X-RAY DIFFRACTION INVESTIGATION OF THE STRUCTURE OF CONCENTRATED IONIC SOLUTIONS (*)

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The existence of correlations of positions taken up by heavy ions in aqueous solutions was demonstrated using X-ray diffraction [1]. The existence of a (local) arrangement of hydrated light ions in concentrated electrolytic solutions was suggested [2] [3] for interpreting similar X-ray diffraction experiments; some of those cation hydrates have a defined structure.

Cations that have not shown well-defined coordination hydration shells in aqueous solutions were investigated. Correlations of positions taken up by hydrated cations in concentrated aqueous solutions of indium nitrate and sulphate and of calcium nitrate are reported. The X-ray diffraction pattern of each solution shows (fig. 1), among others, one interference maximum at $q \sim 1$ Å^{-1} (q, momentum transfer divided by $\hbar$). The value of q corresponding to this interference maximum varies with the cation concentration C according to the law $q \propto C^{1/3}$, (fig. 2 and table).

Results obtained with concentrated aqueous solutions of other inorganic salts of metallic cations and the influence of the atomic number of the anions on the intensity of the interference maxima will be discussed in a forthcoming publication.

The X-ray diffraction patterns were obtained with two different wavelengths: Cu K_α and Mo K_α.

(*) Results presented at the Conference of the Portuguese Physics Society (Lisbon, February 1978).

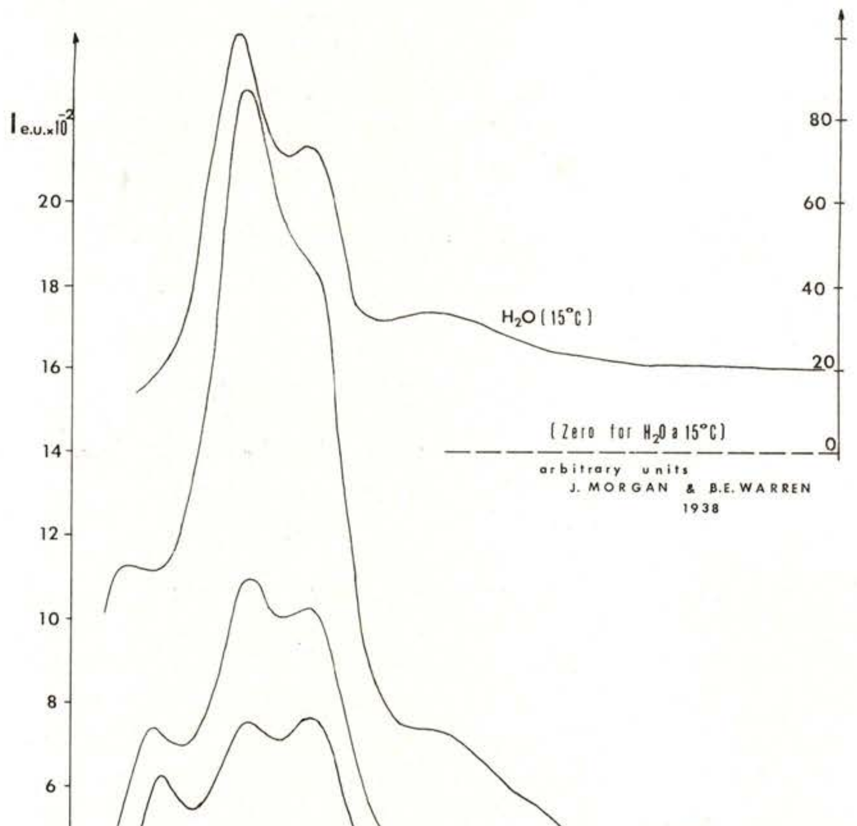

Fig. 1 — X-ray diffraction intensities, corrected for absorption and polarization, of concentrad aqueous solutions of calcium nitrate. H_2O diffraction intensities are given (in arbitrary units) for comparison. Here S has the same meaning as q.

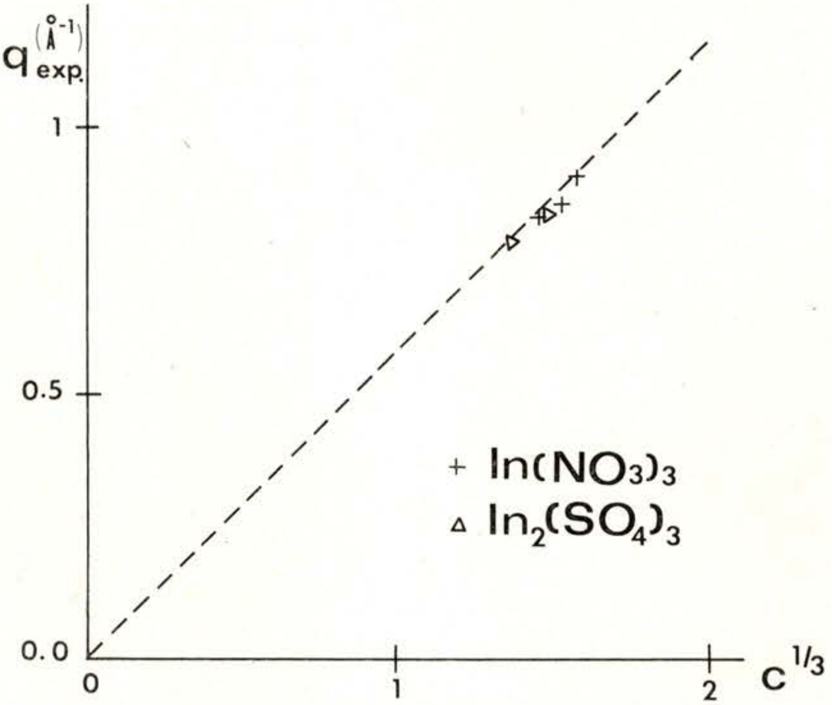

Fig. 2—Momentum transfer, $q_{exp.}$, corresponding to the inner diffraction ring, versus $C^{1/3}$.

TABLE

Solute salt	Molarity $g.mol.l^{-1}$	Density (*)	Mol. H_2O per cation	Moving Diffraction Maximum	
				$q_{exp.}$ (Å^{-1})	q_{theor} (**) (Å^{-1})
$Ca(NO_3)_2$	5.3	1.55	7.2	1.01	1.01
	3.8	1.41	11.6	0.89	0.90
	2.8	1.31	16.8	0.80	0.82
	1.88	1.21	26.5	0.72	0.72
$In(NO_3)_3$	3.9	1.88	10.0	0.90(?)	0.91
	3.6	1.80	11.2	0.84	0.89
	3.1	1.71	13.6	0.81	0.85
$In_2(SO_4)_3$	1.59	1.68	15.0	0.82	0.85
	1.26	1.55	19.7	0.78	0.79

(*) Densities were measured at 20°C.

(**) q_{theor} corresponds to an assumed quasi-close packing of hydrated cations.

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