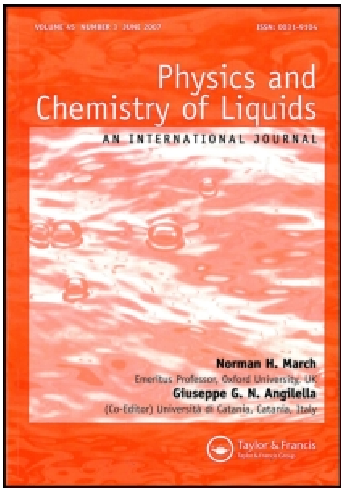

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Thermodynamics of Transfer and Solvent Transport of Silver(I) Sulphate, Bromate and Iodate in Ethanol-Pyridine Mixtures

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THERMODYNAMICS OF TRANSFER AND SOLVENT TRANSPORT OF SILVER(I) SULPHATE, BROMATE AND IODATE IN ETHANOL-PYRIDINE MIXTURES

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The Gibbs energies of transfer and the solvent transport numbers of silver(I) salts viz. silver sulphate, silver bromate and silver iodate have been determined in ethanol-pyridine mixtures over the complete range of compositions at 30°C. The solubility of all the salts passes through a maximum near $X_{py}=0.6$, $X_{py}=0.5$ and $X_{py}=0.6$ for silver sulphate,bromate and iodate respectively and decreases subsequently with further addition of pyridine. The standard Gibbs energies of transfer from ethanol to ethanol-pyridine mixtures were calculated from the thermodynamic solubility products of the salts in these mixtures and found to decrease up to $X_{py}=0.3$, $X_{py}=0.3$ and $X_{py}=0.6$ for silver sulphate, bromate and iodate respectively and then increase with the addition of pyridine. The ionic free energy of transfer of silver ion, determined on the basis of negligible liquid junction potential method, was found to be negative and decreases continuously while that of anions is positive and increases with the addition of pyridine. A large positive value of the solvent transport number,Δ is observed for all the salts in these mixtures. These results indicate that all the silver salts are heteroselectively solvated ie the silver ion is preferentially solvated by pyridine and anions by ethanol in this mixed solvent system.

Keywords: Silver(I) salts; ethanol-pyridine mixtures; solvent transport number

INTRODUCTION

Many physico-chemical properties like solubilities of electrolytes, rates of chemical reactions, redox potentials, phase separation between two

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partially miscible liquids are strongly affected by the sorting of solvent components by ions in binary mixed solvents [1]. Some interesting applications based on these observations, have been reported in electrodeposition, electrorefining [2, 3, 4], and in the choice of suitable solvent-electrolyte combination in high energy density batteries [5,6]. In earlier communications from this laboratory, the preferential solvation of silver (I) and copper (II) salts in several binary mixed solvents consisting of water and other dipolar aprotic solvents such as acetonitrile [7], dimethylsulphoxide (DMSO) [8, 9], dimethylformamide (DMF) [10,11] and pyridine (PY) [12,13] have been reported. These studies have been extended in the present work which deals with the solvation behaviour of some silver (I) salts, in a new mixed solvent system viz. ethanol-pyridine over the complete range of solvent compositions. This solvent system is reported to be pseudo-ideal in nature [14] and hence it is interesting to study the ion-solvation in these mixtures and to compare the results with other related systems such as water-pyridine.

EXPERIMENTAL AND RESULTS

a) Materials

Pyridine (GR,Merck) was purified following the procedure of Vogel [15]. It was initially refluxed over KOH pellets for 8 hours and then distilled with careful exclusion of moisture. The middle fraction boiling at 115°C was collected and stored over KOH. The purified sample had a density, $d^{25} = 0.9789$ g cm^{-3} and viscosity $\eta = 0.8870$ cP at 25°C which are in good agreement with the values reported in literature [16]. Ethanol was purified by distillation over magnesium and iodine following the procedure of Vogel [17]. It had a boiling point $= 78.2$°C, density $d^{25} = 0.7820$ g cm^{-3} and $\eta_{25} = 1.0720$ cP, in good agreement with the literature values [18].

Conductivity water was employed in the preparation of solvent mixtures. Silver sulphate (E.Merck) was dried over P_2O_5 under vacuum before use. Silver bromate and iodate were prepared by the double decomposition of silver nitrate with the respective potassium salts in aqueous solution. The precipitated salts were filtered, washed several times with conductivity water followed by alcohol and dried over P_2O_5 under vacuum at 80°C, to constant weight. The purity of all the salts was checked by the analysis of silver content by potentiometric titration with potassium iodide. Silver perchlorate was prepared according to the procedure described previously [19]. Silver electrodes were prepared by electrolytically depositing silver on platinum spiral electrodes sealed in glass tubes following the procedure of Carmody [20]. Only freshly prepared electrodes whose bias potentials were less than 0.5 mV were used in all EMF measurements. A Keithley soild state electrometer (Model 602) having an input impedance greater than 10^{14} Ω was used in all EMF measurements. All measurements were carried out at 30 ± 0.1°C.

b) Solubility measurements

Saturated solutions of salts were prepared as described previously [21]. The solubilities were determined by estimating the silver content by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, ARL-3410 with minitorch), using suitable calibration curve obtained at 328.07 nm. The results were further checked by potentiometric titration with standard KI. Separate experiments performed with the salts in various compositions of the mixed solvents according to the method of de Ligny *et al.* [22] revealed no solvate formation.

c) Determination of $\Delta G_t^\circ(Ag^+)$

The standard Gibbs transfer energies of silver ion, $\Delta G_t^\circ(Ag^+)$from the reference solvent (ethanol) to the solvent mixtures (ethanol-pyridine) were determined by the negligible liquid junction potential (nLJP) method of Parker *et al.* [23] using the cell A,

$$Ag\left|\begin{array}{c} AgClO_4(0.01m) \\ AN \end{array}\right\|\begin{array}{c} Et_4NPic(0.1m) \\ AN \end{array}\left\|\begin{array}{c} AgClO_4(0.01m) \\ R\ Or\ S \end{array}\right| Ag \cdots \quad (A)$$

where R is the reference solvent and S is the solvent mixture.

d) Determination of solvent transport number, Δ

The solvent transport number, Δ was determined by employing a galvanic cell (B),

$$M\left|\begin{matrix} MX\ (satd.) \\ X'_{py} = 1 - X'_E \end{matrix}\right|\begin{matrix} MX\ (satd.) \\ X''_{py} = 1 - X''_E \end{matrix}\left|M\right. \quad \cdots\cdots\cdots \qquad (B)$$

where MX $= Ag_2SO_4$, $AgBrO_3$, $AgIO_3$ and E = Ethanol as proposed by Wagner [24] in which the two half cells containing saturated solutions of the salts in solvent mixtures differing only slightly in solvent composition (ie $X''_{py} - X''_{py} = 0.1$, maintained throughout). A U-type cell fitted with ground joints at the top and a G_3 frit in the middle was used in these measurements.

The dielectric constant, D of the various solvent mixtures was determined with a DK-meter 60 GK (Franz Kustner Nachf KG, Dresden) at 30°C. The D values are accurate to within ±0.2%.

DISCUSSION

The solubilities s, of Ag_2SO_4, $AgIO_3$ and $AgBrO_3$ are related to their respective thermodynamic solubility products by

$$\left.\begin{matrix} K_{sp}(AgIO_3 \text{ and } AgBrO_3) = s^2\gamma_\pm^2 \\ K_{sp}(Ag_2SO_4) = 4s^3\gamma_\pm^3 \end{matrix}\right| \quad \cdots\cdots\cdots \qquad (1)$$

where $\gamma\pm$ is the mean molal activity coefficient of the electrolyte under consideration and it was calculated from the extended Debye-Hückel equation,

$$-\log\gamma_\pm = \frac{A|z^+z^-|\mu^{1/2}}{1 + a\,B\,\mu^{1/2}} \quad \cdots\cdots\cdots \qquad (2)$$

where A and B are the Debye-Hückel constants, μ is the ionic strength of the solution and 'a' refers to the ion-size parameter with a $= 6.5$Å for silver iodate and silver bromate and a $= 6.0$Å for silver sulphate [25]. In view of the high solubility of silver sulphate and silver bromate in these solutions, an extended activity coefficient expression valid at high concentrations of salt, viz. modified Pitzer's equation [26] given by

$$\ln\gamma_\pm = -\left(\frac{500}{M_1}\right)^{1/2} \cdot A \cdot \left\{\left(\frac{2}{\rho}\right)^{3/2} \cdot \ln\left(1+\frac{\rho}{\sqrt{2}}x_2^{1/2}\right) + (x_2^{1/2}-x_2^{3/2})\Big/\left(1+\frac{\rho}{\sqrt{2}}x_2^{1/2}\right)\right\} \quad \cdots\cdots \tag{3}$$

where X_2 = molefraction of the salt

M_1 = average molecular weight of the solvent mixture
$\rho = (1000/M_1)^{1/2}$. a
A = Debye – Hückel constant
a = ion – size parameter

was used for obtaining $\gamma_\pm$ and these data were utilised to obtain ΔG_t°. No significant difference in ΔG_t° between this method and the earlier method was observed. It is thus seen that the ΔG_t° data of Table II are not affected by the high solubility of silver sulphate and silver bromate in these mixtures.

TABLE I Solubilities(s) and solubility products $(pK_{sp})^{a)}$ of silver(I) sulphate,bromate and iodate in ethanol-pyridine mixtures at 30°C

X_{py}	$D^{b)}$	Ag_2SO_4		$AgBrO_3$		$AgIO_3$	
		$s^{c)}$	pK_{sp}	$s^{c)}$	pK_{sp}	$10^4 s^{c)}$	pK_{sp}
0.0	24.0	$0.0481\text{x}10^{-3}$	12.6	$0.0594\text{x}10^{-3}$	8.50	0.0518	10.60
0.1	23.5	0.237	4.88	0.931	1.38	1.66	7.64
0.2	23.0	0.831	3.78	1.11	1.28	3.28	7.07
0.3	21.8	1.22	3.62	1.46	1.17	4.26	6.87
0.4	19.8	1.28	4.05	1.63	1.25	5.16	6.74
0.5	18.3	1.54	4.29	1.93	1.28	5.48	6.71
0.6	17.7	2.31	4.07	1.83	1.39	5.58	6.70
0.7	16.3	1.74	4.86	1.61	1.65	5.02	6.81
0.8	15.1	1.62	5.47	1.53	1.87	4.48	6.92
0.9	13.3	0.664	7.23	1.43	2.24	3.48	7.16
1.0	12.3	0.0581	9.66	1.34	2.51	2.22	7.53

a) $pK_{sp} = -\log K_{sp}$
b) dielectric constants
c) solubilities in mol kg^{-1}; accuracy, ± 0.2%

TABLE II Gibbs transfer energies ΔG°_t, of silver(I) salts and ions from ethanol to ethanol–pyridine mixtures at 30°C

X_{py}	ΔG°_t						
	Ag_2SO_4	$AgBrO_3$	$AgIO_3$	Ag^+	SO_4^-	BrO_3^-	IO_3^-
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.1	−44.6(−36.1)*	−41.3(−31.5)*	−17.1(−17.1)*	−31.4	18.2	−9.9	14.3
0.2	−50.9	−41.9	−20.4	−42.2	33.5	0.37	21.8
0.3	−51.9(−37.9)	−42.6(−31.5)	−21.6(−21.5)	−43.7	35.6	1.20	22.1
0.4	−49.4	−42.1	−22.3	−46.7	44.1	4.7	24.4
0.5	−48.0(−33.6)	−41.9(−30.5)	−22.5(−22.3)	−50.8	53.6	8.9	28.3
0.6	−49.2	−41.2	−22.5	−53.4	57.6	12.2	30.9
0.7	−44.6(−29.0)	−39.7(−27.7)	−21.9(−21.6)	−54.9	65.2	15.2	33.0
0.8	−41.1	−38.4	−21.2	−56.2	71.3	17.8	35.0
0.9	−30.9(−21.9)	−36.3(−26.7)	−19.9(−19.4)	−57.4	84.0	21.2	37.6
1.0	−18.8(−15.4)	−34.8(−21.9)	−17.7(−17.2)	−58.9	99.0	24.1	41.2

Gibbs transfer energies (kJ mol^{-1}) of the salts are accurate to ±0.2%.

*values in the brackets are those based on calculation of association constant, K_A using Fuoss equation.

Gibbs transfer energies of silver(I)bromate and iodate calculated using modified Pitzer's equation (eqn 3) is given as

X_{py}	0.0	0.1	0.3	0.5	0.7	0.9	1.0
$AgBro_3$	0.0	−39.3	−39.2	−35.9	−32.0	−24.5	−22.4
$AgIO_3$	0.0	−17.2	−21.6	−22.5	−21.9	−19.8	−17.8

The standard Gibbs transfer energies of the salts were calculated from

$$\Delta G^\circ_t(salt) = -RT\ln\frac{K_{sp}(S)}{K_{sp}(R)} \quad \cdots\cdots\cdots \quad (4)$$

(R = ethanol and S = ethanol-pyridine mixture)

The Gibbs transfer energy of the silver(I) ion, $\Delta G^\circ_t(\mathrm{Ag}^+)$ from ethanol (R) to ethanol-pyridine mixtures (S) was calculated from the relation,

$$\Delta G^\circ_t(Ag^+) = F(E_{s(v-c)} - E_R) - RT\ln\frac{a_{Ag}\cdot(S)}{a_{Ag}\cdot(R)} \quad \cdots\cdots\cdots \quad (5)$$

where E_S and E_R refer to the EMF's of the cell (A) in the solvent mixture and reference solvent *ie.* ethanol respectively. The activity of the silver ion (eqn 5) was calculated from the molal concentration of silver ion in the two solutions and the molal activity coefficient of the ion employing equation 2.

The transfer free energy of the anions was calculated from,

$$\Delta G_t^\circ(\mathrm{AgX}) = \Delta G_t^\circ(\mathrm{Ag}^+) + \Delta G_t^\circ(\mathrm{X}^-) \quad \cdots\cdots\cdots \qquad (6)$$

(where $X^- = BrO_3^-$ or IO_3^-) and

$$\Delta G_t^\circ(\mathrm{Ag_2SO_4}) = 2\Delta G_t^\circ(\mathrm{Ag}^+) + \Delta G_t^\circ(\mathrm{SO_4}^{2-}) \cdots\cdots \qquad (7)$$

The solubility (s), solubility product (K_{sp}) of the salts and the dielectric constants (D) of the solvent mixtures at 30°C are given in Table I. The transfer energies of the salts and the ions Ag^+, BrO_3^- and SO_4^{2-} are given in Table II and their variation with solvent composition is shown in Figure 1. The values in the brackets are ΔG_t°'s calculated taking the association constants of the salts (determined by conductance measurements in the case of $AgBrO_3$ and by applying Fuoss equation [27] in the case of Ag_2SO_4 and $AgIO_3$) into consideration. A comparison of experimental ΔG_t° values and those calculated after taking ion association into account shows that on average, the difference is only about 11 kJ mol^{-1} in the case of Ag_2SO_4 and $AgBrO_3$ while it is negligible in the case of $AgIO_3$. It is seen (Tab. I) that the solubility of all the salts passes through a maximum near $X_{py} = 0.6$, $X_{py} = 0.5$ and $X_{py} = 0.6$ for silver sulphate, bromate and iodate respectively and then decreases with further addition of pyridine. However, the transfer energies of the salts (Tab. II and Fig. 1) viz. silver sulphate, silver bromate and silver iodate decrease up to $X_{py} = 0.3$, $X_{py} = 0.3$ and $X_{py} = 0.6$ respectively and then increase with the addition of pyridine. The standard Gibbs energy of transfer of silver ion from ethanol to ethanol-pyridine mixtures is negative and decreases continuously with the addition of pyridine indicating that its transfer from ethanol to ethanol-pyridine mixtures is thermodynamically favoured and thus a preferential solvation of Ag^+ ion by pyridine in these mixtures is inferred. The selective solvation of silver ion by pyridine in these mixtures can be rationalised on the basis of soft-soft interactions as pyridine is a soft solvent (DN = 33.1) which can interact strongly with soft cations such as Ag^+ [28]. The specific silver ion-pyridine interaction may be explained to occur

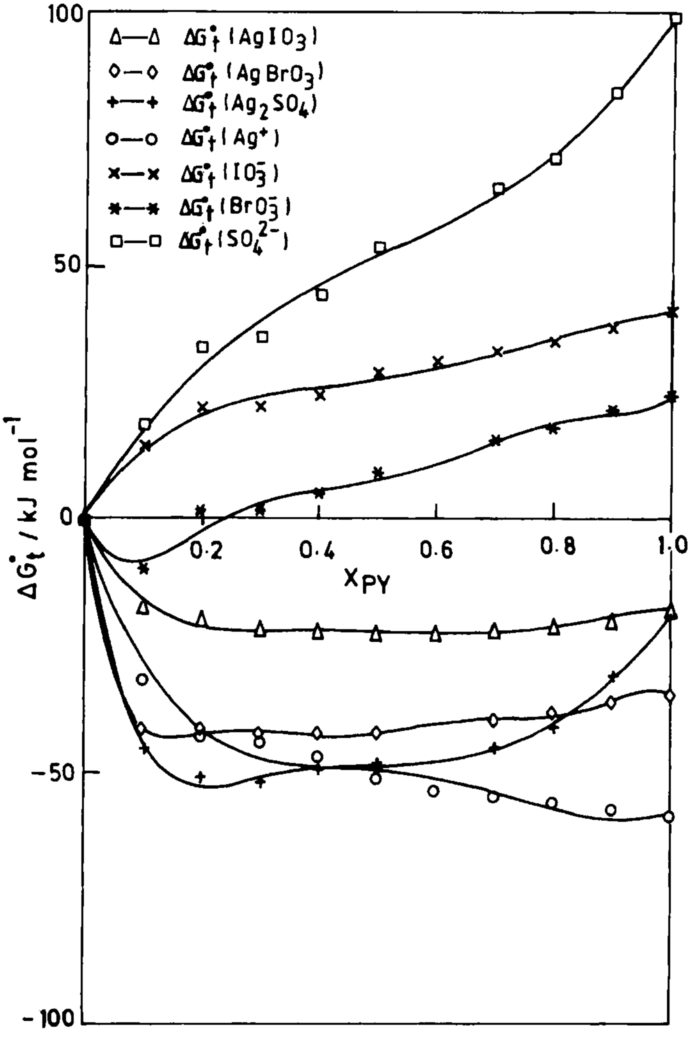

FIGURE 1 Variation of ΔG_t° of $AgIO_3$, $AgBrO_3$, Ag_2SO_4, Ag^+, IO_3^-, BrO_3^- and $SO_4{}^{2-}$ ions (from ethanol to ethanol-pyridine mixtures) with molefraction of pyridine (X_{PY}) at 30°C.

through nitrogen atom of the pyridine molecule which co-ordinates with silver cation. Actually, a complex of silver ion with pyridine of the composition $Ag(C_5H_5N)^+{}_2$, has been reported [16]. The standard Gibbs transfer energies of the anions are positive and increase continuously with the addition of pyridine and this can be explained as arising due to the hard-hard interactions between the anions viz.sulphate, bromate and iodate with ethanol. The interaction of anions with ethanol occurs via. the hydrogen bonding between the hydroxylic H-atom of ethanol and the anions. Thus a selective solvation of the anions by ethanol is observed in these mixtures.

A comparison of the transfer free energy data of the silver cation and the anions with the corresponding results in the related water-pyridine mixtures [29] at a representative molefraction $X_{py} = 0.5$,($\Delta G°_t$ (W– > W + Py)(kJ mol^{-1}) of $Ag^+ = -47.6$, $SO_4^{2-} = 81.7$, $BrO_3 = 27.0$ and $IO_3 = 32.7$) shows that while the differences in $\Delta G°_t(Ag^+)$ between the two systems is quite small, in the case of $SO_4^{2-}$and BrO_3^- ions large differences are noted. These results show that the anion-water interactions are much stronger than anion-ethanol interactions for these two anions. This presumably arises due to the inductive effect of $-C_2H_5$ group in ethanol which increases the electron density on the oxygen atom of –OH group and thereby reduces the positive character of H-atom of the hydroxyl group. As a result the anion-ethanol interactions become weaker as compared to those in water. It is interesting to note that the strong anion-water interactions persist in water-pyridine mixtures despite the fact that the excess free energy and enthalpy of mixing data [30] indicate strong water-pyridine interactions and even formation of water-pyridine complexes of definite composition.

The solvent transport number, Δ of *py* in these mixtures was calculated from the EMF data of the cell (B) using the relation

$$E = -\frac{RT}{F}\frac{X''_{py} - X'_{py}}{X_{py}(1 - X_{py})} \cdot \Delta \cdot \left(1 + \frac{d \ln f_{py}}{d \ln X_{py}}\right) \cdots\cdots\cdots \quad (8)$$

where the various terms have their usual significance [19]. The activity coefficient term in equation (8) accounts for the deviation of the solvent mixtures from ideal behaviour. From the vapour pressure data of ethanol-pyridine mixtures [14], it is reported that the mixtures are pseudo-ideal and thus the activity coefficient term is taken as zero in these mixtures. The solvent transport numbers, Δ calculated from the EMF of the cell (B) for the three salts are given in Table III. The variation of Δ with X_{py} is graphically shown in Figure 2.

TABLE III EMF's of the cell (B) and solvent transport number Δ, of pyridine for silver (I) salts in ethanol-pyridine mixtures at 30°C

X_{py}	Ag_2SO_4		$AgBrO_3$		$AgIO_3$	
	$-E(mV)$	Δ	$-E(mV)$	Δ	$-E(mV)$	Δ
0.15	5.5±1.0	0.27±0.06	5.8±1.0	0.28±0.05	26.0±2.0	1.3±0.15
0.25	9.2±1.0	0.66±0.07	4.4±0.5	0.32±0.03	21.3±1.0	1.5±0.07
0.35	18.3±1.0	1.60±0.04	8.4±0.5	0.73±0.05	21.5±0.5	1.9±0.05
0.45	25.5±0.5	2.43±0.04	16.5±1.0	1.6±0.10	22.3±1.0	2.1±0.09
0.55	25.8±1.0	2.44±0.10	18.5±1.0	1.8±0.10	22.5±1.0	2.4±0.09
0.65	28.0±0.5	2.44±0.04	16.0±0.5	1.4±0.05	18.3±0.5	1.6±0.04
0.75	21.0±0.5	1.5±0.03	12.5±0.5	0.90±0.03	15.5±0.5	1.1±0.04
0.85	17.4±1.0	0.85±0.05	11.0±1.0	0.54±0.05	13.1±0.5	0.64±0.02
0.95	14.8±1.0	0.27±0.02	11.5±0.5	0.21±0.01	20.3±1.0	0.37±0.02

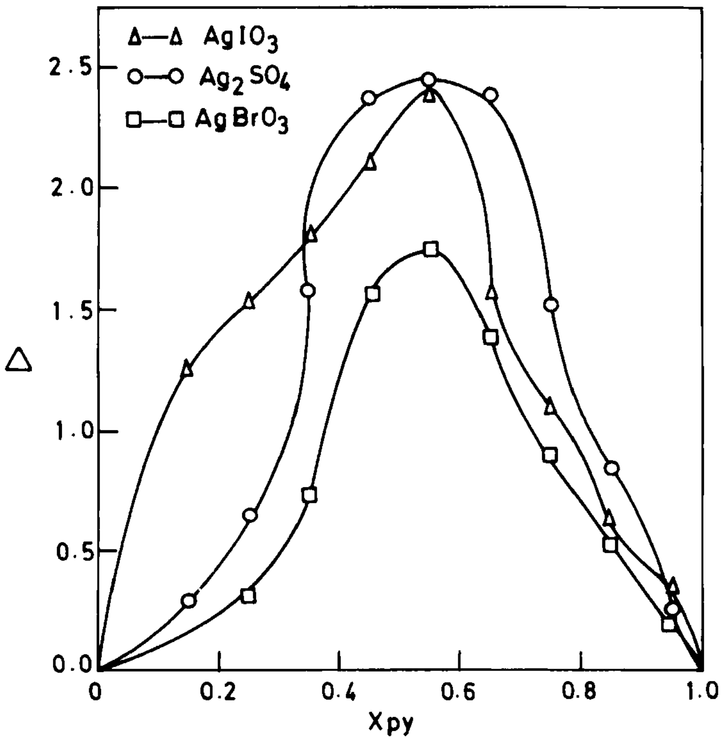

FIGURE 2 Solvent transport number of pyridine, Δ_{py}, for the salts $AgIO_3$, Ag_2SO_4 and $AgBrO_3$ in ethanol-pyridine mixtures at 30°C.

It is observed that Δ values for all the three salts are positive throughout and pass through a maximum viz. $\Delta_{\max} = 2.4$ at $X_{py} = 0.55$ for silver iodate, $\Delta_{\max} = 2.4$ at $X_{py} = 0.55$ for silver sulphate and $\Delta_{\max} = 1.8$ at $X_{py} = 0.55$ for silver bromate. Δ is related (in the case of $AgIO_3$ and $AgBrO_3$) to the molefractions of solvent components and the solvation numbers of the cations and anions according to

$$\Delta_{py} = (x_E\, n^+_{py} - x_{py}\, n^+_E)t_+ - (x_E\, n^-_{py} - x_{py}\, n^-_E)t_- \ldots\ldots \qquad (9)$$

where x_E and x_{py} represent the molefractions of ethanol, pyridine n^+, n^- are the solvation numbers of cation and anion by the inidicated solvent components and t's are the transport numbers of the ions. In the case of Ag_2SO_4, the t_- in the second term of equation (9) has to be divided by 2. For heteroselectively solvated salts $n_{py}{}^+$ and $n_E{}^-$ are large while $n_{py}{}^-$ and $n_E{}^+$ are small resulting in large positive Δ values as observed in this system. Thus there is an increase of 2.4, 2.4 and 1.8 moles of pyridine for silver iodate, silver sulphate and silver bromate respectively per Faraday relative to the mean molar velocity of the respective solvent mixtures as reference [31] in the cathode compartment when solutions of these salts are electrolysed in ethanol-pyridine mixtures at the above stated compositions. The enrichment of pyridine in the cathode compartment arises through the transport of pyridine by the silver ion while the anion transports ethanol in the opposite direction, *ie.* towards anode. As a result of the additive nature of these two effects, Δ is seen to be large for all salts and these observations further support the conclusions that these salts are heteroselectively solvated in these mixtures, with the silver cation being preferentially solvated by pyridine and the anions by ethanol.

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