

The hydration of divalent cations in aqueous solution : an x-ray investigation with isomorphous replacement

Citation for published version (APA):

Bol, W., Gerrits, G. J. A., & Panthaleon baron van Eck, van, C. L. (1970). The hydration of divalent cations in aqueous solution : an x-ray investigation with isomorphous replacement. *Journal of Applied Crystallography*, 3(Pt. 6), 486-492. <https://doi.org/10.1107/S0021889870006738>

DOI:

[10.1107/S0021889870006738](https://doi.org/10.1107/S0021889870006738)

Document status and date:

Published: 01/01/1970

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

The Hydration of Divalent Cations in Aqueous Solution. An X-ray Investigation with Isomorphous Replacement

BY W. BOL, G. J. A. GERRITS AND C. L. VAN PANTHALEON VAN ECK

Laboratorium voor Algemene Chemie, Eindhoven University of Technology, The Netherlands

(Received 2 February 1970)

With the method of isomorphous replacement direct information about the hydration of cations has been obtained. The study comprises two groups of isomorphous aqueous solutions, *viz.* one group composed of cadmium and calcium nitrate solutions and another with solutions of the nitrates of zinc, nickel, cobalt and magnesium. The divalent cations appear to have a clear-cut shell of 6 neighbouring water molecules. The cation-water distance is in close agreement with the distances mentioned in the literature for the unit $M(H_2O)_6^{2+}$ in crystalline substances. A second hydration shell of about 12 molecules of water can be discerned at a distance of about 4.2 \AA of the cation.

Introduction

Information about the environment of cations in aqueous solutions has been obtained by various experimental and theoretical methods as described in the literature. The work has resulted in the determination of hydration numbers, cation-water distances, ionic volumes, heats and entropies of hydration, *etc.*

Cation-water distances have been determined by da Silveira & Marques (1965) by Raman spectroscopic methods (2.08 \AA for $Mg-H_2O$ and 2.10 \AA for $Zn-H_2O$) and by Wertz & Kruh (1969) by X-ray diffraction (2.1 \AA for $Co-H_2O$). These values agree very well with the values that have been found in crystalline substances (see Table 1).

Less uniform results have been obtained in the determination of the coordination number of ions in aqueous solutions. For example, values of 6.6 up to 37.5 have been reported for the hydration of Mg^{2+} (see Azam, 1960). Therefore, a number of 'hydration shells' is usually adopted round the ions, a first hydration shell of more or less tightly bound water molecules and a second (and also a third if any) of less tightly bound water molecules. Apparently, in some techniques (*e.g.* dialysis experiments) a greater part of these shells has been taken into account than in others.

The most elucidative results have been obtained from the absorption spectra of Co^{2+} and Ni^{2+} in aqueous solution. Close agreement between the spectra of crystalline substances with sixfold coordinated cations and the spectra of the corresponding aqueous solutions has led to the conclusion that Co^{2+} and Ni^{2+} in aqueous solution have an inner hydration shell of six water molecules (Ballhausen, 1962).

The hypothesis of sixfold coordination has sometimes been adopted also for the ions Mg^{2+} , Zn^{2+} , Cd^{2+} and Ca^{2+} because in crystalline substances with divalent ions coordination by six water molecules often occurs (Table 1). Moreover the rate constant for H_2O substitution is low, especially in the case of Mg^{2+} , Co^{2+} and

Ni^{2+} (Eigen, 1963). Therefore it is likely that the first hydration shell has a well defined structure.

In this paper we describe an experimental method which has led to the description of hydration of divalent cations with hydration numbers and cation-water distances. Thermodynamic values, ionic volume *etc.* have not been evaluated.

Experimental

For the method of isomorphous replacement two solutions have been used, one of the electrolyte CA and one of the electrolyte $C'A$ in water. The solutions had the same mole fractions of electrolyte.

By an Enraf-Nonius liquid jet diffraction camera the diffraction patterns of the two solutions were evaluated. In the camera a vertical jet of a solution (diameter 0.5 mm) was irradiated with a horizontal beam of $Mo K\alpha$ radiation. Monochromatization was performed with a set of balanced filters as described by Bol (1967).

The intensity of the diffracted radiation was measured with a scintillation counter as a function of $s = 4\pi \sin \theta / \lambda$ from $s = 0.9$ with intervals of 0.1 up to $s = 10.3$. The intensity obtained was normalized by the method of Krogh Moe (1956) after correction for absorption and polarization. The coherent scattering factors of the cations were taken from Cromer & Waber (1965).

The incoherent scattering factors of the cations were calculated from the values for the free atoms of Cromer & Mann (1967) and Cromer (1969), by subtracting two electron-equivalents from the tabulated values for $\sin \theta / \lambda > 0.5$ and extrapolation to $I_{inc} = 0$ for $\sin \theta = 0$. The coherent scattering factor of the water molecule was calculated from the electron density function of water as given by Bishop, Hoyland & Parr (1963).

The coherent and incoherent scattering of the other species were taken from *International Tables for X-ray Crystallography* (1962).

One-molar solutions of the four couples

- (i) $\text{Co}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$
- (ii) $\text{Ni}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$
- (iii) $\text{Zn}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$
- (iv) $\text{Cd}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2$

were chosen as isomorphous solutions.

As can be seen in Table 1, within each of these couples the distances between cation and water molecule in crystalline substances lie close together. The electrical charges of the ions are equal and there is no evidence of strong structural deviation as in the case of *e.g.* hydrated Cu^{2+} since the water molecules round the latter ion are known to form a strongly distorted octahedron owing to the Jahn–Teller effect.

For each of the four groups of isomorphous solutions a set of the normalized intensity functions was calculated. After subtraction the resulting intensity functions no longer contain the contribution of the H_2O – H_2O distances, H_2O –anion and anion–anion distances.

Using the method described in the next chapter, we transformed the results into an electron distribution function $E(r)$. Numerical evaluation of this function was performed along the lines previously described by Bol (1968). A synthetic distribution function $G(r)$ was calculated using the formula

$$G(r) = \int_0^\infty N \frac{r'}{R} \sqrt{2\pi/B} \exp[-2\pi^2(r'-R)^2/B] \times \int_0^{s_{\max}} f_{\text{H}_2\text{O}} \sin(sr) \sin(sr') ds dr' \quad (1)$$

The use of $f_{\text{H}_2\text{O}}$ in this formula is based on the assumption that in the immediate neighbourhood of the cat-

ions there are only water molecules and no anions or other cations.

The coordination number N , the mean distance R and the temperature factor B were chosen optimally following an iterative procedure which minimizes the value of K .

$$K = \sum_{r_1}^{r_2} [G(r) - E(r)]^2 \quad (2)$$

with r given in intervals of 0.1 Å.

For r_1 and r_2 the values of 1.7 and 2.4 Å respectively were chosen (in the case of Cd and Ca, 1.8 and 2.5 Å respectively). Detailed numerical results of measurements and calculations have been reported separately by Bol (1970).

Theoretical

There are three types of radial distribution functions which will be described below.

Starting from Huygens's principle, the intensity of coherent radiation diffracted in the direction S (where $|S| = 2 \sin \theta$) is found to be [James (1962), pp. 464, 109]

$$I = \sum_p \sum_q \int_p \int_q \gamma_p \gamma_q \exp[ik(\mathbf{r}_p - \mathbf{r}_q) \cdot S] dV_p dV_q \quad (3)$$

where I is the measured intensity divided by the factor

$$\frac{1}{R^2} \left(\frac{e^2}{mc^2} \right)^2 \frac{1 + (\cos 2\theta)^2}{2}$$

and $k = 2\pi/\lambda$ (λ = wavelength of the X-rays used). $\gamma_p dV_p$ and $\gamma_q dV_q$ are the average numbers of electrons in the elements of volume dV_p and dV_q whose mid-points are defined by the vectors \mathbf{r}_p and \mathbf{r}_q .

Table 1. Distance between sixfold coordinated cations and water molecules occurring in various crystalline substances

Cation	Crystalline substance	Cation–water distance (Å)	Mean distance (Å)	
Mg^{2+}	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2.053–2.061–2.063	2.066	Braibanti, A. (1969).
	$\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$	2.091–2.037–2.088–2.071		Baur, W. H. (1962).
	$\text{MgS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$	2.118–2.046–2.042		Baggio, S., Amzel, L. M. & Becka, L. N. (1969).
Co^{2+}	$\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$	2.11–2.05–2.14–2.13–2.12–2.11	2.100	Zalkin, A., Ruben, H. & Templeton, D. H. (1962).
	$\text{Co}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	2.107–2.106–2.070		Montgomery, H., Chastain, R. V., Natt, J. J., Witkowska, A. M. & Lingafelter, E. C. (1967).
Ni^{2+}	$\text{NiSO}_3 \cdot 6\text{H}_2\text{O}$	2.043–2.076	2.062	Baggio, S. & Becka, L. N. (1969).
	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	2.02–2.07–2.10		O'Connor, B. H. & Dale, D. H. (1966).
	$\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	2.05–2.03–2.03		Grimes, N. W., Kay, H. F. & Webb, M. W. (1963).
	$\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	2.086–2.053–2.084–2.039		Gallezot, P., Weigel, D. & Prettre, M. (1967).
Zn^{2+}	$\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$	2.089	2.096	Morosin, B. (1967).
	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	2.064–2.083–2.104–2.129–2.130		Ferrari, A., Braibanti, A., Lanfredi, A. M. & Tiripicchio, A. (1967).
Ca^{2+}	$\text{CaBr}_2 \cdot 2(\text{CH}_2)_6\text{N}_4 \cdot 10\text{H}_2\text{O}$	2.316–2.330–2.345	2.330	Mazzarella, L., Kovaco, A. L., De Santis, P. & Liquori, A. M. (1967).
Cd^{2+}	$\text{Cd}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	2.241–2.298–2.297	2.279	Montgomery, H. & Lingafelter, E. C. (1966).

Element dV_p is in atom p and dV_q in atom q .

$\sum_p \sum_q \int_p \int_q$ stands for: integration over the whole volume of atom p and of atom q followed by summation over all N atoms of the sample successively in position p and position q (including the cases that p and q are identical).

Defining the mid-points of the atoms p and q by the vectors \mathbf{R}_p and \mathbf{R}_q , the vector $\mathbf{r}_p - \mathbf{r}_q$ can be written in three ways.

- (i) $(\mathbf{r}_p - \mathbf{r}_q)$ as it was
- (ii) $(\mathbf{r}_p - \mathbf{R}_p) + (\mathbf{R}_p - \mathbf{r}_q)$
- (iii) $(\mathbf{r}_p - \mathbf{R}_p) + (\mathbf{R}_p - \mathbf{R}_q) + (\mathbf{R}_q - \mathbf{r}_q)$

The three possibilities lead to three modifications of equation (3):

(i) Equation (3) as it was.

$$(ii) I = \sum_p \sum_q f_p \int_q \gamma_q \exp [ik(\mathbf{R}_p - \mathbf{r}_q) \cdot \mathbf{S}] dV_q, \quad (4)$$

$$(iii) I = \sum_p \sum_q f_p f_q \exp [ik(\mathbf{R}_p - \mathbf{R}_q) \cdot \mathbf{S}], \quad (5)$$

$$f_p \text{ standing for } \int_q \gamma_p \exp [ik(\mathbf{r}_p - \mathbf{R}_p) \cdot \mathbf{S}] dV_p$$

and f_q for the same expression with subscript q .

For practical reasons the double summation is divided into two parts, one for the N cases that p and q are identical, leading to a term Nf^2 (supposing there is only one type of atoms) and another for the $N(N-1)$ cases when p and q are different. The equations (3), (4) and (5) lead to three different concepts.

$$(3) \rightarrow I = Nf^2 + N \int_0^\infty \sigma(r) \frac{\sin(sr)}{sr} dr \quad (6)$$

$$(4) \rightarrow I = Nf^2 + Nf \int_0^\infty 4\pi r^2 \gamma(r) \frac{\sin(sr)}{sr} dr \quad (7)$$

$$(5) \rightarrow I = Nf^2 + Nf^2 \int_0^\infty 4\pi r^2 \varrho(r) \frac{\sin(sr)}{sr} dr. \quad (8)$$

$\sigma(r)$ is the electron product function (Patterson function or EPF),

$\gamma(r)$ is the mean electron density in electrons. \AA^{-3} in the elements of volume at a distance r from the reference atom,

$\varrho(r)$ is the mean atomic density in atoms. \AA^{-3} in the elements of volume at a distance r from reference atom.

As far as nomenclature is concerned the electron product function $\sigma(r)$ has been called electron distribution function in previous publications (Finbak, 1949; Bol, 1968). It is better, however, to use the words electron distribution function (EDF) for $4\pi r^2 \gamma(r)$ in analogy with atomic distribution function (ADF) for $4\pi r^2 \varrho(r)$. As an example, Fig. 1 shows the three functions for

liquid water. The first curve has been obtained by calculating the Fourier transform of the expression

$$s \left(\frac{I - Nf^2}{N} \right).$$

The third curve has been sharpened by multiplying this expression by $1/f^2$. The nature of the second curve is between those of the two; it has been sharpened by multiplying the expression by $1/f$. In liquids containing more than one type of atom the situation is slightly more complicated. If, for instance, we have a cation C and an anion A in a solvent S the first term of the right-hand side of (7) becomes $N_c f_c^2 + N_A f_A^2 + N_s f_s^2$.

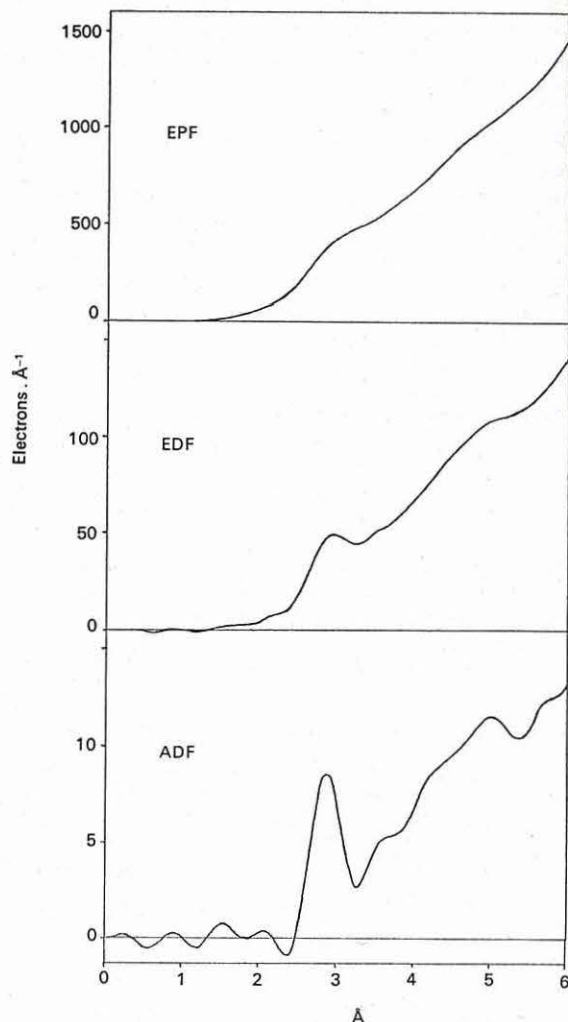


Fig. 1. Electron product function (EPF), electron distribution function (EDF) and atomic distribution function (ADF) of the same liquid (water). The first curve is a one-dimensional Patterson function and represents the mean electron density if the origin is placed in one of the electrons of the system. The second curve represents the electron density if the origin is placed in the centre of one of the atoms. The third curve gives the density of atoms (atomic centres) with the origin in the centre of one of the atoms. (In this case a molecule of water is considered to be a quasi atom).

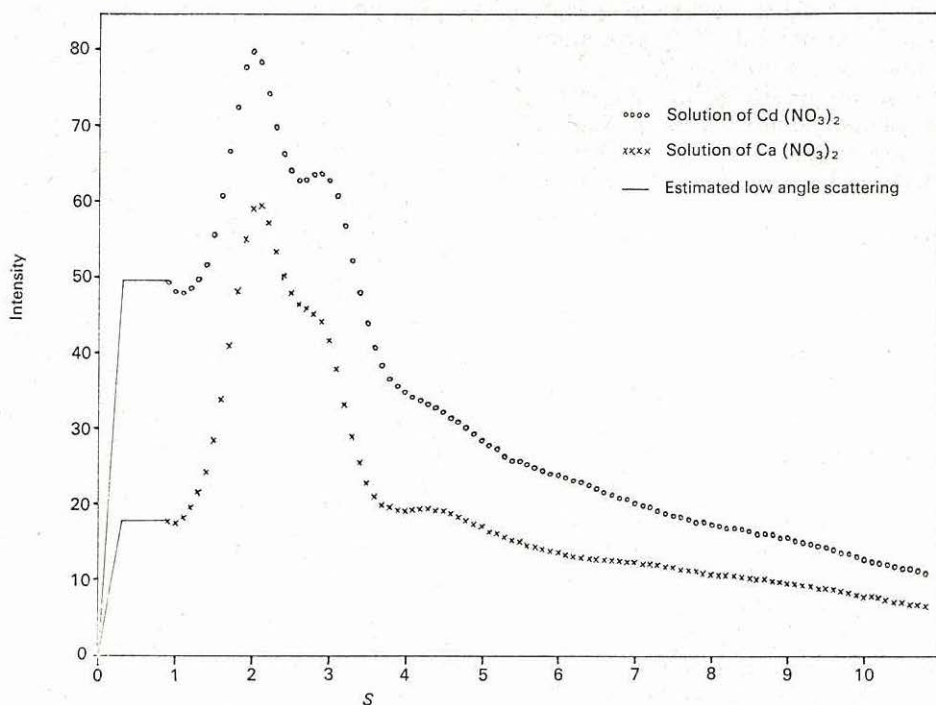


Fig. 2. Normalized intensity of scattered radiation.

The second term of the same equation gives rise to nine terms, $I_{CC} + I_{CA} + I_{CS} + I_{AC} + I_{AA} + I_{AS} + I_{SC} + I_{SA} + I_{SS}$. Each of them can be written as an integral analogous to the second term of (7)

$$\text{for instance } I_{CA} = N_C f_C \int_0^{\infty} 4\pi r^2 \gamma_{CA} \frac{\sin(sr)}{sr} dr.$$

γ_{CA} is a function of r and equals the mean electron density at a distance r from cation C , including only the electrons of the anions A .

When C and A are interchanged the contribution to intensity remains unchanged, (although $\gamma_{CA} \neq \gamma_{AC}$, $N_C \neq N_A$ and $f_C \neq f_A$) so $I_{CA} = I_{AC}$, $I_{CS} = I_{SC}$ and $I_{AS} = I_{SA}$.

The total intensity is

$$I = N_C f_C^2 + N_A f_A^2 + N_S f_S^2 + (I_{CC} + I_{AA} + I_{SS} + 2I_{CA} + 2I_{CS} + 2I_{AS}). \quad (9)$$

When comparing two isomorphous solutions, one with cation C and the other with cation C' , both with the same anion A and solvent S , then the consequence of isomorphism is that γ_{CA} , γ_{CS} , γ_{AA} , γ_{AS} , γ_{SA} and γ_{SS} are the same for the two solutions. In consequence, the contributions I_{AA} , I_{SS} and I_{AS} to the intensity are equal so that after subtraction of the two experimental intensities these contributions are eliminated. Likewise the terms $N_A f_A^2$ and $N_S f_S^2$ are eliminated.

As $f_C \neq f_{C'}$ the other contributions to intensity are not eliminated. Of these contributions $I_{CA} - I_{C'A}$ and $I_{CS} - I_{C'S}$ are easily evaluated as $\gamma_{CA} = \gamma_{C'A}$ and $\gamma_{CS} = \gamma_{C'S}$. The contribution $I_{CC} - I_{C'C'}$ however is

more difficult as both $f_C \neq f_{C'}$ and $\gamma_{CC} \neq \gamma_{C'C'}$. What is the same in the two liquids is the atomic density function $\rho_{CC} = \rho_{C'C'}$.

Therefore in accordance with (8)

$$I_{CC} - I_{C'C'} = N_C (f_C^2 - f_{C'}^2) \int_0^{\infty} 4\pi r^2 \rho_{CC} \frac{\sin(sr)}{sr} dr.$$

When introducing a new electron density function

$$\gamma_{\overline{CC}} = \frac{\gamma_{CC} + \gamma_{C'C'}}{2}$$

then

$$\begin{aligned} & \int_0^{\infty} 4\pi r^2 \gamma_{\overline{CC}} \frac{\sin(sr)}{sr} dr \\ &= \sum_q \int_q \gamma_{\overline{CC}} \exp[ik(\mathbf{R}_p - \mathbf{r}_q) \cdot \mathbf{S}] dV_q \\ &= \sum_q \frac{f_C + f_{C'}}{2} \exp[ik(\mathbf{R}_p - \mathbf{R}_q) \cdot \mathbf{S}] \\ &= \frac{f_C + f_{C'}}{2} \int_0^{\infty} 4\pi r^2 \rho_{CC} \frac{\sin(sr)}{sr} dr = \frac{I_{CC} - I_{C'C'}}{2N_C(f_C - f_{C'})}. \end{aligned}$$

The difference between the intensities diffracted by the two isomorphous solutions becomes

$$\begin{aligned} I &= m_C (f_C^2 - f_{C'}^2) \\ &+ m_C (f_C - f_{C'}) \int_0^{\infty} 4\pi r^2 (2\gamma_{\overline{CC}} + 2\gamma_{CA} + 2\gamma_{CS}) \frac{\sin(sr)}{sr} dr. \end{aligned} \quad (10)$$

Here the mol fraction $m_C = N_C/N$ is introduced, whereas N is omitted because the normalization procedure implies multiplication of the intensity by $1/N$.

In (10) the mean electron density γ_0 must be introduced in the proper way [see James (1962), p. 466] in order that the integrand of (10) converges for $r = \infty$. Furthermore, the incoherent scattering must be taken into account.

Subsequent Fourier inversion yields the EDF

$$E(r) = 4\pi r^2 (\gamma_{CC} + \gamma_{CA} + \gamma_{CS}) \\ = 4\pi r^2 \gamma_0 + \frac{r}{\pi} \int_0^\infty s \frac{\Delta I - m_C(f_C^2 - f_{C'}^2 + I_{inc} - I'_{inc})}{m_C(f_C - f_{C'})} \sin(sr) ds \quad (11)$$

Results

Fig. 2 shows the normalized intensity of radiation, scattered by one-molar solutions of $\text{Ca}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2$ at 25°C. For the other couples the curves are analogous.

At low scattering angles ($s < 0.9$) an extrapolation was used. This extrapolation is justified by our own orientating measurements in this region and by the results of Hyman (1963). The difference between the two sets of intensities has been calculated and with the help of equation (11) the electron distribution functions.

The results for the four couples have been plotted in Fig. 3. In the four cases there appears to be a clear-cut peak near 2 Å, which must be ascribed to the water molecules that are the nearest neighbours of the cation. A second, less clear-cut peak is seen at about 4 Å. It can be described to be the picture of the 'second hydration shell'.

Numerical evaluation using equation (1) as mentioned previously leads to satisfactory results for the nearest neighbour peak. The results are summarized in Table 2. The number of molecules in the first hydration shell appears to be in all cases near to six. The deviations from the value of six are not significant (less than 2 standard deviations). This is a confirmation of the generally adopted octahedral structure of the first hydration shell. The hypothesis of a fully occupied octahedron of six water molecules is furthermore supported by the fact that the electron density from 2.7 to 3.5 Å from cation is very low, since it is impossible for a water molecule to approach a fully occupied octahedron closer than 4 Å from the centre.

Table 2. The cation-water distance R and the number of water molecules in the first hydration shell

Values calculated from the EDF's of the four couples of one-molar nitrate solutions, (with standard deviations). Temperature 25°C.

Couple	R	N
$\text{Co}^{2+} - \text{Mg}^{2+}$	2.108 (0.006) Å	5.9 (0.2)
$\text{Ni}^{2+} - \text{Mg}^{2+}$	2.065 (0.006)	5.7 (0.2)
$\text{Zn}^{2+} - \text{Mg}^{2+}$	2.108 (0.006)	6.2 (0.2)
$\text{Cd}^{2+} - \text{Ca}^{2+}$	2.263 (0.006)	5.8 (0.2)

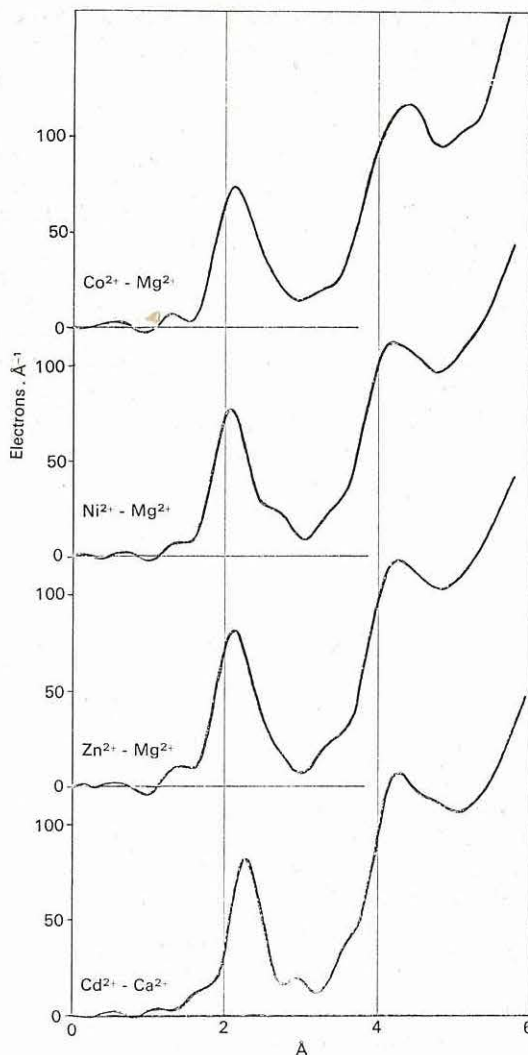


Fig. 3. Electron density function (EDF) calculated for four couples of one-molar solutions. The ordinate is in electrons. Å⁻¹, the abscissa in Å. Temperature 25°C.

The values of the cation-water distance mentioned in Table 2 are in good agreement with the values found in crystalline substances (Table 1). Even better agreement is obtained when minor deviations from isomorphy between the solutions are taken into account.

If the diffracted intensities of two solutions, one with cation C and the other with cation C' with different cation-water distances R_C and $R_{C'}$ are subtracted, an EDF results with a cation-water distance $R_{C-C'}$ which is given by

$$(Z_C - Z_{C'})R_{C-C'} = R_C Z_C - R_{C'} Z_{C'} \quad (12)$$

(supposing that the difference between R_C and $R_{C'}$ is not great).

On this basis the values of $R_{C-C'}$ can be re-examined. If R is assumed to be 2.066 ± 0.02 Å for $\text{Mg}^{2+} - \text{H}_2\text{O}$ and 2.330 ± 0.02 Å for $\text{Ca}^{2+} - \text{H}_2\text{O}$, then, for the heavier ions, R can be calculated to be

Table 3. Characteristics of second hydration shell

Couple of cations	N=10		N=12		N=14	
	R	B	R	B	R	B
Co ²⁺ -Mg ²⁺	4.07 Å	2.0	4.15 Å	3.3	4.22 Å	4.6
Ni ²⁺ -Mg ²⁺	4.07	1.4	4.14	2.3	4.21	3.2
Zn ²⁺ -Mg ²⁺	4.12	1.3	4.20	2.0	4.26	2.6
Cd ²⁺ -Ca ²⁺	4.14	1.4	4.22	2.0	4.28	2.6

N = number of water molecules; R = cation-water distance; B = temperature factor.

for Co ²⁺ -H ₂ O	2.091 ± 0.015 Å
for Ni ²⁺ -H ₂ O	2.065 ± 0.015
for Zn ²⁺ -H ₂ O	2.093 ± 0.015
for Cd ²⁺ -H ₂ O	2.289 ± 0.013

The agreement with the values of Table 1 is very good. The agreement with the results of da Silveira & Marques (1965) (2.08 for Mg-H₂O and 2.10 for Zn-H₂O) and of Wertz & Kruh (1969) (2.1 for Co-H₂O) is also good.

The temperature factor *B* is not mentioned in Table 2 because it appears to be very low. In fact, it is only possible to state that *B* < 0.3. This result may be an artifact of the subtraction procedure. A decrease in *B* may be caused by the following circumstances:

(i) any difference in cation-water distance between subtrahend cation and minuend cation;

(ii) temperature factor *B* greater for the subtrahend ions (Ca²⁺ and Mg²⁺) than for the minuend ions (Cd²⁺, Co²⁺, Ni²⁺ and Zn²⁺);

(iii) distortion of the (H₂O)₆ octahedron greater for the subtrahend ions than for the minuend ions;

As the difference in cation-water distance is very

limited (it might account for a fall of *B* from 2.0 to at least 1.6), it is likely that the low value of the resulting temperature factor is caused by a difference in the temperature factors of the two solutions or a difference in the regularity of their (H₂O)₆ octahedrons. This result is not in accordance with the conclusion of Furlani (1957) that the Ni(H₂O)₆²⁺ octahedron is strongly distorted, because in that case the peak in EDF would have been broadened. The second hydration shell is not easily evaluated quantitatively with equation (1) since the result appears to be strongly dependent on the value chosen for *r*₁ and *r*₂ in (2). In fact, this difficulty is the same as that encountered when hydration is determined in other physico-chemical ways. The difference between water molecules in a second hydration shell and in the bulk of the liquid is vague.

The peak in EDF at 4.2 Å can be accounted for if we assume a second hydration shell of 12 ± 2 water molecules. With more than 14 or less than 10 molecules the result is not quite acceptable. Within the region from 10 to 14 it is not possible to say which value is best (see Fig. 4, Table 3).

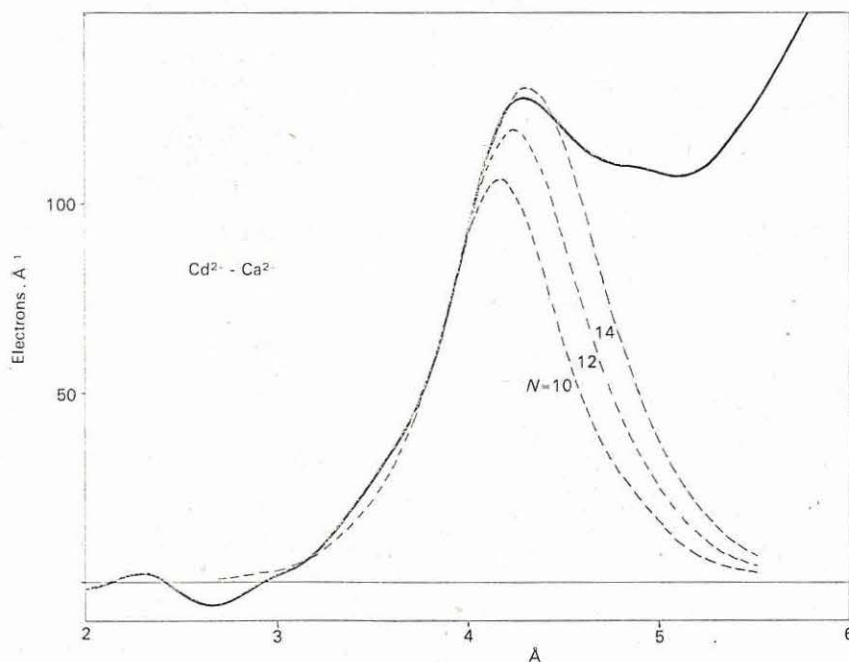


Fig. 4. Best fitting curves for the second hydration shell. The EDF is the EDF of the couple Cd²⁺-Ca²⁺ after elimination of the peak at 2.26 Å using equation (1). With 10 up to 14 water molecules in the second shell the result is satisfactory. With fewer molecules or with more the result is not quite acceptable.

The water molecules of the second hydration shell can have two different types of contact with the six water molecules of the inner shell. There may be a hydrogen bond ($\pm 2.85 \text{ \AA}$) and there may be a van der Waals contact ($> 3.4 \text{ \AA}$).

In the latter case the molecules of the second shell can be calculated to be at least at a distance of 4.15 \AA from the cations (both in the case of cations with $r=2.1 \text{ \AA}$ and with $r=2.3 \text{ \AA}$).

In the case of a hydrogen bond the distance depends on the cation-water-water angle. A distance of 4.2 \AA corresponds with an angle of 112° , which is a normal value.

The second hydration shell is greater than a pentadodecahedron as occurring in some hydrates, but it contains a smaller number of water molecules (20 in dodecahedron, 12 in second shell). A simple structure of the second shell is therefore not probable. The structure is greatly determined by that of the surrounding bulk water (the anions in a one-molar solution are at a mean distance of about 8 \AA from the cations, so they are not greatly involved in the peak at 4.2 \AA).

Further investigation will be directed towards (i) evaluation of ionic volumes and (ii) subtraction of the C-A, C-S and C-C contributions from the electron product function of the electrolyte solution. In this way the S-S, S-A and A-A contributions will be left behind.

For both purposes the accuracy of the experiments must be increased, especially at high S values ($S > 10$) and at low S values ($S < 1$).

The authors wish to thank Mr S. P. Bertram for his contributions to the experimental work and the computer programming.

References

- AZZAM, A. M. (1960). *Canad. J. Chem.* **38**, 993.
 BAGGIO, S. & BECKA, L. N. (1969). *Acta Cryst.* **B25**, 1150.
 BAGGIO, S., AMZEL, L. M. & BECKA, L. N. (1969). *Acta Cryst.* **B25**, 2650.
 BALLHAUSEN, C. J. (1962). *Ligand Field Theory*, pp. 256, 261. New York: McGraw Hill.
 BAUR, W. H. (1962). *Acta Cryst.* **15**, 815.
 BISHOP, D. M., HOYLAND, J. R. & PARR, R. G. (1963). *Mol. Phys.* **6**, 467.
 BOL, W. (1967). *J. Sci. Instrum.* **44**, 736.
 BOL, W. (1968). *J. Appl. Cryst.* **1**, 234.
 BOL, W. (1970). *The Hydration of Divalent Cations in Aqueous Solution. Detailed Numerical Results*. Report 150170 T. H. Eindhoven.
 BRAIBANTI, A. (1969). *Acta Cryst.* **B25**, 354.
 CROMER, D. T. (1969). *J. Chem. Phys.* **50**, 4857.
 CROMER, D. T. & MANN, J. B. (1967). *J. Chem. Phys.* **47**, 1892.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.
 EIGEN, M. (1963). *Pure Appl. Chem.* **6**, 97.
 FERRARI, A., BRAIBANTI, A., LANFREDI, A. M. M. & TIRICCHIO, A. (1967). *Acta Cryst.* **22**, 240.
 FINBAK, C. (1949). *Acta Chem. Scand.* **3**, 1293.
 FURLANI, C. (1957). *Z. Phys. Chem.* **10**, 291.
 GALLEZOT, P., WEIGEL, D. & PRETTRE, M. (1967). *Acta Cryst.* **22**, 699.
 GRIMES, N. W., KAY, H. F. & WEBB, M. W. (1963). *Acta Cryst.* **16**, 823.
 HYMAN, A. (1963). Thesis. Rutgers, The State University, New Brunswick, New Jersey, U.S.A.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 202, 205. Birmingham: Kynoch Press.
 JAMES, R. W. (1962). *The Optical Principles of the Diffraction of X-rays*. London: Bell.
 KROGH MOE, J. (1956). *Acta Cryst.* **9**, 951.
 MAZZARELLA, L., KOVACS, A. L., DE SANTIS, P. & LIQUORI, A. M. (1967). *Acta Cryst.* **22**, 65.
 MONTGOMERY, H. & LINGAFELTER, E. C. (1966). *Acta Cryst.* **20**, 728.
 MONTGOMERY, H., CHASTAIN, R. V., NATT, J. J., WITKOWSKA, A. M. & LINGAFELTER, E. C. (1967). *Acta Cryst.* **22**, 775.
 MOROSIN, B. (1967). *Acta Cryst.* **23**, 630.
 O'CONNOR, B. H. & DALE, D. H. (1966). *Acta Cryst.* **21**, 705.
 SILVEIRA, A. DA, MARQUES, M. A. & MARQUES, N. M. (1965). *Mol. Phys.* **9**, 271.
 WERTZ, D. L. & KRUEH, R. F. (1969). *J. Chem. Phys.* **50**, 4313.
 ZALKIN, A., RUBEN, H. & TEMPLETON, D. H. (1962). *Acta Cryst.* **15**, 1219.