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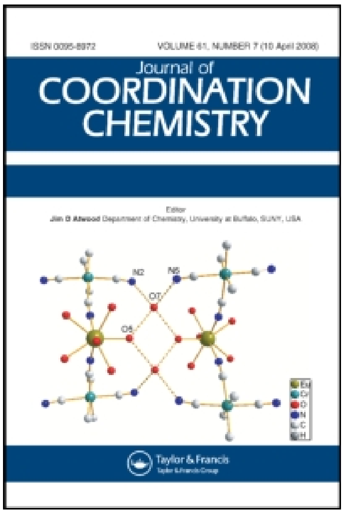

## Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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Guo Li[a]; Liang Chun-Yu[a]; Yang Jia-Zhen[a]; Liu Qi-Tao[a]
[a] Department of Chemistry, Liaoning University, Shenyang, Peoples' Republic of China

**To cite this Article** Li, Guo , Chun-Yu, Liang , Jia-Zhen, Yang and Qi-Tao, Liu(1990) 'The Influence of Medium on the Stability of Coordination Compounds. III. The System $CuSO_4$-$NaClO_4$-Organic Solvents-$H_2O$', Journal of Coordination Chemistry, 21: 1, 43 — 53

**To link to this Article: DOI:** 10.1080/00958979009408182

**URL:** http://dx.doi.org/10.1080/00958979009408182

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*J. Coord. Chem.* 1990, Vol. 21. pp. 43–53
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# THE INFLUENCE OF MEDIUM ON THE STABILITY OF COORDINATION COMPOUNDS. III. THE SYSTEM $CuSO_4$-$NaClO_4$-ORGANIC SOLVENTS-$H_2O$

GUO LI, LIANG CHUN-YU, YANG JIA-ZHEN and LIU QI-TAO

*Department of Chemistry, Liaoning University, Shenyang, Peoples' Republic of China.*

*(Received May 10, 1989)*

The concentration stability constants for $CuSO_4$ in various mixed solvents, *viz* ethanol–water, isopropanol–water and dioxane–water, having a composition of organic solvent of 0, 5, 10, 15, 20 and 25 mass per cent were measured spectrophotometrically at 298 $\pm 0.5$ K using $NaClO_4$ as supporting electrolyte. The total ionic strength range of the solutions are 0.06–4.0 mol $dm^{-3}$ and pH = 4–5. The thermodynamic stability constants $CuSO_4$ were obtained by a polynomial approximation based on Pitzer's theory. Finally, the standard free energies of transfer of the coordination reaction, $\Delta G^{\circ}_{..}$, from pure water to mixed solvent were obtained and the electrostatic part of $\Delta G^{\circ}_{..}$ was calculated based on Beveridge's theory.

**Keywords:** $CuSO_4$, complex, stability constants, mixed solvents, free energy of transfer

## INTRODUCTION

The thermodynamic behaviour of complexes in mixed solvents has long been a subject of interest. Complex formation reactions in solution are significantly influenced by the solvents employed. In studies of complex equilibria in different mixed aqueous solvents, the organic solvent certainly plays an important role. Water has always been a component of the mixed solvents, while the other component is usually an amphiprotic organic species. The solvent mixtures under investigation containing 0, 5, 10, 15, 20 and 25 mass per cent of ethanol, isopropanol, or dioxane were chosen.

The variation of the stability constants of complexes with solvent composition must be attributed to properties of the mixed solvents. The variation in proportion of water–organic solvent changes the dielectric constant of the medium and therefore it must have a pronounced effect on the values of the stability constants. Thermodynamic stability constants of complexes reflect intrinsic properties of complex formation reactions. A determination activity coefficient of the species in the complex equilibria is the key of obtaining thermodynamic stability constants. Davies[1] and Vasil'ev[2] have used the extended Debye–Hückel equation to calculate activity coefficients. Recently Pitzer[3] developed a series of equations for the thermodynamic properties of electrolyte solution on the basis of statistical mechanics. These equations are able to be applied formally to any dielectric medium. The theory has been quite successful in predicting the properties of aqueous electrolyte solutions at concentrations up to several molal. It has however been applied but rarely to mixed solvents.[4,5] Liang chun-yu *et al.*,[6] have proposed methods for determining thermodynamic stability constants of coordination compounds in aqueous solutions by a curve fitting technique and a polynomial approximation based on Pitzer's theory, and have extended these methods to complex formation in mixed solvents.[7,8]

This paper reports the spectrophotometric determination of the concentration stability constant, $K_1$, for the complex formation reaction (*1*),

$$Cu^{++} + SO_4^{--} \leftrightharpoons CuSO_4 \qquad (1)$$

in three kinds of mixed solvents at 298.2±0.5 K. On the basis of Pitzer's theory, the thermodynamic stability constants for the 2–2 neutral complex, $CuSO_4$, were obtained by a polynomial approximation. The results have been compared with those obtained by using the Vasil'ev method. Finally, the standard free energies of transfer for the coordination reaction, $\Delta G^{\circ}..$, are examined. The electrostatic part of $\Delta G^{\circ}..$ has been calculated using Beveridge's theory, and non-electrostatic contribution to $\Delta G^{\circ}..$ obtained.

## EXPERIMENTAL

All organic solvents, *viz* ethanol, isopropanol and dioxane were A.R. grade and were distilled by a standard method.[9] The desired mixed solvent was prepared by mixing distilled organic solvent and double-distilled water by weight with pH = 4–5 (adjusted by $HClO_4$ (C.R.) $Na_2SO_4$ and $NaClO_4$ (A.R.) were dried at 180°C and 220–230°C, respectively, after recrystallization. $Cu(ClO_4)_2$ was prepared using CuO (A.R.) dissolved in 50% $HClO_4$ (A.R.) and the concentration was checked by spectrophotometric measurement.

The absorbance measurement was carried out using a Shimadzu UV-240 spectrophotometer equipped with a thermostatted 1 cm cell at 298.2±0.5 K at 250 nm.

### *Determination of molar absorptivity*

A method similar to that of Dadgar and Atkinson[10] was used to determine the difference, $\Delta\varepsilon$, of molar absorptivity between complex, $CuSO_4$, and ion, $Cu^{++}$, using equations (*2*) to (*4*),

$$ab/\Delta A = (a+b-x)/\Delta\varepsilon + 1/(\Delta\varepsilon K_1) \qquad (2)$$

$$\Delta A = A - A' \qquad (3)$$

$$\Delta\varepsilon = \varepsilon_1 - \varepsilon_0 \qquad (4)$$

where a is the stoichiometric molality of $Cu(ClO_4)_2$, b is the stoichiometric molality of $Na_2SO_4$, x is molality of $CuSO_4$, A is the optical density of the test solution when measured in a cell of the length 1 cm, A′ is the optical density of the reference solution, $\varepsilon_0$ is molal extinction coefficient of $Cu^{++}$ ions, and $\varepsilon_1$, is the molal extinction coefficient of the complex $CuSO_4$. In order to determine $\Delta\varepsilon$, a series of test solutions were prepared. In the test solutions the concentration of $Cu^{++}$, a, was constant and the concentration of $SO_4^{--}$, b, was a variable. The ionic strength of all solutions was adjusted by $NaClO_4$ to $I = 0.1\ mol\,dm^{-3}$. The composition of the relevant reference solution is the same as the test solution except b = 0. $\Delta\varepsilon$ can be obtained by an iterative computer program.

### *Determination of the stability constants of the complex $CuSO_4$ in different mixed solvents and at different ionic strength*

At the selected wavelength, 250 nm, the optical density, A, of the $Cu^{++} + SO_4^{--}$ system, in which $[Cu^{++}]$ and $[SO_4^{--}]$ were constant and ionic strength varied from 0.6 to 4.0 mol dm$^{-1}$, was measured for different compositions of mixed solvent. The concentration stability constant, $K_1$, was calculated from equation (*5*).

$$K_1 = (\Delta A/\Delta\varepsilon)/[a-(\Delta A/\Delta\varepsilon)]/[b-(\Delta A/\Delta\varepsilon)] \tag{5}$$

TABLE I

Molar absorptivity values for $CuSO_4$ in mixed solvents.

| | ΔA | | | | |
|---|---|---|---|---|---|
| $b \times 10^2$ | wt% ethanol | | | | |
| (mol dm$^{-2}$) | 0 | 5 | 10 | 15 | 20 |
| 1.120 | 0.220 | 0.289 | 0.392 | 0.528 | 0.690 |
| 1.494 | 0.276 | 0.367 | 0.486 | 0.643 | 0.832 |
| 1.734 | 0.312 | 0.408 | 0.538 | 0.719 | 0.906 |
| 2.116 | 0.354 | 0.473 | 0.616 | 0.804 | 1.019 |
| 2.490 | 0.402 | 0.522 | 0.674 | 0.876 | 1.104 |
| 2.739 | 0.424 | 0.549 | 0.710 | 0.917 | 1.153 |
| Δε | 233.7 | 257.8 | 307.5 | 354.2 | 407.7 |

$a = 4.937 \times 10^{-3}$ mol dm$^{-3}$

| | ΔA | | | | |
|---|---|---|---|---|---|
| $b \times 10^2$ | wt% isopropanol | | | | |
| (mol dm$^{-3}$) | 5 | 10 | 15 | 20 | 25 |
| 1.120 | 0.307 | 0.399 | 0.557 | 0.719 | 0.902 |
| 1.494 | 0.373 | 0.500 | 0.670 | 0.849 | 0.975 |
| 1.734 | 0.413 | 0.554 | 0.738 | 0.934 | 1.036 |
| 2.116 | 0.471 | 0.632 | 0.839 | 1.049 | 1.185 |
| 2.490 | 0.523 | 0.702 | 0.906 | 1.122 | 1.257 |
| 2.739 | 0.549 | 0.726 | 0.952 | 1.152 | 1.300 |
| Δε | 240.4 | 332.2 | 365.5 | 391.9 | 465.4 |

$a = 4.831 \times 10^{-3}$ mol dm$^{-3}$

| | ΔA | | | | |
|---|---|---|---|---|---|
| $b \times 10^2$ | wt% dioxane | | | | |
| (mol dm$^{-3}$) | 5 | 10 | 15 | 20 | 25 |
| 1.120 | 0.295 | 0.373 | 0.480 | 0.624 | 0.666 |
| 1.494 | 0.362 | 0.458 | 0.590 | 0.752 | 0.799 |
| 1.734 | 0.402 | 0.506 | 0.651 | 0.826 | 0.877 |
| 2.116 | 0.462 | 0.580 | 0.742 | 0.926 | 0.974 |
| 2.490 | 0.513 | 0.644 | 0.800 | 1.000 | 1.042 |
| 2.739 | 0.542 | 0.662 | 0.838 | 1.030 | 1.076 |
| Δε | 255.8 | 289.5 | 329.3 | 367.7 | 368.6 |

$a = 4.992 \times 10^{-3}$ mol dm$^{-3}$

## RESULTS AND DISCUSSION

$CuSO_4$ and $Cu^{++}$ have absorption distinctly different at the selected wavelength of 250 nm. Although the absorption spectra of the other components in the systems showed that ethanol and dioxane also absorbed a little at the same wavelength, these absorptions can be ignored since the concentration of ethanol and dioxane in the relevant reference and the test solutions were the same. Molar extinction coefficients obtained by an iterative computing program are shown in Table I. The concentration stability constants computed from equation (*5*) are listed in Tables II, III and IV.

TABLE II
Concentration stability constants for $CuSO_4$ in ethanol–water mixed solvent.

| wt% ethanol | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 0 | | 5 | | 10 | | 15 | | 20 | |
| I | $\log K_1$ | I | $\log K_1$ | I | $\log K_1$ | I | $\log K_1$ | I | $\log K_1$ |
| 0.0686 | 1.457 | 0.0599 | 1.603 | 0.0599 | 1.697 | 0.0597 | 1.801 | 0.0599 | 1.914 |
| 0.110 | 1.299 | 0.0995 | 1.476 | 0.0995 | 1.555 | 0.100 | 1.637 | 0.100 | 1.739 |
| 0.130 | 1.258 | 0.125 | 1.402 | 0.125 | 1.491 | 0.126 | 1.560 | 0.125 | 1.660 |
| 0.169 | 1.182 | 0.155 | 1.316 | 0.155 | 1.423 | 0.159 | 1.475 | 0.154 | 1.577 |
| 0.200 | 1.138 | 0.200 | 1.281 | 0.200 | 1.319 | 0.200 | 1.390 | 0.200 | 1.498 |
| 0.269 | 1.066 | 0.269 | 1.192 | 0.269 | 1.247 | 0.269 | 1.287 | 0.269 | 1.378 |
| 0.329 | 0.994 | 0.324 | 1.121 | 0.324 | 1.180 | 0.324 | 1.241 | 0.324 | 1.299 |
| 0.444 | 0.912 | 0.445 | 1.044 | 0.445 | 1.098 | 0.445 | 1.122 | 0.445 | 1.183 |
| 0.500 | 0.897 | 0.500 | 0.991 | 0.500 | 1.032 | 0.500 | 1.082 | 0.500 | 1.130 |
| 0.618 | 0.869 | 0.618 | 0.933 | 0.610 | 0.987 | 0.610 | 1.034 | 0.610 | 1.065 |
| 0.777 | 0.825 | 0.775 | 0.912 | 0.775 | 0.945 | 0.802 | 0.941 | 0.852 | 0.958 |
| 1.000 | 0.735 | 1.000 | 0.824 | 1.000 | 0.825 | 1.000 | 0.862 | 1.000 | 0.894 |
| 1.161 | 0.723 | 1.156 | 0.819 | 1.299 | 0.772 | 1.156 | 0.844 | 1.156 | 0.852 |
| 1.312 | 0.706 | 1.299 | 0.788 | 1.500 | 0.764 | 1.306 | 0.820 | 1.300 | 0.834 |
| 1.500 | 0.687 | 1.500 | 0.658 | 1.751 | 0.756 | 1.500 | 0.804 | 1.500 | 0.783 |
| 1.746 | 0.675 | 1.656 | 0.701 | 2.000 | 0.714 | 1.750 | 0.763 | 1.750 | 0.771 |
| 2.000 | 0.632 | 1.830 | 0.697 | 2.249 | 0.740 | 2.000 | 0.716 | 2.000 | 0.737 |
| 2.190 | 0.675 | 2.000 | 0.675 | 2.500 | 0.691 | 2.268 | 0.753 | 2.268 | 0.737 |
| 2.500 | 0.622 | 2.236 | 0.719 | 2.743 | 0.740 | 2.500 | 0.723 | 2.500 | 0.774 |
| 2.750 | 0.679 | 2.500 | 0.675 | 3.033 | 0.800 | 2.743 | 0.767 | 2.750 | 0.837 |
| 3.000 | 0.688 | 2.750 | 0.719 | | | 3.000 | 0.797 | | |
| 3.255 | 0.767 | 3.020 | 0.764 | | | | | | |
| 3.500 | 0.782 | 3.180 | 0.784 | | | | | | |
| 3.741 | 0.885 | | | | | | | | |

### *Estimation of the thermodynamic stability constant for $CuSO_4$ in different mixed solvents*

The relationship between the concentration stability constant, $K_1$, and the thermodynamic stability constant, $K_0$, of the complex is expressed as in (*6*),

$$\log K_0 = \log K_1 + \Sigma v_{1j} \log \gamma_{ij} \qquad (6)$$

where $\gamma_{ij}$ is the mean ionic activity coefficient of the electrolyte, ij, in the given solvent

## TABLE III

Concentration stability constants for $CuSO_4$ in isopropanol–water mixed solvent.

| wt% isopropanol | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 5 | | 10 | | 15 | | 20 | | 25 | |
| I | $\log K_I$ | I | $\log K_I$ | I | $\log K_I$ | I | $\log K_I$ | I | $\log K_I$ |
| 0.052 | 1.658 | 0.0653 | 1.653 | 0.0664 | 1.766 | 0.0615 | 1.937 | 0.0468 | 2.053 |
| 0.083 | 1.548 | 0.105 | 1.519 | 0.105 | 1.619 | 0.0999 | 1.754 | 0.0888 | 1.829 |
| 0.094 | 1.500 | 0.137 | 1.428 | 0.138 | 1.558 | 0.136 | 1.637 | 0.125 | 1.697 |
| 0.114 | 1.458 | 0.164 | 1.376 | 0.165 | 1.466 | 0.164 | 1.582 | 0.155 | 1.610 |
| 0.173 | 1.348 | 0.200 | 1.305 | 0.200 | 1.395 | 0.200 | 1.493 | 0.200 | 1.507 |
| 0.233 | 1.258 | 0.257 | 1.227 | 0.258 | 1.300 | 0.257 | 1.388 | 0.246 | 1.419 |
| 0.352 | 1.146 | 0.323 | 1.151 | 0.325 | 1.223 | 0.326 | 1.292 | 0.313 | 1.323 |
| 0.471 | 1.074 | 0.413 | 1.067 | 0.414 | 1.143 | 0.410 | 1.202 | 0.407 | 1.216 |
| 0.589 | 1.035 | 0.500 | 1.039 | 0.500 | 1.069 | 0.500 | 1.121 | 0.500 | 1.127 |
| 0.812 | 0.958 | 0.624 | 0.980 | 0.625 | 1.006 | 0.623 | 1.054 | 0.619 | 1.062 |
| 0.827 | 0.998 | 0.780 | 0.916 | 0.716 | 0.909 | 0.777 | 0.961 | 0.801 | 0.954 |
| 1.114 | 0.978 | 1.000 | 0.822 | 1.000 | 0.860 | 1.000 | 0.873 | 1.000 | 0.865 |
| 1.314 | 0.984 | 1.183 | 0.797 | 1.184 | 0.788 | 1.185 | 0.836 | 1.662 | 0.850 |
| 1.516 | 0.948 | 1.365 | 0.771 | 1.366 | 0.782 | 1.362 | 0.796 | | |
| 1.818 | 0.954 | 1.500 | 0.727 | 1.500 | 0.772 | 1.500 | 0.783 | | |
| 2.120 | 0.942 | 1.664 | 0.749 | 1.665 | 0.730 | 1.686 | 0.733 | | |
| 2.472 | 0.982 | 2.000 | 0.603 | 1.860 | 0.719 | | | | |
| 2.824 | 1.024 | 2.249 | 0.749 | 2.000 | 0.710 | | | | |
| 3.277 | 1.008 | | | 2.250 | 0.739 | | | | |
| | | | | 2.484 | 0.742 | | | | |

## TABLE IV

Concentration stability constants for $CuSO_4$ in dioxane–water mixed solvent.

| wt% dioxane | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 5 | | 10 | | 15 | | 20 | | 25 | |
| I | $\log K_I$ | I | $\log K_I$ | I | $\log K_I$ | I | $\log K_I$ | I | $\log K_I$ |
| 0.0531 | 1.591 | 0.0522 | 1.721 | 0.0511 | 1.763 | 0.0501 | 1.884 | 0.0481 | 2.053 |
| 0.0862 | 1.464 | 0.0732 | 1.657 | 0.0723 | 1.662 | 0.0831 | 1.753 | 0.0715 | 1.890 |
| 0.123 | 1.377 | 0.0931 | 1.594 | 0.0981 | 1.566 | 0.121 | 1.618 | 0.0915 | 1.789 |
| 0.166 | 1.305 | 0.123 | 1.532 | 0.124 | 1.502 | 0.164 | 1.519 | 0.126 | 1.721 |
| 0.224 | 1.212 | 0.154 | 1.430 | 0.154 | 1.419 | 0.223 | 1.402 | 0.153 | 1.611 |
| 0.330 | 1.092 | 0.200 | 1.351 | 0.200 | 1.316 | 0.329 | 1.244 | 0.203 | 1.554 |
| 0.445 | 1.035 | 0.306 | 1.246 | 0.306 | 1.161 | 0.445 | 1.135 | 0.305 | 1.366 |
| 0.583 | 0.811 | 0.406 | 1.176 | 0.397 | 1.042 | 0.582 | 1.011 | 0.395 | 1.279 |
| 0.740 | 0.829 | 0.537 | 1.028 | 0.533 | 0.902 | 0.897 | 0.986 | 0.596 | 1.200 |
| 0.899 | 0.445 | 0.777 | 0.957 | 0.758 | 0.734 | 1.058 | 0.958 | 0.717 | 1.079 |
| 1.059 | 0.311 | 0.988 | 0.861 | 0.982 | 0.625 | 1.218 | 0.944 | 1.032 | 0.900 |
| 1.212 | 0.287 | 1.348 | 0.872 | 1.318 | 0.549 | 1.314 | 0.941 | 1.333 | 0.860 |
| 1.598 | 0.274 | 1.648 | 0.807 | 1.570 | 0.525 | 1.318 | 0.914 | 1.633 | 0.842 |
| 1.817 | 0.287 | 1.918 | 0.831 | 1.823 | 0.513 | 1.596 | 0.898 | | |
| | | 2.158 | 0.846 | 2.018 | 0.549 | 1.942 | 0.911 | | |
| | | 2.308 | 0.827 | 2.186 | 0.555 | 2.319 | 0.906 | | |

of ionic strength I, $v_{ij}$ is the (mole) number of ions per mole of electrolyte, and ij represents products and reactants in reaction (*1*).

The ion interaction model of Pitzer[3,12] has been very successful in describing activity coefficients. Following this model the equation for the mean activity coefficient of electrolyte MX for multicomponent electrolyte solutions is given as shown below, (*7*) to (*12*).

$$\begin{aligned}\ln\gamma_{mx} = {} & |Z_H Z_X| f^r + 2v_M/v\Sigma_a m_a[B_{ma} + (\Sigma mZ)C_{ma} + v_x/v_H\theta_{xa}] \\ & + 2v_x/v\Sigma_o m_o[B_{ox} + (\Sigma mZ)C_{ox} + v_m/v_x\theta_{mo}] \\ & + \Sigma_c\Sigma_a m_o m_a\{Z_M Z_X|B'_{oa} + v^{-1}[2v_M Z_M C_{oa} + v_M\Psi_{Moa} + v_x\Psi_{oax}]\} \\ & + 1/2\Sigma_a\Sigma_{a'} m_a m_{a'}[v_M/v\Psi_{Maa'} + |Z_M Z_X|\theta'_{aa'}] \\ & + 1/2\Sigma_o\Sigma_{o'} m_o m_{o'}[v_x/v\Psi_{oo'x} + |Z_N Z_x|\theta'_{oo'}]\end{aligned} \qquad (7)$$

where $f^r$ is defined as

$$f^r = -A\varphi[I^{1/2}/(1 + bI^{1/2}) + (2/b)\ln(1 + bI^{1/2})] \qquad (8)$$

$$A\varphi = 1/3(2\pi Nd/1000)^{1/2}[e^2/(DkT)]^{3/2} \qquad (9)$$

and $B_{ij}$, $B'_{ij}$ by

$$B_{ij} = \beta^{(0)} + (2\beta^{(1)}/\alpha^2 I)[1-(1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})] \qquad (10)$$

$$B'_{ij} = (2\beta^{(1)}/\alpha^2 I^2)[(1-\alpha I^{1/2} + 1/2\alpha^2 I)\exp(-\alpha I^{1/2})-1] \qquad (11)$$

$$C_{ij} = C^F{}_{ij}/(2|Z_i Z_j|^{1/2}) \qquad (12)$$

Herein $f^r$ is the Debye–Hückel function for the activity coefficient with parameter $A\varphi$. $A\varphi$ (with dimensions of $kg^{1/2}\,mol^{-1/2}$) is the Debye–Hückel constant for the osmotic coefficient. The parameter b has the standard value $1.2\,kg^{1/2}\,mol^{-1/2}$. The parameter α has the value $2.0\,kg^{1/2}\,mol^{-1/2}$. The second and third virial coefficients of a pure electrolyte, ij, are $B_{ij}$ and $C_{ij}$ and have dimensions of $kg\,mol^{-1}$ and $kg^2\,mol^{-2}$, respectively. The second virial coefficient $B_{ij}$, is assumed to have some dependence upon ionic strength, as represented above in equation (*10*) by two adjustable parameters, $\beta^{(0)}{}_{ij}$ and $\beta^{(1)}{}_{ij}$. $B'_{ij}$ is a derivative of $B_{ij}$ with respect to I, with dimensions of $kg^2\,mol^{-2}$. The $\beta^{(0)}{}_{ij}$ and $\beta^{(1)}{}_{ij}$ terms are parameters specific to the electrolyte, ij. The third virial coefficient $C_{ij}$ is independent of the ionic strength. $Z_i$ and $Z_j$ are the ionic charges. The quantitiy ΣmZ is the total electric positive (or negative) charge molality, *i.e.*, $\Sigma mZ = \Sigma m_o Z_o = \Sigma m_a|Z_a|$. The mixing coefficients θ, θ′ and ψ are independent of the ionic strength of solution.

To apply Pitzer's equation to any system simply and conveniently, the activity coefficients of the electrolyte are determined by a polynomial approximation, so as to avoid using Pitzer's parameters which are not easily available for mixed solvents. First, on the suggestion of Pitzer,[3,11,12] mixing parameters θ, θ′ and ψ are omitted, and this will cause little error. Secondly, the concentration, m, of the supporting electrolyte was considered only in the sum of the equation (7), since the concentration of metal ion and ligand is usually quite low under the experimental conditions used for determining the stability constant and the concentration of the supporting electrolyte is very high. Then the following equation was derived from equation (*7*).

$$\ln\gamma_{MX} = |Z_M Z_X| f^{\gamma} + 2\nu_M \cdot m_y/\nu[B_{My} + m_y Z_y C_{My}] + 2\nu_x \cdot m_s/\nu]B_{sx} + m_s Z_s C_{sx}] + m_s m_y[|Z_M Z_x| B'_{sy} + 2\nu_m Z_n C_{sy}/\nu] \tag{13}$$

The total ionic strength I, is approximately equal to $I_{sy}$, which was contributed by the supporting electrolyte, SY,

$$\begin{aligned} I_{sy} &= (1/2)\Sigma m_i Z_i^2 \\ m &= 2I/(\nu_{sy}|Z_{sy}|) \end{aligned} \tag{14}$$

where $\nu_{sy} = \nu_s + \nu_y$, $\nu_s$, $\nu_y$ are the numbers of cation and anions dissociated from the supporting electrolyte, SY, respectively, and $Z_s$ and $Z_y$ are the charges on cation and anion of supporting electrolyte, SY, respectively. The concentration of the cation, $m_s$, and that of anion, $m_y$, are derived as in (*15*).

$$m_s = 2\nu_s I/(\nu_{sy}|Z_s Z_y|),\ m_y = 2\nu_y I/(\nu_{sy}|Z_s Z_y|) \tag{15}$$

From equations (*13*) and (*15*), we obtain (*16*).

$$\begin{aligned} \ln\gamma_{MX} = {} & |Z_M Z_x| f^{\gamma} + [(4\nu_M \nu_y I)/(\nu\,\nu_{sy}|Z_s Z_y|)][B_{MV} + (2\nu_y I C_{sy})/(\nu_{sy} Z_s)] \\ & + [(4\nu_x \nu_s I)/(\nu\,\nu_{sy}|Z_s Z_y|)][B_{sx} + (2\nu_s I C_{sx})/(\nu_{sy} Z_y)] \\ & + [(4\nu_s \nu_y I^2)/(\nu_{sy}|Z_M Z_y|)^2][|Z_M Z_x| B'_{sy} + (2\nu_M Z_M C_{sy})/\nu] \end{aligned} \tag{16}$$

Considering equations (*10*)–(*12*) and (*16*), the following equations are deduced

$$\ln\gamma = |Z_M Z_x| f^{\gamma} + a_1 f_1 + a_2 f_2 + a_3 f_3 + a_4 f_4 \tag{17}$$

where $a_1$ (i = 1,. . .,4) are constants unrelated to ionic strength, I, but depending on $\beta^{(0)}$, $\beta^{(1)}$, ν and Z of the electrolytes in solution.

$$\begin{aligned} f_1 &= I \\ f_2 &= I^2 \\ f_3 &= [1-(1+\alpha I^{1/2})\exp(-\alpha I^{1/2})] \\ f_4 &= [(1+\alpha I^{1/2} + 1/2\alpha^2 I)\exp(-\alpha I^{1/2})-1] \end{aligned} \tag{18}$$

From equations (*6*) and (*17*) and $\nu_{Mx}|Z_M Z_x| = \nu_M Z_M{}^2 + \nu_x Z_x{}^2$, we get

$$\log K_1 - (\Delta Z^2 A\Phi.\Delta)/\ln 10 = \log K_0 + A_1 f_1 + A_2 f_2 + A_3 f_3 + A_4 f_4 \tag{19}$$

$$\Delta \equiv [I^{1/2}/(1 + bI^{1/2}) + (2/b)\ln(1 + bI^{1/2})] \tag{20}$$

where $A_1$ (i = 1,. . .,4) are constants unrelated to ionic strength, I, and which are the combination of $a_1$ for electrolytes. $\Delta Z^2$ is the difference between charge squares of products and reactants. The density, d, and dielectric constant, D, of the mixed solvents were taken from references 13, 14 and 15. Values of the parameter AΦ in each mixed solvent were calculated by using equation (*9*). The thermodynamic stability constants for the complex $CuSO_4$ in mixed solvents were calculated by using a polynomial approximation technique based on Pitzer's theory. The quantity

($\log K_1 - \Delta Z^2 A\Phi / \ln 10$) on the left side of equation (*19*) was approximated to the polynomial of $f_1$, $f_2$, $f_3$, $f_4$ and $\log K_0$, and therefore $\log K_0$ in each mixed solvent can be obtained. Table V summarizes the results concerning thermodynamic stability constants, $\log K_0^P$, together with the sum of square-error, R.

TABLE V
Thermodynamic stability constants for $CuSO_4$ in mixed solvents.

| Organic Solvent | wt% (org.) | X | D | $\log K_o^P$ | $\log K_o^v$ | R ($\times 10^2$) | S ($\times 10^2$) | r |
|---|---|---|---|---|---|---|---|---|
| | 0.00 | 0.0000 | 78.54 | 2.24 | 2.17 | 7.22 | 12.1 | 0.98 |
| | 5.00 | 0.0202 | 75.74 | 2.38 | 2.37 | 3.75 | 10.6 | 0.96 |
| ethanol | 10.00 | 0.0416 | 72.80 | 2.52 | 2.50 | 5.31 | 8.15 | 0.98 |
| | 15.00 | 0.0646 | 69.82 | 2.69 | 2.64 | 2.59 | 6.21 | 0.99 |
| | 20.00 | 0.0891 | 67.00 | 2.86 | 2.80 | 1.63 | 10.1 | 0.96 |
| | 5.00 | 0.0155 | 74.95 | 2.40 | 2.34 | 7.22 | 41.4 | 0.89 |
| | 10.00 | 0.0322 | 71.40 | 2.57 | 2.52 | 12.4 | 12.2 | 0.93 |
| isopropanol | 15.00 | 0.0502 | 67.74 | 2.69 | 2.70 | 4.18 | 6.76 | 0.98 |
| | 20.00 | 0.0697 | 64.10 | 2.89 | 2.91 | 0.673 | 2.92 | 0.99 |
| | 25.00 | 0.0908 | 60.52 | 3.01 | 3.03 | 0.426 | 0.77 | 0.98 |
| | 5.00 | 0.0106 | 74.10 | 2.33 | 2.42 | 42.8 | 44.3 | 0.74 |
| | 10.00 | 0.0222 | 69.69 | 2.47 | 2.58 | 82.9 | 10.8 | 0.98 |
| dioxane | 15.00 | 0.0348 | 65.23 | 2.58 | 2.68 | 0.527 | 14.8 | 0.85 |
| | 20.00 | 0.0486 | 60.79 | 2.85 | 2.94 | 6.81 | 41.0 | 0.56 |
| | 25.00 | 0.0638 | 56.36 | 3.08 | 3.19 | 3.21 | 23.3 | 0.94 |

To compare the method based on Pitzer's theory with the traditional method based on the extended Debye–Hückel equation, the thermodynamic stability constants, $\log K^u{}_0$, were calculated by using the method of Vasil'ev,[2] as follows

$$\log K_1 - (A\Delta Z^2 I^{1/2}) / (1 + B_a I^2) = \log K_0 + bI \qquad (21)$$

where $A = (2\pi N/1000)^{1/2}.(e^2/(2.303k^{3/2})\}\{1/[(DT)^{3/2}]\} = 1.8246 \times 10^6/(DT)^{3/2}$ $mol^{-1/2}\,dm^{3/2}\,K^{3/2}$ and where b is a constant independent of I (on the suggestion of Vasil'ev $Ba = 1.6$ $mole^{-1/2}\,dm^{-3/2}$). A plot of the quantity on the left side of equation (*21*) against I should be linear with intercept $\log K_0^u$. The thermodynamic stability constants, $\log K_0^u$, obtained by using the Vasil'ev method are also listed in Table V, in which r is the correlation coefficient and s is the sum of square-error.

The results in Table V show that the thermodynamic stability constants obtained by using the methods of Vasil'ev based on the extended Debye–Hückel equation and by the polynomial approximation based on Pitzer's theory are in approximate agreement and s resulting from the Vasil'ev method is larger than R resulting from Pitzer's method. The latter is thus a better method to estimate the thermodynamic stability constants.

At the same time, we compare our results in aqueous solution with others in the literature. The value of $\log K^u{}_0$ (2.17) obtained by the Vasil'ev method is equal to the value (2.17) reported by Liu Qi Tao[17] under the same conditions. The log $K^P_0$ value in the same system calculated with Pitzer's method was 2.24, which is more consistent with other literature values (2.26–2.37).[18–23] The result shows that the method used to determine the thermodynamic stability constants for the system in mixed solvents by the polynomial approximation on the basis of Pitzer's theory is more accurate than the Vasil'ev method.

### *Free energy of transfer*

The results in Table V show that log $K_o$ increases with increasing mole fraction of the organic solvent, X, and the reciprocal of dielectric constant, 1/D, in mixed solvents. This means that the organic solvents in the media are favourable for increasing the thermodynamic stability of the complex. The decrease in dielectric constant of the reaction medium enhances electrostatic forces between oppositely charged ions and thus facilitates the formation of neutral molecular species. From the data, plots of $\log (K_o/K_o^*)$ against the mole fraction, X, of the organic solvent or $(1/D_s - 1/D_H)$ give straight lines for each organic-water mixture over the entire region studied, and the linear correlation coefficients are greater than 0.99;

$$\log (K_o/K_o^*) = k_x X \qquad (22)$$

$$\log (K_o/K_o^*) = k_D(1/D_s - 1/D_H) \qquad (23)$$

where the subscripts s and w mean mixed solvent and pure water, $k_x$ and $k_D$ are empirical constants independent of X and D, and $K_o$ and $K_o^*$ are thermodynamic stability constants for the complex in pure water and in mixed solvents, respectively.

The difference between the standard free energy change for the complex reaction in mixed solvent and in pure water is defined as the standard free energy of transfer for the complex reaction, (*24*).

$$\Delta G^\circ_{tr} = RT \ln(K_o/K_o^*) \qquad (24)$$

The free energy of transfer for a complex reaction is the sum of the free energy of transfer for each species involved in the complex reaction. Formally, the free energy of transfer for an electrolyte is the sum of free energy of transfer of the separate ions. The free energy of transfer for neutral species and for neutral ion combinations can be derived by rigorous thermodynamic methods. From the data in Table V, the free energy of transfer for the complex reaction, $\Delta G^\circ_{tr}$, calculated with equation (*24*) are listed in Table VI. All values of $\Delta G^\circ_{tr}$ are negative and they become more negative with increasing organic solvent component.

The free energy of transfer for neutral species and for neutral ion combinations is the difference of their solvation free energy in the mixed solvents and in pure water. $\Delta G^\circ_{tr}$ values consist of two parts, electrostatic and non-electrostatic, which are represented by $\Delta G^\circ_{tr,e}$ and $\Delta G^\circ_{tr,n}$, respectively.

$$\Delta G^\circ_{tr} = \Delta G^\circ_{tr,e} + \Delta G^\circ_{tr,n} \qquad (25)$$

The electrostatic part can be calculated on the basis of the concentric continua model proposed by Beveridge.[24] The electrostatic free energy of solvation of an ion has been calculated by using the model in which an ion of radius a and dielectric constant

TABLE VI

Standard free energy of transfer for the coordination reaction.

| organic solvent | wt% (org.) | $\Delta G^\circ_{tr}$/ kJ mol$^{-1}$ | $\Delta G^\circ_{tr,e}$/ kJ mol$^{-1}$ | $\Delta G^\circ_{tr,n}$/ kJ mol$^{-1}$ |
|---|---|---|---|---|
| ethanol | 0.00 | 0.00 | 0.00 | 0.00 |
| | 5.00 | −0.799 | −0.865 | 0.066 |
| | 10.00 | −1.60 | −1.85 | 0.25 |
| | 15.00 | −2.57 | −2.92 | 0.35 |
| | 20.00 | −3.54 | −4.03 | 0.49 |
| isopropanol | 5.00 | −0.913 | −1.12 | 0.21 |
| | 10.00 | −1.88 | −2.34 | 0.46 |
| | 15.00 | −2.57 | −3.73 | 1.15 |
| | 20.00 | −3.71 | −5.27 | 1.56 |
| | 25.00 | −4.40 | −6.97 | 2.57 |
| dioxane | 5.00 | −0.514 | −1.40 | 0.82 |
| | 10.00 | −1.31 | −2.97 | 1.67 |
| | 15.00 | −1.94 | −4.78 | 2.84 |
| | 20.00 | −3.48 | −6.83 | 3.35 |
| | 25.00 | −4.80 | −9.21 | 4.41 |

$\varepsilon_1 = 1$ is surrounded by a solvent layer of thickness (b–a) and dielectric constant $\varepsilon_1 = 2$ and immersed in the bulk solvent of dielectric constant $\varepsilon_o$. We restate an equation derived by Beveridge and Schnuelle as follows.

$$\Delta G^\circ_e = (1/2)\Sigma_{n=o}\{[(n+1)(1-\varepsilon'_a)(Q_n/a^{2n+1})]/[(n+1)\varepsilon'_a + n]$$
$$+ (n+1)(1-\varepsilon_b)[1-n(1-\varepsilon'_a)/\{(n+1)\varepsilon'_a + n\}](Q_n/b^{2n+1})/[(n+1)\varepsilon_b + n]\} \quad (26)$$

$$\varepsilon'_a = \varepsilon_a\{1 + [(n+1)(1-\varepsilon_a)(1-\varepsilon_b)a^{2n+1}]/[\{(n+1)\varepsilon_b + n\}b^{2n+1}]\}^{-1} \quad (27)$$

The terms $\varepsilon_a = \varepsilon_1/\varepsilon_1$ and $\varepsilon_b = \varepsilon_o\varepsilon_1$, so that for the usual case in which $\varepsilon_1$ is set equal to unity, $\varepsilon_a = \varepsilon_1$. Since $\varepsilon_1 = 2$ for many nonaqueous solvents, we set for all solvents $\varepsilon_1 = 2$ as a fixed value. The first term in equation (*26*), n = 0, corresponds to the ion charging energy, and the higher term, n = 1, corresponds to dipole polarisation.

For n = 0, $Q_o = Z^2$ where Z is the charge on the ion. In this paper we consider only $Cu^{2+}$ and $SO_4{}^{2-}$ ions, so that $Q_o = 4$. The equations (*26*) and (*27*) lead to (*28*).

$$\Delta G^\circ_{e,i} = (Q_o/4)\{2/(b\varepsilon_o) - 1/a - 1/b\} \quad (28)$$

For n = 1, $Q_1 = \mu^2$, where $\mu$ is the dipole moment of the complex $CuSO_4$. From equations (*26*) and (*27*) we derive (*29*) and (*30*).

$$\Delta G^\circ_{e,d} = (Q_1/2)\{[2(1-\varepsilon'_a)]/[2\varepsilon'_a + 1)a^3]$$
$$+ [(2-\varepsilon_o)\{1-(1-\varepsilon'_a)/(2\varepsilon'_a + 1)\}]/[(\varepsilon_o + 1)b^3] \quad (29)$$

$$\varepsilon'_a = 2[1 + \{(\varepsilon_o - 2)a^3\}/\{(\varepsilon_o + 1)b^3\}] \quad (30)$$

The subscripts i and d in the above equations represent the ion and dipole, respectively. The thickness of the first solvent layer, (b – a), is quite close to the radius of a solvent molecule. In mixed solvents, as in our investigation, the molecules in the first solvation layer are assumed to be only water molecules; thus (b – a) is the radius of the water molecule, $r_w = 1.45$ Å.[25] The terms $a^+$ and $a^-$ are ionic crystal radii of $Cu^{2+}$ and $SO_4^{2-}$, taken as 0.72 Å[14] and 2.58 Å,[26] respectively. The radii a and b remain to be fixed in various mixed solvents; $a_2$ is the centre-to-centre distance between $Cu^{2+}$ and $SO_4^{2-}$ in the complex $CuSO_4$, and can be estimated by using the sum of ionic crystal radii of $Cu^{2+}$ and $SO_4^{2-}$. Hence, in mixed solvents, *viz* ethanol–water, isopropanol–water and dioxane–water, $a_2$ is fixed at 3.30 Å.

From the definition of free energy of transfer, the electrostatic part of the free energy of transfer for ion and dipole, $\Delta G°_{tr,i}$ and $\Delta G°_{tr,d}$, can be calculated by using equations (*28*) and (*29*) for free energy of solvation for ion and dipole, respectively. Thus, the electrostatic part of the free energy of transfer for the complex can be obtained and results are given in Table VI. From free energy of transfer for the complex reaction and its electrostatic part the non-electrostatic part of the complex reaction, $\Delta G°_{tr,n}$, can be calculated, and obtained results are also listed in Table VI. No adjustable parameters are used in the calculation, which requires only a knowledge of the solvent bulk dielectric constant, and the method has considerable predictive power. We conclude that since the thermodynamic stability constants for the complex $CuSO_4$ increase with increasing organic component in mixed solvents, this is simply a result of increased electrostatic action.

## REFERENCES

1. C.W. Davies, "Ion Association," (Butterworths, London, 1962).
2. V.P. Vasil'ev, *Zhur. Neorg. Khim.*, 7, 1788 (1962).
3. K.S. Pitzer, *J. Phys. Chem.*, 77, 268 (1973).
4. A.R. Gupta, *J. Phys. Chem.*, 83, 2986 (1979).
5. K. Donald, S.P. Khoo and C.C. Yan, *J. Solution Chem.*, 14, 635 (1985).
6. Liang Chunyu, Yang Jiazhen and Liu Qitao, *Acta Chimica Sinica, (Chinese Edition)*, 39, 837 (1981).
7. Liang Chunyu, Yang Jiazhen, Liu Qitao and Yang Xiaoqiu, *Acta Chimica Sinica*, 45, 26 (1987).
8. Liang Chunyu, Yang Jiazhen, Liu Qitao and Chen Zeihua, *inorg. Chem., (Chinese Edition)*, 3, 24 (1987).
9. A. Weissberger, "Technique of Organic Chemistry," (Wiley, New York, 1955).
10. A. Dadgar, D. Khorsandl and G. Atkinson, *J. Phys. Chem.*, 86, 3829 (1982).
11. K.S. Pitzer and G. Mayorga, *J. Phys. Chem.*, 77, 2300 (1973).
12. K.S. Pitzer and J.J. Kim, *J. Am. Chem. Soc.*, 96, 5701 (1974).
13. D. Jannakoudakis, G. Papanastasion and P.G. Mavridis, *J. Chim. Phys.*, 73, 156 (1976).
14. Handbook of Chemistry and Physics, ed. R.C. Weast, 63rd ed., (CRC., Boca Roton, Florida, 1983).
15. G. Akerlof, *J. Am. Chem. Soc.*, 54, 52 (1932).
16. V.P. Vasil'ev, *Zhur. Neorg. Khim.*, 22, 1160 (1977).
17. Liu Qitao and Yang Ming, *Acta Chimica Sinica, (Chinese Edition)*, 43, 126 (1985).
18. G.W. Davies, R.J. Otter and J.E. Prue, *Diss. Faraday Soc.*, 24, 103 (1957).
19. G. Atkinson, M. Yokoi and C.J. Hallada, *ibid.*, 83, 1570 (1961).
20. R.A. Matheson, *J. Phys. Chem.*, 69, 1537 (1965).
21. P.A.H. Izatt, D. Eatough, J.J. Christenser and C.H. Bartholomew, *J. Chem. Soc.*, 47 (1969).
22. P.A.H. Izatt, *Trans. Faraday Soc.*, 47, 656 (1951).
23. B.B. Owen and R.W. Gurry, *J. Amer. Chem. Soc.*, 60, 307 (1938).
24. D.L. Beveridge and G.W. Schnuelle, *J. Phys. Chem.*, 79, 2562 (1975).
25. Huang Zhiqing, "Introduction to Theory of Electrolyte Solution," (Science Edition (China), 1983).
26. H.D. Jenkins and K.P. Thakur, *J. Chem. Educ.*, 56, 576 (1979).