscosity of the system. The relative viscosity, η_r , specific viscosity η_{sp} and intrinsic viscosity, $[\eta]$ is also recorded in Table 1. The intrinsic viscosity, $[\eta]$ for samarium alkanoates (pentanoate and hexanoate) obtained by intercept of the curves of η_{sp}/C vs. C . The values of intrinsic viscosity, $[\eta]$ increase with increase in chain length.

It is therefore concluded that the equations by Einstein, Moulik, Vand and Jones-Dole are applicable to dilute solution of samarium alkanoates (pentanoate and hexanoate). The values of CMC and molar volume of these alkanoates, calculated from these equations are in close agreement. And micellar and bulk behavior (molar volume, rheology) of these alkanoates can be explained by using density and viscosity measurements.

Table-1: Parameters from density and viscosity measurements of the solutions of samarium alkanoates in the mixture of benzene-methanol (6:4 v/v) at 40±0.05°C.

Parameters	Derived from	Samarium Pentanoate		Samarium Hexanoate	
Critical micellar concentration, CMC(mol dm ⁻³)	k vs C, ρ vs C and η vs C	CMC(I) 0.037	CMC(II) 0.066	CMC(I) 0.033	CMC(II) 0.063
Density of solvent, ρ ₀ (g cm ⁻³)	ρ vs. C	0.8300		0.8300	
Limiting apparent molar volume, ϕ ⁰ (cm ³ mol ⁻¹)	ϕ _v vs C ^{1/2}	4.30×10 ⁻²		4.58×10 ⁻²	
Constant, S _v	ϕ _v vs C ^{1/2}	8.2×10 ⁻²		11.25×10 ⁻²	
Viscosity of solvent, η ₀	η vs C	0.4712		0.4712	
Molar volume, V _m (mol ⁻¹ dm ³)	η _{sp} vs C	0.23		0.33	
Moulik's constant(M and K)	(η/η ₀) ² vs C ²	M=1.00	K=29	M=1.02	K=50
Constants of Jones-Dole's equation(A and B)	η _{sp} /C ^{1/2} vs C ^{1/2}	A=0.04	B=0.2	A=0.08	B=0.25
Interaction coefficient, θ	1/C vs 1/log(η/η ₀)	8.0		8.0	
Relative viscosity, η _r	(η/η ₀)	1.0036		1.0125	
Specific viscosity, η _{sp}	(η _r -1)	0.0036		0.0125	
Intrinsic viscosity,[η]	η _{sp} /C vs C	0.02		0.43	
Fluidity, Φ	(1/η)	2.115		2.096	



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