Viscosities of Solutions of Cadmium Halides in Aqueous Acetone

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Viscosities and relative viscosities of CdX₂ (X = Cl, Br, I) in aq. acetone (80%, w/w) were measured as a function of salt concentration at 30°. The data have been analysed in terms of the Jones-Dole equation and the results discussed in terms of the effects of salts on the structure of the solvent. CdCl₂ and CdBr₂ are suggested to be structure breakers while CdI₂ is structure promoter.

MIXED binary aqueous solvent systems behave differently in an unexpected manner as compared with the behaviour of mixed non-aqueous systems. These observations have given a new impetus to a detailed study of the structure of aqueous solutions. Mixed binary aqueous solvent systems have received much less attention in the literature than its aqueous analogues. While the behaviour of mixed non-aqueous systems has been studied in detail, much less attention has been given to the study of the structure of aqueous solutions. While the behaviour of mixed binary aqueous solvent systems has been studied in detail, much less attention has been given to the study of the structure of aqueous solutions. While the behaviour of mixed binary aqueous solvent systems has been studied in detail, much less attention has been given to the study of the structure of aqueous solutions.

For preparing the aqueous solutions of acetone, triply distilled water (specific conductance ~ 10⁻⁶ ohm⁻¹ cm⁻¹) was used. Acetone (BDH) of AR grade was dried over anhydrous calcium sulphate and distilled for the present study were 0.78521 g m⁻¹ and 0.0032 mP respectively at 25° and these values agree well with the literature values. AR grade salts, after drying over P₂O₅, were used for the present study and the solutions were made by weight under dry conditions. Conversion between molar concentration and molality was done by the relation:

\[ m = 1/(\rho M - M_s/1000) \]

where \( M \) represents the molarity, \( m \) the molality, \( \rho \) the density of the salt solution and \( M_s \) the molecular weight of the salt used. The density of the solution needed for viscosity was determined with the help of a double capillary pycnometer. For absolute viscosities, the viscometer was calibrated with water and pure toluene of known viscosity.

The viscosity data reported here have an accuracy of ± 0.001 (cp). From Table 1 it is clear that the viscosity increases with the increase of concentration of the salt. The variation of viscosity with concentration can be represented by the Jones-Dole equation (Eq. 2):

\[ \eta /\eta_0 = 1 + AC + BC \]

where \( \eta \) and \( \eta_0 \) are the viscosities of the salt solution and solvent (aqueous acetone) respectively. The coefficients \( A \) and \( B \) are adjustable parameters, either positive or negative, that accounts for ion-solvent interaction. Value of \( B \) was determined from the slope of the linear plot of \( (\eta /\eta_0 - 1) / \sqrt{C} \) versus \( \sqrt{C} \). The values of \( B \) for CdCl₂, CdBr₂ and CdI₂ are -3.13, -0.46 and -0.27 respectively. Since coefficient \( B \) of the Jones-Dole equation is a characteristic of ion-solvent interaction, the negative values of \( B \) for CdCl₂ and CdBr₂ suggest that these salts behave as structure breakers, while the positive values of \( B \) for CdI₂ indicate that it acts as structure promoter.

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References
Stannous Chloride Catalysed Polymerization of n-Butyl Vinyl Ether

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The kinetics of cationic polymerization of the system n-butyl vinyl ether-stannous chloride-n-hexane at 13° have been studied. The initial rate of polymerization is found to be directly proportional to [monomer]^{3/2} and [stannous chloride]. The average degree of polymerization of the polymer varies with the monomer concentration according to the relation \( \bar{DP} = K_2[M] \) and is independent of [stannous chloride]. The polymer is saturated as evidenced by bromination and IR spectral studies.

Using several reagents like boron trifluoride etherate, boron trifluoride, stannic chloride, ferric chloride, etc., n-butyl vinyl ether has been polymerized. In the present study, the polymerization of n-butyl vinyl ether has been carried out in n-hexane solution using stannous chloride as the initiator and the kinetics of the homogeneous polymerization system have been studied.

The monomer, solvent and other chemicals used were of analytical grade and they were further purified and dried using standard procedures. The solvent and requisite amount of initiator were placed in a small standard joint flask and the monomer was injected by a hypodermic syringe through a rubber seal. A dry box was used for handling the materials in order to protect the reaction system from moisture. After a definite time period of polymerization, in a thermostatic bath at 13°, the polymer was precipitated by the addition of excess ammoniacal methanol. It was centrifuged, washed and dried in \( \textit{vacuo} \) at 50° to constant weight. Number average molecular weight was determined by depression in freezing point method in benzene.

The per cent conversion versus time plots for the system (Figs. 1 and 2) are reproducible and pass through origin indicating the adequacy of the purification of reagents and absence of any induction period. The lack of dependence of degree of polymerization on increasing conversion per cent and on [stannous chloride] conform to a normal cationic polymerization system.

Figs. 1 and 2 represent the dependence of the rate of polymerization (\( R_p \)) on [monomer] and [stannous chloride] respectively at 13°. The corresponding \( \log R_p \) versus [M] and \( \log R_p \) versus \( \log [\text{SnCl}_2] \) plots show the order of the reaction with respect to [monomer] to be about 1·5 and that with respect to [stannous chloride] to be about one.

Data regarding the dependence of the number average degree of polymerization (\( \bar{DP} \)) of the polymers on monomer concentration are shown in Table 1. The results may be represented by Eq. (1),

\[
\bar{DP} = K_2[M]
\]

which indicates absence of chain transfer to monomer.