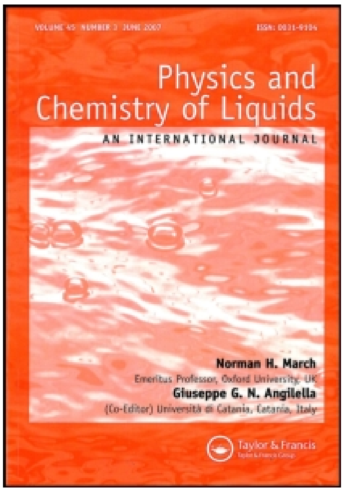

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Ion-Solvation Studies of Some Substituted Copper(II) Benzoates in Water-DMSO Mixtures

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ION-SOLVATION STUDIES OF SOME SUBSTITUTED COPPER(II) BENZOATES IN WATER—DMSO MIXTURES

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The preferential solvation of some substituted copper(II) benzoates viz *p*-CH_3, *p*-NO_2 and *o*-OH copper(II) benzoates was investigated in water—DMSO mixtures at 30°C by Gibbs transfer energy and solvent transport number measurements. While the standard Gibbs energy of transfer of copper(II) ion is negative and decreases with the addition of DMSO, the transfer energies of the anions are positive and increase under the same conditions. The solvent transport number, Δ_{DMSO}, for all salts is positive and passes through a maximum with Δ_{max} = ranging from about 1.5 to 2.0 around $X_{DMSO} = 0.35$. These results were interpreted in terms of the selective solvation of copper(II) ion with DMSO and the anions by water.

KEY WORDS: Substituted copper(II) salts, water—DMSO mixtures, solvent transport measurements.

Selective solvation of ions by the components of a binary solvent mixture profoundly affects[1,2] many physico-chemical phenomena such as solubilities, phase separation in partially miscible systems, redox behaviour, rates of reactions etc. It is also of potential technological value[3] in areas such as electrodeposition, electrorefining, choice of suitable electrolyte—solvent combination in non-aqueous high energy density batteries[4]. In earlier investigations from this laboratory, the preferential solvation of a number of silver(I) salts in several binary solvent mixtures was investigated and the present status in this field has been recently reviewed[5]. However, such investigations involving multivalent unsymmetrical electrolytes is scarce[6–8] and the present work deals with the solvation behaviour of some substituted copper(II) benzoates in water—DMSO mixtures at 30°C in order to compare the results with the unsubstituted salts and thereby to understand the effect of substituents on the ion solvation.

EXPERIMENTAL AND RESULTS

a) Materials

Anhydrous copper(II) *p*-methyl and *p*-nitro benzoates were prepared following the procedure of Lewis[9]. Hydrated copper(II) salicylate was prepared by a procedure similar to that of copper(II) benzoate and dried in the same way.

Dimethylsulphoxide (B.D.H., L.R.) was purified as described earlier[6]. Conductivity water, prepared as described previously[6] was used in the preparation of water—DMSO mixtures.

Tetraethylammonium picrate, used as bridge electroyte in EMF measurements was prepared by neutralisation of tetraethyl ammonium hydroxide with a methanolic solution of picric acid. The resultant product was twice recrystallised from methanol.

b) *Electrodes*

Copper electrodes were prepared by electrolytically depositing copper onto platinum spiral electrodes according to the procedure of Blokhra *et al.*[10] The coated electrodes were washed with conductivity water and preserved in a solution of neutral copper(II) sulphate. Only freshly prepared bright copper electrodes whose bias potentials were less than ± 0.5 mV were used in all EMF measurements.

A Keithley solid state electrometer (Model 602, Keithley Instruments, Germany) having an input impedance greater than $10^{14}\ \Omega$ was used in all EMF measurements. The EMF values were often cross checked with a Philips rms digital multimeter.

c) *Solubility measurements*

The method of preparation of saturated solutions of the salts in the various solvent mixtures has been described previously[11]. The analysis of the saturated solutions was performed by two methods. For fairly soluble salts, UV-Visible spectrophotometry (PMQ II Carl Zeiss spectrophotometer, Germany) was adopted. The method involves the displacement of copper from the saturated solution by addition of zinc powder, dissolving the copper in few drops of conc HNO_3, removing the excess acid by addition of urea and forming the blue copper-ammonia complex by addition of ammonia. The absorbance of this complex was measured at 625 nm (λ_{max}). In the case of slightly soluble salts the solubility was determined by atomic absorption spectrometry (Varian spectra AA 20, air-acetylene flame, $\lambda_{max} = 218.2$ nm) using a calibration graph with standard copper(II) sulphate solutions whose copper content ranged from 20 ppm to 80 ppm.

d) *Solvent transport number measurements*

The solvent transport number Δ, of DMSO for all the salts was determined using a concentration cell with transference as suggested by Wagner[12]. For this purpose the cell

$$\mathrm{Cu}\left|\begin{matrix}\mathrm{CuX_2\,(satd)}\\ X'_{\mathrm{DMSO}} = 1 - X'_{\mathrm{W}}\end{matrix}\middle|\begin{matrix}\mathrm{CuX_2\,(satd)}\\ X''_{\mathrm{DMSO}} = 1 - X''_{\mathrm{W}}\end{matrix}\right|\mathrm{Cu} \qquad \mathrm{(A)}$$

was employed where $X =$ *p*-methyl, *p*-nitro or *o*-hydroxy benzoate ions was set up in which X represents the mole fraction of the solvent component in the two half cells. The cell consists of the two half cells containing saturated solutions of the respective copper(II) salts in solvent mixtures differing only slightly in composition ($X''_{\mathrm{DMSO}} - X'_{\mathrm{DMSO}} = 0.1$) which was maintained constant throughout.

The details of EMF measurements using the above cell have been described earlier[6].

e) Determination of $\Delta G_t^0(\mathrm{Cu}^{2+})$

The standard Gibbs transfer energies of copper(II) ion $\Delta G_t^0(\mathrm{Cu}^{2+})$ from the reference solvent (RS), water to the solvent mixtures of water + DMSO (S) were determined by the negligible liquid junction potential (nLJP) method of Parker *et al.*[13] using the cell

$$\mathrm{Ag}\left|\begin{matrix}\mathrm{AgClO_4(0.01\ m)}\\ \mathrm{AN}\end{matrix}\right\|\begin{matrix}\mathrm{Et_4NPic\ (0.1\ m)}\\ \mathrm{AN}\end{matrix}\left\|\begin{matrix}\mathrm{Cu(ClO_4)_2(0.01\ m)}\\ \mathrm{RS\ or\ S}\end{matrix}\right|\mathrm{Cu} \qquad \mathrm{(B)}$$

where the bridge electrolyte $\mathrm{Et_4NPic}$ is tetraethylammonium picrate and AN refers to acetonitrile, RS and S refer to water and water—DMSO mixtures respectively. All measurements were made at 30 ± 0.1°C.

DISCUSSION

The solubilities of the copper(II) salts are related to their respective thermodynamic solubility products, K_{sp} by

$$K_{\mathrm{sp}}(\mathrm{CuX_2}) = 4s^3\tau\pm^3 \qquad (1)$$

where s = solubility in mol kg^{-1} of the solvent and $\tau\pm$ is the mean molal activity coefficient of the salt under consideration. It was calculated from the extended Debye–Huckel equation

$$-\log \tau\pm = \frac{AZ_+Z_-\sqrt{\mu}}{1 + aB\sqrt{\mu}} \qquad (2)$$

where A and B are the Debye–Huckel constants, μ is the ionic strength of the solution and "a" refers to the ion size parameter with a = 13 Å for copper(II) *p*-methyl and *p*-nitro benzoate and a = 12 Å for copper(II) salicylate[14]. The standard Gibbs energy of transfer of the salts was calculated from

$$\Delta G_t^0(\mathrm{salt}) = -RT \ln \frac{K_{\mathrm{sp}}(S)}{K_{\mathrm{sp}}(RS)} \qquad (3)$$

where S and RS have the significance already mentioned earlier. The standard Gibbs energy of transfer of Cu^{2+} ion $\Delta G_t^0(\mathrm{Cu}^{2+})$, from water to water—DMSO mixtures was calculated from the equation

$$\Delta G_t^0(\mathrm{Cu}^{2+}) = 2F(E_S - E_{RS}) - RT \ln \frac{{}^{a}\mathrm{Cu}^{2+}(S)}{{}^{a}\mathrm{Cu}^{2+}(RS)} \tag{4}$$

where E_S and E_{RS} are the EMF's of the cell B and ${}^{a}\mathrm{Cu}^{2+}$ is the activity of Cu^{2+} ion in water + DMSO mixtures and water respectively.

The transfer energies of the anions were calculated from

$$\Delta G_t^0(X^-) = [\Delta G_t^0(\mathrm{CuX}_2) - \Delta G_t^0(\mathrm{Cu}^{2+})]/2 \tag{5}$$

(where $X = p$-CH_3, p-NO_2, o-OH benzoate ions)

The solubility (s) and solubility product (K_{sp}) of the salts at 30°C are given in Table 1. The dielectric constants of water—DMSO mixtures required for calculating the mean molal activity coefficient of the salts were taken from literature[6].

The transfer energies of the salts, copper(II) and various substituted benzoate ions are given in Table 2. Their variation with solvent composition is shown in Figure 1. The values given in brackets are those calculated by correcting for ion association of the salts by applying the Fuoss equation[15]. A comparison of the experimental ΔG_t^0 and those calculated as above, shows that the difference between them for any salt at a given composition does not exceed 4 kJ mol^{-1} and furthermore they are negative and thus do not alter the general conclusions as will be seen later. It is thus clear that the ion association of the salts has no effect on the conclusions based on transfer energy results.

It is seen (Table 1) that the solubility of p-NO_2 and o-OH substituted benzoates increases continuously with the addition of DMSO similar to that of unsubstituted salt viz copper(II) benzoate[6] while in the case of p-CH_3 copper(II) benzoate the solubility passes through a maximum at $X_{\mathrm{DMSO}} = 0.4$ and subsequently decreases. Thus, while the transfer energies of the former two salts decrease continuously, the ΔG_t^0 of p-CH_3 copper(II) benzoate decreases upto $X_{\mathrm{DMSO}} = 0.4$ and then increases. However, ΔG_t^0 of the salts is negative in all mixtures indicating that their transfer from water to water—DMSO mixtures is thermodynamically favoured.

The standard Gibbs energy of transfer of Cu^{2+} ion, ΔG_t^0 (Cu^{2+}) is negative and decreases continuously (Table 2) with the addition of DMSO which indicates that its transfer from water to water—DMSO mixtures is thermodynamically favoured. This suggests that copper(II) ion is preferentially solvated by DMSO in water—DMSO mixtures. The specific copper(II)—DMSO interactions arise from its higher charge density, hard nature and co-ordination capacity. Also, the donicity and hence the basicity of DMSO is greater than that of water. The incomplete d-orbitals of copper(II) ion make it possible for the formation of crystal field stabilised mixed complexes which are entropically and enthalpically stable[16]. The preferential solvation of copper(II) ion by DMSO is marked between $X_{\mathrm{DMSO}} = 0.3$ and $X_{\mathrm{DMSO}} = 0.7$ which is characterised by considerable changes in the slope $d\Delta G_t^0(\mathrm{Cu}^{2+})/dX_{\mathrm{DMSO}}$ in the region. The relatively small variation in $\Delta G_t^0(\mathrm{Cu}^{2+})$ with X_{DMSO} subsequently (at

Table 1 Solubilities *s* and solubility products $_pK_{sp}$ of copper(II) *p*-methyl benzoate, *p*-nitro benzoate and *o*-hydroxy benzoate in water—DMSO mixtures at 30°C.

X_{DMSO}	D^a	$Cu(p\text{-}CH_3C_6H_4COO)_2$		$Cu(p\text{-}NO_2C_6H_4COO)_2$		$Cu(o\text{-}OHC_6H_4COO)_2$	
		$10^2\ s^b$	$_pK_{sp}$	$10^3\ s^b$	$_pK_{sp}$	$10^2\ s^b$	$_pK_{sp}$
0.0	76.8	0.617	6.29	0.747	8.90	3.054	4.37
0.1	74.8	3.55	4.18	3.80	6.89	4.17	4.01
0.2	72.4	5.02	3.78	6.06	6.33	4.52	3.93
0.3	69.5	5.58	3.67	8.05	6.01	4.60	3.93
0.4	66.3	5.79	3.66	10.09	5.76	4.87	3.89
0.5	62.8	5.76	3.70	11.43	5.63	5.29	3.83
0.6	59.4	5.49	3.80	11.55	5.65	5.71	3.78
0.7	55.9	4.98	3.96	12.26	5.62	6.22	3.73
0.8	52.5	4.23	4.20	15.42	5.38	6.90	3.66
0.9	49.3	3.24	4.57	21.09	5.07	7.59	3.61
1.0	46.0	2.01	5.17	28.90	4.75	8.14	3.53

[a] Dielectric constant; [b] Solubilities in mol kg^{-1}; accuracy, ±0.5%.

Table 2 Gibbs transfer energies (kJ mol^{-1}) of copper(II) salts and ions from water to water—DMSO mixtures at 30°C.

X_{DMSO}	ΔG_t^0						
	Cu^{2+}	$Cu(p\text{-}CH_3C_6H_4COO)_2$	$Cu(p\text{-}NO_2C_6H_4COO)_2$	$Cu(o\text{-}OHC_6H_4COO)_2$	$p\text{-}CH_3C_6H_4COO^-$	$p\text{-}NO_2C_6H_4COO^-$	$o\text{-}OHC_6H_4COO^-$
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.1	−7.1	−12.2 (−10.1)*	−11.6 (−11.2)*	−2.1 (−1.5)*	−2.6	−2.3	2.5
0.2	−12.7	−14.5	−14.9	−2.5	−1.0	−1.1	5.1
0.3	−17.9	−15.2 (−11.3)	−16.8 (−15.8)	−2.5 (−1.6)	1.4	0.6	7.7
0.4	−24.3	−15.3	−18.2	−2.7	4.5	3.0	10.8
0.5	−32.4	−15.0 (−11.4)	−18.9 (−17.4)	−3.1 (−1.6)	8.7	6.7	14.7
0.6	−41.9	−14.5	−18.8	−3.4	13.7	11.5	19.2
0.7	−48.6	−13.5 (−9.8)	−19.0 (−17.2)	−3.7 (−1.5)	17.5	14.8	22.5
0.8	−49.8	−12.2	−20.4	−4.1	18.8	14.7	22.8
0.9	−50.5	−10.0 (−6.7)	−22.2 (−19.1)	−4.4 (1.2)	20.2	14.1	23.0
1.0	−56.4	−6.5	−24.0	−4.9	25.0	16.2	25.0

* Values in the brackets are those based on calculation of association constant, K_A using Fuoss equation. Gibbs transfer energies of salt are accurate to ±0.2 kJ mol^{-1}.

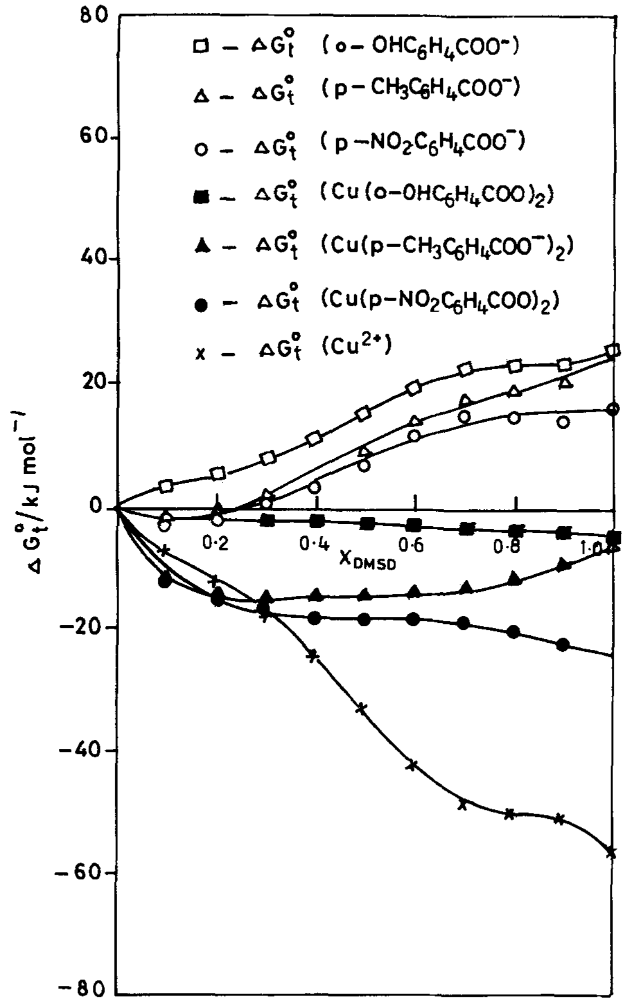

Figure 1 Standard Gibbs free energies of transfer for the various copper(II) salts and ions in water—DMSO mixtures at 30°C.

higher compositions of DMSO) suggests that the primary solvation shell of copper(II) ion is fully occupied at about $X_{\text{DMSO}} = 0.7$. Similar observations on Cu^{2+} solvation by DMSO were made by Lewandowski[17]. A comparison of the $\Delta G_t^0(Cu^{2+})$ with those of others[18] on silver(I) ion solvation shows that whereas $\Delta G_t^0(Ag^+) \approx 0.0$ kJ mol^{-1} up to $X_{\text{DMSO}} = 0.1$ in water—DMSO mixtures, $\Delta G_t^0(Cu^{2+}) = 7.0$ kJ mol^{-1} which reflects the effect of greater charge density of copper(II) ion on transfer energy values.

The transfer energies of all the anions are generally positive and increase continuously with the addition of DMSO, thereby indicating a preferential solvation of these anions by water in these mixtures. However, in the case of p-CH_3 and p-NO_2

copper(II) benzoates the ΔG_t^0's are small and negative up to $X_{\text{DMSO}} = 0.2$ and thereafter steadily increase. This indicates that in this water rich region, the water—DMSO interactions are slightly stronger than the anion-water interactions.

The anion solvation is mainly governed by charge density and basicity of the anion as the oxyanions normally interact with protic solvents like water through H-bonding and ion-dipole forces[19]. Comparison of ΔG_t^0 values of the various anions together with that of unsubstituted benzoate ion ($\Delta G_t^0 = 25.0\ \text{kJ mol}^{-1}$)[6] shows that the preferential hydration of the anions for transfer from pure water to pure DMSO is in the order,

$$o\text{-OHC}_6\text{H}_5\text{COO}^- > \text{C}_6\text{H}_5\text{COO}^- \approx p\text{-CH}_3\text{C}_6\text{H}_5\text{COO}^- > p\text{-NO}_2\text{C}_6\text{H}_5\text{COO}^-.$$

While the o-OH and p-CH_3 copper(II) benzoate anions do not exhibit any significant substituent effect vis a vis the unsubstituted benzoate anion, the ΔG_t^0 difference between p-NO_2 copper(II) benzoate ion and that of benzoate ion is large i.e. about $9.0\ \text{kJ mol}^{-1}$. Presumably, this arises as a result of the electron withdrawing nature of —NO_2 group making the H-bonded interactions between this anion and water weaker so that its transfer to DMSO is more easily facilitated compared to benzoate ion.

The solvent transport number, Δ, of DMSO in these mixtures was calculated from the EMF data of cell A using the relation

$$E = -\frac{RT}{F}\,\frac{X''_{\text{DMSO}} - X'_{\text{DMSO}}}{X_{\text{DMSO}}(1 - X_{\text{DMSO}})}\cdot\Delta\cdot\left(1 + \frac{d\ln f_{\text{DMSO}}}{d\ln X_{\text{DMSO}}}\right) \tag{6}$$

where the various terms have their usual significance[19]. The activity coefficient term in Eq. (6) accounts for the deviation of the solvent mixtures from ideal behaviour and has been calculated using the vapour pressure data of Cox and Mctigue[20].

The solvent transport numbers calculated as above for the different salts are given in Table 3 and their variation with solvent composition is shown in Figure 2. It is

Table 3 EMF data and solvent transport number of DMSO for copper(II) salts in water—DMSO mixtures at 30°C.

X_{DMSO}	$\frac{d \ln f_{DMSO}}{d \ln X_{DMSO}}$	$Cu(p\text{-}CH_3C_6H_4COO)_2$		$Cu(p\text{-}NO_2C_6H_4COO)_2$		$Cu(o\text{-}OHC_6H_4COO)_2$	
		−E (mV)	Δ	−E (mV)	Δ	−E (mV)	Δ
0.05	0.175	—	—	—	—	5.0 ± 0.5	0.07 ± 0.01
0.15	0.245	6.5 ± 1.0	0.25 ± 0.02	7.5 ± 0.5	0.29 ± 0.02	9.3 ± 0.5	0.36 ± 0.02
0.25	0.365	20.4 ± 0.5	1.07 ± 0.02	11.0 ± 1.0	0.58 ± 0.06	12.0 ± 1.0	0.63 ± 0.05
0.35	0.515	25.2 ± 0.5	1.45 ± 0.03	35.0 ± 0.5	2.01 ± 0.02	26.0 ± 0.5	1.49 ± 0.03
0.45	0.705	24.0 ± 1.0	1.33 ± 0.05	10.5 ± 0.5	0.58 ± 0.05	17.5 ± 0.5	0.97 ± 0.03
0.55	0.920	12.0 ± 0.5	0.59 ± 0.02	14.0 ± 1.0	0.69 ± 0.05	13.5 ± 0.5	0.65 ± 0.03
0.65	1.155	—	—	9.0 ± 0.5	0.36 ± 0.02	—	—
0.75	1.235	7.5 ± 0.5	0.24 ± 0.01	12.8 ± 0.5	0.41 ± 0.01	4.5 ± 0.5	0.14 ± 0.02
0.85	1.235	15.0 ± 1.0	0.33 ± 0.01	7.8 ± 0.5	0.17 ± 0.01	6.4 ± 0.5	0.14 ± 0.02
0.95	1.235	12.0 ± 0.5	0.19 ± 0.02	4.0 ± 1.0	0.03 ± 0.00	10.4 ± 1.0	0.08 ± 0.00

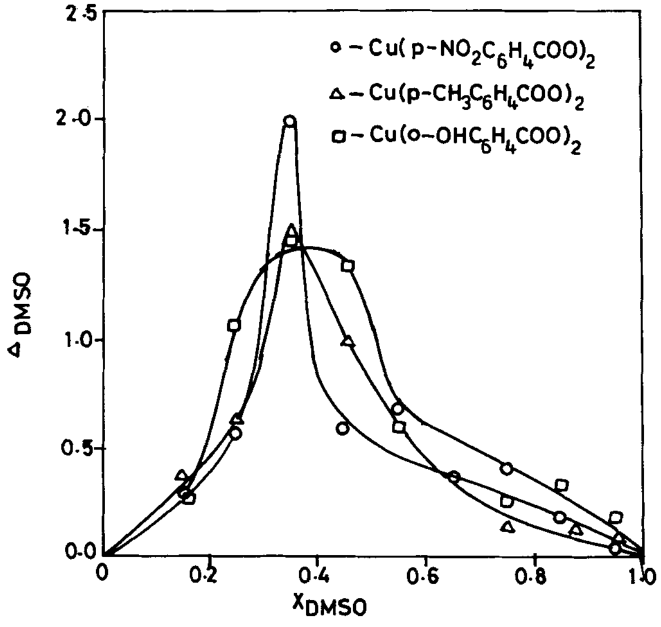

Figure 2 Solvent transport number of DMSO, Δ_{DMSO} for the various copper(II) salts in water—DMSO mixtures at 30°C.

seen that the values for all the salts are positive and pass through a maximum viz $\Delta_{\max} = 1.45$, for copper(II) p-methyl benzoate, $\Delta_{\max} = 2.01$, for copper(II) *p*-nitro benzoate and $\Delta_{\max} = 1.49$ for copper(II) salicylate at $X_{\mathrm{DMSO}} = 0.35$ in all cases. Δ is related to the molefractions of solvent components (X's) and the solvation numbers of cations and anions (n's) according to

$$\Delta_{\mathrm{DMSO}} = (X_W n^{+2}_{\mathrm{DMSO}} - X_{\mathrm{DMSO}} n^{+2}_W) t_+/2 - (X_W n^{-}_{\mathrm{DMSO}} - X_{\mathrm{DMSO}} n^{-}_W) t_- \tag{7}$$

Generally, in the case of heteroselectively solvated salts n^{+2}_{DMSO} and n^{-}_W are large while n^{+2}_W and n^{-}_{DMSO} are small which results in large Δ values as observed in the present case. The values viz 1.45, 2.01 and 1.49 also represent the number of moles of DMSO transported into the cathode compartment when the solutions of these salts are electrolysed at $X_{\mathrm{DMSO}} = 0.35$.

The enrichment of DMSO in the cathode arises through the transport of DMSO by copper(II) ion while the anions transport water in the opposite direction i.e. towards anode. These two effects add together giving rise to large Δ values. Thus these results also support the earlier conclusion that the salts are heteroselectively solvated with Cu^{2+} being selectively solvated by DMSO and the anions by water.

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