Molar volume and rheology of anionic surfactants in non-aqueous media

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Abstract: The apparent molar volume, and fluidity for the solution of anionic surfactants ie. zinc hexanoate and decanoate as mono-alkanoates and butanedioate and hexanedioate as dialkanoates in a mixture of benzene-methanol (50% v/v) at 30°C have been evaluated from the data of density and viscosity. The value of CMC decreases with increasing chain length of fatty acid constituent. The limiting apparent molar volume has been calculated by Masson’s equation.

Keywords: Anionic surfactants, metal alkanoates, density, 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, 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.

While major developments have taken place in the study of metal alkanoates of mono-carboxylic acid, the study of di-alkanoates of di-carboxylic acid is almost untouched. Burrows et al. synthesized di-carboxylic acid metal alkanoates by metathesis and Ikhuoria et al. studied the effect of temperature on the stability of metal alkanoates of dicarboxylic acids. Suzuki prepared and investigated the thermal dehydration of manganese(II) dialkanoate anhydrides in various atmospheres. Liu et al. synthesized different metal dialkanoates such as calcium glutarate, zinc glutarate, calcium sebacate and zinc sebacate and discussed their use as thermal stabilizers for PVC material. Barbara and Lacz studied the thermal decomposition of cadmium butanedioate dihydrate. A number of workers have reported ultrasonic, conductometric, and rheometric measurements of metal alkanoates for the determination of ion-solvent interaction in organic solvents. Viscometric and conductometric measurements of lanthanide and transition metal alkanoates have been reported in different organic solvents.

The focus of this paper is to look into the bulk behavioral aspects like apparent molar volume and rheology (viscosity/ fluidity) of zinc mono-(hexanoate and decanoate) and di-(butanedioate and hexanoate) alkanoate by using density and viscosity measurements in a mixture of benzene and methanol (50% v/v) at 30±0.05°C.

II. Experimental

All the chemicals used were of BDH/AR grade. Solvents benzene and methanol were purified by distillation under reduced pressure. Zinc mono- (hexanoate and decanoate) alkanoates were synthesized by direct metathesis of corresponding potassium alkanoates as mentioned in our earlier publications, while di-alkanoates of zinc were synthesized by metathesis in alcohol solution. The zinc di-alkanoates (butanedioate and hexanedioate) were first prepared by dissolving the dicarboxylic acid in hot ethanol, followed by treatment with potassium hydroxide solution. To this mixture, solution of the zinc salt was added slowly with continuous stirring. The precipitated alkanoates of the dicarboxylic acid was filtered off, washed with hot water and air-dried. The alkanoates were purified by recrystallization with alcohol and dried under reduced pressure. The purity was checked by their melting points (hexanoate-130.0°C decanoate-92.0°C and butanedioate-310.0°C hexanoate-263.0°C) and absence of hydroxyl 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 zinc mono- and di-alkanoates were prepared by dissolving a known amount of alkanoates in a benzene-methanol mixture (50% v/v) and were kept for 2 hr in a thermostat at 30±0.05°C temperature. The zinc mono- and dialkanoates 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 pyknometer. The Pyknometer 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

Apparent Molar Volume

The density, ρ of zinc mono-(hexanoate and decanoate) and di-alkanoate (butanedioate and hexanoate) in the mixture of benzene-methanol (50% v/v) at 30⁰C (Fig.1) is found to increase with increasing solute concentration, C as well as increasing chain length of alkanoates. The plot ρ-C (Fig.1) of zinc mono-alkanoates is characterized by an intersection of two straight lines at a critical concentration, CMC (Table I). While the plots (Fig.1) of di-alkanoates is characterized by two breaks at definite solute concentration which corresponds to the critical micellar concentration, CMC (I) and CMC (II) in dialkanoate solution (Table I). The appearance of CMC (I) and CMC (II) can be explained on the basis of the formation of ionic and neutral micelles in the surfactant solution. The concentration at which micelles formation starts known as critical micellar concentration (CMC), beyond this concentration the bulk properties of the surfactant, such as osmotic pressure, turbidity, solubilization, surface tension, viscosity, ultrasonic velocity and conductivity changes abruptly. If the micelles are formed in non-aqueous medium the aggregates are called “reversed micelles” in this case the polar head groups of the surfactant are oriented in the interior and the lyophilic groups extended outwards in the solvent. The values of CMC (I) and CMC (II) vary with the chain length of alkanoates molecule which may be due to the increase in micelle stability and increasing tendency to aggregate. The plots (Fig.1) of density vs. concentration of solution of zinc alkanoates below CMC have been extrapolated to zero surfactant concentration; the extrapolated values of density, ρ₀ for these alkanoates are in agreement with the experimental value of density of solvent mixture. The equation by W.C. Roots¹ has been applied to dilute anionic surfactant solutions below CMC to evaluate the Roots constants¹ (A and B). The order: A > B was found, suggest that the solute-solvent interactions predominate in dilute solutions of zinc alkanoates and micellization only begins at the CMC.

The density data (Fig.1) are used to evaluate the apparent molar volume, φᵥ (solute-solvent interaction) by employing equation¹²

$$\phi_v = \frac{M}{\rho} - \frac{10^3(\rho - \rho_0)}{C_0 \rho_0}$$  \hspace{1cm} (1)

Where M, ρ, ρ₀ and C represent the molecular weight of the zinc alkanoates, density of solution, density of solvent and concentration of the surfactant solution, respectively. It is obvious that increase in surfactant concentration, and chain length of molecule apparent molar volume φᵥ (solute-solvent) increases (φᵥ decreases) below the CMC and the same decreases (φᵥ increases) above the CMC. The limiting apparent molar volume, φᵥ⁰ has been obtained by extrapolating the linear plot of φᵥ vs. Cⁱ/² and found to be increase with increase in chain length (Table I) for dilute alkanoates solutions (below the CMC) according to Masson’s equation¹³ for electrolytes. (φᵥ = φᵥ⁰ + Sᵥ Cⁱ/²). The limiting apparent molar volume, φᵥ⁰ and the experimental limiting slopes, Sᵥ (Table I) are measures of solute-solvent and solute-solute interactions, respectively. The positive values of Sᵥ indicates strong solute-solute interactions leading to a fair chance of micellization in these surfactants 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 (Zn²⁺ ion), with its strong electric field, packs polar solvent molecules around itself in a smaller volume than they occupy in the bulk solvent.

Rheology

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. 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 dissolved, the solution consist of a distribution ions supported by the solvent (electrolyte solution). In dilute solution of zinc alkanoates, the cations Zn²⁺ ion, and anions, RCOO⁻ and R(COO)₂⁻ 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 of solution of zinc mono-and dialkanoates as a function of solute concentration, C manifest the cited fact i.e. the fluidity (Table I) decreases (viscosity increases) with increasing chain length and concentration of alkanoates solution owing to the formation of large entities (micelles) at higher concentration of surfactant solutions.

The plots (Fig.2) of viscosity vs. alkanoates concentration, (η - C) are characterized by an intersection of two straight lines at CMC (Table I) in a mixture of benzene-methanol (50% v/v). The viscosity, η of the dilute solution of zinc surfactants increases with increase in solute concentration which may be due to the tendency of surfactant molecule to form aggregate (micelle) with the increase in alkanoates concentration in non-aqueous
medium. The viscosity for solvent mixture, \( \eta \), are evaluated (Table I) by extrapolating \( \eta - C \) plots (Fig. 2) to zero surfactant concentration. The viscosity data have been interpreted in the light of following well known equations\(^{14-17}\) proposed by Einstein\(^1\), Moulik\(^5\), Vand\(^6\) and Jones-Dole\(^7\). Einstein type plots \( \eta_{sp} - C \) are used to evaluate molar volume, \( V_m \) of solution of zinc alkanoates (Table I), the values molar volume increases with increasing in chain length of fatty acid constituent in anionic surfactants. The interaction coefficient, \( \theta \) was obtained by employing Vand type plots \( [1/C vs 1 / \log (\eta / \eta_0) ] \). The values of interaction coefficient, \( \theta \) (Table I) were found almost independent of chain length. The values of Moulik’s constants (M and K) were evaluated from \( (\eta / \eta_0)^2 \) vs. \( C^2 \) plots following the order: \( K > M \) (Table I) indicating the predominance of solute-solute interactions (good probability of micellization). The values of M (solute-solvent interaction) were found to be almost constant with increase in chain length. The constants A and B from Jones-Dole’s equation have been evaluated by employing plots of \( \eta_{sp} / \sqrt{C} \) vs. \( \sqrt{C} \). The results (Table I) suggest that solute-solvent interaction constant, B are larger than the A (solute-solute interaction), suggest that the anionic surfactant molecules do not aggregate appreciably in the premicellar region (below the CMC) but there is a sudden change in the aggregation at CMC. This may be attributed to the fact that the aggregation of surfactant molecules boost up the electrokinetic forces causing more intake of the solvent resulting in the increasing viscosity of the system. The relative viscosity, \( \eta_r \), specific viscosity \( \eta_{sp} \) and intrinsic viscosity, \([\eta]\) increases with increasing chain length of fatty acid constituent recorded in Table I. The intrinsic viscosity, \([\eta]\) for zinc mono- and dialkanoates obtained by intercept of the curves of \( \eta_{sp} / C \) 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 zinc mono- (hexanoate and decanoate) and di-(butanediolate and hexanediolate) alkanoates. 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 anionic surfactants can be explained by using density and viscosity measurements and also suggest that solute-solvent interaction is predominant in premicellar region.

**Acknowledgements**

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**References**


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Table: 1. Parameters from density and viscosity measurements of the solutions of zinc alkanoates in the mixture of benzene-methanol (50% v/v) at 30°C.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Derived from</th>
<th>Hexanoate</th>
<th>Decanoate</th>
<th>Butane dioate</th>
<th>Hexane dioate</th>
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<tbody>
<tr>
<td>Critical micellar concentration, CMC (mol dm⁻³)</td>
<td>k vs C, ρ vs C, η vs C</td>
<td>6.3 x 10⁻³</td>
<td>5.6 x 10⁻³</td>
<td>(I) 3.1 x 10⁻⁴</td>
<td>(II) 6.3 x 10⁻⁴</td>
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<tr>
<td>Density of solvent, ρ (g cm⁻³)</td>
<td>ρ vs C</td>
<td>0.800</td>
<td>0.800</td>
<td>0.809</td>
<td>0.800</td>
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<tr>
<td>Limiting apparent molar volume, Vₐ (cm³ mol⁻¹)</td>
<td>ρ vs C</td>
<td>-6.88 x 10⁻³</td>
<td>-9.12 x 10⁻³</td>
<td>-8.21 x 10⁻³</td>
<td>-8.40 x 10⁻³</td>
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<tr>
<td>Constant, Sₙ</td>
<td>ρ vs C</td>
<td>3.86 x 10⁻³</td>
<td>4.64 x 10⁻³</td>
<td>11.41 x 10⁻³</td>
<td>11.94 x 10⁻³</td>
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<td>Viscosity of solvent, ηₜ</td>
<td>ηₜ vs C</td>
<td>0.451</td>
<td>0.451</td>
<td>0.452</td>
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<td>Molar volume, Vₘ (mol³ dm⁻³)</td>
<td>η₀ vs C</td>
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<td>82.67</td>
<td>9.16 x 10⁻³</td>
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<td>Moulik’s constant (M and K)</td>
<td>(η/η₀)² vs C²</td>
<td>M=1.09</td>
<td>K=8.09 x 10⁻²</td>
<td>M=1.15</td>
<td>K=7.33 x 10⁻²</td>
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<tr>
<td>Constants of Jones-Dole’s equation (A and B)</td>
<td>ηₜ/η₀ vs C²</td>
<td>A=4.69</td>
<td>B=77.76</td>
<td>A=6.03</td>
<td>B=70.20</td>
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<td>Interaction coefficient, θ</td>
<td>1/C vs 1/log(η/η₀)</td>
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<td>0.1397</td>
<td>0.0135</td>
<td>0.0315</td>
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<td>Relative viscosity, ηₘ</td>
<td>(η/η₀)</td>
<td>1.0444</td>
<td>1.0467</td>
<td>1.0040</td>
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<td>Specific viscosity, ηₛ</td>
<td>(ηₛ-1)</td>
<td>0.0444</td>
<td>0.0467</td>
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<td>Intrinsic viscosity, [η]</td>
<td>ηₛ/η₀ vs C</td>
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<td>Fluidity, Ψ</td>
<td>(1/η)</td>
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<td>2.1231</td>
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