

Viscosities of Potassium Halides in Water-Pyridine & Water- γ -Picoline Mixtures

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The relative viscosities of 0.025M to 0.2M solutions of potassium chloride, potassium bromide and potassium iodide in 20%, 40%, 60% and 80% aqueous pyridine and aqueous γ -picoline at 35°C and 65°C have been determined. The relative viscosity is found to fit the Jones-Dole equation, $\eta/\eta_0 = 1 + AC^{1/2} + BC$. The coefficient B is found to increase with increase in temperature as well as cosolvent concentration. This increase is larger in the case of γ -picoline compared to that for pyridine. B is very large at 60% and 80% cosolvent concentrations. The large values of B have been explained in terms of the ion-solvent interactions and also solvent-solvent interactions in the mixed solvent.

THE viscosity data of electrolyte solutions have been widely used to provide information concerning the nature of ion-solvent interactions, based on Jones-Dole equation. In the title study, pyridine and γ -picoline have been chosen as the cosolvents, since both these solvents have tendency to interact with water molecules¹.

Materials and Methods

Potassium halides (AR) were dried at 110°C for 4 hr prior to use. Reagent grade pyridine and γ -picoline were distilled over KOH beads and the middle fractions collected.

Viscosity was determined using a Cannon Fenske direct flow viscometer. The kinetic energy factor of the viscometer was found to be within experimental error. The viscometer was calibrated frequently with freshly distilled water. For the viscosity measurement a concentration range of 0.025 to 0.2M was used. The viscosity values were generally reproducible within $\pm 0.3\%$. Density was determined in a bicapillary pycnometer calibrated with distilled water and was accurate to 2×10^{-5} g ml⁻¹. Viscosity and density measurements were made in a thermostated water-bath, the temperature of which was controlled to within $\pm 0.01^\circ\text{C}$. All the solutions were made by weight and vacuum correction done for weighing.

Results and Discussion

The relative viscosities and densities of potassium chloride, bromide and iodide have been determined in 20%, 40%, 60% and 80% water-pyridine and water- γ -picoline mixtures at 35°C and 65°C. The relative viscosities of the halides increase with increase in temperature. In the case of potassium chloride, the viscosity increases with increase in

concentration of the electrolyte for all cosolvent compositions. However, in the case of potassium bromide and iodide the viscosities increase above 20% cosolvent composition.

The viscosity data have been analysed by means of the Jones-Dole² equation

$$\eta_r = \eta/\eta_0 = 1 + AC^{1/2} + BC \quad \dots(1)$$

It is seen that Jones-Dole equation is valid under present experimental conditions (Fig. 1). In the present study, A -values decrease with increase in

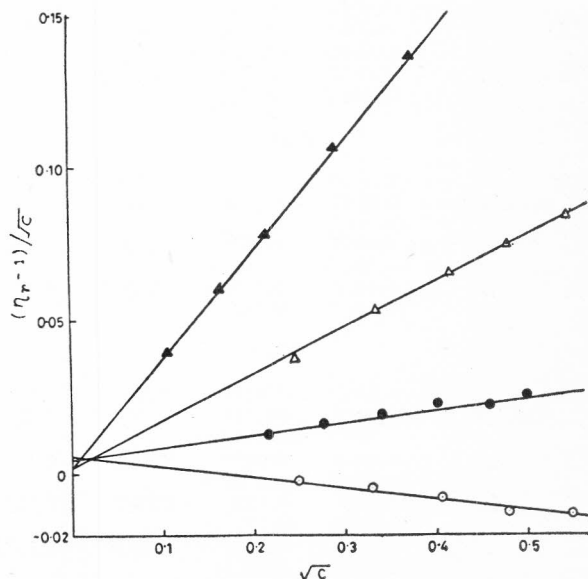


Fig. 1 — Variation of the coefficients A and B of Eq. (1) for KI in 20% (○); 40% (●); 60% (Δ) and 80% (▲) pyridine solutions at 35°C.

concentration of the cosolvent, indicating decrease in ion-ion interaction (Table 1). It is known that potassium and halide ions behave as structure-breakers in aqueous solution³. The B -values in the present case for all the three halides rapidly increase with increase in concentration of the cosolvent (Table 1). It is interesting to note that KI gives the steepest curve, in a plot of B versus pyridine concentration, followed by KBr and KCl.

In order to evaluate the different factors contributing to B -values, we have examined the effect of addition of pyridine and γ -picoline to water from the viscosity data of the binary mixture. The viscosity of the mixed solvent increases to a maximum with increase in cosolvent percentage and then decreases. The viscosity of such binary mixtures can be interpreted with the help of Grunberg and Nissan⁴ equation

$$\ln \eta_{\text{mix}} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d' \quad \dots(2)$$

where η_{mix} is the viscosity of the mixture, η_1 is the viscosity of the liquid one, η_2 of the second liquid, and x_1 and x_2 are the mole fractions of the components of the mixture, d' is proportional to w/RT (w is the interchange energy). According to Guggenheim⁵ d' is a measure of the strength of interaction between the components in solution. The data for d' along with excess viscosity

$$\eta_{\text{ex}} = \eta_{\text{mix}} - (x_1 \eta_1 + x_2 \eta_2) \dots \dots \dots (3)$$

are given in Table 2. It is seen from Table 2 that d' is positive and η_{ex} is also positive and large. The presence of pyridine and γ -picoline therefore leads to the formation of solvent complexes. Such complexes may have only weaker interactions with solute ions.

Therefore, a decrease in η^D value due to change in the water-structure by the cosolvent cannot be ruled out (η^D is the negative contribution to viscosity due to structure-breaking by solute ions of highly structured liquids). η^D also might decrease due to decrease in ionic field effect resulting from the shielding effect of the large cosolvent or the larger solvent complex.

Increase in B -coefficient might be partly due to increase in η^E also (η^E is the contribution to viscosity due to Einstein effect). With increase in the percentage of cosolvent, the water-structure is gradually broken down releasing free water molecules which are more easily oriented by the solute ions. The possibility of solvation of the solute ions by the cosolvent is also likely to add to η^E effect. It has been argued⁶ that larger size of solvent molecules would lead to larger η^E values for solvated species and η^A effect would also be greater (η^A is the contribution to viscosity due to orientation of the solvent molecules surrounding the ion). In mixed solvent systems, partial solvation by both the solvents are likely. It is, therefore, interesting to see the effect of the additional $-\text{CH}_3$ group in the case of γ -picoline as a cosolvent. It is known from IR spectroscopic studies⁷ that γ -picoline has a stronger tendency for complex formation with methanol than pyridine. Such tendency might prevail in aqueous solution also. The values of d' and η_{ex} in Table 2 suggest stronger association in aqueous γ -picoline mixed solvent.

The B -value of potassium chloride, which is positive in pure water, increases with increase in pyridine concentration. The increase is steeper at higher cosolvent composition. It is known⁶ that potassium and chloride ions are strongly solvated in pure water giving rise to large η^E and η^A . In the present case the η^E and η^A effects might be stronger due to stronger ion-dipole interactions. The positive dB/dT indicates that KCl is capable of breaking the solvent complex at lower temperature and at higher temperature the solvent complex quickly dissociates. The B -value of KCl in aqueous γ -picoline is larger and supports the above view.

TABLE 1 — VALUES OF COEFFICIENTS A AND B FOR POTASSIUM HALIDES IN AQUEOUS PYRIDINE AND AQUEOUS γ -PICOLINE MIXED SOLVENTS

Solvent	35°C		65°C	
	A	B	A	B
KCl				
Water	0.0055*	0.0098*	0.0060	0.0460
20% pyridine	0.0050 (0.0050)	0.0312 (0.0700)	0.0050	0.0690
40% "	0.0042 (0.0050)	0.0800 (0.1600)	0.0040	0.1380
60% "	0.0032 (0.0030)	0.1430 (0.1775)	0.0030	0.1800
KBr				
Water	0.0050	—0.0260	0.0060	0.0130
20% pyridine	0.0048 (0.0045)	—0.0020 (0.0048)	0.0045	0.0344
40% "	0.0045 (0.0045)	0.0512 (0.1010)	0.0040	0.1090
60% "	0.0028 (0.0045)	0.1298 (0.1410)	0.0035	0.1780
KI				
Water	0.0052*	—0.0485*	0.0060	0.0130
20% pyridine	0.0057 (0.0092)	—0.0248 (—0.0348)	0.0055	0.0202
40% "	0.0044 (0.0065)	0.0400 (0.070)	0.0050	0.1020
60% "	0.0030 (0.0025)	0.1500 (0.1913)	0.0032	0.2020
80% "	0.0025 (0.0020)	0.3540 (0.4125)	0.0028	0.3675

*Values quoted from reference 6.

Values in parentheses are in aq. γ -picoline.

TABLE 2 — VALUES OF THE CONSTANT d' IN EQ. (2) AND η_{ex} IN EQ. (3) FOR AQUEOUS PYRIDINE AND AQUEOUS γ -PICOLINE

[Cosolvent] (%)	Pyridine		γ -Picoline	
	d'	η_{ex}	d'	η_{ex}
20	7.09	0.00333	9.77	0.00420
40	5.53	0.00666	7.40	0.00861
60	4.14	0.00897	5.30	0.01155
80	2.72	0.00721	3.41	0.00964

Also the more steady values at higher concentrations of γ -picoline support stronger shielding effect of γ -picoline.

The B -coefficient of KBr which has a negative value in pure water becomes positive at 40% pyridine concentration. Here also the rise is sharp, but the B -coefficient has always lower value than the corresponding B -value of KCl, indicating less solvation and more effective structure-breaking as evidenced by the larger dB/dT .

The negative B -coefficient of KI in pure water increases slowly in the beginning and then more steeply at higher pyridine concentration. The B -value is suggestive of primary solvation of the ions. The derivative dB/dT is positive in pure water, increases in the intermediate concentration and then decreases. It is known that iodide ion is least solvated in pure water. The increase in B -coefficient here seem to be due to the combined effects of stronger ion-dipole interaction with the cosolvent and shielding effect of the cosolvent reducing the large distance structure-breaking effects. At 80% pyridine concentration where dB/dT is low, structure-breaking is apparently

negligible. It is also interesting to note that the B -values of KI in 20% pyridine and 20% γ -picoline are similar. Their crease in η^A effect is, therefore, compensated here by the stronger structure-breaking of the more stabilized water structure due to hydrophobic exchange effect of the additional CH_3 group in γ -picoline.

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