THERMODYNAMIC AND RELATED STUDIES OF AQUEOUS COPPER(II) SULFATE SOLUTIONS

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This thesis is presented for the degree of Doctor of Philosophy of Murdoch University
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I declare that this thesis is my own account of my research and contains as its main content work which has not previously been submitted for a degree at any tertiary education institution.

Chandrika Akilan
Abstract

This thesis describes a systematic investigation of the thermodynamic quantities associated with the interaction between Cu$^{2+}$ and SO$_4^{2-}$ in aqueous solution. A variety of techniques including UV-Visible spectrophotometry, Cu(II) ion-selective electrode potentiometry, dielectric relaxation spectroscopy and titration calorimetry have been used.

The values for the CuSO$_4^0$(aq) association constants determined by UV-Vis spectrophotometry in NaClO$_4$ media as a function of ionic strength were in good agreement with published data but were lower than the values obtained from Cu(II) ion-selective electrode potentiometry. The source of this difference was traced to the presence of solvent-separated ion pairs which are only partially detected by UV-Vis spectrophotometry. This was shown by a detailed investigation of CuSO$_4$(aq) over a wide range of concentrations using modern broad-band dielectric relaxation spectroscopy (DRS). This technique revealed the presence of three ion-pair types: double solvent-separated, solvent-shared and contact ion pairs.

Calorimetric titrations using the log $K_A$ values determined by potentiometry, have provided for the first time reliable values for the enthalpy and entropy changes associated with complex formation between Cu$^{2+}$(aq) and SO$_4^{2-}$(aq) system over range of ionic strengths (in NaClO$_4$ media). These data were fitted to a specific ion interaction model to obtain the standard state value which was in excellent agreement with the values obtained in other studies and from the DRS work in this study.

In addition, investigations have been carried out into the physicochemical properties, (osmotic coefficients, densities, heat capacities, solubilities and viscosities) of ternary mixtures of CuSO$_4$(aq) with Na$_2$SO$_4$(aq) or MgSO$_4$(aq). The isopiestic measurements (water activities) of the mixtures were in general well described by Zdanovskii’s rule,
especially for the mixtures of CuSO$_4$ with MgSO$_4$. The densities of the ternary mixtures of CuSO$_4$ with MgSO$_4$ were found to follow Young’s rule of mixing but those of CuSO$_4$ with Na$_2$SO$_4$ deviated from linearity. The solubilities of the salts in their ternary mixtures agree well with literature data and show that the solubility of MgSO$_4$ or CuSO$_4$ decreases with increasing Na$_2$SO$_4$ concentration. The viscosities of all the ternary mixtures show clear negative departures from 'Young’s rule' type behaviour.
Publications

The following publications have arisen from work completed by the candidate for the present thesis.


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Abbreviations and symbols

\( a \)  activity of the solute
\( \dot{a} \)  mean distance of the closest approach of the ions
\( A \)  Debye-Hückel constant
\( A \)  absorbance
\( A_L \)  Debye-Hückel parameter for enthalpies
\( \text{Å} \)  angstrom \((10^{-10} \text{ m})\)
\( \text{AMD} \)  acid mine drainage
\( \text{aq} \)  aqueous
\( \text{AR} \)  analytical reagent
\( \alpha \)  polarisability
\( B \)  second Debye-Hückel constant
\( \alpha, \beta \)  empirical exponents for Equation 4.8
\( b \)  cell path-length
\( \text{BL} \)  Beer-Lambert law
\( B, C, D \)  adjustable parameters
\( c \)  concentration
\( c_i \)  concentration of the species i
\( ca. \)  circa
\( \text{cal} \)  calorimetry
\( \text{CIP} \)  contact ion-pair
\( {^\circ}\text{C} \)  degrees Celsius
\( c_{\text{app}} \)  apparent water concentration
\( c_i^\circ \)  analytical (total) concentration of water
\( c_p \)  heat capacity
\( C_{\text{pp}} \)  apparent molar heat capacities
\( \text{CN}_{\text{+}}, \text{CN}_{\text{-}} \)  sum of the first-shell coordination numbers
\( \text{Cu}^{2+}\text{-ISE} \)  copper ion selective electrode
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>3D</td>
<td>three Debye</td>
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<tr>
<td>D-H</td>
<td>Debye-Hückel</td>
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<td>DRS</td>
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<tr>
<td>$\Delta H^o$</td>
<td>standard enthalpy change</td>
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<td>potentials of any liquid junctions</td>
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$I$ ionic strength
IP ion-pair
ISE ion-selective electrode
$I_T, I_I$ monochromatic radiant power transmitted by, and incident upon, the medium.
k kilo-, $10^3$ (as in kg)
k Boltzmann constant
κ conductivity
κ_e effective conductivity
$K_A$ overall ion association constant
$K_A^o$ standard ion association constant
$K_1, K_2, K_3$ stepwise association constants
$K_{out}$ outer sphere complex
$K_{in}$ inner sphere complex
λ wavelength
$L_1$ relative partial molar enthalpy of water
l length of the constant-bore capillary
L litre (cubic decimeter, dm$^3$)
$L^{a-}$ anion
ln natural logarithm
LJP liquid junction potential
M molar (mol/L solution)
$M^{m+}$ cation
m milli-, $10^{-3}$ (as in mL)
m metre
m molal (mol/kg solvent)
MHg mercury amalgam electrode
$m^*, m'_i$ equilibrium molalities of the reference and sample
mol mole
n general number
n  Number of electrons involved in the electrochemical reaction

$N$  total number of titration points

$N_A$  Avogadro’s number

$n_e$  number of parameters to be optimised

$N_{lc}$  number of ligands specified in the SPECFIT model

$n_p$  total number of electrodes

$\eta$  viscosity

OBJE  objective function

$p$  indicates negative log (as in pH, pK)

$p$  number of metal ions present in a particular species

$p$  Pico-, $10^{-12}$ (as in ps)

$Pa$  pascal

$pH$  $\log[-H^+]$

$ppm$  parts per million

PTFE  polycrystalline ethylene

$\pi$  pi constant: 3.14159

$\phi^*, \phi$  osmotic coefficients of the reference and the mixed-electrolyte solution

$\bar{P}(t)$  time-dependent electric polarization

$\bar{P}_{i*,}$  orientational polarization

$\bar{P}_a$  induced polarization

$q$  arbitrary distance

$Q_c$  heat of complexation

$Q_r$  heats of reaction

$Q_d$  heats of dilution

$r$  ionic radius

$r$  number of moles of water

$r^2$  correlation coefficient

$R$  universal gas constant ($8.314 \, \text{J} \, \text{K}^{-1} \, \text{mol}^{-1}$)
$r$ radius of the constant-bore capillary

$\sigma$ experimental standard deviation

$\rho, \rho_0$ density of an electrolyte solution, and the pure solvent

SIP solvent-shared ion-pair

$\sigma_p$ standard deviation

2SIP double solvent-separated ion-pair

SIT specific ion interaction theory

$S_j$ Dispersion amplitude

$s$ second

(s) solid

Sol solubility

$s^2$ variance

SD standard deviation

$T$ thermodynamic temperature (in Kelvin, K)

t Temperature (in Celsius, °C)

$\tau$ dielectric relaxation time

$\mu$ Micro-, $10^{-6}$ (as in µm)

$\tau^2$ vibration period of the tube

$\mu$ dipole moment

$\mu$ chemical potential of a solute

$\mu^0$ standard potential of a solute

$\mu_{IP}$ dipole moments

$U$ objective function

$V$ volt

$\bar{V}$ Partial molal volume

$V$ total volume

VNA vector network analyser

$v$ frequency

$V_\phi$ apparent molal volumes

$v^*, v_i$ stoichiometric ionization numbers
\( \omega \) field frequency
\( W \) watts
\( w \) mass
\( W_o \) baseline power applied to the cells
\([X]\) concentration of species X
\( y_i \) ionic strength fraction
\( z_i \) charge on species i
\( z_+ \) charge number of the cation
\( z_- \) charge number of the anion
\( Z_{IB} \) effective solvation number