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Ion Solvation of Some Copper(II) Salts in Water + *N*-Methyl-2-pyrrolidinone Solvent Mixtures at 30 °C

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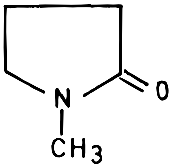
The preferential solvation of copper(II) iodate, benzoate, formate, salicylate, *p*-methylbenzoate, and *p*-nitrobenzoate has been studied in water + *N*-methyl-2-pyrrolidinone mixtures at 30 °C by Gibbs energies of transfer and solvent transport number measurements. The Gibbs transfer energies of the salts were split into their ionic values using the transfer energies of copper ion determined on the basis of the negligible liquid junction potential method. These results were also compared with those obtained on the basis of the tetraphenylarsonium tetraphenylborate method. These results have been interpreted in terms of heteroselective solvation of all the salts with the copper ion being selectively solvated by *N*-methyl-2-pyrrolidinone and anions by water.

Introduction

N-Methyl-2-pyrrolidinone (NMP) which has the structure



is an important dipolar aprotic solvent with a fairly high relative permittivity ($\epsilon = 32.0$ at 25 °C). Its mixtures with water form an important group of binary solvent mixtures among protic + dipolar aprotic solvent mixtures covering a wide range of relative permittivities and basicities because of the high Lewis basicity of NMP. Such solvent mixtures are of considerable fundamental and technological value (Parker 1969, 1981; Salomon, 1987). However, only a few thermodynamic and electrochemical investigations in this mixed solvent system have been reported hitherto. In earlier communications from our laboratory the solvation behavior of some silver(I) salts (Varadarajan et al., 1995a) has been reported in these solvent mixtures by Gibbs transfer energies and solvent transport number measurements. These studies have now been extended to a few unsymmetrical salts, viz., copper(II) iodate, formate, benzoate, etc., to understand the nature of ion−solvent interactions in these mixtures.

Experimental Section

(a) Materials. *N*-Methyl-2-pyrrolidinone (NMP) (SISCO Research Laboratories, Mumbai) was purified as reported earlier (Perrin and Armerago, 1988). The purified sample had a boiling point of 76 °C (at 0.66 kPa) (reported 76 °C at 0.66 kPa) and density $d^{30} = 1.0331$ g cm^{-3} which is in good agreement with literature values $d^{30} = 1.0330$ (Perrin and Armerago, 1988). It had a water content of 85 mg/L from analysis by the Karl Fischer method. Acetonitrile (E. Merck) was purified by following the procedure of Jayadevappa (1969). Copper(II) benzoate was prepared by following the procedure of Lewis et al. (1965) by the addition of a slight excess of a concentrated aqueous solution of copper(II) sulfate to a solution of sodium benzoate whose pH was adjusted to pH = 5.0. The precipitated salt was repeatedly washed with an aqueous acidic solution of pH = 4.0, dried in air, and then dried over anhydrous $CaCl_2$ under vacuum. It was finally dried over P_2O_5 at 110−120 °C in vacuum for over 2 days to yield the anhydrous compound. Anhydrous copper(II) salicylate and copper(II) *p*-methyl- and *p*-nitrobenzoates were prepared in a similar manner. Copper(II) iodate and formate were prepared as reported earlier (Sneed, 1954; Ullmann, 1986). Tetraethylammonium picrate, used as the bridge electrolyte in emf measurements was prepared and purified as described earlier (Sreekumar et al., 1994). Copper(II) perchlorate was prepared as described earlier (Lewandowski, 1986). The purity of the salts was checked by estimating their copper content by spectrophotometry (Hiroshi Onishi, 1986) and was found to be >99%. Deionized water, used for the preparation of water + NMP mixtures, was prepared as described earlier (Glasstone, 1960).

(b) Electrodes. Silver electrodes were prepared according to the method of Carmody (1928). Copper electrodes were prepared by electrolytically depositing copper onto platinum spiral electrodes according to the procedure of Blokhra et al. (1976). The freshly coated electrodes were repeatedly washed with deionized water and preserved in a solution of neutral copper(II) sulfate. Fresh electrodes whose bias potentials were less than ±0.5 mV were used in all emf measurements. A Keithley solid state electrometer (Model 602, Keithley Instruments, Germany) having an input impedance greater than 10^{14} Ω was used in all emf measurements. The emf values were often cross checked with a Philips RMS digital multimeter (PM 2527).

(c) Solubility Measurements. The method of preparation of saturated solutions of the salts in the various solvent mixtures has been described previously (Kalidas and Schneider, 1980), and the solubility was evaluated from estimating the copper content determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, ARL-3410 with mini torch) at a λ_{max} of 324.754 nm. An appropriate volume of clear saturated solution was suitably diluted and analyzed for the copper content. A calibration curve was drawn previously using standard copper(II) sulfate pentahydrate solution in the range of metal ion content from 3 mg/L to 50 mg/L. These results were independently checked by atomic absorption spectrometry

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(Varian spectra, AA 20, air−acetylene flame, $\lambda_{\max} = 218.2$ nm) also using standard copper(II) sulfate solutions for calibration in the range of copper concentration from 20 mg/L to 80 mg/L. The agreement between the two sets of measurements was better than ±0.1%. All measurements were carried out at (30 ± 0.1) °C. Separate experiments were performed with the various salts in solvent mixtures of different compositions according to the method of Deligny et al. (1969) to detect solvate formation. For this purpose, a known amount of dry salt was taken and kept over each solvent mixture for a period of 1 week. An increase of about 0.1% by weight only was observed in all cases, which indicated that no solvates were formed in these studies.

(d) Determination of $\Delta_tG°(Cu^{2+})$. The Gibbs transfer energies $\Delta_tG°(\mathrm{Cu}^{2+})$ from the reference solvent (RS), i.e., water to the solvent mixtures (water + NMP), were determined by employing the negligible liquid junction potential method proposed by Alexander et al. (1972) by employing cell A

$$\begin{array}{c|c||c||c|c} \mathrm{Ag} & \mathrm{AgClO_4}\ \ (0.01\ \mathrm{M}) & \mathrm{Et_4NPic}\ \ (0.1\ \mathrm{M}) & \mathrm{Cu(ClO_4)_2}\ \ (0.01\ \mathrm{M}) & \mathrm{Cu} \\ & \mathrm{AN} & \mathrm{AN} & \mathrm{RS\ or\ S} & \end{array} \qquad \mathrm{(A)}$$

where AN = acetonitrile, $\mathrm{Et_4NPic}$ = tetraethylammonium picrate, RS = reference solvent (water), and S = water + NMP or pure NMP.

(e) Solvent Transport Number Measurements. The solvent transport number, Δ of NMP, for all the salts was determined using a concentration cell (B) with transference as suggested by Wagner (1966)

$$\begin{array}{c|c:c|c} \mathrm{Cu} & \mathrm{CuY_2(satd)} & \mathrm{CuY_2(satd)} & \mathrm{Cu} \\ & x'_{\mathrm{NMP}} = 1 - x'_{\mathrm{H_2O}} & x''_{\mathrm{NMP}} = 1 - x''_{\mathrm{H_2O}} & \end{array} \qquad \mathrm{(B)}$$

where Y = *p*-methyl-, *p*-nitro-, or *o*-hydroxybenzoate, iodate, benzoate, or formate ions and *x* is the mole fraction of the solvent components. The two half-cells contained saturated solutions of the respective copper(II) salts in solvent mixtures differing only slightly in composition ($x''_{\mathrm{NMP}} - x'_{\mathrm{NMP}} = 0.1$) which has been maintained constant throughout.

(f) Relative Permittivity Measurements. The relative permittivities, ϵ, of water + NMP mixtures were determined with a DK meter 60 GK (Franz Kustner Nachf. KG, Dresden) at 30 ± 0.1 °C. The instrument was initially calibrated with pure dioxane ($\epsilon = 2.1$), pyridine ($\epsilon = 12.3$), acetone ($\epsilon = 20.3$), methanol ($\epsilon = 31.5$), DMSO ($\epsilon = 46.8$), and water ($\epsilon = 76.7$) at 30 ± 0.1 °C. Using the relative permittivities of various liquids, a calibration plot of meter reading versus ϵ was made. The ϵ of the various solvent mixtures used in the present work were read from the calibration plot. The values thus determined are found to be precise to within ±0.2%. Solvent mixtures were prepared by weight and are precise to within ±0.1%.

Results and Discussion

The thermodynamic solubility products, K_{sp}, of all the salts were determined from the solubility data using the relation

$$[\mathrm{Cu}^{2+}][\mathrm{anion}^-]^2 = K_{\mathrm{sp}} = 4S^3\gamma_{\pm}{}^3 \tag{1}$$

where *S* is the solubility in mol kg^{-1} and $\gamma_{\pm}$ is the mean molal activity coefficient calculated from the extended Debye−Huckel equation

Table 1. Relative Permittivity (ϵ_r) and Debye−Huckel Constants *A* and *B* for (1 − *x*)Water + (*x*)NMP Mixtures at 30 °C

x	ϵ_r	A^a	$10^{-8}B^b$
0.0	76.3	0.5152	0.3299
0.1	69.2	0.5999	0.3470
0.2	62.5	0.6996	0.3653
0.3	56.4	0.8164	0.3846
0.4	53.4	0.8879	0.3955
0.5	46.1	1.1040	0.4254
0.6	41.9	1.2740	0.4462
0.7	38.5	1.4550	0.4664
0.8	35.4	1.6380	0.4851
0.9	33.2	1.8100	0.5015
1.0	31.5	1.9520	0.5143

[a] $A = 1.825 \times 10^6/(DT)^{3/2}$ mol L$^{1/2}$ (deg K)$^{3/2}$. [b] $B = 50.29 \times 10^8/(DT)^{1/2}$ cm^{-1} mol$^{-1/2}$ L$^{1/2}$ (deg K)$^{1/2}$.

$$-\log \gamma_{\pm} = \frac{AZ_+Z_-I^{1/2}}{1 + aBI^{1/2}} \tag{2}$$

in which *A* and *B* are the Debye−Huckel constants, *I* is the ionic strength, and *a* is the ion size parameter with *a* = 13 Å for copper(II) *p*-methyl- and *p*-nitrobenzoates, *a* = 12 Å for copper(II) salicylate and benzoate, *a* = 10.5 Å for copper(II) iodate, and *a* = 9 Å for copper(II) formate (Kielland, 1937). The values of *A* and *B* and the relative permittivities of the solvent mixtures, ϵ, at various compositions are given in Table 1.

The standard Gibbs transfer energies of the salts were calculated from

$$\Delta_tG°(\mathrm{salt}) = -RT \ln \frac{K_{\mathrm{sp}}\,(S)}{K_{\mathrm{sp}}\,(RS)} \tag{3}$$

The solubilities and solubility products (pK_{sp}) of the salts are given in Table 2, while their Gibbs transfer energies are presented in Table 3.

The emf data of cell A and the standard Gibbs transfer energies of copper(II) ion in various mixtures, calculated from

$$\underset{RS \to S}{\Delta_tG°(\mathrm{Cu}^{2+})} = 2F(E_S - E_{RS}) - RT \ln \frac{a_{\mathrm{Cu}^{2+}}(S)}{a_{\mathrm{Cu}^{2+}}(RS)} \tag{4}$$

are given in Table 4.

The transfer energies of all the anions were computed from the relation

$$\Delta_tG°(\mathrm{CuY_2}) = \Delta_tG°(\mathrm{Cu}^{2+}) + 2\Delta_tG°(\mathrm{Y}^-) \tag{5}$$

where Y = $\mathrm{IO_3}^-$, $\mathrm{C_6H_5COO^-}$, $\mathrm{HCOO^-}$, $\mathrm{C_6H_4(OH)COO^-}$, $\mathrm{C_6H_4(CH_3)COO^-}$, $\mathrm{C_6H_4(NO_2)COO^-}$, and these data are summarized in Table 5. The data given in parentheses are those based on the reference electrolyte method determined by us earlier (Varadarajan et al., 1995b). A comparison of $\Delta_tG°$ values based on the two methods shows that the agreement between the two sets of values is satisfactory in the mixed solvent system with the maximum difference in $\Delta_tG°$ being about 10 kJ mol^{-1}.

The transfer energy of Cu^{2+} [$\Delta_tG°(\mathrm{Cu}^{2+})$] is negative throughout (Table 5) and decreases continuously with the addition of NMP. Thus its transfer from water to water + NMP and to pure NMP is thermodynamically favored and it may be inferred that Cu^{2+} is preferentially solvated by NMP in these mixtures. This may be explained on the basis of the differences in the softness between the two

Table 2. Solubilities s and Solubility Products pK_{sp} of Copper(II) Iodate, Benzoate, Formate, Salicylate, p-Methylbenzoate, and p-Nitrobenzoate in $(1 - x)$Water + (x)NMP Mixtures at 30 °C

	copper iodate		copper benzoate		copper formate		copper salicylate		copper p-methylbenzoate		copper p-nitrobenzoate	
x	10^3s^a	pK_{sp}	10^2s^a	pK_{sp}	s^a	pK_{sp}	10^3s^a	pK_{sp}	10^2s^a	pK_{sp}	10^4s^a	pK_{sp}
0.0	3.37	7.04	1.11	5.60	0.3600	1.46	0.53	9.34	0.71	6.13	7.62	8.87
0.1	3.01	7.17	0.80	6.00	0.2200	2.15	0.57	9.26	1.20	5.53	4.92	9.94
0.2					0.1600	2.62	0.68	9.05	1.37	5.42	1.31	11.10
0.3	1.71	7.90	0.74	6.20	0.0541	4.01	0.86	8.80	1.52	5.36	0.98	11.50
0.4					0.0522	4.14	1.68	8.85	1.75	5.26	0.56	12.20
0.5	0.85	8.70	2.81	4.70	0.0262	5.01	1.87	8.22	1.91	5.24	1.47	11.00
0.6					0.0114	6.02	2.23	7.79	2.77	4.90	2.23	10.50
0.7	0.59	9.30	6.53	3.70	0.0098	6.27	2.32	7.70	7.19	3.89	2.36	10.50
0.8					0.0065	6.79	3.24	7.48	10.90	3.51	3.72	9.96
0.9	0.34	9.90	7.02	3.80	0.0112	6.31	3.82	7.36	13.70	3.33	3.74	9.98
1.0	0.30	10.10	6.82	3.90	0.0169	5.97	4.26	7.28	15.20	3.28	3.47	10.10

[a] Solubilities in mol kg^{-1}; average of three sets, standard deviation ±0.5%.

Table 3. Gibbs Transfer Energies ($\Delta_tG°$ ^{a}/kJ mol^{-1}) of Various Copper(II) Salts from Water to $(1 - x)$Water + (x)NMP Mixtures at 30 °C

	x										
salts	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$Cu(IO_3)_2$	0.0	1.5		3.2		4.3		13.2		15.0	18.3
$Cu(C_6H_5COO)_2$	0.0	2.4		3.4		−5.4		−10.9		−10.6	−9.8
$Cu(HCOO)_2$	0.0	4.0	6.7	14.8	15.6	20.6	26.5	27.9	31.0	28.2	26.2
$Cu(C_6H_4(OH)COO)_2$	0.0	−0.5	−1.6	−3.1	−4.6	−6.5	−9.0	−9.9	−10.8	−11.5	−11.8
$Cu(C_6H_4(CH_3)COO)_2$	0.0	−3.5	−4.1	−4.5	−5.1	−5.2	−7.2	−13.0	−15.2	−16.3	−16.5
$Cu(C_6H_4(NO_2)COO)_2$	0.0	3.3	13.0	15.2	19.4	12.5	9.6	9.3	6.3	6.4	7.0

[a] Mean of three values: standard deviation ±0.2 kJ mol^{-1}.

Table 4. EMF Data of Cell A and Standard Gibbs Transfer Energies of the Cu^{2+} Ion from Water to $(1 - x)$Water + (x)NMP Mixtures at 30 °C

x	$-E$/V	$\Delta_tG°$ ^{a}(Cu^{2+})/kJ mol^{-1}
0.0	0.175	0.0
0.1	0.200	−4.3
0.3	0.275	−18.5
0.5	0.305	−24.0
0.7	0.308	−24.2
0.9	0.313	−24.9
1.0	0.320	−26.7

[a] Precision ±0.2 kJ mol^{-1}.

solvents, i.e., the greater polarizability of electron pairs on nitrogen in NMP than that on the oxygen in water. Further, the carbonyl group of NMP is a stronger donor than the water molecule which results in strong interactions between this group and the divalent Cu^{2+} cation. The higher Lewis basicity, the electron pair donor ability of NMP (donor number = 27.3) (Mayrhofer, 1990) compared to water, and the high charge density, coordinating capacity of the Cu^{2+} ion result in specific Cu(II)−NMP interactions and explain the large negative $\Delta_tG°$ values of this ion.

The selective solvation of Cu^{2+} by NMP in these mixtures is consistent with the observation of Gritzner (1977) that NMP, being a relatively softer solvent (compared to water), interacts more strongly with borderline or soft cations like Cu^{2+}. The free energies of transfer of all the anions are positive and increase with the addition of NMP, thus indicating a preferential solvation of anions by water. The anion−water interactions mainly arise through H-bonding between the negative charge of the anions and the hydrogen centers of water molecules and are mainly controlled by the charge density and basicity of anions. A comparison of $\Delta_tG°$ of the unsubstituted benzoate anion with those of substituted benzoate anions shows that the effect of the nitro substituent is much stronger compared to methyl or hydroxy groups. The strong electron-withdrawing tendency of the nitro group reduces the electron density on the carboxyl group and thus makes the $\Delta_tG°$ of the nitro-substituted benzoate more positive compared to the unsubstituted benzoates.

A comparison of $\Delta_tG°$ between Ag^+ ($\Delta_tG°(Ag^+) = -18.4$ kJ mol^{-1}) (Varadarajan et al., 1995a) and Cu^{2+} ($\Delta_tG°(Cu^{2+}) = -26.4$ kJ mol^{-1}) shows that it is more negative in the case of Cu^{2+}, presumably due to the higher charge of Cu^{2+} resulting in more stronger interaction with NMP than Ag^+. An examination of the free energies of transfer of the copper(II) ion and anions from water to DMF, DMSO, NMP, and pyridine (Table 6) shows that as the donor number of solvent increases, the transfer energy of Cu^{2+} (either on nLJP or TATB method) becomes more negative; i.e., the donor strength toward Cu^{2+} increases.

The solvent transport number of NMP (Δ_{NMP}) was evaluated from the emf data of cell B using the relation

$$\Delta_{NMP} = -\frac{FE}{RT}\,\frac{(x_{NMP})(1 - x_{NMP})}{(x''_{NMP} - x'_{NMP})}\,\frac{1}{1 + \dfrac{d\ln f_{NMP}}{d\ln x_{NMP}}} \qquad (6)$$

In eq 6, x''_{NMP} and x'_{NMP} represent the mole fractions of NMP in the two half-cells of cell B, $x_{NMP} = (x''_{NMP} + x'_{NMP})/2$, and f_{NMP} is the rational activity coefficient of NMP referred to pure water as the standard state. E refers to the emf of cell B, F is the Faraday constant, R is the gas constant, and T is the temperature in degrees Kelvin (Rajendran and Kalidas, 1986). In view of the nonavailability of vapor pressure data of water + NMP mixtures, a quantity Δ' defined by

$$\Delta'_{NMP} = \Delta\left(1 + \frac{d\ln f_{NMP}}{d\ln x_{NMP}}\right) \qquad (7)$$

was calculated.

The emf of cell B and the calculated Δ'_{NMP} are given in Table 7. It is observed that Δ'_{NMP} for all the salts is positive and passes through a maximum. The values of

Table 5. Standard Gibbs Transfer Energies ($\Delta_t G^\circ$ [a]/kJ mol^{-1}) of Various Ions from Water to $(1 - x)$Water + (x)NMP Mixtures at 30 °C[b]

ions	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Cu^{2+}	0.0	−4.3 (−7.3)		−18.5 (−8.4)		−24.0 (−15.9)		−24.2 (−22.0)		−24.9 (−22.6)	−26.7 (−38.5)
IO_3^-	0.0	2.9 (4.4)		10.8 (5.8)		14.2 (10.1)		18.7 (17.6)		20.0 (18.8)	22.5 (28.4)
$C_6H_5COO^-$	0.0	3.3 (4.9)		10.9 (5.9)		9.3 (5.3)		6.7 (4.5)		7.1 (6.3)	8.4 (11.0)
$HCOO^-$	0.0	3.8 (5.7)		16.6 (11.6)		22.3 (18.3)		26.1 (24.9)		26.7 (25.4)	26.5 (32.3)
$C_6H_4(OH)COO^-$	0.0	1.9 (3.4)		7.9 (2.6)		8.7 (4.7)		8.4 (6.5)		7.7 (5.5)	8.5 (13.3)
$C_6H_4(CH_3)COO^-$	0.0	0.3 (1.9)		6.7 (5.9)		9.4 (5.1)		5.0 (4.5)		3.8 (3.2)	4.5 (11.0)
$C_6H_4(NO_2)COO^-$	0.0	3.8 (5.3)		14.6 (11.8)		18.3 (14.2)		9.7 (15.6)		9.1 (14.7)	10.5 (22.7)

[a] Average of three sets: standard deviation ±0.2 kJ mol^{-1}. [b] Values in parentheses are those based on TATB values.

Table 6. Comparison of Transfer Free Energies of the Copper(II) Ion and the Anions Iodate, Benzoate, Formate, Salicylate, and *p*-Methyl- and *p*-Nitrobenzoates from Water to Other Solvents

		$\Delta_t G^\circ$/kJ mol^{-1}						
solvent	donor no.	Cu^{2+}	IO_3^-	$C_6H_5COO^-$	$HCOO^-$	$C_6H_4(OH)COO^-$	$C_6H_4(CH_3)COO^-$	$C_6H_4(NO_2)COO^-$
DMF	26.6[e]	−17.9[g] (−23.2)[a]	36.5[g]	7.7[g]				
NMP	27.3[f]	−26.7[h] (−38.5)[b]	28.4[h]	8.4[h]	26.4[h]	8.5[h]	4.5[h]	10.5[h]
DMSO	29.8[e]	−43.4[i] −41.0[c] (−50.2)[d]	24.2[k]	25.2[k]		25.0[l]	25.0[l]	16.2[l]
pyridine	33.1[e]	−73.0 (−50.2)[j]	55.2[k]	34.7[k]			30.9[j]	30.0[j]

[a] Lewandowski and Gritzner, 1993. [b] Varadarajan et al., 1995b. [c] Cox et al., 1974. [d] Chaudry and Persson, 1994. [e] Gutman, 1978. [f] Mayhrofer and Gritzner, 1990. [g] Lewandowski, 1985. [h] Present study. [i] Lewandowski, 1986. [j] Haridas, 1986. [k] Rajendran et al., 1989. [l] Sreekumar and Kalidas, 1994.

Table 7. EMF Data and Solvent Transport Number of NMP (Δ') for Various Copper(II) Salts in $(1 - x)$Water + (x)NMP Mixtures at 30 °C

	copper iodate		copper formate		copper benzoate		copper salicylate		copper *p*-methylbenzoate		copper *p*-nitrobenzoate	
x	$-E$/mV	Δ'	$-E$/mV	Δ'	$-E$/mV	Δ'	$-E$/mV	Δ'	$-E$/mV	Δ'	$-E$/mV	Δ'
0.05	11.5 ± 0.5	0.2 ± 0.03			12.0 ± 1.0	0.2 ± 0.01	6.0 ± 0.5	0.1 ± 0.02	17.0 ± 0.5	0.3 ± 0.05	8.5 ± 0.5	0.2 ± 0.03
0.15	8.7 ± 0.5	0.4 ± 0.04	8.0 ± 1.0	0.4 ± 0.02	28.0 ± 0.5	1.4 ± 0.02	9.2 ± 1.0	0.5 ± 0.03	25.0 ± 0.5	1.2 ± 0.05	8.2 ± 1.0	0.4 ± 0.05
0.25	21.0 ± 1.0	1.5 ± 0.02	15.5 ± 0.5	1.1 ± 0.03	19.0 ± 0.5	1.4 ± 0.05	10.3 ± 1.0	6.7 ± 0.02	28.0 ± 1.0	2.0 ± 0.02	12.6 ± 1.0	0.9 ± 0.05
0.35	28.0 ± 0.5	2.4 ± 0.01	38.5 ± 0.5	3.3 ± 0.03	27.0 ± 0.5	2.4 ± 0.03	12.1 ± 0.5	1.1 ± 0.05	39.5 ± 0.5	3.4 ± 0.04	10.2 ± 0.5	0.9 ± 0.05
0.45	45.0 ± 1.0	4.3 ± 0.01	65.0 ± 1.0	6.2 ± 0.04	11.0 ± 1.0	1.0 ± 0.02	16.0 ± 1.0	1.5 ± 0.02	56.0 ± 1.0	6.3 ± 0.02	9.2 ± 0.5	1.0 ± 0.04
0.55	29.5 ± 1.0	2.7 ± 0.02	85.5 ± 1.0	8.1 ± 0.05	5.0 ± 1.0	0.5 ± 0.03	15.1 ± 0.5	1.4 ± 0.03	40.0 ± 1.0	3.8 ± 0.02	45.2 ± 1.0	4.3 ± 0.02
0.65	21.0 ± 1.0	1.8 ± 0.03	80.0 ± 1.0	5.7 ± 0.02	7.5 ± 1.0	0.6 ± 0.02	15.2 ± 0.5	1.3 ± 0.02	22.5 ± 0.5	1.9 ± 0.03	49.4 ± 1.0	4.0 ± 0.05
0.75	20.0 ± 0.5	1.4 ± 0.02	46.2 ± 0.5	3.3 ± 0.01			10.8 ± 0.5	0.8 ± 0.03	10.5 ± 0.5	0.7 ± 0.04	13.5 ± 0.5	1.0 ± 0.03
0.85	23.0 ± 0.5	1.1 ± 0.03	32.1 ± 1.0	1.6 ± 0.2	12.0 ± 0.5	0.6 ± 0.03	3.0 ± 0.5	0.4 ± 0.02	13.0 ± 1.0	0.6 ± 0.03	23.0 ± 1.0	1.1 ± 0.04
0.95	19.0 ± 1.0	0.3 ± 0.03	30.0 ± 1.0	0.5 ± 0.03	20 ± 0.5	0.4 ± 0.02			8.5 ± 0.5	0.1 ± 0.05	18.0 ± 1.0	0.4 ± 0.04

the maxima are

$$\Delta'_{NMP} = 4.3 \text{ at } x_{NMP} = 0.45 \text{ for copper iodate}$$

$$\Delta'_{NMP} = 8.1 \text{ at } x_{NMP} = 0.55 \text{ for copper formate}$$

$$\Delta'_{NMP} = 2.4 \text{ at } x_{NMP} = 0.35 \text{ for copper benzoate}$$

$$\Delta'_{NMP} = 1.5 \text{ at } x_{NMP} = 0.45 \text{ for copper salicylate}$$

$$\Delta'_{NMP} = 6.3 \text{ at } x_{NMP} = 0.45 \text{ for copper } p\text{-methylbenzoate}$$

$$\Delta'_{NMP} = 4.3 \text{ at } x_{NMP} = 0.65 \text{ for copper } p\text{-nitrobenzoate}$$

These results show that there is an enrichment of 4.3, 8.1, 2.4, 1.5, 6.3, and 4.3 moles of NMP in the cathode compartments when 1 f of charge is passed through the saturated solutions of the salts at the given composition in cell B. The Δ'_{NMP} can also be related to the solvation numbers (n) and transport numbers (t) using the equation

$$\Delta'_{NMP} = (x_W n^{2+}_{NMP} - x_{NMP} n^{2+}_W) t_+/2 - (x_W n^-_{NMP} - x_{NMP} n^-_W) t_- \quad (8)$$

n_W and n_{NMP} in eq 8 represent the solvation numbers of cation and anion by water or NMP, and t's are the transport numbers of the respective ions in the various solvent mixtures. For heteroselectively solvated salts, n^{2+}_{NMP} and n^-_W are large whereas n^-_{NMP} and n^{2+}_W are small which results in large Δ'_{NMP} values, as observed in these mixtures.

The enrichment of NMP in the cathode compartments arises largely through their transport by the copper(II) ion while the anions transport water in the opposite direction, i.e., toward the anode. These two effects are additive, resulting in large positive Δ'_{NMP} values.

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