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A study on rheology, density and molar volume of aqueous transition metal dodecylsulhates

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ABSTRACT

The apparent molar volume, ϕ_v ($cm^3 mol^{-1}$) and fluidity, ϕ (P^{-1} or rhe) for the aqueous solutions of transition metal [Cr(II), Mn(II), Co(II)] dodecylsulphates at different temperatures (30°-50°C) have been evaluated from the data of density, ρ (g cm^{-3}) and viscosity, η(P), respectively. The limiting apparent molar volume, $\phi°_v$ (cm^3 mol^{-1}) has been computed employing Masson's equation. Both viscosity and density for these aqueous solutions are found to increase with increasing surfactant concentration. The CMCs determind from η-C and ρ-C plots are in good agreement. The present investigation reveals that transition metal dodecylsulphates exhibit a greater tendency to undergo micellization in water even at low surfactant concentration (0.008-0.010 mol dm^{-3}). Higher fluidity for these aqueous surfactant solutions is suggestive of the fact that these are free flowing solutions even after the onset of micellization. Partial molar expansibility data, $E°_{surf}$ have been evaluated for these systems utilizing the temperature dependence of partial molar volume, $\phi°_v$. $E°_{surf}$ increases with increasing temperature which may be attributed to a decrease in electrostriction as well as loosening of water structure at higher temperatures.

Key words : Rheology, Fluidity, Density, Molar volume, Transition metal dodecylsulphates.

Research workers have used viscosity (Abdel-Rahem *et al.*, 2005; Blockhra and Verma, 1977; Franks and Chickenden, 1968; Franks *et al.*, 1968 and Glasstone *et al.*, 1941) and density (Grant *et al.*, 2006; Hu and Matthys, 1997; Hugerth, 2001; Jones and Dole, 1929 and Kay and Evans, 1966) data to detect critical micelle concentration (CMC) for different surfactant solutions. J.A. Shashkina and co-workers (Kay and Evans, 1966), through their study on rheology of viscoelastic solutions of cationic surfactant, observed the effect of added macromolecule to the system. Molar volume and rheology have been used to probe into the bulk behaviour of Uranyl (II) stearate (Kumar, 1994). Recent references (Millero, 1968, 1979; Montalvo *et al.*, 2000 and Moulik, 1968) on rheological aspects appear in literature to deduce important consequences about solution behaviour of various surfactants. The present study on rheology, density and molar volume of aqueous transition metal (Cr(II), Mn(II)), Fe(II), Co(II)) dodecylsulphates has been initiated with a view to probe various aspects of the solution behaviour for these micellar systems. The study suggests that there is a greater tendency for these systems to undergo micellisation in water even at such a low surfactant concentration as (8-10) × 10^{-3} mol dm^{-3}. The results suggest that the fluidity of these systems is restored even after the onset of micellisation.

MATERIALS AND METHODS

As the dodecylsulphates of Cr, Mn, Fe, Co are not commercially available, these compounds were all prepared in our laboratory using GR grade (Merck/BDH) chromium oxide, manganese acetate, ferric chloride, cobalt nitrate, sodium dodecylsulphate and toluene. The respective dodecylsulphates were prepared by refluxing the stoichiometric amounts of chromium oxide/manganese acetate/ferric chloride/cobalt nitrate with sodium dodecylsulphate in toluene for about 5-6 hrs. The products so obtained were washed with methanol-benzene and vacuum dried. The crystalline grey-green chromium, grey-brown manganese, dull-brown iron and light-pink cobalt dodecylsulphates thus obtained were found to decompose in the temperature range, 220-270ºC. The synthesis and the purity of the compounds were confirmed by CHNS (elemental) and IR techniques.

Ostwald's type viscometer used for measuring the viscosity (± 0.002) of the aqueous surfactant solutions satisfies to a great extent the conditions assumed in the discussion of Poiseuille's law. The cleaning up of the apparatus before each day's determination was done with chromic acid. It was also kept filled with chromic acid even when not in use. The oven dried viscometer was calibrated time and again by determining the time of flow for water. The much needed density data for viscosity evaluation was obtained by employing high quality pyrex glass dilatometer bearing a 15 ml reservoir. The accuracy of the calibrated dilatometer was checked by using any suitable liquid of known density. Viscosity data for aqueous surfactant solution was evaluated as: