



## Solvation of Ions, Part XXX. Thermodynamics of Transfer of Copper Ions from Water to Solvent Mixtures

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*Free energies and Walden products show that the  $\text{Cu}^+$  and  $\text{Ag}^+$  ions are specifically solvated by acetonitrile (AN), 2-hydroxycyanoethane (HAN), and by pyridine (Py) whereas  $\text{Na}^+$  is specifically solvated by water, in mixtures of these organics with water. The  $\text{Cu}^{2+}$  ion is specifically solvated by pyridine in pyridine-water mixtures, but by water in acetonitrile-water mixtures. Ion-solvent, coordinated solvent-bulk solvent, and solvent-solvent interactions produce large entropy losses in the order  $\text{Cu}^+ \gg \text{Ag}^+ > \text{Na}^+$  for transfer of these ions from water to dilute acetonitrile-water. The metallurgically important oxidations of copper, silver,  $\text{CuS}$  and  $\text{Cu}_2$  with  $\text{CuSO}_4$  in water are strongly favored in an enthalpic and free energy sense by the addition of acetonitrile, but addition of acetonitrile also produces a large loss of entropy for the reactions.*

**KEY WORDS:** Thermodynamic transfer quantities; acetonitrile; pyridine; 2-hydroxycyanoethane; aqueous organic solvent mixtures;  $\text{Cu}^{2+}$ ,  $\text{Cu}^+$ , and  $\text{Ag}^+$  ions; hydrometallurgy.

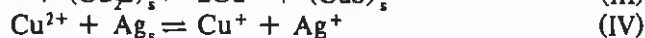
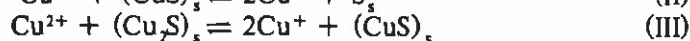
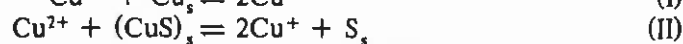
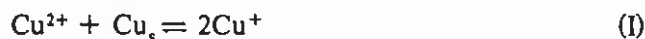
### 1. INTRODUCTION

There been several studies of the thermodynamic transfer properties of ions, electrolytes and non-electrolytes from water to mixtures of water and acetonitrile.<sup>(1-6)</sup> However, the transfer properties of  $\text{Cu}^{+(5,7)}$  have not been studied in detail. They are of special interest because the  $\text{Cu}^+$  ion has a strong interaction of the  $d^{10}$  cations with acetonitrile, because mixtures of  $\text{Cu}^+$  with other ions such as  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$  in acetonitrile-water (AN- $\text{H}_2\text{O}$ ) exhibit hetero-selective solvation<sup>(8,9)</sup> and because solutions of copper (I) salts in AN- $\text{H}_2\text{O}$  may have applications in the extractive metallurgy of copper and silver.<sup>(10)</sup>

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In dilute AN-H<sub>2</sub>O, Na<sup>+</sup> and Cu<sup>2+</sup> have highly aqueous solvation shells and form hydrophilic species like Na(H<sub>2</sub>O)<sub>x</sub><sup>+</sup> and Cu(H<sub>2</sub>O)<sub>y</sub><sup>2+</sup>. In the same solvent, Cu<sup>+</sup> and Ag<sup>+</sup> have AN rich solvation shells and exist as hydrophobic species such as Ag(AN)<sub>2</sub><sup>+</sup> and Cu(AN)<sub>3</sub><sup>+</sup>.<sup>(4,9)</sup> Free energies, enthalpies and entropies of transfer of these four ions will be influenced by changes in ion-solvent interactions and by changes in coordinated solvent-bulk solvent interactions on transfer from water to AN-H<sub>2</sub>O mixtures.<sup>(1,3,11)</sup> It is likely that such changes for the formation of hydrophobic Cu(AN)<sub>3</sub><sup>+</sup> will be very different from those for formation of hydrophilic Cu(H<sub>2</sub>O)<sub>y</sub><sup>2+</sup>, in the same solvent. Examination of these changes is one aspect of this paper.

The temperature dependence of equilibria such as (I) - (IV) in AN-H<sub>2</sub>O mixtures is of interest to hydrometallurgists, because of the prospect of leaching copper and silver from appropriate materials then recovering pure metals by thermal disproportionation of the resulting solutions of Cu<sub>2</sub>SO<sub>4</sub> and Ag<sub>2</sub>SO<sub>4</sub> in AN-H<sub>2</sub>O.<sup>(10)</sup>



This paper reports thermodynamic data for single ions and equilibria in water, in AN-H<sub>2</sub>O mixtures and in some other mixtures where hetero-selective solvation also takes place. All single ion values in this paper are based on the TATB assumption<sup>(12)</sup> that  $X(\text{Ph}_4\text{As}^+) = X(\text{BPh}_4^-)$  where  $X$  is any thermodynamic quantity.<sup>(14)</sup>

## 2. EXPERIMENTAL

Conventional polarographic and potentiometric measurements were made using a PAR170 electrochemical system.<sup>(12)</sup> Calorimetry used an LKB 8700-1 precision calorimeter or a Guild solution calorimeter 400.<sup>(13)</sup> Solvents and chemicals were of AR quality. An especially pure sample of NaBPh<sub>4</sub> was required for reproducible results. It was dissolved in the minimum of dry acetone and toluene was added to slight opalescence. The solution was warmed and a small amount of dry toluene was added. White crystals appeared and were filtered from the hot solution. The crystals were dried under vacuum at 78°C. It was not possible to obtain dry Ph<sub>4</sub>AsCl or Cu(ClO<sub>4</sub>)<sub>2</sub> so they were used as concentrated aqueous solutions and heats of dilution were measured. All heats of solution, precipitation, or dilution were the mean of five

Table I. Free Energies of Transfer of Ions from Water to 5.7 mole% Organic-Water Mixtures at 25°C

| Organic <sup>c</sup> | $\Delta G_{tr}(\text{Na}^+)$ | $\Delta G_{tr}(\text{Ag}^+)$ | $\Delta G_{tr}(\text{Cu}^+)$ | $\Delta G_{tr}(\text{Cu}^{2+})$ |
|----------------------|------------------------------|------------------------------|------------------------------|---------------------------------|
| AN                   | -1.9 <sup>a</sup>            | -10.3 <sup>d</sup>           | -30.8 <sup>a</sup>           | +4.4 <sup>a</sup>               |
| HAN                  | -2 <sup>b</sup>              | -12 <sup>b</sup>             | -36 <sup>b</sup>             | -2 <sup>b</sup>                 |
| Py                   | +3 <sup>b</sup>              | -29 <sup>b</sup>             | -55 <sup>b</sup>             | -37 <sup>b</sup>                |
| DMF                  | -0.5 <sup>a</sup>            | -2 <sup>d</sup>              | -                            | -                               |
| DMSO                 | 0 <sup>a</sup>               | -2.4 <sup>d</sup>            | -                            | -1.8 <sup>a</sup>               |
| Urea                 | 0 <sup>b</sup>               | -1 <sup>b</sup>              | -                            | -                               |
| S-Urea               | 0 <sup>b</sup>               | -79 <sup>b</sup>             | -                            | -                               |
| PC                   | -2 <sup>b</sup>              | -2 <sup>b</sup>              | -                            | -                               |
| MeOH                 | 0 <sup>b</sup>               | -0.5 <sup>b</sup>            | -                            | -                               |

<sup>a</sup>Values of  $\Delta G_{tr}(\text{M}^+) - \Delta G_{tr}(\text{Ag}^+)$  were measured by polarography or potentiometry of the cells  $\text{M}/\text{MClO}_4(0.01\text{M})/0.01\text{M}\text{Et}_4\text{NClO}_4/\text{Et}_4\text{NPic}(0.1\text{M})//\text{sce}$  and  $\text{Ag}/\text{AgClO}_4(0.01\text{M})//\text{sce}$ .  $\Delta G_{tr}(\text{M}^+)$  was calculated using  $\Delta G_{tr}(\text{Ag}^+)$  (TATB) from Ref. 2. Units;  $\text{kJ}\cdot\text{mol}^{-1}$ . <sup>b</sup>Assuming negligible liquid junction potential for highly aqueous mixtures in the cell  $\text{M}/\text{MClO}_4(0.01\text{M})//\text{sce}$  (cf Ref. 2, 4 and 7). These values are expected to be within  $\pm 3 \text{ kJ}\cdot\text{mol}^{-1}$  of those based on the TATB assumption (Ref. 2). <sup>c</sup>Abbreviations are: AN, acetonitrile; HAN 2-hydroxycyanoethane; Py, pyridine; S-urea, thiourea; PC, propylene carbonate. <sup>d</sup>From Ref. 2.

measurements to within  $\pm 0.5 \text{ kJ}\cdot\text{mol}^{-1}$ . Sodium amalgams were prepared by electrolysis of excess NaOH solutions at a mercury electrode to give a  $2 \times 10^{-3}\text{M}$  sodium amalgam under a nitrogen atmosphere.

### 3. RESULTS

#### 3.1. Free Energies of Transfer

$\Delta G_{tr}(\text{Na}^+)$  from water to AN-H<sub>2</sub>O mixtures were obtained from polarographic half-potentials for the reversible reduction of  $\text{Na}^+$  on a dropping mercury electrode, from  $10^{-3}\text{M}$  NaClO<sub>4</sub> in  $0.1\text{M}$  Et<sub>4</sub>NClO<sub>4</sub> by using the relationship,  $\Delta G_{tr}(\text{Na}^+) = -F[(E_{1/2})_{\text{AN-H}_2\text{O}} - (E_{1/2})_{\text{H}_2\text{O}}]$  where  $F$  is the Faraday constant. Potentials were measured against a standard calomel reference electrode (sce) using a  $0.1\text{M}$  Et<sub>4</sub>NPic salt bridge in the solvent mixture. In other solvent mixtures, a sodium amalgam electrode ( $2 \times 10^{-3}\text{M}$ ) was used in the cell,

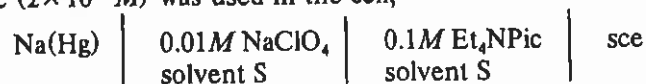


Table II. Free Energies of Transfer of Ions from Water to Aqueous Solvent Mixtures at 25°C<sup>a,c</sup>

| Mole% Organic | $\Delta G_{tr}(\text{Na}^+)$ | $\Delta G_{tr}(\text{Ag}^+)^b$ | $\Delta G_{tr}(\text{Cu}^+)$ | $\Delta G_{tr}(\text{Cu}^{2+})$ |
|---------------|------------------------------|--------------------------------|------------------------------|---------------------------------|
| 5.7 AN        | -1.9 (0.5)                   | -10.3 (-8.4)                   | -30.8 (-33.0)                | 4.4                             |
| 12.7 AN       | -5.0 (1.4)                   | -15.1 (-12.5)                  | -41.7 (-39.7)                | 3.1                             |
| 25.4 AN       | -0.8 (3.3)                   | -17.5 (-15.5)                  | -42.8 (-43.9)                | 7.0                             |
| 65.9 AN       | 5.4 (9.4)                    | -20.5 (-17.2)                  | -50.9 (-47.7)                | 11.4 (12.5)                     |
| 100.0 AN      | 18.0 (16.6)                  | -22.0 (-17.6)                  | -50.0 (-48.1)                | 68.0 (55.2)                     |
| 2.5 DMSO      | -0.3 <sup>d</sup>            | -1.0 <sup>e</sup>              | -                            | -0.5 <sup>e</sup>               |
| 5.4 DMSO      | -0.6 <sup>d</sup>            | -2.4 <sup>e</sup>              | -                            | -1.8 <sup>e</sup>               |
| 13.8 DMSO     | -1.7 <sup>d</sup>            | -6.4 <sup>e</sup>              | -                            | -6.2 <sup>e</sup>               |
| 25.7 DMSO     | -3.9 <sup>d</sup>            | -13.2 <sup>e</sup>             | -                            | -15.1 <sup>e</sup>              |
| 100.0 DMSO    | -13.0 <sup>d</sup>           | -34.1                          | -50                          | -43.0 <sup>e</sup>              |

<sup>a</sup>See footnote a Table I. <sup>b</sup>Ref. 2. <sup>c</sup>Values in parentheses from Ref. 4, based on negligible liquid junction potential assumption. <sup>d</sup> $\Delta G_{tr}(\text{Na}^+) - \Delta G_{tr}(\text{Ag}^+)$  calculated from  $\Delta G_{tr}(\text{AgCl})$  of J. P. Morel, *Bull. Soc. Chim. France*, 896 (1968) and  $\Delta G_{tr}(\text{NaCl})$  of D. Feakins, B. E. Hickey, and P. J. Voice, *J.C.S. Faraday I* 75, 907 (1979). <sup>e</sup> $\Delta G_{tr}(\text{Cu}^{2+}) - \Delta G_{tr}(\text{Ag}^+)$  from, W. E. Waghorne, Ph.D. Thesis, Australian National University (1972).

The cell potential was used to estimate  $\Delta G_{tr}(\text{Na}^+)$ .<sup>(12,13)</sup>

For other ions, potentials were measured at 25°C versus the sce reference with a 0.1M Et<sub>4</sub>NPic salt bridge, for the half cells, Ag/AgNO<sub>3</sub> 0.01M; Cu/Cu<sub>2</sub>SO<sub>4</sub>(0.005M) and Pt/CuSO<sub>4</sub>(0.01M), Cu<sub>2</sub>SO<sub>4</sub>(0.005M). All measured potentials contain a significant liquid junction potential between the sce and the Et<sub>4</sub>NPic salt bridge in the non-aqueous solvent.<sup>(2)</sup> This problem was overcome by calculating  $\Delta G_{tr}(\text{M}^+) - \Delta G_{tr}(\text{Ag}^+)$ , from two cell potentials versus the sce to give values which do not contain a significant liquid junction potential. Where available,  $\Delta G_{tr}(\text{Ag}^+)$  values<sup>(2)</sup> were then used to calculate  $\Delta G_{tr}(\text{M}^+)$  for the other cations.  $\Delta G_{tr}(\text{M}^+)$  values are in Tables I and II, together with those based on the assumption of the negligible liquid junction potential in the above cells.

### 3.2. Enthalpies of Transfer

Heats of solution of soluble salts in the various solvents at 25°C (Table III) were measured using the LKB calorimeter. The data were

Table III. Heats of Solution and Heats of Transfer of Electrolytes from Water to 5.7 Mole% AN-H<sub>2</sub>O at 25°C<sup>g</sup>

| Electrolyte                        | $\Delta H_s$ (H <sub>2</sub> O) | $\Delta H_s$ (AN-H <sub>2</sub> O) | $\Delta H_{tr}$          |
|------------------------------------|---------------------------------|------------------------------------|--------------------------|
| NaCl                               | 3.9 <sup>a</sup>                | 2.1 <sup>d</sup>                   | -1.8                     |
| AgCl                               | 65.7 <sup>b</sup>               | 41.9 <sup>c</sup>                  | -23.8                    |
| NaClO <sub>4</sub>                 | 13.9 <sup>a</sup>               | -                                  | -1.8 <sup>e</sup>        |
| NaBPh <sub>4</sub>                 | -20.1 <sup>a</sup>              | -7.6 <sup>d</sup>                  | 12.5                     |
| AgBPh <sub>4</sub>                 | 87.0 <sup>b</sup>               | 77.4 <sup>c</sup>                  | -9.6                     |
| Cu(ClO <sub>4</sub> ) <sub>2</sub> | -                               | -                                  | -3.5 <sup>e</sup>        |
| CuBPh <sub>4</sub>                 | -                               | 60.7 <sup>c</sup>                  | -                        |
| Ph <sub>4</sub> AsCl               | -10.7 <sup>a</sup>              | -                                  | 16.3 <sup>e</sup>        |
| Ph <sub>4</sub> AsBPh <sub>4</sub> | 36.2 <sup>c</sup>               | 64.3 <sup>c</sup>                  | 28.1 (30.5) <sup>f</sup> |

<sup>a</sup> Ref. 1. <sup>b</sup> Ref. 12. <sup>c</sup> This work, by the heat of precipitation,  $\pm 1$  kJ·mol<sup>-1</sup> uncertainty.

<sup>d</sup> This work, by direct heat of solution,  $\pm 0.1$  kJ·mol<sup>-1</sup>. <sup>e</sup> This work, by heat of dilution method (see text). <sup>f</sup> Calculated via  $\Delta H_{tr}(\text{Ph}_4\text{AsCl}) + \Delta H_{tr}(\text{MBPh}_4) - \Delta H_{tr}(\text{MCl})$  for M as Na<sup>+</sup> or Ag<sup>+</sup>. <sup>g</sup> Units: kJ·mol<sup>-1</sup>.

analyzed by the Regnault-Pfaundler method<sup>(15)</sup> for solution concentrations between 10<sup>-3</sup> and 5 × 10<sup>-3</sup> M. The concentration dependence was negligible. With Cu(ClO<sub>4</sub>)<sub>2</sub> and Ph<sub>4</sub>AsCl, which could not be obtained dry, the heat of dilution of 1 ml of a 1 M solution of the salt in water, when diluted with 100 ml of water and with 100 ml of 5.7 mole% AN-H<sub>2</sub>O was used to estimate  $\Delta H_{tr}$ , after allowing for the measured heat of transfer of the water in the 1 ml of concentrated salt solution.

The heats of solution of the very slightly soluble salts, AgCl, AgBPh<sub>4</sub>, CuBPh<sub>4</sub>, and Ph<sub>4</sub>AsBPh<sub>4</sub> (Table III) were estimated from the heats of precipitation measured using the Guild calorimeter, by adding a small volume of 0.5 M NaBPh<sub>4</sub> in the solvent to 100 ml of 0.01 M MNO<sub>3</sub> in the solvent where M = Ag, Cu or Ph<sub>4</sub>As.

The heat of the reaction of CuSO<sub>4</sub> with copper powder to give Cu<sub>2</sub>SO<sub>4</sub> solutions was measured by mixing exceptionally fine freshly prepared copper powder with well stirred excess CuSO<sub>4</sub> in 0.01 M H<sub>2</sub>SO<sub>4</sub> in the appropriate solvent under an argon atmosphere to avoid oxide formation. The copper powder was prepared by rapid thermal disproportionation of a saturated Cu<sub>2</sub>SO<sub>4</sub> solution in 20 vol.% AN-H<sub>2</sub>O.

Since Cu<sup>+</sup> is unstable in water,  $\Delta H_{tr}$  of copper (I) salts cannot be estimated directly. However,  $\Delta H^\circ$  for Cu<sup>2+</sup> + Cu<sub>s</sub> → 2Cu<sup>+</sup> is 78.7 in water<sup>(16)</sup> and we found it to be -59.0 in 5.7 mole% AN-H<sub>2</sub>O (Table V) so that  $\Delta H_{tr}(\text{Cu}^+)$  is  $\frac{1}{2}[-137.7 \text{ kJ}\cdot\text{mol}^{-1} + \Delta H_{tr}(\text{Cu}^{2+})]$  for transfer

Table IV. Free Energies, Enthalpies and Entropies of Transfer of Ions from Water to Solvents at 25°C

| Solvent                         | Na <sup>+</sup>  |                  |                  | Ag <sup>+</sup>  |                  |                  | Cu <sup>+</sup>  |                  |                  | Cu <sup>2+</sup> |                 |                  |
|---------------------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|-----------------|------------------|
|                                 | $\Delta G_{tr}$  | $\Delta H_{tr}$  | $-\Delta S_{tr}$ | $\Delta G_{tr}$  | $\Delta H_{tr}$  | $-\Delta S_{tr}$ | $\Delta G_{tr}$  | $\Delta H_{tr}$  | $-\Delta S_{tr}$ | $\Delta G_{tr}$  | $\Delta H_{tr}$ | $-\Delta S_{tr}$ |
| 5.7 mole% AN-H <sub>2</sub> O   | -2 <sup>a</sup>  | -3 <sup>e</sup>  | 1                | -10 <sup>a</sup> | -25 <sup>e</sup> | 15               | -31 <sup>a</sup> | -72 <sup>i</sup> | 41               | 4 <sup>a</sup>   | -5 <sup>e</sup> | 10               |
| 5.7 mole% DMSO-H <sub>2</sub> O | -1 <sup>a</sup>  | 2 <sup>f</sup>   | -3               | -2 <sup>a</sup>  | -                | -                | -                | -                | -                | -                | -               | -                |
| 5.7 mole% DMSO/PC               | 9 <sup>b</sup>   | -22 <sup>g</sup> | 31               | -6 <sup>b</sup>  | -58 <sup>g</sup> | 52               | -                | -                | -                | -                | -               | -                |
| AN                              | 18 <sup>c</sup>  | -13 <sup>h</sup> | 31               | -22 <sup>c</sup> | -53 <sup>h</sup> | 31               | -50 <sup>c</sup> | -                | -                | 68 <sup>c</sup>  | -               | -                |
| PC                              | 17 <sup>d</sup>  | -7 <sup>h</sup>  | 24               | 16 <sup>d</sup>  | -13 <sup>h</sup> | 29               | -                | -                | -                | 73 <sup>d</sup>  | -               | -                |
| DMSO                            | -13 <sup>b</sup> | -28 <sup>h</sup> | 15               | -34 <sup>c</sup> | -55 <sup>h</sup> | 21               | -50 <sup>c</sup> | -                | -                | -43 <sup>c</sup> | -               | -                |

<sup>a</sup> Table I. <sup>b</sup> Ref. 4 and Table I. <sup>c</sup> Table II. <sup>d</sup> Ref. 11. <sup>e</sup> Applying the TATB Assumption to the appropriate  $\Delta H_{tr}$  data in Table III. <sup>f</sup> R. Fuchs and C. P. Hagan, *J. Phys. Chem.* 77, 1797 (1973). <sup>g</sup> Ref. 12 and B. G. Cox, W. E. Waghorne and C. K. Pigott, *J.C.S. Faraday Trans I* 75, 227 (1979). <sup>h</sup> Ref. 12. <sup>i</sup> Calculated from  $\frac{1}{2}(\Delta H_{tr}(\text{Reaction I}) + \Delta H_{tr}(\text{Cu}^{2+}))$  from this Table] see text.

Table V. Thermodynamic Quantities for Various Equilibria in Water and Organic-H<sub>2</sub>O Mixtures at 25°C<sup>e</sup>

| Equilibrium  | Solvent  | $\Delta G^{\circ}$ | $\Delta H^{\circ}$ | $-T\Delta S^{\circ}$ |
|--|--|--------------------|--------------------|----------------------|
| $\text{Cu}^{2+} + \text{Cu}_s = 2\text{Cu}^+$                              | H <sub>2</sub> O <sup>a</sup>                    | 35.6 <sup>b</sup>  | 79.5               | -43.9                |
|  | 5.7% AN  | -27.4 <sup>b</sup> | -59.0 <sup>c</sup> | 31.6                 |
|  | 5.7% HAN   | -31.0 <sup>b</sup> | -56.5 <sup>c</sup> | 25.5                 |
|  | 5.7% Py  | -37.6 <sup>b</sup> | -23.4 <sup>c</sup> | -14.2                |
|  | NH <sub>3</sub> -H <sub>2</sub> O <sup>a,d</sup> | -19.2              | 46.4               | -65.6                |
| $\text{Cu}^{2+} + (\text{CuS})_s = 2\text{Cu}^+ + \text{S}_s$              | H <sub>2</sub> O <sup>a</sup>                    | 88.7 <sup>b</sup>  | 132.1 <sup>b</sup> | -43.4                |
|  | 5.7% AN  | 25.7 <sup>b</sup>  | -6.4 <sup>b</sup>  | 32.1                 |
| $\text{Cu}^{2+} + (\text{Cu}_2\text{S})_s = 2\text{Cu}^+ + (\text{CuS})_s$ | H <sub>2</sub> O <sup>a</sup>                    | 69.9               | 107.9 <sup>b</sup> | -38.0                |
|  | 5.7% AN  | 6.9 <sup>b</sup>   | -30.6 <sup>b</sup> | 37.5                 |
| $\text{Cu}^{2+} + \text{Ag}_s = \text{Cu}^+ + \text{Ag}^+$                 | H <sub>2</sub> O <sup>a</sup>                    | 61.9               | 113.0 <sup>b</sup> | -51.1                |
|  | 5.7% AN  | 19.7               | 21.6 <sup>b</sup>  | -1.9                 |

<sup>a</sup> P. Doby, *The Thermodynamic Properties of Aqueous Inorganic Copper Systems* INCRA Monograph 4, (1977). <sup>b</sup> Calculated from the transfer properties for the ions in Tables I - III. <sup>c</sup> Experimental result, this work. <sup>d</sup> For  $\text{Cu}(\text{NH}_3)_2^+$  and  $\text{Cu}(\text{NH}_3)_4^{2+}$  in infinitely dilute H<sub>2</sub>O. <sup>e</sup>Units: kJ-mol<sup>-1</sup>

from water to 5.7 mole% AN-H<sub>2</sub>O. Similar procedures were used to calculate  $\Delta H_{tr}(\text{Cu}^+)$  for 5.7 mole% Py-H<sub>2</sub>O and 5.7 mole% HAN-H<sub>2</sub>O.

#### 4. DISCUSSION

The free energies of transfer of Na<sup>+</sup>, Ag<sup>+</sup>, Cu<sup>+</sup> and Cu<sup>2+</sup> ions given in Tables I and II reflect well known principles of donor-acceptor interaction between organic bases and cations and fit the coordination model for cation solvation.<sup>(1,4,11)</sup>  $\Delta G_{tr}(\text{Na}^+)$  values act as a reference point, because Na<sup>+</sup> cations do not have specific interactions with most solvents. Table II compares the data for transfer of cations between water and mixtures of water with AN and with dimethylsulfoxide (DMSO). AN is a weaker solvator than water for most cations, except the d<sup>10</sup> cations, whereas DMSO is a stronger solvator than water for all cations and also exhibits weak d<sup>10</sup>- $\pi^*$  back bonding with Ag<sup>+</sup> and Cu<sup>+</sup> ions, as shown in Table II by  $\Delta G_{tr}(\text{Cu}^+)$  being more negative than  $\Delta G_{tr}(\text{Cu}^{2+})$ , despite the greater charge density of the Cu<sup>2+</sup> ion.  $\Delta G_{tr}$  for the Na<sup>+</sup> and Cu<sup>2+</sup> ions are negligible for transfer from water to

highly aqueous aquo-organic mixtures when water is the active solvent for the cation in the mixture. For transfer from water to dilute pyridine-water,  $\Delta G_{tr}(\text{Cu}^{2+})$  is strongly negative whereas  $\Delta G_{tr}(\text{Na}^+)$  is positive since pyridine, rather than water, coordinates with  $\text{Cu}^{2+}$ .<sup>(9)</sup>  $\Delta G_{tr}$  for the  $\text{Cu}^+$  and  $\text{Ag}^+$  ions are strongly negative for transfer of these  $d^{10}$  cations from water to AN-H<sub>2</sub>O, HAN-H<sub>2</sub>O, thiourea-H<sub>2</sub>O and Py-H<sub>2</sub>O mixtures whereas  $\Delta G_{tr}(\text{Na}^+)$  is negligible. This is because of preferential coordination of the organic component via  $d^{10}-\pi^*$  back-bonding interactions.<sup>(4,7,10)</sup> For transfer from water to mixtures of water with dilute DMSO, dimethylformamide (DMF), urea, methanol and propylene carbonate,  $\Delta G_{tr}$  for the  $\text{Ag}^+$  and  $\text{Na}^+$  ions are small and comparable because water is the active solvator of both cations in these mixtures. In more concentrated DMSO-H<sub>2</sub>O there is some evidence for specific solvation of  $\text{Ag}^+$  compared to  $\text{Na}^+$  (Table II).

When back bonding occurs with the organic component,  $\Delta G_{tr}(\text{Cu}^+)$  is much more negative than  $\Delta G_{tr}(\text{Ag}^+)$  because the charge density is greater on the smaller  $\text{Cu}^+$  ion and its nucleus is less effectively shielded. This observation highlights the inadequacy of the hard and soft acids and bases theory (HSAB)<sup>(17)</sup> when dealing with  $d^{10}-\pi^*$  interactions. The HSAB theory would predict (incorrectly) that the larger more polarizable  $\text{Ag}^+$  would be softer than  $\text{Cu}^+$  and thus it would have stronger interactions with soft solvents such as AN, Py, and thiourea than would  $\text{Cu}^+$ .

The changes in  $\Delta G_{tr}$  for  $\text{Cu}^+$  and  $\text{Ag}^+$  ions parallel the changes in the limiting single ion Walden products for transfer of these same ions from anhydrous AN to AN-H<sub>2</sub>O mixtures (Figs. 1a and 1b).<sup>(9)</sup> Differences in  $(\lambda_{\sigma}^{\eta})_{tr}$  for  $\text{Na}^+$  and  $\text{Cu}^+$  ions were attributed to heterosolvation, with  $\text{Na}^+$  coordinating water to form  $\text{Na}(\text{H}_2\text{O})_x^+$  and  $\text{Cu}^+$  coordinating AN to form hydrophobic  $\text{Cu}(\text{AN})_3^+$  in AN-H<sub>2</sub>O<sub>x</sub> mixtures. The same explanation applies to the different  $\Delta G_{tr}$  ion values for  $\text{Na}^+$  and  $\text{Cu}^+$ .<sup>(1,4)</sup>

Walden products of transfer of  $\text{Cu}^+$  from water to Py-H<sub>2</sub>O suggested that  $\text{Cu}^+$  was specifically solvated by pyridine to form hydrophobic  $\text{Cu}(\text{Py})_2^+$ . The very negative  $\Delta G_{tr}(\text{Cu}^{2+})$  for transfer to Py-H<sub>2</sub>O, support this view.  $\Delta G_{tr}$  suggest that pyridine has stronger interactions than acetonitrile with  $\text{Cu}^+$  and  $\text{Ag}^+$  ions.

With the exception of transfer to Py-H<sub>2</sub>O mixtures, there is an excellent linear free energy relationship of the form

$$\Delta G_{tr}(\text{Cu}^{2+}) = 3.8 \Delta G_{tr}(\text{Na}^+) + \text{constant}$$



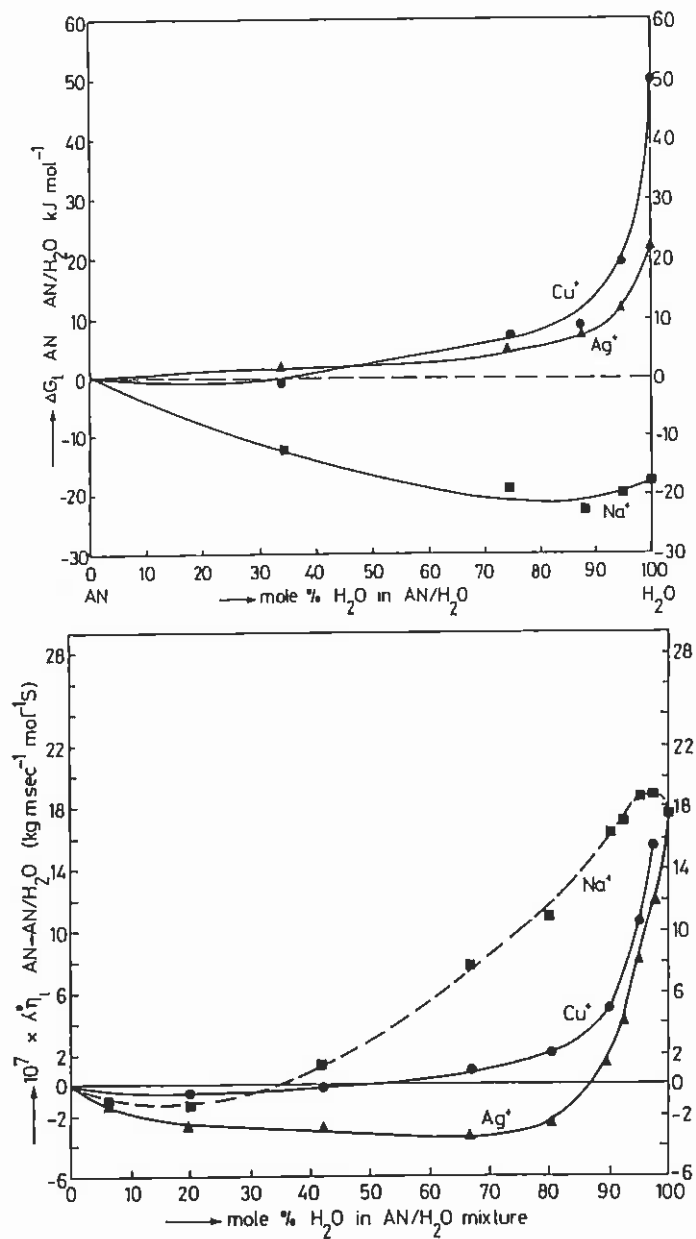


Fig. 1. Free energy (1a) and Walden product of transfer (1b) of Cu<sup>+</sup>, Ag<sup>+</sup> and Na<sup>+</sup> from acetonitrile to acetonitrile-water mixtures at 25°C. TATB Assumption.

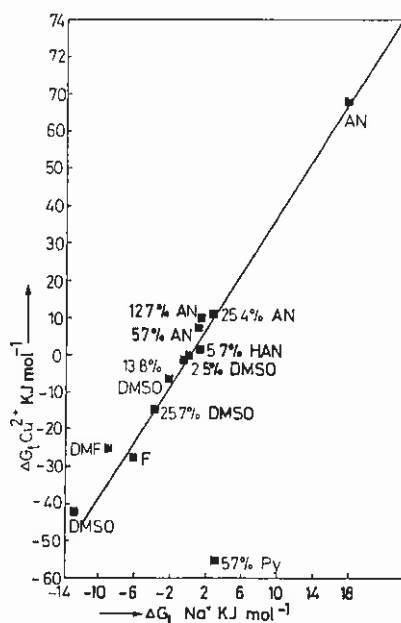


Fig. 2. Linear free energy relationship.  $DG_{tr}(Cu^{2+}) = 3.8 \Delta G_{tr}(Na^{+}) + \text{constant}$  for transfer between oxygenated solvents.

(see Fig. 2) for transfer from water to a variety of oxygenated solvents. On purely electrostatic grounds (Born equation),  $\Delta G_{tr}(Cu^{2+})$  should be four times more sensitive to solvent transfer than  $\Delta G_{tr}(Na^{+})$ , as suggested by Fig. 2, so for once the Born concept has some predictive value.

#### 4.1. Enthalpies and Entropies of Transfer of Ions

Cox and Waghorne<sup>(1)</sup> have concluded that in mixed solvent systems, preferential solvation causes characteristic variations in  $\Delta G_{tr}$ ,  $\Delta H_{tr}$  and  $\Delta S_{tr}$ .  $\Delta H_{tr}$  rather than  $\Delta S_{tr}$  reflect ion-immediate solvent neighbor interaction. Coordinated solvent-bulk solvent interactions and structural changes in mixed solvents contribute to  $\Delta S_{tr}$  and  $\Delta H_{tr}$  values by amounts which largely compensate.<sup>(1)</sup> Thus, although  $\Delta G_{tr}$  variations, as discussed above, are simpler to interpret, a great deal more information about specific solvation can be obtained if  $\Delta H_{tr}$  and  $\Delta S_{tr}$  values are also available.

Table IV shows  $\Delta G_{tr}$ ,  $\Delta H_{tr}$  and  $-T\Delta S_{tr}$  at 25°C for transfer of  $Na^{+}$ ,  $Ag^{+}$ ,  $Cu^{+}$  and  $Cu^{2+}$  ions from water to mixed and pure solvents.

Table VI. Equilibrium Constants (Molar Scale) for Reactions in AN-H<sub>2</sub>O Mixtures at 25°C

| Reaction   | Log <i>K</i> <sup>b</sup> |                   |                    |                    |                    |                   |
|--|---------------------------|-------------------|--------------------|--------------------|--------------------|-------------------|
|  | 0% <sup>c</sup>           | 5.7% <sup>c</sup> | 12.7% <sup>c</sup> | 25.4% <sup>c</sup> | 65.9% <sup>c</sup> | 100% <sup>c</sup> |
| $\text{Cu}^{2+} + \text{Cu}_s = 2\text{Cu}^+$                              | -6.2 <sup>a</sup>         | 4.8               | 7.8                | 9.4                | 13.1               | 23.2              |
| $\text{Cu}^{2+} + (\text{CuS})_s = 2\text{Cu}^+ + \text{S}_s$              | -15.5 <sup>a</sup>        | -4.5              | -1.5               | 0.1                | 3.8                | 13.9              |
| $\text{Cu}^{2+} + (\text{Cu}_2\text{S})_s = 2\text{Cu}^+ + (\text{CuS})_s$ | -12.2 <sup>a</sup>        | -1.2              | 1.8                | 3.3                | 7.1                | 17.2              |
| $\text{Cu}^{2+} + \text{Ag}_s = \text{Cu}^+ + \text{Ag}^+$                 | -10.8 <sup>a</sup>        | -3.4              | -1.5               | 0.3                | 3.2                | 13.7              |

<sup>a</sup> Footnote a, Table V. <sup>b</sup> log *K* calculated from  $\Delta G_{ir}$  data in Table II. <sup>c</sup> Mole% AN.

$\Delta H_{ir}$  is exothermic for transfer of ion from water to 5.7 mole% AN-H<sub>2</sub>O in the order  $\text{Cu}^+ > \text{Ag}^+ > \text{Cu}^+, \text{Na}^+$ . This is a consequence of decreasing strength of the acetonitrile-ion interaction in the order  $\text{Cu}^+ > \text{Ag}^+ > \text{Cu}^{2+} > \text{Na}^+$ . Specific coordination of acetonitrile to form the hydrophobic  $\text{Cu}(\text{AN})_3^+$  and  $\text{Ag}(\text{AN})_2^+$  ions produces a large loss of entropy on transfer from water to a highly aqueous AN-H<sub>2</sub>O mixture. Solvation of the second kind or hydrophobic interactions<sup>(18)</sup> for  $\text{Cu}(\text{AN})_3^+$  in dilute AN-H<sub>2</sub>O cause a large loss of entropy compared to the entropy associated with solvation of the first kind, when  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  is formed in pure water.<sup>(11)</sup> The effect is less pronounced for transfer of  $\text{Ag}^+$ , which coordinates fewer AN molecules and these less strongly than  $\text{Cu}^+$  in an enthalpic sense (Table IV). Very little entropy is lost in transfer of  $\text{Na}^+$  from water to dilute AN-H<sub>2</sub>O, because  $\text{Na}^+$  is specifically solvated by water in both structured solvents.

For transfer of cations from water to one component non-aqueous solvents, there is a large loss of entropy which is independent of the ion and the strength of the ion-solvent interaction.<sup>(1,11,13)</sup> Table IV provides a good example with identical  $\Delta S_{ir}(\text{Na}^+)$  and  $\Delta S_{ir}(\text{Ag}^+)$  values for transfer from water to dry AN, despite very different  $\Delta H_{ir}$  for the two cations.

For transfer to two component mixed solvents containing water, the strength of specific interactions, the hydrophilic or hydrophobic nature<sup>(1,18)</sup> of the resulting coordinated solute, and the structure of the mixture strongly influence  $\Delta S_{ir}$  ion values.<sup>(11)</sup> The values of  $-\Delta S_{ir}$  for  $\text{Cu}^+$  (41), for  $\text{Ag}^+$  (15), and for  $\text{Na}^+$  (1 kJ·mol<sup>-1</sup>·K<sup>-1</sup>) from Table IV for transfer from water to 5.7 mole% AN-H<sub>2</sub>O, when compared to the

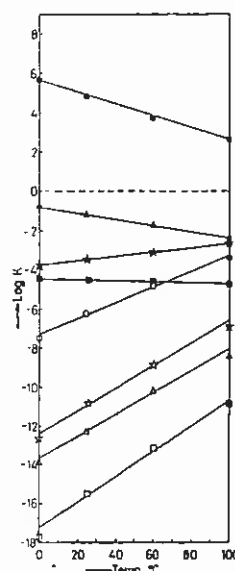


Fig. 3. Equilibrium constants at 0 - 100°C for Reactions (I)-(IV) in water and in 5.7 mole% AN-H<sub>2</sub>O. Open symbols ○, □, △, ☆ - H<sub>2</sub>O; Filled symbols ●, ■, ▲, ★ - 5.7 mole% AN-H<sub>2</sub>O: ○, ● Reaction (I); □, ■ Reaction (II); △, ▲ Reaction (III); ☆, ★ Reaction (IV).

same value of 31 kJ·mol<sup>-1</sup> for  $-T\Delta S_{tr}$  for Ag<sup>+</sup> and Na<sup>+</sup> for transfer to dry acetonitrile, well illustrate the difference between transfer of specifically interacting ions to one component vs. two component solvents containing water.

#### 4.2. Equilibria

Table V contains thermodynamic data for four equilibria involving copper ions in water and in an AN-H<sub>2</sub>O mixture. Table VI shows how equilibrium constants increase in mixtures of increasing AN content. Table VII shows very unfavorable entropies of transfer of the reactions from water to dilute mixtures of organics in water.

All four reactions are highly endoenergetic in water, but in 5.7 mole% AN, all four equilibria are displaced further to the right, because of favorable solvation of Cu<sup>+</sup> and Ag<sup>+</sup> by the acetonitrile compared to water. Despite the more favorable equilibrium, water containing more than 20 mole% acetonitrile is needed to achieve high concentrations of Cu<sup>+</sup> from Reactions (II), (III) and (IV) (Table VI).

All four reactions are very strongly favored (> 100 kJ·mol<sup>-1</sup>) to

Table VII. Entropy Changes Associated with Transfer of Reactions from Water to Organic-Water Mixtures at 25°C<sup>b</sup>

| Reaction   | Solvent                           | $\Delta S_{tr}$ |
|--|-----------------------------------|-----------------|
| $\text{Cu}^{2+} + \text{Cu}_s = 2\text{Cu}^+$                              | H <sub>2</sub> O                  | 0               |
| $\text{Cu}^{2+} + (\text{CuS})_s = 2\text{Cu}^+ + \text{S}_s$              | 5.7% AN-H <sub>2</sub> O          | -253            |
| $\text{Cu}^{2+} + (\text{Cu}_2\text{S})_s = 2\text{Cu}^+ + (\text{CuS})_s$ | 5.7% HAN-H <sub>2</sub> O         | -233            |
|  | 5.7% Py-H <sub>2</sub> O          | -100            |
|  | NH <sub>3</sub> -H <sub>2</sub> O | 73              |
| $\text{Cu}^{2+} + \text{Ag}_s = \text{Cu}^+ + \text{Ag}^+$                 | H <sub>2</sub> O                  | 0               |
|  | 5.7% AN-H <sub>2</sub> O          | -165            |

<sup>a</sup> Calculated from data in Table V. <sup>b</sup> Units: J-K<sup>-1</sup>-mol<sup>-1</sup>.

the right in an enthalpic sense by addition of 5.7 mole% acetonitrile to water. The exothermic nature of the reaction is consistent with a strong interaction of acetonitrile with Cu<sup>+</sup>,<sup>(9)</sup> but more importantly, is associated with solvent-solvent interactions resulting from formation of hydrophobic Cu(AN)<sub>3</sub><sup>+</sup> from hydrophilic Cu(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>.<sup>(11)</sup> Structure-making solvation of the second kind is an exothermic process for large hydrophobic cations, just as hydrophilic solvation is often an endothermic process, for solution from the ionic crystals.<sup>(11)</sup>

All four reactions suffer a very substantial loss of entropy (up to 250 J-K<sup>-1</sup>-mol<sup>-1</sup> on transfer from water to 5.7 mole% acetonitrile) in water. This is expected because of formation of hydrophobic Cu(AN)<sub>3</sub><sup>+</sup> from hydrophilic Cu(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> as discussed above. Reaction (I) loses 150 units less entropy for transfer to dilute Py-H<sub>2</sub>O than to dilute AN-H<sub>2</sub>O (Table VII) from water. This is because on transfer to Py-H<sub>2</sub>O, both Cu(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> and Cu(H<sub>2</sub>O)<sub>4</sub><sup>+</sup> form hydrophobic ions, Cu(Py)<sub>3</sub><sup>+</sup> and Cu(Py)<sub>4</sub><sup>+</sup> from aquo ions. Thus the entropy of both sides of the equilibrium are strongly but more or less equally effected by the change (Table I). On transfer to NH<sub>3</sub>-H<sub>2</sub>O, the ammonia ligand, unlike AN, is hydrophilic and unlike AN more ammonia binds to form Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> than to form Cu(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> from the aquo ions. Thus, Reaction (I) has a gain of entropy of 73 on transfer from water and of 326 J-K<sup>-1</sup>-mol<sup>-1</sup> on transfer from 5.7 mole% AN-H<sub>2</sub>O to NH<sub>3</sub>-H<sub>2</sub>O.<sup>(11)</sup>

#### 4.3. Temperature Dependence of Equilibrium Constants

Figure 3 shows log *K* for equilibria (I)-(IV) at 0-100°C. Reac-

tions (I)-(III) give greater proportions of  $\text{Cu}^+$  at lower temperatures, whereas Reaction (IV) gives greater proportions of  $\text{Cu}^+$  and  $\text{Ag}^+$  at higher temperatures in  $\text{An-H}_2\text{O}$ . The reverse is true for Reactions (I)-(III) in water. In hydrometallurgical leaching using acetonitrile, the aim is to maximize the concentration of  $\text{Cu}^+$  and  $\text{Ag}^+$  for subsequent recovery of the metals.<sup>(10)</sup> Thus, these temperature effects are of significance.

## 5. ACKNOWLEDGEMENT

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