22.2-04   SOLUTION CHEMISTRY: A CONTRIBUTION FROM THE X-RAY DIFFRACTION TECHNIQUE. By M. Magini , Laboratorio Chimica Fisica, CNEN, CSN-Casaccia, Rome, Italy.

The ionic hydration and complex formation phenomena occurring in aqueous metal ionic solutions have been investigated with a wide variety of techniques.

During the last twenty years a remarkable contribution to the knowledge of the coordination of metal ions in solution has been provided by χ-ray diffraction studies. The description of the structure of the solutions has been first limited to the first coordination shell of the ions in terms of distances, geometries and coordination numbers without considering correlations between the ions (the so-called First Neighbors Model). Later, both complex formation (mononuclear and polynuclear) and description of the second coordination shell of the cations have been successfully provided by this technique (Caminiti,Licheri,Piccaluga,Pinna and Magini, Rev.Inorg. Chem. 1,333(1979)).

In a diffraction experiment the quantity obtained is the intensity of the scattered radiation as a function of the scattering angle. This quantity is related to the radial distribution function which gives the first direct structural information on the system, i.e.: (i) characteristic distances corresponding to the main peaks of the curves, (ii) the range of distances chracterized by meaningful order phenomena. Further information on the system can be obtained in several ways. With solutions of heavy atoms, information on the dominant intramolecular interactions can be obtained from the high-angle part of the structure function by a least squares procedure which yields the bond lengths and the frequency of the distances, while the low-angle part can be used to extract information on packing of the solvent molecules. With light atom solutions, the scattered intensities from the cations are levelled off to the other contribution in solution: a complete model is needed to perform a least squares procedure, and, for its formulation, the greatest amount of information must be drawn from the experimental radial curves.

The main limit on the information obtainable from a scattering experiment is due to the one dimensional information contained in the scattering pattern. However the non-uniqueness of the solution models is greatly reduced if the scattering measurements are carried out for solutions of different concentrations and/or composition and containing different cations and/or counter ions and the results are combined with equilibrium analysis and crystal structure determinations. The use of difference curves between radial distribution functions of such solutions is often revealing, in fact, as far as the structuring of the ions in different chemical conditions is concerned.

Transition metal ions, such as Cr(III), Fe(III), Co(II), Ni(II), Cu(II), Th(IV), have been investigated at different concentrations in acidic, neutral and hydrolysed solutions in different chemical conditions. For demonstration of the method, mononuclear complex formation between metal ions and typical inorganic and organic anions will be illustrated (Fe(III)-SO_4^{2-}, J.Chem.Phys. 70,317 (1979); Fe(III)-Cl⁻, J.Chem.Phys. 71,4255 (1979); Cr(III)-Cl⁻, J.Chem.Phys. 73,2499 (1980); Fe(III)-$C_2O_4^{2-}$, Chem.Phys.Letters in press; Co(II),Ni(II), Cu(II)-Cl⁻; J.Chem.Phys. in press).Polynuclear complex formation will be illustrated by Th(IV) hydrolysed solutions where structural units containing from few up to several tens of atoms have been found to occur (Acta Chem. Scand., A30, 437 (1976)).

22.2-05   A NEUTRON DIFFRACTION STUDY ON THE HYDRATION OF Ni(II), Mn(II) AND Cu(II) IN AQUEOUS SOLUTION BY SUBSTITUTION METHODS. By M. Sandström[a], G. W. Neilson[b] and J. R. Newsome[b], [a]Department of Inorganic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden, [b]H. H. Wills Physics Laboratory, Royal Fort, Tyndall Avenue, Bristol BS81TL, England.

Introduction

Direct information about the detailed arrangement of the water molecules around the ions in aqueous solution can be obtained by neutron diffraction difference methods, using data from structurally similar solutions (1). Isotopic substitution exploits the fact that structurally identical solutions with different isotopic compositions give different neutron diffraction intensities. In isomorphic substitution the two solutions compared differ by the exchange of one ion against another in a structurally similar environment. In the isotopic case, or when one of the isomorphically substituted ions M' has a neutron scattering length b = 0, the structure factor only contains ion-water or ion-ion terms involving the other ion M , i.e. M-O, M-D, M-X and M-M in a four-component system of composition MX_n or MXO_n in D_2O.

Experimental

Neutron diffraction data (λ = 0.7 Å) were gathered on the D4 diffractometer at the I.L.L., Grenoble, on five aqueous (D_2O) solutions. The intensity data were corrected and normalized using standard procedures (2).

Results

Isotopic substitution: A Fourier transformation of the intensity difference between two $Ni(ClO_4)_2$ solutions with different Ni isotopes gives a distribution function dominated by two sharp peaks. They were identified as due to Ni-O and Ni-D interactions in the first hydration sphere.

Isomorphic substitution: The pair of solutions, $Cu(ClO_4)_2$ and $Ni(ClO_4)_2$ with b_{Ni} = 0, was combined to study the possible distortion due to Jahn-Teller effects of the Cu^{2+} hydration sphere. Only one slightly broadened Cu-O peak at 1.97 Å and one Cu-D peak at 2.6 Å were found in the distribution function.

Another isomorphic pair studied is the 4.3 M $NiCl_2$-$MnCl_2$ solutions. The results are given in Table 1 below.

Table 1. Cation hydration determined by neutron diffraction (N = natural isotopic composition)

Ion M	Solute	Conc. mol/l	M-O Å	M-D Å	Coord. No.	Θ^{a}
N_{Ni2+}	$Ni(ClO_4)_2$	3.8	2.07	2.67	6	39 ± 10°
Ni^{2+} (b=0)						Ni^{2+}
N_{Ni2+}	MCl_2	4.3	2.09	2.69	5	43 ± 10°
N_{Mn2+}						Mn^{2+}
Cu^{2+}	$M(ClO_4)_2$	3.8	1.97	2.60	6	39 ± 10°
Ni^{2+} (b=0)						Cu^{2+}

$^{a}\Theta$ is the angle between the metal ion-oxygen axis and the plane of the water molecule according to the figure.
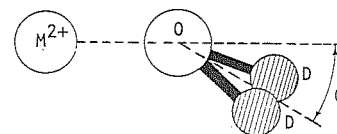
References
1. Enderby, J. E. and Neilson, G. W. in 'Water, A Comprehensive Treatise', Vol.6, Ch.1, Plenum, N.Y. 1979.
2. Page, D. I. Ibid, Vol.1, Ch.9.