X-Ray Diffraction on Electrolyte Solutions in the Low Angle Range

G. Pálinkás and E. Kalman

Central Research Institute for Chemistry of the Hungarian Academy of Sciences,
Budapest, Hungary

Z. Naturforsch. **36a**, 1367—1370 (1981); received October 24, 1981

Aqueous cobalt, nickel, zinc, cadmium and aluminium-chloride, -nitrate, -sulphate and Ph_4AsCl solutions at 25 °C were studied by small angle X-ray diffraction. The scattered intensities of chloride, nitrate and $CdSO_4$ solutions show the so-called "prepeak". The concentration dependence of the peak positions is discussed.

Introduction

The low angle behaviour of the X-ray and neutron scattering intensity of some aqueous electrolyte solutions is a long standing problem in the literature. The total scattered intensities of some solutions show a low angle pre-peak at $k = (4\pi/\lambda) \cdot \sin(\vartheta/2) \approx 1$ Å^{-1}. The origin of the pre-peaks has been discussed for a long time and has been interpreted in contradictory ways by different authors.

The first observation of this phenomenon was reported by Dorosh and Skryshewskii [1] in a series of X-ray measurements of divalent metal cation aqueous solutions. From the position of the observed pre-peaks the authors evaluated mean cation-cation distances in the solution investigated. Later on, similar low angle maxima were found in the X-ray intensity functions of $Cd(NO_3)_2$, $In_2(SO_4)_3$, $In(NO_3)_3$, $InCl_3$, $InBr_3$, $Al_2(SO_4)_3$ and $NiCl_2$ aqueous solutions by Marques and Marques [2] and $Fe(NO_3)_3$ aqueous solutions by Caminiti and Magnini [3]. The existence of a peak in the Ni-Ni structure factor itself for $NiCl_2$ solutions was first established with neutron diffraction experiments by Howe, Howells and Enderby [4]. In a later study of the total neutron scattering of $NiCl_2$ solutions, the position of the pre-peak was found to be consistent with the $M^{1/3}$ law (M=molarity); this dependence was interpreted [5—6] as a consequence of a quasi-lattice arrangement of Ni^{++} ions in the solutions. Introduction of the highly ordered quasi lattice structure of Ni^{++} ions was based (a) on the linear dependence of the peak position k_0 on $M^{1/3}$, because a cubic lattice structure would imply that the closest distance of approach is equal to the mean separation of the ions, so that k_0 should be proportional to $M^{1/3}$ [6], and (b) on the existence of a well defined peak in $S_{\mathrm{NiNi}}(k)$ at ≈ 1 Å^{-1}. The concept of the quasi-lattice is not well-defined [7] but is nowadays taken to mean long range order substantially in excess of that predicted by primitive models.

In contradiction to this, in the X-ray investigations of $NiCl_2$ solutions of Caminiti, Licheri, Piccaluga and Pinna [8], the same pre-peak could be interpreted only in terms of ion-water and water-water interactions, although, as recognized by these workers, the ion-ion contribution to the total pattern is difficult to identify. Although the $M^{1/3}$ law was also supported in the x-ray work of Marques et al. on indium solutions, there the origin of the pre-peaks was interpreted by the authors with interactions between hydrated cations.

The X-ray diffraction data of iron nitrate solutions have shown that the concentration dependence of the position of pre-peaks is consistent with an $M^{1/4}$ law which leads to the rejection of the hypothesis of a quasi-lattice structure for the solutions investigated [3].

In all cases except one, the authors have found the concentration dependence of the positions of the maxima to be consistent with a cube root law $k_0 = AM^{1/3}$.

Questions: 1) Is the cube root law general for all solutions?

2) Can the effect in all cases be unambigously related only to the cation-cation interactions?

3) Is the quasi lattice structure of ions deducible from the diffraction pattern of solutions?

Reprint requests to Dr. G. Pálinkás, Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Pusztaszeri u. 59/67, 1025 Budapest, II, Hungary.

0340-4811 / 81 / 1200-1367 $ 01.00/0. — Please order a reprint rather than making your own copy.

X-ray Diffraction Measurements

The aim of this paper is to study the X-ray scattering of aqueous Al, Co, Ni, Zn, Cd-chloride, -nitrate and -sulphate solutions in order to investigate the concentration dependence of the position of the observable low angle peaks.

The X-ray experiments were carried out using transmission geometry and monochromatic MoK$_\alpha$ radiation with a flat LiF monochromator and a flat plane-parallel specimen holder. The windows of the thermostated (25 °C) specimen holder had been prepared from 0.1 mm thick plates of single quartz crystal. The details of this technique are described elsewhere [9]. All measurements were made with strict conditions on the slit system in order to get appropriate resolution of low angle measurements. The intensity data were corrected for the scattering of the specimen holder, absorption and polarization. The concentration dependence of the peak positions was investigated in the concentration range from 1 molar up to saturation. The densities were measured by a digital densimeter (Anton Paar K. G.).

A low angle peak could be observed in the measured intensity functions of all the solutions except Al, Co, Zn, Ni-sulphate. The typical behaviour of the peaks is illustrated in Figs. (1—3) for Al(NO$_3$)$_3$, AlCl$_3$ and NiCl$_2$ solutions.

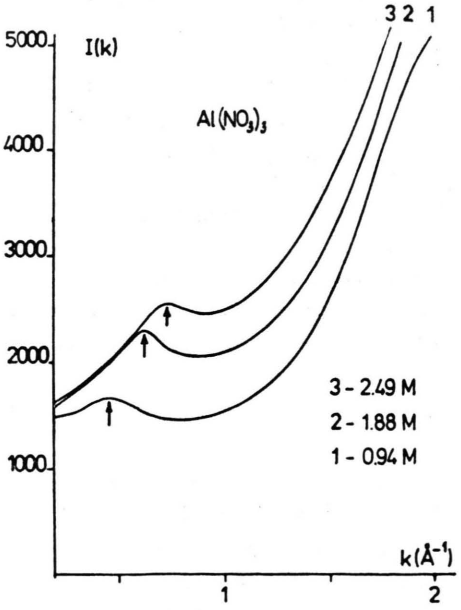

Fig. 1. Low angle X-ray scattering of aqueous Al(NO$_3$)$_3$ solutions.

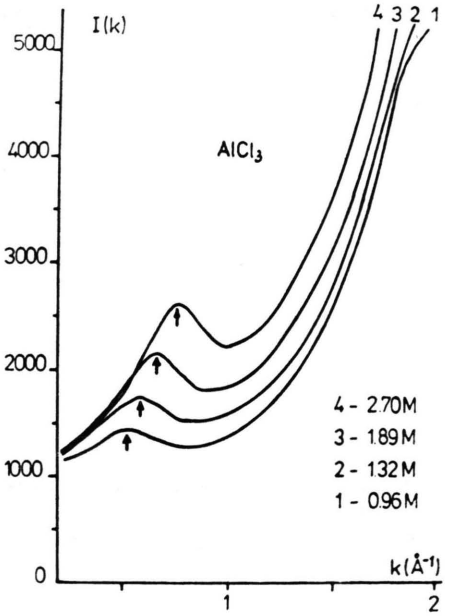

Fig. 2. Low angle X-ray scattering of aqueous AlCl$_3$ solutions.

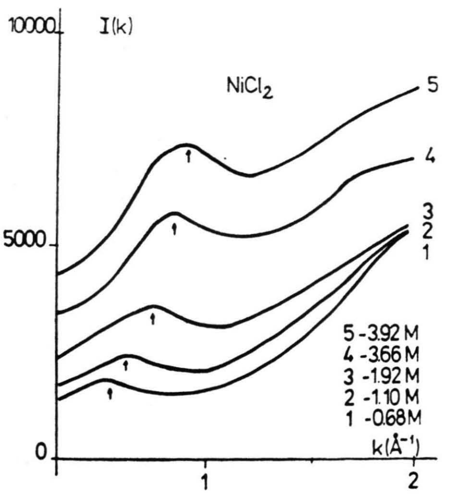

Fig. 3. Low angle X-ray scattering of aqueous NiCl$_2$ solutions.

The present work leads to the following observations:

a) The effect can be observed at high and low concentrations in the case of both heavy and light ions.

b) The height of the peaks increases with increasing salt concentration and the peak position k_0

varies strictly lineary with M^B

$$k_0 = AM^B$$

with different power values B for the various solutions (Table 1).

c) The peak positions k_0 are at higher scattering variables than the expected values calculated from the mean cation-cation distances based on the stoichiometric volume of the cations k_+. In most cases the peak positions k_0 are between the k_+ and k_-.

d) In the cases of Al, Co, Ni, Zn-sulphate solutions the peaks are not observable.

e) The position of the low angle X-ray peak for the $NiCl_2$ solution varies with the concentration with a $M^{1/4}$ law in contradiction to neutron scattering data.

The presence of the peak even in the case of dilute $AlCl_3$ solutions makes it quite questionable to relate the origin of the maxima only to the cation-cation interactions. The Al^{+++}-Al^{+++} interactions have very low weight (C) in the total diffraction pattern (Table 2).

Table 1. Coefficients B for different solutions.

	$k_0 = AM^B$ B Cl^-	NO_3^-	SO_4^{2-}
Al^{3+}	0.37 ± 0.01	0.47 ± 0.02	—
Co^{2+}	0.47 ± 0.02	0.36 ± 0.01	—
Ni^{2+}	0.25 ± 0.01	0.40 ± 0.01	—
Zn^{2+}	0.52 ± 0.02	0.32 ± 0.01	—
Cd^{2+}	0.35 ± 0.01	0.30 ± 0.03	0.6 ± 0.2

Table 2. Averaged contributions of different interactions to the X-ray scattering of aqueous $AlCl_3$ solutions.

M	C% ++	+−	−−	+w	−w	ww
0.96	0.03	0.3	0.8	3	15.5	80.3
1.89	0.08	0.9	2.4	4.8	25.0	66.0
2.7	0.16	1.7	4.7	5.2	32.0	55.0

Low-angle Scattering of Aqueous Ph_4AsCl Solutions

The low angle scattering of the Ph_4AsCl solutions was first predicted by Friedman, Zebolsky and Kalman [10].

The authors have calculated ion-ion pair correlation functions for Ph_4AsCl solutions based on a primitive model of electrolyte solutions which incorporates a Gurney cosphere overlap term in the ion-ion interactions. The model was fitted to osmotic coefficient data. Models with predominantly $+-$(D1) and $++$(K1) ion pairing were about equally successful. The concentration dependence of the model pcf's was rather weak. The partial cation-cation structure functions derived from pcf's by Fourier transformation show a low-angle peak $k_0 = 0.65$ Å^{-1} for the D1 model and $k_0 = 0.8$ Å^{-1} for the K1 model (Figure 4). It also was shown that the great scattering power (197 electrons) of Ph_4As^+ may render possible the observation of the $h_{++}(k)$ partial structure function in the total X-ray structure function. The X-ray scattering intensities, which have been measured to check the prediction of the model, show a low angle peak. The height of the peak increases with increasing salt concentration. The comparison of the predicted peak positions for the D1 and K1 models with the experimental data shows better agreement for the K1 model [11].

A detailed reproduction of the experimental total intensity functions meets difficulties because the primitive model does not contain ion-solvent and solvent-solvent interactions while such effects give predominant contributions in the total diffraction pattern. The positions of the low angle peaks show no significant concentration dependence (Figure 5).

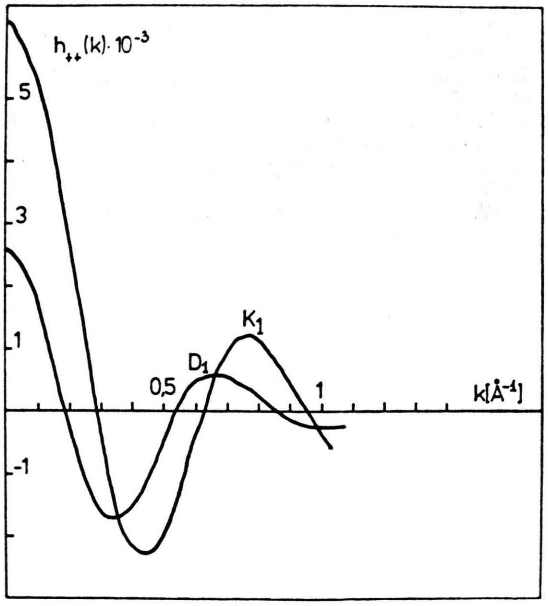

Fig. 4. Structure functions of D1 and K1 models of Ph_4AsCl.

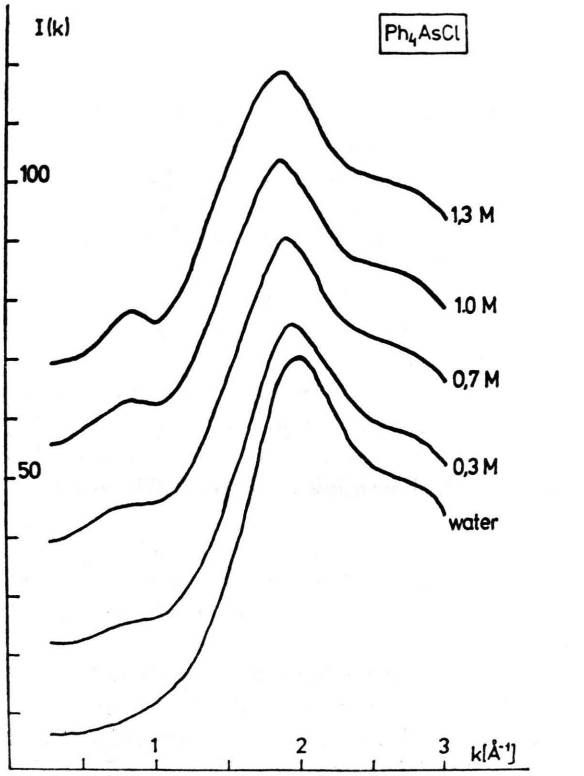

Fig. 5. Low angle x-ray scattering of aqueous Ph_4AsCl solutions.

Conclusions

Consideration of the above observations made from x-ray measurements leads to the following conclusions:

1) Both cations and anions may contribute to the pre-peaks. Indeed, direct evidence for a major contribution from the anions for the case of $NiCl_2$ has already appeared [7].
2) The effect is complicated by ion-solvent and solvent-solvent interactions (see also [12]).
3) The concentration dependence of the peak positions is different for the different solutions.
4) In the case of the Ph_4AsCl solutions no concentration dependence of the peak positions could be observed.
5) The interpretation of the origin of low angle peaks in total diffraction patterns needs models which include ion-solvent and solvent-solvent interactions.
6) Based only on total diffraction data one cannot establish the existence of any quasi-lattice structure of ions. However, if the individual $S_{++}(k)$, $S_{+-}(k)$ and $S_{--}(k)$ are known as function of molarity, detailed comparisons with the prediction of models can then be made.

[1] A. K. Dorosh and A. F. Skryshewski, J. Struct. Chem. **8**, 300 (1967).
[2] M. A. Marques and M. I. Marques, Proc. Kon. Ned. Akad. Wt. **B77**, 286 (1974).
[3] R. Caminiti and M. Magnini, Chem. Phys. Lett. **54**, 600 (1978).
[4] R. A. Howe, W. S. Howells, and J. E. Enderby, J. Phys. **C7**, L111 (1974).
[5] J. E. Enderby, Proc. Roy. Soc. London **A345**, 107 (1975).
[6] G. W. Neilson, R. A. Howe, and J. E. Enderby, Chem. Phys. Lett. **33**, 284 (1975).
[7] J. E. Enderby and R. A. Howe, Adv. Phys. **29**, 323 (1980).
[8] R. Caminiti, G. Licheri, G. Piccaluga, and G. Pinna, Disc. Faraday Soc. **66**, 13 (1978).
[9] F. Hajdu and G. Pálinkás, J. Appl. Cryst. **5**, 392 (1972).
[10] H. Friedman, D. Zebolsky, and E. Kálmán, J. Sol. Chem. **5**, 853 (1976).
[11] E. Kálmán, G. Pálinkás, and H. L. Friedman to be published.
[12] J. E. Enderby, R. A. Howe, and W. S. Howells, Chem. Phys. Lett. **21**, 109 (1973).