Hence for the initial concentrations $[\mathrm{Am(III)}]_0$ and $[\mathrm{Am(VI)}]_0$ in the mixtures, the equilibrium concentrations of americium species may be calculated:

$$[\mathrm{Am(IV)}] = [\mathrm{Am(V)}] = [\mathrm{Am(III)}]_0 - [\mathrm{Am(III)}] = \Delta$$
$$[\mathrm{Am(VI)}] = [\mathrm{Am(VI)}]_0 - [\mathrm{Am(IV)}] = [\mathrm{Am(VI)}]_0 - \Delta$$

This serves to express K in the form

$$K = \frac{\Delta^2}{[\mathrm{Am(III)}]\{[\mathrm{Am(VI)}]_0 - \Delta\}}$$

The values of K for the different mixtures investigated is given in Table II. The mean constant obtained, $K = 11.20 \pm 1.5$, is consistent with the results summarized in Figure 9, and the anticipated value of K for a potential difference of 60 mV is equal to 10.

Conclusions

The possible coexistence of americium in four oxidation states in sodium bicarbonate–carbonate medium 1.2 M < $[\mathrm{HCO_3^-} + \mathrm{CO_3^{2-}}]$ < 2.3 M in the pH range from 9.5 to 10.5 is a particularly remarkable occurrence. Hitherto this property was only known for plutonium in dilute acidic medium.[17]

The difficulty of obtaining pure americium(IV) in carbonate media with the pH above 11 is not explained by the nearness of the apparent normal potentials of the two couples Am(IV)/Am(III) and Am(VI)/Am(V) but by the tendency of Am(IV) to disproportionate, experimentally observed at pH >11.5.

In fact, according to the measurements summarized in Figure 9, the difference between the potentials of the two systems increases with $\mathrm{CO_3^{2-}}$ concentration, i.e. with the pH. Contrary to what could be concluded from this reading alone, the stability of Am(VI) is greater in media with higher pH than that of Am(IV). This positively implies the involvement of a data element supplementary to that of the redox potentials of the couples investigated: the variation in potential of the couple Am(IV)/Am(V), whose dependence on pH is foreseeable, because it is related to the possibility of ionic Am(V) in the americyl form. The study of this important reaction, which has simply been touched on here, is a subject for investigation in its own right.

Registry No. Americium, 7440-35-9; disodium carbonate, 497-19-8; sodium bicarbonate, 144-55-8.

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Coordination of Copper(II) in Aqueous $\mathrm{CuSO_4}$ Solution

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Received May 28, 1982

An aqueous copper(II) sulfate solution has been examined by X-ray diffraction. The existence of a distorted arrangement of six water molecules around $\mathrm{Cu^{2+}}$ ions has been established by distribution curve inspection and direct fitting of the structure function. The structural parameters of the aquocopper(II) ion have also been determined.

Introduction

It is well-known that the d^9 electronic configuration is expected to be subjected to Jahn–Teller distortions; Cu(II) is the species for which the greatest number of distorted coordinations have been found in solid crystalline compounds. Different kinds of distortions have also been identified in $\mathrm{CuL_6}$ complexes; they can be partly ascribed to crystal-packing requirements. In the liquid phase and in solution these constraints fail, and it is therefore interesting to investigate the variety of geometries observed under these conditions.

A good example of tetragonally distorted sixfold coordination has recently been given in an X-ray diffraction study of $\mathrm{Cu(ClO_4)_2}$ aqueous solutions.[1] Four water molecules, w_{eq} (equatorial position), lie in a square-planar configuration at a distance of 1.97–1.98 Å from the central ion, and two others, w_{ax} (axial position), are placed above and below the plane at 2.34–2.39 Å.

In $\mathrm{CuCl_2}$ solutions[2] the same technique has successfully described the occupancy of equatorial sites according to the mean configuration $\mathrm{Cu(H_2O)_{2.8}Cl_{1.2}}$, although the axial positions were not unambiguously determined. This result suggests that some solvent effect may exist so that more weakly bonded ligands may prefer the stabilization due to the solvent rather than occupy the axial sites.

Difficulties in describing unequivocally the environment of Cu(II) in $\mathrm{CuCl_2}$ solutions have been confirmed by Neilson[3] in a neutron diffraction investigation carried out with the isotopic substitution technique. The existence of two different coordination distances for Cu(II)–water pairs was not evident in a neutron diffraction study[4] of copper(II) perchlorate solutions.

In order to have more data on the coordination of aqueous Cu(II), we examined by X-ray diffraction a solution of $\mathrm{CuSO_4}$. Because of the solubility limit of this salt, just one solution has been investigated, with a concentration (1.37 mol/L at 20 ± 1 °C) smaller that that used in the study[1] of $\mathrm{Cu(ClO_4)_2}$ samples.

Experimental Details, Data Treatment, and Results

The saturated solutions was prepared by dissolving crystalline $\mathrm{CuSO_4{\cdot}5H_2O}$ in doubly distilled water at 20 ± 1 °C. The copper content was determined by direct titration with standard EDTA and after cation exchange on a cationic resin (Dowex 50W-X8). The molarity turned out to be 1.375 M, and the density was 1.207 g/mL, so that the stoichiometric coefficient x in the unit $\mathrm{(CuSO_4)_x(H_2O)_{1-x}}$ had the value 0.0245.

The ϑ–ϑ X-ray diffractometer and the procedure of data collection and reduction have been previously described.[5,6]

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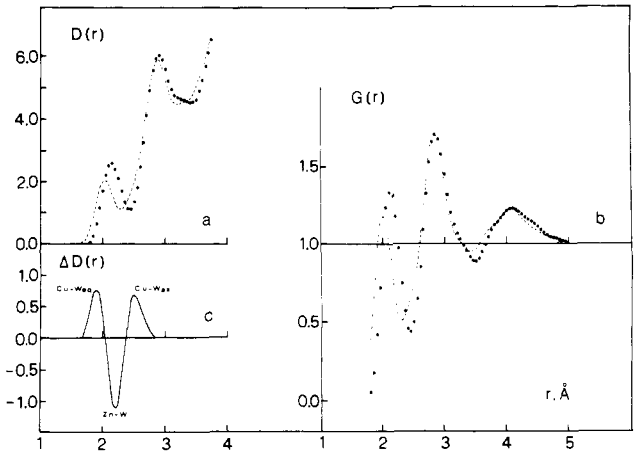

Figure 1. (a) Experimental radial distribution functions of $CuSO_4$ (---) and $ZnSO_4$ (···) solutions. (b) Experimental correlation functions of $CuSO_4$ (---) and $ZnSO_4$ (···) solutions. (c) $\Delta D(r) = D(r)_{CuSO_4} - D(r)_{ZnSO_4}$.

The radial distribution curve and the correlation function were calculated from the structurally sensitive part of the scattering data, $i(s)$, by a Fourier transformation according to

$$G(r) = \frac{D(r)}{4\pi r^2 \rho_0} = 1 + \frac{1}{2\pi^2 r \rho_0}\int_{s_{\min}}^{s_{\max}} s\, i(s)\, M(s) \sin(rs)\, ds \quad (1)$$

Here ρ_0 is the average bulk density of stoichiometric units, s is the usual scattering variable ($s = 4\pi(\sin \vartheta)/\lambda$, where ϑ is half the scattering angle and λ is the wavelength of the radiation employed, Mo $K\alpha$), $M(s)$ is a damping factor $e^{-0.005s^2}$ used to minimize the truncation errors, and $s_{\min}$ (0.65 $Å^{-1}$) and $s_{\max}$ (16.18 $Å^{-1}$) are the lower and upper limits of the experimental data.

In order to evaluate the $i(s)$ function, the fraction of incoherent radiation reaching the counter through the monochromator (the so-called discrimination function) was estimated by a customary semiempirical procedure.[5,6] The incoherent intensity is measured at high angles with use of a Zr filter and is extrapolated to the theoretical values at low angle. Systematic errors arising from imprecision in the evaluation of the incoherent intensity (as well as from uncertainties in the tabulated scattering amplitudes, caused by imperfections in diffraction geometry from double-scattering effects)[5,7] are corrected by a method based on the removal of nonphysical peaks at low r. Since this procedure is more effective if a rather extended range of distances can be used to this end, intramolecular real peaks appearing at low r (in the present case, the S–O peak at about 1.45–1.50 Å) were also removed.

$D(r)$ and $G(r)$ functions obtained in this way are shown in Figure 1a,b. The first peak position coincides with the distance $r_{Cu^{2+}-W_{eq}}$ estimated in $Cu(ClO_4)_2$ solutions[1] within the limits of experimental uncertainties. The second peak comes from the usual H_2O–H_2O distances always present in aqueous systems. Contrary to what happens in $Cu(ClO_4)_2$ solutions, in the radial curves there is no peak in correspondence with the distance $r_{Cu^{2+}-W_{ax}}$ at about 2.40 Å; only a slight enlargement near the base of the water–water peak is observable. However, this is not sufficient proof of the existence of Cu^{2+}–W_{ax} distances, since also O–O distances inside sulfate ions (O_S–O_S pairs) are expected to fall within this region.

In order to have clearer experimental indications, we compared the results reported here with those obtained (via the same data treatment) from a 1.5 M $ZnSO_4$ solution investigated[8] previously. Considering the similarity in the composition of the two solutions and in the scattering power of Zn^{2+} and Cu^{2+}, differences in their radial curves are to be ascribed to different structural behavior. The radial curves of 1.5 M $ZnSO_4$ are superimposed in Figure 1a,b on those of the $CuSO_4$ solution. It appears that the peak at 2.10 Å, which in $ZnSO_4$ solution is diagnostic of Zn^{2+}–water pairs, is higher than the peak at 2.00 Å of $CuSO_4$, thus indicating that the number of direct Zn^{2+}–water contacts is greater than number of the shortest Cu^{2+}–water contacts included in the first peak. However, at about 2.40 Å, the $CuSO_4$ radial curve is higher than that of $ZnSO_4$. O–O interactions in sulfate ions being equal, this means that longer Cu^{2+}–water interactions are present. This is even more evident in the difference curve $\Delta D(r) = D(r)_{CuSO_4} - D(r)_{ZnSO_4}$ shown in Figure 1c.

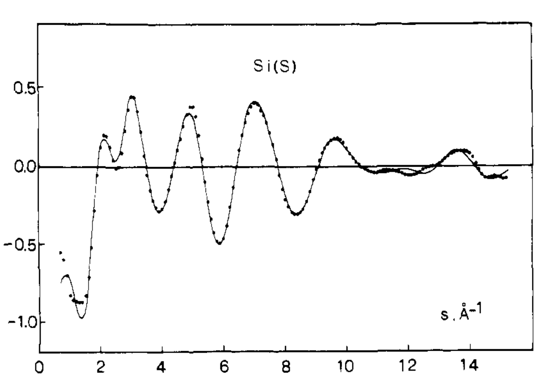

Figure 2. Experimental (···) and model (—) structure functions.

Two peaks clearly appear at two distance values that correspond to $r_{Cu^{2+}-W_{eq}}$ and $r_{Cu^{2+}-W_{ax}}$ evaluated in the $Cu(ClO_4)_2$ solutions; the minimum in the middle corresponds to Zn^{2+}–water distances.

In this way the existence of a distorted coordination polyhedron around Cu^{2+} ions has been strongly suggested.

As will be discussed in the following, in our opinion, the differing evidence of the longer Cu^{2+}–water distances in the radial curves of $Cu(ClO_4)_2$ and $CuSO_4$ solutions cannot be explained on the basis of the slight difference in concentrations. Anyway, before going on to a more quantitative analysis, we wanted to check further on the correctness of the $CuSO_4$ correlation function. When ϑ–ϑ geometry is used with the monochromator placed on the diffracted beam, a critical point in data processing is the correct evaluation of the incoherent radiation fraction that reaches the counter. The method described above is quite arbitrary at the point in which experimental data must be connected to theoretical incoherent intensities at low angles. Although the method of correction of systematic errors generally makes up for inaccurate determination of the monochromator transmission factor, it is possible that some error persists and alters the real peaks (particularly the minor ones). Therefore, a method of data normalization proposed by Habenschuss and Spedding[9] and successfully employed in a series of rare-earth chloride[9-11] solutions was used here. In this procedure the corrected intensities $I_c(s)$ are fitted by least squares to a smooth curve

$$I_c(s) = [\textstyle\sum x_i(f_i^2(s)) + \sum x_i(I_i^{\rm Inc}(s))][A + \sum B_j \exp(-C_j s^{D_j})] \quad (2)$$

where A, B_j, C_j, and D_j are parameters. In (2) f_i and $I_i^{\rm Inc}$ values are coherent and incoherent scattering amplitudes of the

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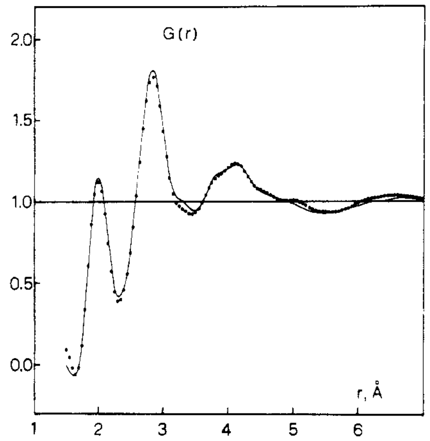

Figure 3. Experimental (···) and model (—) correlation functions.

various species. In this formulation the monochromator discrimination function is absorbed into the empirical term; this is sufficiently smooth so that real distance contributions in $I_c(s)$ are not affected. The normalization constant is given by $K = (A + \sum B_j)^{-1}$. While referring the reader to the original papers for further details about the method, we wish to add that in the present case two exponential terms were used in the fit. Structure and correlation functions thus obtained are reported in Figure 2 and 3, respectively. Note that experimental intensities were not smoothed; the smooth shape of $s\ i(s)$ was obtained through inverse Fourier transformation of the corrected $D(r)$.[9] The comparison of the $G(r)$'s shows that the two normalization methods provide identical results. Since the Habenschuss–Spedding method gives lower spurious peaks at short distances in the radial curves, in the following analysis the $s\ i(s)$ function of Figure 2 has been used.

Discussion

To obtain a set of quantitative parameters describing the coordination of the copper ion, we used the usual least-squares refinement procedure.[5-7] Accordingly, experimental and calculated structure functions are compared until best fits are obtained, with an assumed model, by varying the structural parameters. Since the analysis of the experimental radial curve suggested the existence of a distorted coordination polyhedron around Cu^{2+} ions, the cation was thought of as having the same tetragonal geometry proposed in the study of $Cu(ClO_4)_2$ solutions,[1] this geometry being the most common form of distortion for Cu^{2+}. A second hydration shell was also included in the model; its existence is suggested by the peak at 4.10–4.20 Å in the radial curve, by analogy from results on bi- and trivalent ion solutions.[7] A hydration shell was ascribed to sulfate ions; in the following w_A will denote hydration water molecules. The pair distances in water-anion complexes give small contributions to the reduced intensities (consequently, sulfate–water interactions are not observable in the radial curves); in an investigation of $ZnSO_4$ solutions[12] we showed that including these water-anion complexes is a useful description of the state of sulfate ions, in that it permits a more trustworthy description of the counterions.

The synthetic $s\ i(s)$ from the best fit is shown in Figure 2 and the corresponding $G(r)$ in Figure 3. The excellent agreement between model and "experimental" functions is apparent; the usual[13] agreement factor R was estimated as 11.73. The final parameters describing the discrete interactions are given in column 1 of Table I; for comparison, the parameters obtained for Cu^{2+} in the 2 M $Cu(ClO_4)_2$ solution[1] and for sulfate in the 1.5 M $ZnSO_4$ solution[8] are reported in columns 2 and 3.

Table I. Mean Distances r (Å), Mean Square Deviations σ (Å), and Frequency Factors N for Discrete Interactions

	1	2	3
$r_{Cu^{2+}-w_{eq}}$	2.006 (4)	1.976	
$\sigma_{Cu^{2+}-w_{eq}}$	0.09 (1)	0.053	
$r_{Cu^{2+}-w_{ax}}$	2.33 (2)	2.339	
$\sigma_{Cu^{2+}-w_{ax}}$	0.23 (2)	0.097	
$r_{Cu^{2+}-w_{II}}$	4.197 (9)	3.95	
$\sigma_{Cu^{2+}-w_{II}}$	0.202 (9)	0.335	
$r_{w_I-w_{II}}$	2.79 (1)	2.73	
$\sigma_{w_I-w_{II}}$	0.03	0.07	
$N_{Cu^{2+}-w_{II}}$	7.6 (3)	11.6	
$r_{O_S-O_S}$	2.50		2.49
$\sigma_{O_S-O_S}$	0.09		0.09
$r_{O_S-w_A}$	2.88 (1)		2.82
$\sigma_{O_S-w_A}$	0.06 (2)		0.08
r_{S-w_A}	3.78 (1)		3.91
σ_{S-w_A}	0.17 (1)		0.20
N_{S-w_A}	8.2 (4)		7.8

[a] Values given in column 1 are those used in the final calculation of the $CuSO_4$ synthetic structure function; standard errors for the refined parameters are given in parentheses. For comparison, the parameters obtained for Cu^{2+} in the 2 M $Cu(ClO_4)_2$ solution and for the sulfate ion in the 1.5 M $ZnSO_4$ solution are reported in columns 2 and 3, respectively.

It is clear that the geometric model (distorted octahedron, 4 + 2) proposed for the Cu^{2+} ion in the 2 M $Cu(ClO_4)_2$ solution is completely consistent with experimental data. Both distances, $r_{Cu^{2+}-w_{eq}}$ and $r_{Cu^{2+}-w_{ax}}$, are in good agreement with those quoted for the Cu(II) perchlorate solution. The longer distance has, as expected, a greater error; however, if we omit the relevant term in the calculation of the synthetic $s\ i(s)$, the agreement factor R becomes about 5 units greater, supporting the existence of discrete axial distances. A check of the correctness of these distance values is possible by following the Pauling concepts of bond strength and bond valence. Brown and Shannon[14] proposed an empirical expression that permits the bond valence to be calculated from the observed bond length r

$$V = (r/R_0)^{-N} \tag{3}$$

where R_0 and N are universal parameters fitted empirically for a given atom pair. The bond valences are such that their sum around a cation is equal to the ionic charge. Using the R_0 and N values reported by Brown and Kang Kun Wu[15] for the pair Cu^{2+}–O, we calculated the valences of the bonds Cu^{2+}–w_{eq} and Cu^{2+}–w_{ax} for the r values given in Table I, column 1. From them a valence sum of 1.93 was evaluated, which is in good agreement with the ionic charge.

Going back to Table I, it is interesting to observe that, while the copper(II)–water distances are nearly equal in the two cases compared, the corresponding mean square deviations are much greater in the case of the $CuSO_4$ solution. This fact stresses that in aqueous $CuSO_4$ a greater disorder exists around Cu^{2+} ions. As further proof, the parameters $r_{Cu^{2+}-w_{II}}$ (w_{II} is a water molecule in the second hydration shell) and $r_{w_I-w_{II}}$ (w_I represents either w_{eq} or w_{ax}) are longer in $CuSO_4$ than in $Cu(ClO_4)_2$ solution, while the number of water molecules in the second shell, $N_{Cu^{2+}-w_{II}}$ is smaller. This accounts for the lesser evidence of Cu^{2+}–w_{ax} distances in the $CuSO_4$ radial

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curve; if the values of cation–solvent distances have a great spread, their contributions to the $G(r)$ function are very broadened.

Obviously, this increase in disorder must be attributed to some anionic effect, for instance, to some tendency of the sulfate ion to compete with water molecules for the occupancy of hydration shell positions. This would be in keeping with the differences in the solid structures of the hydrates[16,17] of $CuSO_4$ and $Cu(ClO_4)_2$.[18] In the first case, sulfate ions enter the first coordination sphere of Cu^{2+} ions, while in the second case only water molecules envelop the central copper(II) ion. In this connection it is worth noting that, in a recent EXAFS[19] investigation on crystalline $CuSO_4{\cdot}5H_2O$, the distance $Cu–w_{eq}$ were carefullly determined at 1.97 Å; on the contrary, poor evidence has been found for axial distances at 2.40 Å, which, according to neutron and X-ray diffraction studies, involve O atoms of the sulfate groups. This was explained on the basis of the remarkable degree of dynamic disorder of the bond $Cu^{2+}–O_{ax}$, which greatly affects the EXAFS signal. This hypothesis may be considered consistent with our interpretation.

Finally, we wish to emphasize that our observations on the $CuSO_4$ solution agree very well with the results of an X-ray diffraction investigation by Ohtaki et al.[20] on solutions of divalent transition-metal ions, including $CuSO_4$ and $Cu(ClO_4)_2$ solutions. While in the radial curve of the $Cu(ClO_4)_2$ solution two clear peaks indicate two distinct coordination distances of Cu^{2+} ions, in the $D(r)$ of the $CuSO_4$ solution, besides the peak at 2.00 Å of the pairs $Cu^{2+}–w_{eq}$, only a small hump is present at about 2.40 Å. However, the same coordination geometry was used in the interpretation of both data series.

As already mentioned in the Introduction, the existence of a distorted coordination polyhedron around Cu(II) ions was not evident in a neutron diffraction study[4] of a $Cu(ClO_4)_2$ solution. In this study the use of a "null" isotope of nickel rendered the isomorphic method favorable, but the assumption of isomorphism for the pair Cu(II)–Ni(II) indeed lacks chemical and structural evidence. In the light of the not neglibible differences between the distribution curves of Ni^{2+} and Cu^{2+} solutions (see Figure 5 in ref 4), the conclusion[4] that Ni^{2+} and Cu^{2+} have similar environments deserves to be reexamined.

In conclusion, the existence of a distorted arrangement of six water molecules around Cu^{2+} ions in $CuSO_4$ solution is supported by inspection of the distribution curve and direct fitting of the structure function. This coordination structure appears to be more disordered in $CuSO_4$ than in $Cu(ClO_4)_2$ solutions.

Acknowledgment. Calculations were carried out at the Centro di Calcolo Elettronico of the Universitã Cagliari.

Registry No. $CuSO_4$, 7758-98-7; $Cu(H_2O)_6{}^{2+}$, 14946-74-8.

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Equilibrium and Kinetics of the Extraction of Nickel with 7-Dodecenyl-8-quinolinol (Kelex 100)

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Received October 4, 1982

The equilibrium and kinetics of the extraction of nickel(II) ion with chloroform solutions of 7-dodecenyl-8-quinolinol (Kelex 100, HL) have been studied at an ionic strength of 0.1 and 25 °C. The extracted species was found to be NiL_2, and its extraction constant of $\log K_{ex} = -6.34 \pm 0.11$ was obtained. The measurement of the distribution equilibrium of Kelex 100 as a function of pH exhibited a dependence on stirring rates that suggests that the heterogeneous acid–base equilibrium is dramatically shifted by preferential interfacial adsorption of the anionic form of the ligand. The rate of extraction was found to be best described by a two-term expression, both of which are first order in nickel ion and HL concentrations. The first term has zero dependence on hydrogen ion concentration whereas the second is inversely first order with respect to hydrogen ion concentration. These results support the hypothesis that the rate-determining steps involve two concurrent reactions of nickel ion with neutral and anionic forms of Kelex 100 (HL and L^-). The first reaction takes place in the aqueous phase, whereas the one involving the anion occurs in the interface. This work represents strong evidence that, while the anion of Kelex 100 is surface active, the neutral species is not and demonstrates the feasibility of elucidating extraction systems involving surface-active components.

Introduction

Recent work in this laboratory[2a] has shown that the rates of extraction of metal ions with large chelating extractants, whose anions are surface active, are enhanced considerably under conditions that generate an extensive interfacial region by interfacial adsorption of ligand anions. The systems studied, alkylated dithizones, involved only ligand anions in the rate-determining step because the experiments were conducted in the pH regions close to their pK_a values. In the case of 8-quinolinols,[2b,3] however, where chelate formation occurs in a pH range much lower than the pK_a so that the concentration

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