

Ion-Solvation Behavior of Some Copper(II) Salts in Isodielectric Solvent Mixtures of Methanol and *N*-Methyl-2-pyrrolidinone at 30 °C

T. Kumara Varadarajan, T. Venkatrama Ramakrishna, and Chatty Kalidas*

Department of Chemistry, Indian Institute of Technology, Madras, Chennai 600 036, India

The selective solvation behavior of copper(II) iodate, formate, and benzoate in the isodielectric solvent mixtures of methanol and *N*-methyl-2-pyrrolidinone has been studied using the standard Gibbs transfer energies and solvent transport number measurements. The standard Gibbs transfer energies of various ions were determined on the basis of the tetraphenylarsonium tetraphenylborate (TATB) assumption. The results were interpreted in terms of heteroselective solvation of all the salts with copper(II) ion being selectively solvated by *N*-methyl-2-pyrrolidinone and anions by methanol.

Introduction

Methanol + *N*-methyl-2-pyrrolidinone (NMP) mixtures form an important class of iso-relative permittivity solvent mixtures (relative permittivity, $\epsilon_r = 31.5$ for NMP and $\epsilon_r = 31.0$ for methanol at 30 °C). Such mixtures are valuable for the elucidation of the specific ion–solvent interactions on the thermodynamics of transfer of the various species because of the negligible influence of the effects of relative permittivity of the solvent components on the transfer process.

Apart from the above, NMP is known to solvate cations more strongly, compared to methanol as reflected by its high donor number [donor number = 27.3 (Mayrhofer and Gritzner, 1990), donor number = 19.0 (Fawcett, 1994)]. Also, methanol + NMP mixtures possess strong solvent–solvent interactions and even a hydrogen-bonded complex between the two solvents has been reported by Dupin (1974). It is, therefore, of interest to study the opposing effects of these interactions on the preferential solvation of various ions in these mixtures. In earlier work from this laboratory, the selective solvation of silver(I) salts in methanol + NMP mixtures had been reported (Varadarajan et al, 1997). In continuation of the above studies, the present work studies the solvation behavior of copper(II) iodate, copper(II) formate, and copper(II) benzoate by standard Gibbs transfer energy measurements of the salts and the corresponding ions and the solvent transport numbers for various salts over the complete range of solvent compositions. Since the standard Gibbs transfer energies of the various ions are based on the reference electrolyte method (Kundu and Parker, 1980), the solubility and Gibbs transfer energy data of the reference electrolyte salts required for this purpose are also reported in the paper.

Experimental Section

(a) Materials. *N*-Methyl-2-pyrrolidinone (NMP) (SIS-CO Research Laboratories, extra pure, stated purity >99.5%) was purified following the procedure described earlier (Dyke et al, 1967). The purified sample had a density of $\rho^{30} = 1.0332 \text{ g cm}^{-3}$ measured pycnometrically at (30 ± 0.1 °C) with an accuracy of ± 0.0002 g cm⁻³ and a refractive

index $D_D^{30} = 1.4705$, which are in good agreement with literature values (reported $\rho^{30} = 1.0330 \text{ g cm}^{-3}$ and refractive index = 1.4705) (Perrin and Armerago, 1988). It had a water content of 85 ppm from analysis by the Karl Fisher method. Methanol (LR, E. Merck, India) was purified following the procedure of Vogel (1975). Potassium picrate, tetraphenylarsonium picrate and potassium tetraphenylborate were prepared and purified as described earlier (Popovych and Friedman, 1966). Silver tetraphenylborate was prepared according to the procedure reported earlier (Popovych and Dill, 1969). Copper(II) benzoate was prepared following the procedure of Lewis et al. (1965). Copper(II) formate was prepared by exact neutralization of copper(II) carbonate with formic acid (Ullmann, 1986). Copper(II) iodate was prepared by the double decomposition reaction of copper(II) nitrate and potassium iodate as described previously (Sneed, 1954).

(b) Solubility Measurements. The saturation solubilities of all the salts were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, ARL-3410 with minitorch). While the solubilities of potassium picrate and potassium tetraphenylborate were determined by analyzing for potassium content by ICP-AES at a wavelength of 766.5 nm, the solubility of tetraphenylarsonium picrate was obtained by estimating the arsenic content at a wavelength of 193.7 nm. The solubility of silver tetraphenylborate was determined by estimating the silver content at a $\lambda_{\text{max}} = 328.06 \text{ nm}$. The solubilities of copper(II) iodate, formate, and benzoate were calculated by determining the copper content at a wavelength of 325.54 nm. The method of preparation of saturated solutions has been described in detail earlier (Kalidas and Schneider, 1980). The solutions were analyzed by taking a known volume of clear saturated solution and diluting it suitably in all measurements. The solubility measurements in all cases were repeated thrice independently for each solvent composition. The agreement between them was better than ±0.1%. All the measurements were carried out at (30 ± 0.1 °C).

Results and Discussion

The standard Gibbs transfer energies of the salts, $\Delta_t G^\circ$, from methanol to methanol + NMP mixtures were calculated using

* To whom correspondence to be addressed.

$$\Delta_t G^\circ(\text{salt}) = -2.303RT \log \frac{K_{\text{sp}}(\text{MeOH} + \text{NMP})}{K_{\text{sp}}(\text{MeOH})} \quad (1)$$

The thermodynamic solubility products, K_{sp} , of various salts were calculated using the relation

$$K_{\text{sp}} = s^2 \gamma_{\pm}^2 \quad (2)$$

for the 1:1 reference electrolyte salts and

$$K_{\text{sp}} = 4s^3 \gamma_{\pm}^3 \quad (3)$$

for 2:1 salts, $\text{Cu}(\text{IO}_3)_2$, $\text{Cu}(\text{HCOO})_2$, and $\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2$.

In eqs 2 and 3, s refers to the solubility of the salts in mol kg^{-1} and γ_{\pm} is the mean molal activity coefficient determined by using the extended Debye Hückel equation

$$-\log \gamma_{\pm} = \frac{AZ_+ Z_- I^{1/2}}{1 + \hat{a}BI^{1/2}} \quad (4)$$

where A and B are Debye–Hückel constants, I is the ionic strength of the solution, and \hat{a} is the ion size parameter with $\hat{a} = 6 \text{ \AA}$ for potassium picrate, $\hat{a} = 8 \text{ \AA}$ for tetraphenylarsonium picrate, potassium tetraphenyl borate, $\hat{a} = 7.5 \text{ \AA}$ for silver tetraphenylborate, $\hat{a} = 10.5 \text{ \AA}$ for copper iodate, copper formate and $\hat{a} = 9.5 \text{ \AA}$ for copper benzoate on the basis of Kielland's tabulated ionic size data (Kielland, 1939). The relative permittivities, ϵ_r , the densities d_0 , and the values of A and B of the solvent mixtures at various solvent compositions, x , (mole fraction) are given in Table 1. Since the solubilities of the copper salts are fairly low ($\sim 10^{-3}$) except in the case of copper benzoate at higher compositions of NMP, it is reasonable to assume that γ_{\pm} values calculated from eq 4 will not be significantly affected by small changes in the values of \hat{a} .

The standard Gibbs transfer energy of tetraphenylarsonium tetraphenylborate (TATB) in various compositions of methanol + NMP mixtures was obtained by combining the $\Delta_t G^\circ$ values of KPic, Ph_4AsPic , and KBPh_4 according to the relation

$$\Delta_t G^\circ(\text{Ph}_4\text{AsBPh}_4) = \Delta_t G^\circ(\text{KBPh}_4) + \Delta_t G^\circ(\text{Ph}_4\text{AsPic}) - \Delta_t G^\circ(\text{KPic}) \quad (5)$$

The $\Delta_t G^\circ$ of various ions (on the basis of TATB method) has been calculated by employing the following expressions

$$\Delta_t G^\circ(\text{Ph}_4\text{As}^+) = \Delta_t G^\circ(\text{BPh}_4^-) = 1/2 \Delta_t G^\circ(\text{Ph}_4\text{AsBPh}_4) \quad (6)$$

$$\Delta_t G^\circ(\text{K}^+) = \Delta_t G^\circ(\text{KBPh}_4) - \Delta_t G^\circ(\text{BPh}_4^-) \quad (7)$$

$$\Delta_t G^\circ(\text{Pic}^-) = \Delta_t G^\circ(\text{KPic}) - \Delta_t G^\circ(\text{K}^+) \quad (8)$$

$$\Delta_t G^\circ(\text{Ag}^+) = \Delta_t G^\circ(\text{AgBPh}_4) - \Delta_t G^\circ(\text{BPh}_4^-) \quad (9)$$

It may be emphasized that the evaluation of $\Delta_t G^\circ$ of all the ions from the solubility data of the various salts is based on the extra thermodynamic assumption involving the reference electrolyte method. For this purpose the $\Delta_t G^\circ$ of the reference electrolyte, tetraphenylarsonium tetraphenylborate is split equally between the cation (Ph_4As^+) and anion (BPh_4^-) (eq 6) for reasons discussed previously (Kundu and Parker, 1980).

The standard Gibbs transfer energy of copper(II) ion, $\Delta_t G^\circ(\text{Cu}^{2+})$ (on the basis of the TATB method) was calcu-

Table 1. Relative Permittivity (ϵ_r), Density (d_0), and Debye–Hückel Constants A and B for (1 - x)Methanol + (x)NMP Mixtures at 30 °C

| x | ϵ_r^a | d_0^a | A^b | $10^{-8}B^c$ |
|-----|----------------|---------|--------|--------------|
| 0.0 | 31.0 | 0.7817 | 2.0047 | 0.5189 |
| 0.1 | 33.0 | 0.8613 | 1.8253 | 0.5029 |
| 0.3 | 35.3 | 0.9316 | 1.6498 | 0.4863 |
| 0.5 | 34.5 | 1.0106 | 1.7075 | 0.4919 |
| 0.7 | 32.7 | 1.0188 | 1.8504 | 0.5052 |
| 0.9 | 32.0 | 1.0286 | 1.9114 | 0.5107 |
| 1.0 | 31.5 | 1.0332 | 1.9520 | 0.5156 |

^a Relative permittivity values taken from: Varadarajan, T. K., Ph.D Thesis, Indian Institute of Technology, Madras, 1997. ^b $A = (1.825 \times 10^6)/(DT)^{3/2}$ mol $\text{L}^{1/2}$ (deg K)^{3/2}. ^c $B = (50.29 \times 10^8)/(DT)^{1/2}$ cm^{-1} mol^{-1/2} $\text{L}^{1/2}$ (deg K)^{1/2}.

lated by utilizing the $\Delta_t G^\circ$ of iodate ion determined earlier (Varadarajan et al, 1997) on the same method and combining it with $\Delta_t G^\circ[\text{Cu}(\text{IO}_3)_2]$ according to the equation

$$\Delta_t G^\circ(\text{Cu}^{2+}) = \Delta_t G^\circ[\text{Cu}(\text{IO}_3)_2] - 2\Delta_t G^\circ(\text{IO}_3^-) \quad (10)$$

The standard Gibbs transfer energies of the anions HCOO^- and $\text{C}_6\text{H}_5\text{COO}^-$ were then evaluated using the relation

$$\Delta_t G^\circ(\text{X}^-) = [\Delta_t G^\circ(\text{CuX}_2) - \Delta_t G^\circ(\text{Cu}^{2+})]/2 \quad (11)$$

where $\text{X}^- = \text{HCOO}^-$ and $\text{C}_6\text{H}_5\text{COO}^-$

The solubility data of the reference electrolyte salts, the copper(II) salts, and the corresponding solubility products are given in Table 2.

Variation of Gibbs Transfer Energies of Ions Based on Reference Electrolyte Method

The solubility of all the reference electrolyte salts increases with the addition of NMP except for potassium tetraphenylborate in pure NMP, where a slight decrease is observed beyond $x_{\text{NMP}} = 0.9$. In the case of copper(II) salts, whereas the solubility of copper(II) iodate passes through a maximum at $x_{\text{NMP}} = 0.5$, the solubility of copper(II) formate and benzoate increases with increasing composition of NMP. The standard Gibbs transfer energies of all the salts in various methanol + NMP compositions are given in Table 3, and for the ions the data are given in Table 4.

It is seen (Table 3) that the standard Gibbs transfer energies of Ph_4As^+ and BPh_4^- ions are quite low and positive over the complete range of solvent compositions, which indicates that these ions are preferred neither by NMP nor by methanol. The solvation of these large ions by NMP is inhibited because of the strong methanol + NMP interactions, which overshadow the weak dispersion interactions between these ions and organic cosolvent molecules. The cavity formation effect associated with these large-sized ions, where the central charge is buried deep inside (Das et al, 1981), also considerably affects the $\Delta_t G^\circ$ values.

The $\Delta_t G^\circ$ values of potassium ion are negative throughout and decrease gradually with the addition of NMP up to $x_{\text{NMP}} = 0.5$. Beyond $x_{\text{NMP}} = 0.5$, they tend to remain constant although they are negative. This suggests that potassium ion is preferentially solvated by NMP in these mixtures. The strong ion–dipole type interactions between potassium ion and NMP and the disruption of the structure of methanol around this ion owing to strong methanol + NMP interactions contribute to the stability of the solvated

Table 2. Solubilities s and Solubility Products pK_{sp} of Various Reference Electrolyte Salts and Copper(II) Salts in (1 - x)Methanol + (x)NMP Mixtures at 30 °C

| Reference Electrolyte Salts | | | | | | | | |
|-----------------------------|--------------------------------------|-----------|--------------------------------------|-----------|--------------------------------------|-----------|--------------------------------------|-----------|
| x | potassium picrate | | tetraphenylarsonium picrate | | potassium tetraphenyl borate | | silver tetraphenylborate | |
| | $S^a \times 10^3/\text{mol kg}^{-1}$ | pK_{sp} | $S^a \times 10^3/\text{mol kg}^{-1}$ | pK_{sp} | $S^a \times 10^3/\text{mol kg}^{-1}$ | pK_{sp} | $S^a \times 10^3/\text{mol kg}^{-1}$ | pK_{sp} |
| 0.0 | 0.26 | 7.2 | 0.81 | 8.2 | 2.74 | 5.3 | 0.57 | 14.5 |
| 0.1 | 0.25 | 6.6 | 1.29 | 7.8 | 4.61 | 4.9 | 3.26 | 13.0 |
| 0.3 | 2.96 | 5.2 | 2.74 | 7.2 | 5.33 | 4.7 | 7.85 | 12.2 |
| 0.5 | 7.17 | 4.5 | 3.62 | 6.9 | 6.15 | 4.6 | 13.70 | 11.7 |
| 0.7 | 9.79 | 4.3 | 4.72 | 6.7 | 6.95 | 4.5 | 32.70 | 11.0 |
| 0.9 | 13.10 | 4.1 | 6.72 | 6.4 | 8.75 | 4.4 | 48.70 | 10.6 |
| 1.0 | 16.80 | 3.9 | 8.79 | 6.2 | 7.65 | 4.5 | 93.20 | 10.1 |

| Copper(II) Salts | | | | | | |
|------------------|--------------------------------------|-----------|--------------------------------------|-----------|--------------------------------------|-----------|
| x | copper(II) iodate | | copper(II) formate | | copper(II) benzoate | |
| | $S^a \times 10^3/\text{mol kg}^{-1}$ | pK_{sp} | $S^a \times 10^3/\text{mol kg}^{-1}$ | pK_{sp} | $S^a \times 10^3/\text{mol kg}^{-1}$ | pK_{sp} |
| 0.0 | 0.45 | 9.8 | 0.63 | 7.0 | 8.21 | 6.6 |
| 0.1 | 0.58 | 9.3 | 0.72 | 6.8 | 10.10 | 6.3 |
| 0.3 | 1.03 | 8.8 | 0.89 | 6.5 | 16.10 | 5.7 |
| 0.5 | 2.71 | 7.7 | 1.22 | 6.2 | 26.30 | 5.2 |
| 0.7 | 1.86 | 8.1 | 1.44 | 6.1 | 46.90 | 4.7 |
| 0.9 | 1.70 | 8.3 | 1.58 | 6.0 | 64.70 | 4.3 |
| 1.0 | 0.30 | 10.2 | 1.69 | 6.0 | 71.60 | 4.2 |

^a Mean of three sets; standard deviation $\pm 0.1\%$ **Table 3. Standard Gibbs Transfer Energies of Various Reference Electrolyte Salts, Silver Tetraphenylborate, and Copper(II) Salts (kJ mol^{-1}) from Methanol to (1 - x)Methanol + (x)NMP Mixtures at 30 °C (Molal Scale)**

| x | $\Delta_t G^\circ$ ^a /kJ mol ⁻¹ | | | | | | | |
|-----|---|-----------------------|-------------------|--------------------|------------------------------------|-----------------------------------|-----------------------|--|
| | KPic | Ph ₄ AsPic | KBPh ₄ | AgBPh ₄ | Ph ₄ AsBPh ₄ | Cu(IO ₃) ₂ | Cu(HCOO) ₂ | Cu(C ₆ H ₅ COO) ₂ |
| 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 0.1 | -3.6 | -2.3 | -2.5 | -8.8 | -1.2 | -2.9 | -1.2 | -1.7 |
| 0.3 | -11.6 | -6.0 | -3.2 | -13.2 | 2.4 | -5.8 | -3.0 | -5.1 |
| 0.5 | -15.7 | -7.4 | -3.9 | -16.0 | 4.4 | -11.8 | -4.7 | -8.1 |
| 0.7 | -17.1 | -8.7 | -4.5 | -20.4 | 3.9 | -9.6 | -5.2 | -11.3 |
| 0.9 | -18.3 | -10.4 | -5.5 | -22.4 | 2.4 | -8.1 | -5.5 | -13.2 |
| 1.0 | -19.4 | -11.7 | -4.9 | -25.6 | 2.8 | -2.4 | -6.0 | -13.7 |

^a Values are precise to within ± 0.2 kJ mol⁻¹**Table 4. Gibbs Transfer Energies of Various Ions from Methanol to (1 - x)Methanol + (x)NMP Mixtures at 30 °C (Molal Scale)**

| x | $\Delta_t G^\circ$ ^a /kJ mol ⁻¹ | | | | | | | | |
|-----|---|------------------|---------------------------------|-------------------------------|-----------------|------------------|------------------------------|-------------------|--|
| | K ⁺ | Pic ⁻ | Ph ₄ As ⁺ | BPh ₄ ⁻ | Ag ⁺ | Cu ²⁺ | IO ₃ ⁻ | HCOO ⁻ | C ₆ H ₅ COO ⁻ |
| 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 0.1 | -1.9 | -1.7 | -0.6 | -0.6 | -8.2 | -18.3 | 7.7 | 8.6 | 8.3 |
| 0.3 | -4.4 | -7.2 | 1.2 | 1.2 | -14.4 | -27.8 | 11.0 | 12.4 | 11.3 |
| 0.5 | -6.1 | -9.6 | 2.2 | 2.2 | -18.2 | -25.8 | 7.0 | 10.6 | 8.8 |
| 0.7 | -6.4 | -10.7 | 1.9 | 1.9 | -22.3 | -30.4 | 10.4 | 12.6 | 9.5 |
| 0.9 | -6.7 | -11.6 | 1.2 | 1.2 | -23.6 | -28.3 | 10.1 | 11.4 | 7.5 |
| 1.0 | -6.3 | -13.1 | 1.4 | 1.4 | -27.0 | -30.4 | 14.0 | 12.7 | 8.8 |

^a Values are precise to within ± 0.2 kJ mol⁻¹.

ion. The decrease in $\Delta_t G^\circ$ values with increasing solvent composition is significant only up to $x_{\text{NMP}} = 0.7$, which suggests that the selective solvation of potassium ion by NMP is significant only up to $x_{\text{NMP}} = 0.7$. The small variation of $\Delta_t G^\circ$ beyond $x_{\text{NMP}} = 0.7$ presumably indicates that the primary solvation shell of this ion is fully occupied by NMP molecules and further addition of NMP results in the occupation of secondary solvation shell of this ion by NMP.

The standard Gibbs transfer energies of silver(I) and copper(II) ions (Table 4) are negative and decrease continuously with the addition of NMP. Thus it may be inferred that both silver(I) and copper(II) ions are preferentially solvated by NMP in these mixtures. The preferential solvation of silver ion by NMP in methanol + NMP mixtures is similar to that observed in water + NMP

mixtures and has been discussed in detail earlier (Varadarajan et al, 1995). For copper(II) ion, the $\Delta_t G^\circ$ decreases sharply up to $x_{\text{NMP}} = 0.3$ and thereafter the decrease is relatively small. It is seen (Table 4) that $\Delta_t G^\circ(\text{Cu}^{2+})$ for transfer from pure methanol to NMP is more negative than that of Ag^+ under the same conditions and thus Cu(II)-NMP interactions are stronger than Ag(I)-NMP interactions. This is not only due to higher charge on Cu^{2+} but also due to the presence of incomplete d-orbitals in copper(II) ion which enable the formation of crystal field stabilized complexes with a stabilization energy of $3\Delta/5$ (Hartley et al., 1980). In addition NMP, being more basic than methanol (Dupin, 1974), aids the formation of strong complex with copper ion.

It is observed (Table 4) that the $\Delta_t G^\circ$ of picrate ion decreases (becomes more negative) with increasing com-

Table 5. EMF Data of Cell (A) and Solvent Transport Number of NMP (Δ') for Various Copper(II) Salts in (1 - x)Methanol + (x)NMP Mixtures at 30 °C

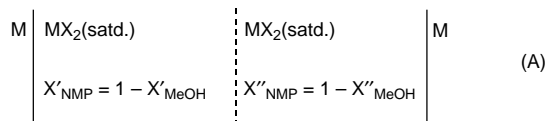
| x | copper iodate | | copper formate | | copper benzoate | |
|------|---------------|------------|----------------|------------|-----------------|------------|
| | -E/mV | Δ' | -E/mV | Δ' | -E/mV | Δ' |
| 0.05 | 18.5 ± 0.5 | 0.3 ± 0.03 | 22.0 ± 0.03 | 0.4 ± 0.03 | 45.0 ± 0.5 | 0.8 ± 0.04 |
| 0.15 | 13.0 ± 0.5 | 0.6 ± 0.05 | 24.5 ± 0.5 | 1.2 ± 0.03 | 27.5 ± 0.5 | 1.3 ± 0.03 |
| 0.25 | 16.5 ± 1.0 | 1.2 ± 0.02 | 25.0 ± 1.0 | 1.8 ± 0.02 | 29.0 ± 0.5 | 2.1 ± 0.03 |
| 0.35 | 22.0 ± 1.0 | 1.9 ± 0.02 | 35.5 ± 0.5 | 3.1 ± 0.02 | 32.5 ± 1.0 | 2.8 ± 0.05 |
| 0.45 | 28.0 ± 1.0 | 2.6 ± 0.03 | 40.0 ± 1.0 | 3.8 ± 0.02 | 38.5 ± 0.5 | 3.6 ± 0.02 |
| 0.55 | 52.0 ± 0.5 | 4.9 ± 0.05 | 50.5 ± 1.0 | 4.8 ± 0.05 | 57.0 ± 1.0 | 5.4 ± 0.02 |
| 0.65 | 43.0 ± 0.5 | 3.7 ± 0.02 | 46.0 ± 1.0 | 4.0 ± 0.05 | 50.5 ± 1.0 | 4.4 ± 0.03 |
| 0.75 | 29.5 ± 0.5 | 2.1 ± 0.02 | 33.5 ± 0.5 | 2.4 ± 0.04 | 41.5 ± 0.5 | 3.0 ± 0.05 |
| 0.85 | 22.0 ± 0.5 | 1.1 ± 0.04 | 35.0 ± 0.5 | 1.7 ± 0.03 | 20.0 ± 1.0 | 1.0 ± 0.05 |
| 0.95 | 20.0 ± 1.0 | 0.4 ± 0.03 | 44.0 ± 0.5 | 0.8 ± 0.03 | 10.5 ± 1.0 | 0.2 ± 0.05 |

position of NMP. This suggests that picrate ion is more stabilized in methanol + NMP mixtures than in methanol.

The standard Gibbs transfer energies of the other anions, viz., iodate, formate, and benzoate are positive and generally increase with the increasing composition of NMP. The slight irregular trend observed in $\Delta_t G^\circ$ of copper(II) ion and the anions in the range $x_{\text{NMP}} = 0.5$ to $x_{\text{NMP}} = 0.9$ is presumably associated with the use of $\Delta_t G^\circ(\text{IO}_3^-)$ data, in the absence of other methods, for the evaluation of $\Delta_t G^\circ$ of these ions. Thus the transfer of these anions from methanol to methanol + NMP mixtures is not thermodynamically favored, and they are preferentially solvated by methanol in these mixtures. This may be explained as arising due to the H-bonded interactions between the oxygen atoms of the anions and the positive hydrogen centers of the methanol molecules.

Solvent Transport Number

The solvent transport number, Δ , for the copper(II) salts was determined by means of a concentration cell with transference in which the two half-cells contain saturated solutions of the copper(II) salts in methanol + NMP mixtures differing slightly in their composition as proposed by Wagner (Wagner, 1966). The cell may be represented as



where M = Cu and $\text{MX}_2 = \text{Cu}(\text{IO}_3)_2$, $\text{Cu}(\text{HCOO})_2$ and $\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2$.

The EMF of the cell is related to the solvent transport number (Δ) according to

$$E = \frac{-RT}{F} \frac{(X'_{\text{NMP}} - X_{\text{NMP}})}{X_{\text{NMP}}(1 - X_{\text{NMP}})} \Delta \left(1 + \frac{d \ln f_{\text{NMP}}}{d \ln X_{\text{NMP}}} \right) \quad (12)$$

where $x_{\text{NMP}} = x'_{\text{NMP}} + x_{\text{NMP}}/2$. The term $d \ln f_{\text{NMP}}/d \ln x_{\text{NMP}}$ accounts for the deviation of the solvent mixture from ideal behavior, and f_{NMP} is the rational activity coefficient of NMP referred to pure methanol as standard state. Owing to the nonavailability of vapor pressure data of methanol + NMP mixtures, Δ'_{NMP} given by

$$\Delta'_{\text{NMP}} = \Delta \left(1 + \frac{d \ln f_{\text{NMP}}}{d \ln x_{\text{NMP}}} \right) \quad (13)$$

was calculated. The emf data of the cell (A) and the Δ' are given in Table 5. The activity coefficient term (eq 13) is

not expected to contribute significantly to Δ' (i.e., about $\pm 0.5\%$) and thus $\Delta' \approx \Delta$.

It is seen (Table 5) that Δ' values for all the copper(II) salts are positive throughout and pass through maxima with $\Delta' = 4.9$ for copper(II) iodate, $\Delta' = 4.8$ for copper(II) formate, and $\Delta' = 5.4$ for copper(II) benzoate, all at $x_{\text{NMP}} = 0.55$. Thus an increase of 4.9, 4.8, and 5.4 mol of NMP per faraday relative to the mean molar velocity of the solvent mixture as reference (Schneider, 1976) is observed in the cathode compartment of a Hittorf cell when solutions of these salts are electrolyzed at the above composition.

Δ' can be expressed in terms of the solvation numbers of cations and anions and the transport numbers according to

$$\Delta' = (x_{\text{MeOH}} n_{\text{NMP}}^{2+} - x_{\text{NMP}} n_{\text{MeOH}}^{2+}) t_+ / 2 - (x_{\text{MeOH}} n_{\text{NMP}}^- - x_{\text{NMP}} n_{\text{MeOH}}^-) t_- \quad (14)$$

where n 's represent the solvation numbers of cation and anion by the respective solvent components and t 's are the transport numbers of the ions. The large positive Δ' values may be explained on the basis that n_{NMP}^{2+} and n_{MeOH}^- are large while n_{NMP}^- and n_{MeOH}^{2+} are small for all the copper(II) salts when they are heteroselectively solvated. The enrichment of NMP into the cathode compartment arises largely through its transport by the copper(II) ion, while the anions transport methanol in the opposite direction. These two effects add together resulting in large Δ' values.

Literature Cited

- Das, K.; Bose, K.; Kundu, K. K. Ion solvent interactions in dimethylformamide-water mixtures *Electrochim. Acta.* **1981**, *26*, 479-485.
- Dupin, M. M. Study of Acid-Base Reactions in methanol-N-Methyl-2-pyrrolidinone Mixtures. *J. Electroanal. Chem.* **1974**, *52*, 75-83.
- Dyke, M. D.; Sears, P. G.; Popov, A. I. Conductances of some uni-univalent electrolytes in N-Methyl-2-pyrrolidinone at 25 °C. *J. Phys. Chem.* **1967**, *71*, 4140-4144.
- Fawcett, W. R. Solvent acidity and basicity in polar media and their role in solvation. Politzner, P., Murray, J. S., Eds.; *Qualitative treatments of solute-solvent interactions. Theoretical and Computational chemistry*; Elsevier Science B. V.: Amsterdam, 1994; Vol. I.
- Hartley, F. R.; Burgess, J.; Allock, R. M. *Solution Equilibria*; Ellis Horwood Ltd.: Chichester, 1980.
- Kalidas, C.; Schneider, H. Solvent transference numbers and solvation energies of silver sulphate in mixtures of methanol and N-Methylformamide. *Z. Phys. Chem., Neue Folge* **1980**, *120*, 145-154.
- Kielland J. Individual activity coefficients of cations in aqueous solutions. *J. Am. Chem. Soc.* **1939**, *59*, 1675-1678.
- Kundu, K. K.; Parker, A. J. Solvation of ions XXVII. Comparison of methods to calculate single ion free energies of transfer in mixed solvents. *J. Solution Chem.* **1980**, *9*, 683-699.
- Lewis, J.; Lin, Y. C.; Royston, L. K.; Thompson, R. C. The chemistry of polynuclear compounds. Part III. Magnetic properties of some

- carboxylic acid derivatives of copper(II). *J. Chem. Soc.* **1965**, 6464–6477.
- Mayrhofer, I. M.; Gritzner, G. Ion solvent interactions in *N*-Methyl-2-pyrrolidinone and *N*-Methyl-thiopyrrolidinone. *J. Chem. Soc., Faraday Trans. 1* **1990**, *86* (5), 823–826.
- Perrin, D. D.; Armerago, W. L. F. *Purification of laboratory chemicals*. 3rd ed.; Pergamon Press: Oxford, 1988; p 231.
- Popovych, O.; Friedman, R. M. Solubilities of potassium, triisoamylbutylammonium and tetrabutylammonium tetrabutyl borides and picrates in water and methanol and their medium effects at 25 °C. *J. Phys. Chem.* **1966**, *70*, 1671–1673.
- Popovych, O.; Dill, A. J. A single scale for ion activities and electrode potentials in ethanol–water solvents based on the triisoamylbutylammonium tetrabutylborate assumption. *Anal. Chem.* **1969**, *41*, 456–462.
- Schneider, H. Ion solvation studied by NMR and electrochemical methods. *Electrochim. Acta* **1976**, *21*, 711–718.
- Sneed, M. C. *Comprehensive organic chemistry*; Van Nostrand: New York, 1954; Vol. II, 102 pp.
- Ullmann's encyclopedia of industrial chemistry*. 4th ed.; VCH Publishers: New York, 1986; Vol A7, p 584.
- Varadarajan, T. K.; Parvathy, R.; Ramakrishna, T. V.; Kalidas, C. Gibbs energies of solvation and solvent transport of some silver(I) salts in water + *N*-Methyl-2-pyrrolidinone solvent mixtures at 30 °C. *J. Chem. Eng. Data* **1995**, *40*, 883–886.
- Varadarajan, T. K.; Ramakrishna, T. V.; Kalidas, C. Preferential solvation of some silver(I) salts in isodielectric mixtures of methanol and *N*-methyl-2-pyrrolidinone at 30 °C. *Ber. Bunsen-Ges. Phys. Chem.* **1997**, *101* (4), 676–680.
- Vogel, A. I. *Practical organic chemistry*, 3rd ed.; Longman: London, 1975.
- Wagner, C. *Advances in electrochemistry and electrochemical engineering*. Delahay, P., Tobias, C. W., Eds. Wiley-Interscience: New York, 1966; Vol. IV, p 1.

Received for review November 5, 1997. Accepted March 5, 1998.

JE970262P