# Gibbs Energies of Solvation and Solvent Transport of Some Silver(I) Salts in Water + *N*-Methyl-2-pyrrolidinone at 30 °C

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The preferential solvation of the silver salts silver(I) bromate, iodate, sulfate, and oxalate in the binary solvent mixtures of water and *N*-methyl-2-pyrrolidinone has been studied by solubility and solvent transport number measurements. The Gibbs transfer energies of the salts from water to water + *N*-methyl-2-pyrrolidinone mixtures, calculated from solubility data, were split into their ionic values by using the transfer energies of silver ion determined on the basis of the negligible liquid junction potential method. These data have also been compared with those obtained on the basis of the tetraphenylarsonium tetraphenylborate method. Solvent transport numbers ($\Delta'$) of *N*-methyl-2-pyrrolidinone were determined for all the salts by employing a concentration cell with transference as suggested by Wagner. The results have been interpreted in terms of heteroselective solvation of all the salts, with silver ion being selectively solvated by *N*-methyl-2-pyrrolidinone and anions by water.

## Introduction

Studies of ion−solvent interactions in binary solvent mixtures are important from both fundamental (*1, 2*) and technological points of view (*3, 4*). Many physicochemical properties like solubilities of salts, rates of reactions, and phase separation phenomena are strongly influenced by the selective solvation of ions in mixed solvents. Dipolar aprotic solvents like acetonitrile, dimethyl sulfoxide, *N,N*-dimethylformamide, and their aqueous mixtures are particularly important in this context, and a literature survey showed that *N*-methyl-2-pyrrolidinone is an important dipolar aprotic solvent with a fairly high relative permittivity ($\epsilon_r = 32$ at 25 °C) (*5*) having basicity comparable to that of dimethyl sulfoxide (*6*). It has versatile applications (i) as an extracting solvent in the petroleum industry (*7*) and (ii) as a solvent medium for the study of aromatic radical anions and their electron transfer reactions by pulse radiolysis (*8*) and several others (*9*). However, very little work involving this solvent in electrochemical investigations especially ion solvation has been reported (*10*).

The present work, therefore, deals with ion-solvation studies of some silver(I) salts in the binary solvent mixtures of water + *N*-methyl-2-pyrrolidinone over a complete range of solvent compositions by Gibbs transfer energy and solvent transport measurements at 30 °C.

## Experimental Section

*N*-Methyl-2-pyrrolidinone (NMP) (SISCO Research Laboratories, extra pure, >99.5%) was initially dried with molecular sieves for a week and was then distilled under vacuum. The middle fraction boiling at 76 °C under a pressure of 5 mmHg was collected and stored out of contact with air. The distilled sample has a density of $\varrho^{30} = 1.0330$ g/cm$^{-3}$, reported $\varrho^{30} = 1.0330$ g cm$^{-3}$, and refractive index of $\eta_D{}^{30} = 1.4705$, reported $\eta_D{}^{30} = 1.4710$ (*11*). Acetonitrile (E. Merck) was purified following the procedure of Jayadevappa (*12*). Freshly prepared conductivity water was used in all experiments.

Silver(I) sulfate (Analytical Reagent, British Drug House) was dried over $P_2O_5$ under vacuum before use. Silver iodate, silver bromate, silver oxalate, and silver perchlorate were prepared and purified following the procedures reported earlier (*13*). The purity of the salts was checked by estimation of their silver content by potentiometric titration with a standard solution of sodium chloride, and their purity was found to be better than 99.5%. Silver electrodes, required for electromotive force (emf) measurements, were freshly prepared following the procedure of Carmody (*14*). A Keithley solid state electrometer (model 602) having an input impedance greater than $10^{14}$ Ω was used in all emf measurements. The data were cross-checked occasionally by means of a Philips RMS digital multimeter (PM2527). All measurements were carried out at (30 ± 0.1 °C).

## Methods Employed

***1. Solubility Measurements.*** The experimental details of the preparation of saturated solutions have been described earlier (*15*). The solubility of the salts in the various solvent compositions was determined by using inductively coupled plasma atomic emission spectrometry (argon flame, wavelength 328.06 nm). An appropriate volume of clear saturated solution was taken and diluted to the desired volume. The solution was analyzed for silver content (expressed as parts per million) after a calibration curve was prepared with various standard solutions of silver(I) nitrate in a suitable range of compositions. In all cases, solubility measurements were repeated twice independently in each solvent composition. The agreement between duplicate experiments was better than ±0.1%.

***2. Determination of $\Delta G_t{}^\circ(Ag^+)_{RS\to S}$.*** (a) The Gibbs transfer energies of silver ion $\Delta G_t{}^\circ(Ag^+)_{RS\to S}$ where RS is the reference solvent (water) and S is the solvent mixture or pure *N*-methyl-2-pyrrolidinone were determined by emf measurements on the basis of the negligible liquid junction potential method proposed by Alexander et al. (*16*) using cell A.

$$\underset{\text{AN}}{\text{Ag}|\text{AgClO}_4\ (0.01\ m)}\|\underset{\text{AN}}{\text{Et}_4\text{NPic}\ (0.1\ m)}\|\underset{\text{RS or S}}{\text{AgClO}_4\ (0.01\ m)|\text{Ag}} \qquad \text{(A)}$$

$Et_4NPic$ = tetraethylammonium picrate

AN = acetonitrile

(b) The same data were also obtained on the basis of the reference electrolyte method using tetraphenylarsonium

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**Table 1. Solubilities ($s$) and Solubility Products (p$K_{sp}$) of $AgIO_3$, $AgBrO_3$, $Ag_2SO_4$, and $Ag_2C_2O_4$ in Water + *N*-Methyl-2-pyrrolidinone at 30 °C**

| | | silver iodate | | silver bromate | | silver sulfate | | silver oxalate | |
|---|---|---|---|---|---|---|---|---|---|
| $x_{NMP}$ | $\epsilon_r$ | $10^4 s^a$/(mol kg$^{-1}$) | p$K_{sp}$ | $10^3 s^a$/(mol kg$^{-1}$) | p$K_{sp}$ | $10^4 s^a$/(mol kg$^{1}$) | p$K_{sp}$ | $10^3 s^a$/(mol kg$^{1}$) | p$K_{sp}$ |
| 0.0 | 76.3 | 1.170 | 7.87 | 6.910 | 4.4 | 441.000 | 4.1 | 0.573 | 9.24 |
| 0.1 | 69.2 | 0.981 | 8.03 | 3.340 | 5.0 | 48.800 | 6.7 | 0.562 | 9.28 |
| 0.2 | 62.5 | 0.970 | 8.04 | | | | | 0.483 | 9.49 |
| 0.3 | 56.4 | 0.910 | 8.10 | 1.350 | 5.8 | 3.864 | 9.8 | 0.476 | 9.53 |
| 0.4 | 53.4 | 0.818 | 8.19 | | | | | 0.462 | 9.60 |
| 0.5 | 46.1 | 0.784 | 8.23 | 0.831 | 6.2 | 2.983 | 10.2 | 0.450 | 9.66 |
| 0.6 | 41.9 | 0.747 | 8.27 | | | | | 0.423 | 9.76 |
| 0.7 | 38.5 | 0.696 | 8.34 | 0.500 | 6.7 | 2.113 | 10.6 | 0.393 | 9.88 |
| 0.8 | 35.4 | 0.433 | 8.75 | | | | | 0.335 | 10.10 |
| 0.9 | 33.2 | 0.802 | 8.22 | 0.390 | 6.9 | 1.902 | 10.8 | 0.344 | 10.10 |
| 1.0 | 31.5 | 0.911 | 8.12 | 0.420 | 6.8 | 3.232 | 10.2 | 0.503 | 9.69 |

[a] Accurate up to ±0.1%.

tetraphenylborate as the reference salt by following a procedure reported earlier (*17*).

***3. Determination of the Solvent Transport Number.*** A concentration cell with transference of type B as suggested by Wagner (*18*) was employed in which the two half-

$$\mathrm{Ag|AgX(satd)} \;\|\; \mathrm{AgX(satd)|Ag} \qquad \text{(B)}$$
$$X'_{\mathrm{NMP}} = 1 - X'_{\mathrm{H_2O}} \quad X''_{\mathrm{NMP}} = 1 - X''_{\mathrm{H_2O}}$$

NMP = *N*-methyl-2-pyrrolidinone

$$\mathrm{AgX} = \mathrm{AgBrO_3, Ag_2SO_4, AgIO_3, Ag_2C_2O_4}$$

cells contained a saturated solution of silver salts in solvent mixtures differing only slightly in solvent composition ($X''_{\mathrm{NMP}} - X'_{\mathrm{NMP}} = 0.1$) for determining the solvent transport number ($\Delta'$). The emf data on the cell (B) are accurate to within ±1 mV.

The relative permittivities of the solvent mixtures were measured with a DK meter, 60GK (Franz Kustner.Nach-f.KG, Dresden), at 30 °C. They are accurate to within ±0.2%.

## Results and Discussion

The solubility product ($K_{sp}$) of various salts was calculated from the solubility data using the relations

$$K_{sp} = 4s^3\gamma_{\pm}^{\,3} \text{ (for the 1:2 salts } \mathrm{Ag_2SO_4} \text{ and } \mathrm{Ag_2C_2O_4}) \qquad (1)$$

$$K_{sp} = s^2\gamma_{\pm}^{\,2} \text{ (for the 1:1 salts } \mathrm{AgIO_3} \text{ and } \mathrm{AgBrO_3}) \qquad (2)$$

where $s$ is the solubility and $\gamma_{\pm}$ is the mean molal activity coefficient. It was calculated by using the modified Debye–Huckel equation given by

$$-\log \gamma_{\pm} = \frac{AZ_+Z_-\mu^{1/2}}{1 + aB\mu^{1/2}} \qquad (3)$$

where $A$ and $B$ are the Debye–Huckel constants, $Z_-$ and $Z_-$ are the charges on the ions, $\mu$ is the ionic strength of the medium, and $a$ is the ion size parameter. In calculating the mean molal activity coefficients, the ion size parameter $a$ has been taken as 6 Å for silver bromate, 7 Å for silver iodate and silver oxalate, and 6.5 Å for silver sulfate (*19*). The solubility and $K_{sp}$ data are given in Table 1.

**Table 2. EMF Data of Cell A and Standard Gibbs Energies of Transfer of Silver Ion $\Delta G_t°(Ag^+)$ (kJ mol$^{-1}$) from Water to Water + *N*-Methyl-2-pyrrolidinone at 30 °C**

| $x_{NMP}$ | $E$/V | $\Delta G_t°(Ag^+)$ | $x_{NMP}$ | $E$/V | $\Delta G_t°(Ag^+)$ |
|---|---|---|---|---|---|
| 0.0 | 0.195 | 0.0 | 0.7 | 0.030 | −15.9 |
| 0.1 | 0.170 | −2.4 | 0.9 | 0.008 | −17.9 |
| 0.3 | 0.130 | −6.4 | 1.0 | −0.023 | −18.4 |
| 0.5 | 0.079 | −11.2 | | | |

The standard Gibbs transfer energy of the salt from water to water + *N*-methyl-2-pyrrolidinone mixtures was calculated from

$$\Delta G_t°(\text{salt}) = -2.303RT \log \frac{K_{sp}(\text{water + NMP})}{K_{sp}(\text{water})} \qquad (4)$$

The Gibbs transfer energy of the silver ion, $\Delta G_t°(Ag^-)$ from water to water + *N*-methyl-2-pyrrolidinone was calculated on the basis of the negligible liquid junction potential method from the difference in the emfs of cell A in the presence of RS ($E_{RS}$) and S ($E_S$) given by

$$E_S - E_{RS} = E_{Ag^-.Ag}(S) - E_{Ag^-.Ag}(RS) + E_j(AN/S) - E_j(AN/RS) \qquad (5)$$

where $E_{Ag^-.Ag}$ refers to the half-cell potential of the right hand electrode in the presence of S and RS as the case may be and $E_j$'s are the liquid junction potentials at the interface, AN/S and AN/RS. Assuming that the $E_j$'s are negligible according to Alexander et al. (*16*), eq 5 may be written as

$$E_S - E_{RS} = E°_{RS} - E°_S + \frac{RT}{F} \ln \frac{a_{Ag^-}(S)}{a_{Ag^-}(RS)} \qquad (6)$$

which gives

$$\Delta G°_t(Ag^-) = F(E_S - E_{RS}) - RT \ln \frac{a_{Ag^-}(\text{water + NMP})}{a_{Ag^-}(\text{water})} \qquad (7)$$

where $E_{RS}$ and $E_S$ represent the emfs of cell A in water and water + *N*-methyl-2-pyrrolidinone, respectively. The values for $R$ and $T$ were taken as 8.3145 J mol$^{-1}$ K$^{-1}$ and 303.15 K, respectively. The emf data of cell A and the calculated Gibbs transfer energies of the silver ion are given in Table 2.

The transfer energies of the salts are related to their respective ions by

$$\Delta G_t°(AgX) = \Delta G_t°(Ag^+) + \Delta G_t°(X^-) \text{ (for 1:1 salts)} \qquad (8)$$

$$\Delta G_t°(Ag_2X) = 2\Delta G_t°(Ag^-) + \Delta G_t°(X^{2-}) \text{ (for 1:2 salts)} \qquad (9)$$

**Table 3. Gibbs Transfer Energies of Silver(I) Salts from Water to Water + *N*-Methyl-2-pyrrolidinone at 30 °C (Molal Scale)[a]**

| | $\Delta G_t^{\circ b}$/(kJ mol$^{-1}$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $x_{NMP}$ | $AgIO_3$ | $AgBrO_3$ | $Ag_2SO_4$ | $Ag_2C_2O_4$ | $Ag^+$ | $IO_3^-$ | $BrO_3^-$ | $SO_4^{2-}$ | $C_2O_4^{2-}$ |
| 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 0.1 | 0.9 | 3.6 | 15.0 | 0.3 | −2.4 | 3.3 | 6.0 | 19.8 | 5.1 |
| | | | | | (−3.5) | (4.4) | (7.1) | (22.0) | (7.3) |
| 0.2 | 1.0 | | | 1.5 | −4.9 | 5.9 | | | 11.3 |
| 0.3 | 1.3 | 8.1 | 33.1 | 1.7 | −6.4 | 7.7 | 14.5 | 45.9 | 15.5 |
| | | | | | (−4.5) | (5.8) | (12.6) | (42.1) | (10.7) |
| 0.4 | 1.8 | | | 2.1 | −8.4 | 10.2 | | | 18.9 |
| 0.5 | 2.1 | 10.5 | 35.2 | 2.4 | −11.2 | 13.3 | 21.7 | 57.6 | 24.8 |
| | | | | | (−8.0) | (10.1) | (18.5) | (36.2) | (18.4) |
| 0.6 | 2.3 | | | 3.0 | −14.0 | 16.3 | | | 31.0 |
| 0.7 | 2.7 | 13.1 | 37.9 | 3.7 | −15.9 | 18.6 | 29.0 | 69.7 | 35.5 |
| | | | | | (−15.0) | (17.6) | (28.65) | (67.8) | (33.6) |
| 0.8 | 5.1 | | | 5.0 | −16.8 | 21.9 | | | 38.6 |
| 0.9 | 2.0 | 14.4 | 38.9 | 5.0 | −17.9 | 19.3 | 32.3 | 74.7 | 40.8 |
| | | | | | (−16.8) | (18.8) | (31.2) | (72.4) | (38.5) |
| 1.0 | 1.4 | 14.1 | 35.4 | 2.6 | −18.4 | 19.8 | 32.5 | 72.2 | 39.4 |
| | | | | | (−26.9) | (28.4) | (40.9) | (89.2) | (56.4) |

[a] Reference solvent water. Values given in parentheses are based on the TATB method. [b] Accurate to ±0.20 kJ mol$^{-1}$.

**Table 4. Comparison of Free Energies of Transfer (kJ mol$^{-1}$) of Silver(I) Ion and Anions, Viz. Iodate, Bromate, Oxalate, and Sulfate from Water to Other Solvents**

| S no. | solvent | donor no. | $Ag^+$ | $IO_3^-$ | $BrO_3^-$ | $C_2O_4^{2-}$ | $SO_4^{2-}$ |
|---|---|---|---|---|---|---|---|
| 1 | DMSO | 29.8[a] | −44.3[d] | 52.5[d] | 38.6[d] | | 123.4[e] |
| 2 | pyridine | 33.1[a] | −52.8[b] | 55.2[b] | 43.6[b] | 104.1[g] | 132.7[b] |
| 3 | NMP | 27.3[f] | −18.4[c] | 19.8[c] | 32.5[c] | 39.4[c] | 72.2[c] |

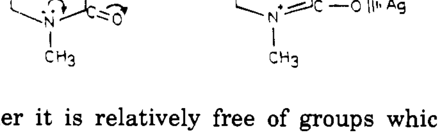
[a] Reference 23. [b] Reference 24. [c] Present study. [d] Reference 25. [e] El-Harakany, A. A.; Schneider, H. *J. Electroanal. Chem.* **1973**, *46*, 255. Data from this reference converted to data from the NLJP method using the conversion factors of Kundu and Parker (*J. Solution Chem.* **1981**, *10*, 847). [f] Reference 9. [g] Haridas, K. R. M.Sc. Dissertation, Indian Institute of Technology, Madras, 1989.

Using the Gibbs free energy of transfer of silver ion in these solvent mixtures determined earlier, the transfer energies of the anions were evaluated.

The transfer energies of the silver ion and the various anions are given in Table 3. The data in parentheses are those based on the tetraphenylarsonium tetraphenylborate method. The agreement between the two sets of values is very satisfactory and justifies the use of the negligible liquid junction potential method as a routine reliable alternative method of evaluation of transfer energies of single ions.

It is seen that the transfer energy of silver ion is negative throughout and decreases continuously with the addition of *N*-methyl-2-pyrrolidinone. Thus, the transfer of silver ion from water to water + *N*-methyl-2-pyrrolidinone is a thermodynamically favorable process. Silver ion possesses $d^{10}$ configuration and is capable of a variety of covalent interactions including back-bonding to suitable ligands (*20*). In addition, because of its smaller size and poorly shielded nucleus ($r_{Ag^-}$ = 1.26 Å), it has strong electrostatic interactions with *N*-methyl-2-pyrrolidinone through the negative end of the carbonyl oxygen of the molecule.

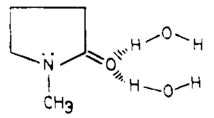
This interaction is aided by the fact that the carbonyl oxygen carries extensive negative charge through resonance structures given by



and further it is relatively free of groups which might interfere with its structuring about silver ion (*26*). Both these interactions result in large negative $\Delta G_t^\circ$ values, and thereby the selective solvation of silver ion by *N*-methyl-2-pyrrolidinone in these mixtures may be inferred.

According to the hard and soft acid and base (HSAB) principle, $Ag^-$ ion is a soft ion, and its interaction with *N*-methyl-2-pyrrolidinone is facilitated because of the softer nature of *N*-methyl-2-pyrrolidinone compared to water (*21*).

Although specific interactions between water and *N*-methyl-2-pyrrolidinone are known to occur leading to the formation of a 2:1 complex of the type (*22*)



these interactions are much weaker in the presence of $Ag^+$ ion.

The transfer energies of all the anions are positive and increase continuously with the addition of *N*-methyl-2-pyrrolidinone, indicating that their transfer from water to water + *N*-methyl-2-pyrrolidinone is not thermodynamically favored. The selective hydration of all the anions may be understood in terms of the hydrogen-bonded interactions between the negative charge of the anions and the positive hydrogen centers in water molecules. These anions may be considered as hard bases, and they will be strongly solvated by hard acid, i.e., water. It may thus be concluded that all silver salts are heteroselectively solvated.

The transfer energy of silver(I) ion and the anions like iodate, bromate, oxalate, and sulfate from water to dimethyl sulfoxide, pyridine, and *N*-methyl-2-pyrrolidinone are presented in Table 4.

It is quite interesting to note, that as the donor number of the solvent (the donor number reflects the behavior of these solvents toward soft cations such as $Ag^-$) increases, the free energy of transfer becomes more negative; i.e., the donor strength toward silver ion increases in the order *N*-methyl-2-pyrrolidinone < dimethyl sulfoxide < pyridine.

**Table 5. Emf's of Cell B and Solvent Transport Number (Δ′) of *N*-Methyl-2-pyrrolidinone for Silver Salts in Water + *N*-Methyl-2-pyrrolidinone at 30 °C**

| | silver iodate | | silver bromate | | silver sulfate | | silver oxalate | |
|---|---|---|---|---|---|---|---|---|
| $x_{NMP}$ | $-E$/mV | Δ′ | $-E$/mV | Δ′ | $-E$/mV | Δ′ | $-E$/mV | Δ′ |
| 0.05 | 16.4 ± 0.5 | 0.3 ± 0.01 | 15.0 ± 1.0 | 0.3 ± 0.01 | 2.5 ± 0.5 | 0.04 ± 0.03 | 11.0 ± 0.5 | 0.4 ± 0.01 |
| 0.15 | 20.5 ± 0.5 | 1.0 ± 0.02 | 12.0 ± 1.0 | 0.6 ± 0.05 | 21.5 ± 1.0 | 1.1 ± 0.05 | 14.0 [illegible] 1.0 | 1.5 ± 0.02 |
| 0.25 | 16.7 ± 0.5 | 1.2 ± 0.02 | 19.5 ± 0.5 | 1.4 ± 0.04 | 6.0 ± 1.0 | 0.4 ± 0.05 | 13.0 ± 1.0 | 2.0 ± 0.04 |
| 0.35 | 28.6 ± 1.0 | 2.5 ± 0.02 | 16.0 ± 0.5 | 1.4 ± 0.03 | 18.5 ± 1.0 | 1.6 ± 0.05 | 16.0 ± 0.5 | 3.0 ± 0.03 |
| 0.45 | 43.2 ± 0.5 | 4.1 ± 0.01 | 15.0 ± 1.0 | 1.4 ± 0.04 | 11.0 ± 0.05 | 1.0 ± 0.04 | 15.5 ± 0.5 | 3.1 ± 0.03 |
| 0.55 | 15.8 ± 1.0 | 1.5 ± 0.05 | 17.0 ± 0.05 | 1.6 ± 0.05 | 10.0 ± 0.5 | 0.9 ± 0.01 | 19.5 ± 0.5 | 3.9 ± 0.05 |
| 0.65 | 16.1 ± 1.0 | 1.4 ± 0.04 | 9.5 ± 0.5 | 0.8 ± 0.01 | 9.5 ± 0.5 | 0.8 ± 0.01 | 28.5 ± 1.0 | 5.3 ± 0.05 |
| 0.75 | 10.4 ± 0.5 | 1.2 ± 0.03 | 10.0 ± 0.5 | 0.7 ± 0.05 | 11.0 ± 0.5 | 0.8 ± 0.01 | 12.0 ± 1.0 | 1.9 ± 0.03 |
| 0.85 | 4.1 ± 1.0 | 0.2 ± 0.03 | 13.0 ± 1.0 | 0.6 ± 0.03 | | | 10.5 ± 0.5 | 1.1 ± 0.03 |
| 0.95 | −21.9 ± 1.0 | −0.4 ± 0.01 | 15.0 ± 1.0 | 0.3 ± 0.01 | 2.0 ± 1.0 | 0.04 ± 0.01 | 6.0 ± 0.5 | 0.2 ± 0.04 |

The reverse is true for anions where water acts as a hard acid toward the anions such as iodate, bromate, oxalate, and sulfate.

## Solvent Transport Number

The solvent transport numbers ($\Delta_{NMP}$) for all the salts were calculated from emf data on cell B using the relation

$$E = -\frac{RT(x''_{NMP} - x'_{NMP})}{Fx_{NMP}(1 - x_{NMP})}\Delta\left\{1 + \frac{(d\ln f_{NMP})}{(d\ln x_{NMP})}\right\} \qquad (10)$$

where all the terms have their usual significance (*18*). Due to the nonavailability of vapor pressure data of water + *N*-methyl-2-pyrrolidinone mixtures, the d ln $f_{NMP}$/d ln $x_{NMP}$ was not evaluated and Δ′ defined by

$$\Delta' = \Delta\left(1 + \frac{d\ln f_{NMP}}{d\ln x_{NMP}}\right) \qquad (11)$$

was calculated.

The emf data of cell B and Δ′ data obtained for various silver salts are given in Table 5. It is observed that Δ′ values for all the salts are positive throughout and pass through a maximum, viz.,

$$\Delta' = 1.6 \text{ at } x_{NMP} = 0.35 \text{ for silver sulfate}$$

$$\Delta' = 1.6 \text{ at } x_{NMP} = 0.55 \text{ for silver bromate}$$

$$\Delta' = 4.1 \text{ at } x_{NMP} = 0.45 \text{ for silver iodate}$$

$$\Delta' = 5.3 \text{ at } x_{NMP} = 0.65 \text{ for silver oxalate}$$

Δ′ may also be expressed as a function of the ionic transport numbers of the salts and the solvation numbers of the cation and anion according to

$$\Delta' = (x_w n_{NMP}^{+} - x_{NMP} n_w^{+})t_+ - (x_w n_{NMP}^{-} - x_{NMP} n^{-}_{w})t_-/2 \text{ (for 1:2 salts)} \qquad (12)$$

$$\Delta' = (x_w n^{+}_{NMP} - x_{NMP} n^{+}_{w})t_+ - (x_w n^{-}_{NMP} - x_{NMP} n^{-}_{w})t_- \text{ (for 1:1 salts)} \qquad (13)$$

where *n*'s are solvation numbers of the ions by respective solvent components, $x_i$'s are the mole fraction of solvent component *i*, and *t*'s are the transport numbers of the ions.

For heteroselectively solvated ions $n^-_{NMP}$ and $n^-_w$ are large while $n^-_w$ and $n^-_{NMP}$ are small which result in large Δ′ values for *N*-methyl-2-pyrrolidinone. The transport of *N*-methyl-2-pyrrolidinone into the cathode compartment arises mainly through silver ions while anions transport water in the opposite direction. Both effects add together, resulting in large positive values of Δ′. The present results thus support the earlier conclusions that all the salts heteroselectively solvated, with silver(I) ion being preferentially solvated by *N*-methyl-2-pyrrolidinone and the anions selectively hydrated in these mixtures.

## Literature Cited

(1) Janardhanan, S.; Kalidas, C. *Rev. Inorg. Chem.* **1984**, *6*, 101.
(2) Schneider, H. In *Solute-solvent Interactions*; Coetzee, J. F., Richie, C. D., Eds.; Marcel-Dekker: New York, 1976.
(3) Parker, A. J. *Pure Appl. Chem.* **1981**, *53*, 1145.
(4) Salomon, M. *J. Power Sources* **1989**, *9*, 26.
(5) Blumenshine, R. L.; Fortune, W. H.; Sears, P. G. *J. Chem. Eng. Data* **1966**, *11*, 406.
(6) Mouton, J. L.; Simcki, C. *J. Electroanal. Chem.* **1973**, *48*, 285.
(7) Gupta, S. K.; Rawat, B. S. *J. Chem. Eng. Data* **1992**, *37*, 139.
(8) Edwards, P. P.; Kadhum, A. A.; Langan, J. K. *J. Radioanal. Nucl. Chem.* **1986**, *101*, 319.
(9) Mayrhofer, W.; Gritzner, G. *J. Chem. Soc., Faraday Trans.* **1990**, *86* (5), 823.
(10) Bates, R. G.; Pawlak, Z. *J. Solution Chem.* **1976**, *5*, 325.
(11) Armarego, W. L. F.; Duperrin, D. *Purification of Laboratory chemicals*, 3rd ed.; Pergamon Press: New York, 1988; p 231.
(12) Jeyadevappa, E. S. *Indian J. Chem.* **1969**, *7*, 1146.
(13) Sreekumar, T. K. Ph.D. Thesis, Indian Institute of Technology, Madras, 1992.
(14) Carmody, W. R. *J. Am. Chem. Soc.* **1928**, *51*, 2901.
(15) Kalidas, C.; Schneider, H. *Z. Phys. Chem. N.F.* **1980**, *120*, 145.
(16) Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. *J. Am. Chem. Soc.* **1972**, *94*, 1148.
(17) Popovych, O. *Crit. Rev. Anal. Chem.* **1970**, *73*, 1.
(18) Wagner, C. In *Advances in Electrochemistry and Electrochemical Engineering*; Delahay, P., Tobias, C. W., Eds.; Wiley-Interscience: New York, 1966; Vol. IV.
(19) Kielland, J. *J. Am. Chem. Soc.* **1963**, *85*, 3533.
(20) Diggle, J. W.; Owensby, D. A.; Parker, A. J. *J. Am. Chem. Soc.* **1974**, *96*, 2682.
(21) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533.
(22) Assarson, P.; Eirich, F. R. *J. Phys. Chem.* **1986**, *72*, 2714.
(23) Gutman, V. *The donor-Acceptor Approach to the molecular interactions*; Plenum: New York, 1978.
(24) Kalidas, C.; Rajendran, G. *J. Chem. Eng. Data* **1986**, *31*, 226.
(25) Janardhanan, S.; Kalidas, C. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2363.
(26) Cox, B. G.; Hedwig, G. R.; Parker, A. J.; Watts, D. W. *Aust. J. Chem.* **1974**, *27*, 477.

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