Ion-Solvent Interactions of Zinc(II) Salts in Water-Pyridine Mixtures*

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The ion-solvent interactions involving zinc(II) salts viz. iodate, fluoride and benzoate in water-pyridine mixtures have been investigated by solubility and solvent transport number measurements. The standard Gibbs transfer energies of the salts (ΔG_t^0), determined from their saturation solubilities in the solvent mixtures, decrease up to $x_{py} = 0.1$ for zinc(II) iodate, but up to $x_{py} = 0.4$ for zinc(II) benzoate, and subsequently increase with the addition of pyridine. For zinc(II) fluoride, however, a continuous increase of ΔG_t^0 with the addition of pyridine is observed. The transfer energy of Zn^{2+} is negative and that of anions is positive with the former decreasing and the latter increasing continuously with the addition of pyridine. The solvent transport number of pyridine (Δ_{py}) is positive and passes through a maximum for all the salts in the range $x_{py} = 0.25$ to 0.55. These results indicate a heteroselective solvation of the salts with Zn^{2+} being preferentially solvated by pyridine and the anions by water.

Introduction

Ion-solvent interactions profoundly influence many chemical phenomena in solutions such as rates of reactions, phase separation processes, solubilities, redox potentials etc. [1]. Studies on ion-solvation are also important from a technological point of view because of their application in electrodeposition [2], metal refining [3], and selection of suitable solvent-electrolyte combinations in high energy density batteries [4]. In particular, the selective solvation in binary mixtures offers interesting possibilities in such applications. In earlier studies from this laboratory we reported the preferential solvation of Ag^+ and Cu^{2+} salts in some binary solvent mixtures involving acetonitrile [5, 6], DMSO [7, 8], DMF [9, 10] and pyridine [11], using solvent transport number, Gibbs energies of transfer and conductance measurements. The present work deals with the solvation behaviour of zinc(II) salts viz. iodate, fluoride and benzoate in water-pyridine mixtures. Although a few results on Gibbs transfer energies of Zn^{2+} in a few mixed solvent systems have been published [12], practically no report is available on the selective solvation of zinc(II) salts in water-pyridine mixtures hitherto.

Experimental

Pyridine (GR, Merck) was purified by the method of Vogel [13]. It was refluxed over KOH pellets and then distilled with the exclusion of moisture. The middle fraction, boiling at 115 °C and 1 atm, was collected and stored over KOH pellets. Zinc(II) iodate was prepared by the metathesis of zinc(II) sulphate and potassium iodate [14]. The anhydrous salt was obtained by heating this sample to 240 °C, and it was stored over $CaCl_2$ under vacuum. Zinc(II) benzoate was prepared by the double decomposition reaction of a solution of sodium benzoate (obtained by exactly neutralising a solution of benzoic acid with NaOH) and zinc(II) sulphate in aqueous solution. The resulting product was recrystallized twice from conductivity water, dried at 110 °C and kept under vacuum. Zinc(II) fluoride was prepared in a similar manner by neutralising aqueous hydrofluoric acid solution with zinc carbonate [15]. The hydrated salt was heated to 120 °C to yield the anhydrous sample, which was stored under vacuum. The purity of all the salts was checked by estimating the zinc content by EDTA titration using eriochrome black-T indicator. The anhydrous nature of all the salts was ensured by thermogravimetric analysis. Amalgamated zinc strips (0.2 cm × 0.5 cm × 6 cm) were used as electrodes in EMF measurements and were prepared following the literature procedure [16]. Freshly prepared electrodes whose bias potentials were less than ±0.1 mV only

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were used in all EMF measurements. A U-type cell, fitted with ground joints at the top and a G_3 frit in the middle to reduce interdiffusion of the electrolyte, was used in these studies. A Keithley solid state electrometer (model 602), having an input impedance greater than $10^{14}\,\Omega$, was used in the EMF measurements. All measurements were carried out at 30 ± 0.1 °C.

Methods

1. *Solubility Measurements*

Saturated solutions of the salts were prepared as described earlier [17]. Solubilities were determined by estimating the zinc content complexometrically by titration with EDTA. All solubility measurements were carried out in duplicate. The reported solubilities are accurate to $\pm 0.2\%$.

2. *Determination of $\Delta G_t^0\,(Zn^{2+})$*

The standard Gibbs transfer energy of zinc(II) ion, $\Delta G_t^0(\mathrm{Zn^{2+}})$ (solvent: water) was evaluated by combining the transfer energy data of $\mathrm{Zn(IO_3)_2}$ with the $\Delta G_t^0(\mathrm{IO_3^-})$ results reported in these mixtures previously [18] on the basis of the negligible liquid junction potential method.

3. *Determination of Solvent Transport Number, Δ_{py}*

The solvent transport number of pyridine, Δ_{py}, for various salts was determined by employing a galvanic cell (A) with transference of the type

$$\begin{array}{c|c|c|c} \mathrm{Zn(Hg)} & \begin{array}{c}\mathrm{ZnX_2\ (statd.)}\\ x'_{py}=1-x'_{w}\end{array} & \begin{array}{c}\mathrm{ZnX_2\ (statd.)}\\ x''_{py}=1-x''_{w}\end{array} & \mathrm{Zn(Hg)}\ldots\mathrm{(A)}, \end{array}$$

where $\mathrm{X=IO_3^-}$, $\mathrm{C_6H_5COO^-}$, $\mathrm{F^-}$, as suggested by Wagner [19], in which the two half cells contain saturated solutions of the salts in solvent mixtures differing by 0.1 mole fraction (i.e. $x''-x'=0.1$ being maintained throughout).

The dielectric constant, D, of the various solvent mixtures was determined [18] with a D_k-meter 60 GK (Franz Kustner Nachf. KG, Dresden) at 30 °C. The D values are accurate to within $\pm 0.2\%$.

Results and Discussions

The solubilities (S) of the sinc salts, viz. $\mathrm{Zn(IO_3)_2}$, $\mathrm{Zn(C_6H_5COO)_2}$ and $\mathrm{ZnF_2}$ are related to their respective thermodynamic solubility products by

$$K_{sp} = 4\,S^3\,\gamma^{\pm 3}, \tag{1}$$

where $\gamma^{\pm}$ is the mean molal activity coefficient of the electrolyte wich has been calculated from the Debye-Hückel expression

$$-\log\gamma^{\pm} = \frac{A\,|Z+Z-|\,\mu^{1/2}}{1+a\,B\,\mu^{1/2}}\,. \tag{2}$$

A and B are Debye-Hückel constants and μ is the ionic strength of the solution. The ion size parameters $a = 10$ Å for $\mathrm{Zn(IO_3)_2}$, $a = 12$ Å for $\mathrm{Zn(C_6H_5COO)_2}$ and $a = 9.5$ Å for $\mathrm{ZnF_2}$ [20] were used in these calculations.

The solubility (s) and solubility product (pK_{sp}) of these salts in water-pyridine mixtures are given in Table 1.

The standard Gibbs energy of transfer, ΔG_t^0, of the salts, from water to water-pyridine mixtures, was calculated from

$$\Delta G_t^0(\mathrm{salt}) = -RT\,\ln\frac{K_{sp}(\mathrm{X})}{K_{sp}(\mathrm{R})}\,, \tag{3}$$

x_{py} [a]	D [b]	$\mathrm{Zn(IO_3)_2}$		$\mathrm{Zn(C_6H_5COO)_2}$		$\mathrm{ZnF_2}$	
		$10^4\,S$ [c]	pK_{sp}	$10^2\,S$ [c]	pK_{sp}	$10^2\,S$ [c]	pK_{sp}
0.0	76.7	51.41	6.537	6.46	3.463	10.14	3.004
0.1	62.7	69.90	6.156	17.28	2.410	7.715	3.490
0.2	50.1	36.88	7.128	50.93	1.303	6.214	3.962
0.3	40.0	23.32	7.719	57.84	1.425	4.959	4.495
0.4	33.0	7.07	9.260	81.65	1.302	4.202	4.969
0.5	28.5	2.54	10.50	88.29	1.479	1.889	6.029
0.6	22.2	1.80	11.04	90.32	2.022	1.637	6.664
0.7	18.2	1.76	11.19	90.66	2.585	0.581	8.155
0.8	15.0	1.58	11.47	90.38	3.266	0.536	8.699
0.9	13.7	1.51	11.60	86.91	3.678	0.406	10.73
1.0	12.3	1.34	11.84	80.89	4.292	0.041	10.89

Table 1. Solubilities, S, and solubility products, pK_{sp}, of zinc(II) iodate, benzoate, and fluoride at 30 °C.

[a] Mole fraction of pyridine.
[b] Dielectric constants.
[c] Solubilities, S, in mol kg^{-1}, accurate to $\pm 0.2\%$.

Table 2. Gibbs transfer energies (kJ mol^{-1}), ΔG_t^0, of $Zn(IO_3)_2$, $Zn(C_6H_5COO)_2$, ZnF_2, Zn^{2+}, IO_3^-, $C_6H_5COO^-$, and F^- from water to water-pyridine mixtures at 30 °C.

x_{py}	$\Delta G_t^0(Zn(IO_3)_2)$	$\Delta G_t^0(Zn(C_6H_5COO)_2)$	$\Delta G_t^0(ZnF_2)$	$\Delta G_t^0(Zn^{2+})$	$\Delta G_t^0(IO_3^-)$	$\Delta G_t^0(C_6H_5COO^-)$	$\Delta G_t^0(F^-)$
0.0	0	0	0	0	0	0	0
0.1	−2.2	−6.1	2.8	−18.6 (−8.8)	8.4 (2.6)	6.5 (2.3)	10.7 (2.8)
0.2	3.4	−12.5	5.6	−24.4	13.9	5.9	15.0
0.3	7.2	−11.8	8.7	−34.4 (−28.7)	20.8 (10.2)	11.3 (8.2)	21.5 (11.4)
0.4	15.8	−12.5	11.4	−38.6	27.2	13.0	25.0
0.5	23.1	−11.5	17.6	−42.4 (−48.7)	32.7 (21.8)	15.4 (16.8)	30.0 (24.6)
0.6	26.1	−8.4	21.3	−49.9	38.0	20.8	35.6
0.7	27.0	−5.1	29.9	−59.0 (−65.6)	43.0 (35.4)	27.0 (27.0)	44.4 (40.2)
0.8	28.6	−1.1	33.0	−66.8	47.7	32.8	49.9
0.9	29.4	+1.3	44.8	−73.2 (−76.4)	51.3 (49.0)	37.2 (37.4)	59.0 (55.7)
1.0	30.8	+4.5	45.8	−79.6	55.2	42.1	62.7

Gibbs transfer energies of the salts are accurate to ±0.1 kJ mol^{-1}. Gibbs transfer energies calculated from QLQC theory, [21], are given in brackets.

where X is the solvent mixture (water-pyridine) and R is the reference solvent (water).

The transfer energy of Zn^{2+} ion, $\Delta G_t^0(Zn^{2+})$, was calculated by combining the transfer free energy data of iodate ion (nLJP method) in water-pyridine mixtures reported earlier [18] with the ΔG_t^0(salt) using the relation

$$\Delta G_t^0(ZnX_2) = \Delta G_t^0(Zn^{2+}) + 2\,\Delta G_t^0(X^-), \qquad (4)$$

where $X^- = IO_3^-$, $C_6H_5COO^-$ and F^-.

The transfer free energy of the other anions was then calculated by using $\Delta G_t^0(Zn^{2+})$ obtained as above. All these results are presented in Table 2. It is seen that the solubility of zinc(II) iodate and zin(II) benzoate increases up to $x_{py} = 0.1$ and $x_{py} = 0.7$, respectively, and then decreases whereas that of zinc(II) fluoride decreases continuously with the addition of Py. Thus the Gibbs transfer energies of these salts (Table 2), viz. zinc(II) iodate and zinc(II) benzoate, decrease up to $x_{py} = 0.1$ and $x_{py} = 0.4$, respectively, and then increase continuously whereas that of zinc(II) fluoride increases with the addition of pyridine.

The Gibbs transfer energy of Zn^{2+}, $\Delta G_t^0(Zn^{2+})$, is negative and decreases with the addition of pyridine, indicating that the transfer of this ion from water to water-pyridine mixtures is thermodynamically favoured. The selective solvation of Zn^{2+} ion by pyridine is thus inferred. The transfer energies of anions are positive and increase continuously with the addition of pyridine, indicating that they are selectively hydrated. Thus, a heteroselective solvation of the salts with Zn^{2+} being preferentially solvated by pyridine and anions by water molecules is observed in these mixtures. The application of the quasi lattice quasi chemical theory of Marcus [21] to the present results also supports the above conclusions, although the calculated ΔG_t^0 at lower compositions ($x_{py} \sim 0.3$) show larger differences from experimental values.

The preferential solvation of anions by water can be explained as arising from the H-bonded interactions between these ions and the H-atoms of water. It is worthwhile to mention that $\Delta G_t^0(F^-)$ is quite high when compared with the other anions. This might be due to the stronger ion-solvent interactions of the fluoride ion, having high charge density on its surface, with water. The preferential solvation of Zn^{2+} by pyridine is attributed to specific interaction of pyridine with Zn^{2+} through Lewis acid-base interactions to form a strong coordinate bond. The solvent transport number, Δ_{py}, of pyridine in these mixtures was calculated from the EMF data of cell (A) using the relation

$$\Delta_{py} = -\frac{F}{RT}\,\frac{x_{py}(1-x_{py})}{(x''_{py}-x'_{py})}\cdot\frac{E}{1+\dfrac{d\ln f_{py}}{d\ln x_{py}}}, \qquad (5)$$

where the various terms have their usual significance [22]. The activity coefficient of the component pyridine, f_{py}, (standard state: water) was evaluated [23] from the vapour pressure data of water-pyridine mixtures, and it accounts for the deviation of the solvent mixtures from ideal behaviour. The EMF of cell (A) and Δ_{py} values of pyridine for all the salts are given in Table 3. It is observed that Δ_{py} for all salts is positive and passes through a maximum with $\Delta_{py} = 4.3$ for zinc(II) benzoate at $x_{py} = 0.55$, $\Delta_{py} = 3.8$ at $x_{py} = 0.25$ for zin(II) fluoride and with $\Delta_{py} = 4.9$ at $x_{py} = 0.35$ for zinc(II) iodate. The low solubility of zin(II) iodate above

Table 3. EMF data and solvent transport numbers, Δ_{py}, of pyridine for zinc(II) salts in water-pyridine mixtures at 30 °C.

x_{py}	$-\frac{d \ln f_{py}}{d \ln X_{py}}$	$Zn(IO_3)_2$		$Zn(C_6H_5COO)_2$		ZnF_2	
		$-E$ (mV)	Δ_{py}	$-E$ (mV)	Δ_{py}	$-E$ (mV)	Δ_{py}
0.15	0.667	4.3 ± 2.0	0.63 ± 0.1	3.2 ± 1.0	0.47 ± 0.1	0.10 ± 0.0	0.02 ± 0.0
0.25	0.637	13.1 ± 2.0	2.6 ± 0.2	5.4 ± 1.0	1.1 ± 0.1	3.4 ± 1.0	0.68 ± 0.1
0.35	0.556	24.8 ± 2.0	4.9 ± 0.1	8.6 ± 2.0	1.7 ± 0.1	4.6 ± 1.0	0.91 ± 0.1
0.45	0.556	7.6 ± 2.0	1.6 ± 0.1	13.5 ± 2.0	2.9 ± 0.1	10.1 ± 2.0	2.2 ± 0.1
0.55	0.444	–	–	25.3 ± 2.0	4.3 ± 0.1	10.5 ± 2.0	2.2 ± 0.1
0.65	0.421	–	–	7.1 ± 1.0	1.1 ± 0.08	6.5 ± 1.0	0.98 ± 0.08
0.75	0.316	–	–	6.3 ± 2.0	0.66 ± 0.1	8.6 ± 2.0	0.91 ± 0.1
0.85	0.250	–	–	5.9 ± 2.0	0.39 ± 0.06	3.5 ± 1.0	0.23 ± 0.08
0.95	0.100	–	–	2.8 ± 1.0	0.06 ± 0.05	–	–

$x_{py} = 0.45$ results in a drift of the EMF of cell (A), and hence it was not possible to calculate Δ_{py} beyond this composition. Thus, there is an enrichment of 4.3, 3.8, and 4.9 moles of pyridine, respectively, per Faraday, relative to the mean molar velocity of the solvent mixture as [24] in the cathode compartment when solutions of these salts, Zn(II) benzoate, fluoride and iodate, are electrolysed in water-pyridine mixtures at the given composition.

Δ_{py} is a composite quantity involving the solvation numbers, n, of the cation and anion by the two solvent components pyridine and water as well as transference numbers, t, of the ions and the mole fractions of the two solvents:

$$\Delta_{py} = (x_w\, n_{py^+} - x_{py}\, n_{w^+}) \frac{t_+}{2} - (x_w\, n_{py^-} - x_{py}\, n_{w^-})\, t_- \,. \tag{6}$$

For heteroselectively solvated salts, n_{py^+} and n_{w^-}, are large while n_{py^-} and n_{w^+} are small resulting in large positive Δ_{py} values as observed in this case. The enrichment of pyridine in the cathode compartment arises through its transport by the zinc ion while the anions transport water in an opposite direction. The large Δ_{py} value, which is characteristic of heteroselective solvation of an electrolyte, is thus a cumulative effect of the above processes.

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