

Viscometric measurements on aqueous dodecylsulphate solutions of Cu (II), Zn (II), Ag (I), Cd (II) at different temperatures (30–50°C)

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ABSTRACT

The study deals with the viscometric measurements on aqueous solutions of transition metal [Cu(II), Zn(II), Ag(I), Cd(II)] dodecylsulphates at different temperatures (30–50°C). The plots of Viscosity coefficient, η as a function of surfactant concentration, C (mol dm^{-3}) are found to intersect at a definite concentration indicating the critical micelle concentration (c.m.c.). Viscosity of these solutions is found to increase with increasing concentration, but decrease with increasing temperature. The knowledge of thermodynamic parameters of viscous flow suggests that only the change in enthalpy ($\Delta H < 0$) favours the viscous flow whereas both the change in entropy ($\Delta S < 0$) and the change in free energy ($\Delta G > 0$) resist the flow in these aqueous surfactant systems.

Key words : Viscosity coefficient, Fluidity, Rheology, molar volume, Critical micelle concentration (c.m.c.), Thermodynamic parameters of viscous flow

The significance of viscometric measurements to the wide surfactant domain is well known. The study has been found useful in elucidating the structure of micelles formed in different surfactant systems. Research workers in the past (Clifton *et al.*, 2007; Davies *et al.*, 2006 and Glasstone *et al.*, 1942) and present (Hu and Matthys, 1997; Hugerth, 2001, Jobling and Robert, 1958; Jones and Dole, 1929; Ketner *et al.*, 2007; Koelsch and Motschmann, 2006; Marchetti *et al.*, 2005; Montalvo *et al.*, 2000, Moulik, 1968 and Panda *et al.*, 2007) have shown keen interest in viscometric measurements in order to study the surfactant demeanour involving their multifarious aspects. The present study is an attempt to probe into the nature of bulk flow in aqueous transition metal [Cu(II), Zn(II), Ag(I), Cd(II)] dodecylsulphates at various temperatures (30–50°C) by resorting to viscometry. Various rheological aspects are envisaged to be brought forth by highlighting such contradictory aspects as fluidity and viscous-drag.

MATERIALS AND METHODS

The dodecylsulphates of Cu(II), Zn(II), Ag(I), Cd(II) are not commercially available. These were prepared in our laboratory using GR grade (Merck/BDH) Zinc oxide, nitrates of copper/silver/cadmium, sodium dodecylsulphate (NaDS) and toluene. The stoichiometric amounts of NaDS and the above cited metal salts were refluxed in toluene for about 5–6 hrs. The metathetic displacement reaction ensured preparation of pale white cadmium(II) and zinc(II), brownish black silver(I) and greenish blue copper(II) dodecylsulphates. The products thus obtained from their respective mother liquors were washed with

methanol-benzene and vacuum dried. The products were further purified by recrystallisation from aniline. The synthesis and purity of the compounds were confirmed by CHNS(elemental) and IR techniques. The compounds do not give sharp m.p. as such, but are found to decompose in the vicinity of 250 °C.

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:

$$\frac{1}{2} = \frac{1}{2} \cdot \frac{t_1}{t_2} \quad \dots (i)$$

where η_1 , η_2 , ρ_1 , ρ_2 and t_1 , t_2 signify for viscosity, density and time of flow for known and unknown solutions, respectively. The measurements were however carried out at different temperatures 30°–50°C ($\pm 0.05^\circ\text{C}$) in a thermostat.

RESULTS AND DISCUSSION

Viscosity, η (millipoise) for the aqueous solutions of transition metal [Cu(II), Zn(II), Ag(I), Cd(II)]