Viscosities of Solutions of Cadmium Halides in Aqueous Acetone

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Viscosities and relative viscosities of CdX_2 (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 ($\eta/\eta_0 = 1+A\sqrt{C}+BC$) and the results discussed in terms of the effects of salts on the structure of the solvent. $CdCl_2$ and $CdBr_2$ are suggested to be structure breakers while CdI_2 is structure promotor.

MIXED binary aqueous solvent systems behave[1,2] 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. While ion-solvent interactions have been studied in detail in aqueous solutions, such effects have received much less attention in mixed binary aqueous solvent systems. In the present note, results of our studies on viscosities of cadmium halides in aq. acetone (80% w/w) at 30° are being reported.

For preparing the aqueous solutions of acetone, triply distilled water (specific conductance $\sim 10^{-6}$ ohm^{-1} cm^{-1}) was used. Acetone (BDH) of AR grade was purified further by refluxing successively with small portions of potassium permanganate until the violet colour persisted. It was then distilled, dried over anhydrous calcium sulphate and distilled again. Density and viscosity of the acetone used for the present study were 0·78521 g ml^{-1} and 0·0032 poise respectively at 25° and these values agree well with the literature values[3].

AR grade salts, after drying over P_2O_5, were used for the present study and the solutions were made by weight under dry conditions. Conversion between molar concentration and molality was done using the relation[4]:

$$m = 1/(\rho/M - M_2/1000)$$

where M represents the molarity, m the molality, ρ the density of the salt solution and M_2 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[5]. For absolute viscosities, the viscometer was calibrated with water and pure toluene of known viscosity using Eq. (1) (ref. 6):

$$V \text{ (kinematic viscosity)} = \eta/\rho = at - b/t \qquad ...(1)$$

where η is the dynamic viscosity, ρ is the density of the liquid, t is the efflux time in seconds, and a and b are the characteristic constants of the viscometer. The viscosity was determined at 30° $\pm 0·01°$ with the help of a capillary type viscometer, the details and working of which are reported elsewhere[7]. The error in the flow-time was $\pm 0·05$ sec. The viscosity data reported here have an accuracy of $\pm 0·001$ (cp).

TABLE 1 — VISCOSITY, DENSITY AND RELATIVE VISCOSITY OF AQUEOUS ACETONE (80%, w/w) SOLUTIONS OF CADMIUM HALIDES AT 30°

Conc. $\times 10^3$ (g mole litre^{-1})	Density (ρ) (g ml^{-1})	Viscosity (η) (cp)	η/η_0
CADMIUM CHLORIDE			
37·49	0·9730	1·1362	1·2614
46·06	0·9736	1·1406	1·2663
55·57	0·9751	1·1504	1·2772
68·78	0·9769	1·1560	1·2834
91·14	0·9808	1·1565	1·2840
112·02	0·9830	1·1629	1·2911
142·74	0·9847	1·1781	1·3080
CADMIUM BROMIDE			
36·98	0·9852	1·0749	1·1934
46·63	0·9855	1·0903	1·2105
57·42	0·9859	1·1135	1·2363
70·72	0·9869	1·1354	1·2606
86·70	0·9879	1·1610	1·2890
101·27	0·9920	1·1716	1·3009
CADMIUM IODIDE			
31·41	0·9917	0·9661	1·0726
42·89	0·9940	0·9949	1·1049
59·16	0·9977	1·0312	1·1449
77·20	0·9986	1·0666	1·1842
99·90	1·0009	1·1170	1·2401
123·83	1·0047	1·1616	1·2000

Values of viscosity, density and relative viscosity of the different aq. acetone solutions of cadmium halides at 30° are given in Table 1.

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 Jones-Dole equation[8] (Eq. 2)

$$\eta/\eta_0 = 1 + AC^{\frac{1}{2}} + BC \qquad ...(2)$$

where η and η_0 are the viscosities of the salt solution and solvent (aqueous acetone) respectively. B is an adjustable parameter, 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 $CdCl_2$, $CdBr_2$ and CdI_2 are $-3·13$, $-0·46$ and 2·63 respectively and the values of the parameter A for $CdCl_2$, $CdBr_2$ and CdI_2 are 1·52, 1·04 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 $CdCl_2$ and $CdBr_2$ suggest that these salts behave as structure breakers, while the positive values of B for CdI_2 indicate that it acts as structure promoter.

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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 porportional to [monomer]$^{3/2}$ and [stannous chloride]. The average degree of polymerization of the polymer varies with the monomer concentration according to the relation $\overline{DP} = K_2[M]$ 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[1], boron trifluoride[2], stannic chloride[3], ferric chloride[4], 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 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 [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.
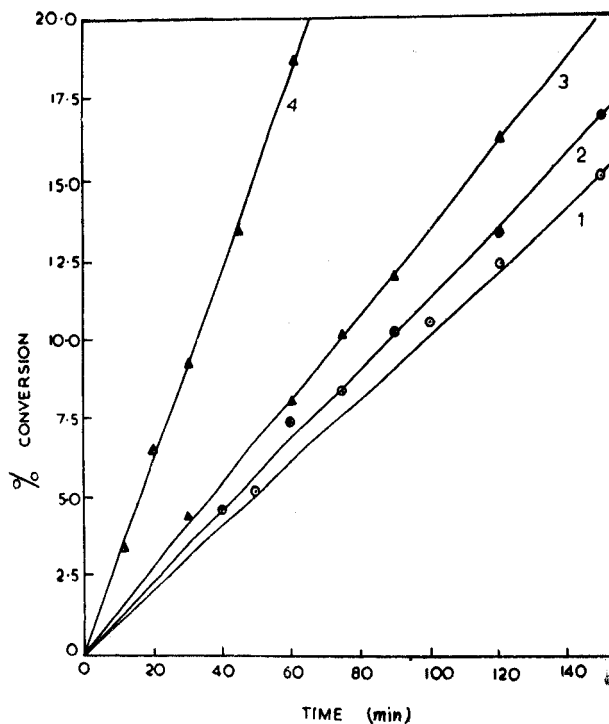

Fig. 1 — Polymerization of n-butyl vinyl ether in n-hexane catalysed by stannous chloride at [SnCl$_2$]=2·2 ×10^{-2}M and 13°; and various [monomer] {Curve 1, [monomer]=1·56M; curve 2, [monomer]=2·34M; curve 3, [monomer]=3·00M; curve 4, [monomer]=3·65M}
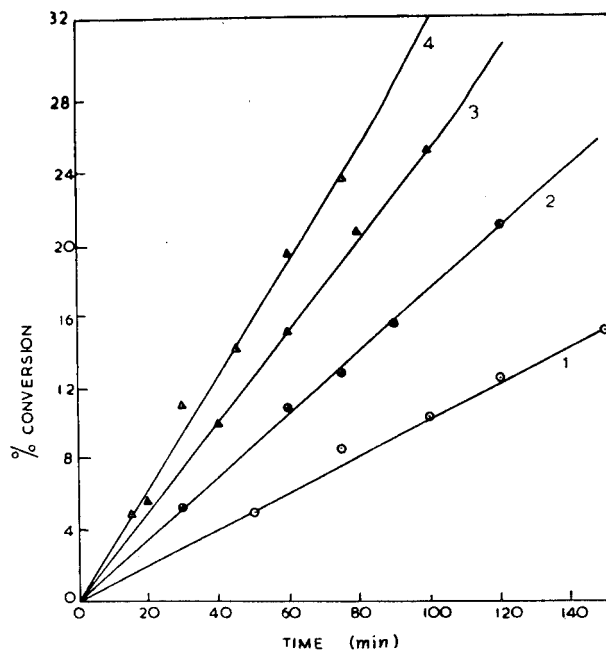

Fig. 2 — Polymerization of n-butyl vinyl ether in n-hexane catalysed by stannous chloride at [monomer]=1·56M and 13° and various [catalyst] {Curve 1, [SnCl$_2$]=2·2 ×10^{-2}M; curve 2, 3·5 ×10^{-2}M; curve 3, 5·5 ×10^{-2}M; curve 4, 6.6 ×10^{-2}M}

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

$$\overline{DP} = K_2[M] \qquad \ldots(1)$$

which indicates absence of chain transfer to monomer.