

# Ion-Solvent and Solvent-Solvent Interactions. X-ray Study of Aqueous Alkali Chloride Solutions

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The first neighbour model, FNM, used frequently for the description of hydration has been modified by dropping the assumption that the structure of the “free” solvent is identical with that of the pure solvent. The modified model, FNM2, reproduces the experimental X-ray structure functions of alkali chloride solutions quite well and enables the study of perturbed solvent-solvent interactions. The refined structural parameters reasonably indicate the dependence of the hydration of the alkali cations on their radius and concentration. The hydration of  $\text{Cl}^-$  has been found to be almost independent of both concentration and the type of counter cation.

The model assumes regular symmetry for the first neighbour coordination sphere, but the high rms deviations of the water-water distances within the shells of the aggregates indicate considerable individual asymmetries.

A further modification of the FNM will be discussed in a following paper.

## Introduction

One way to describe the structure of multi-component liquids is their characterization by atom pair correlation functions. Since 1–1 aqueous electrolyte solutions can be considered as four component liquids ( $\text{O}$ ,  $\text{H}$ ,  $\text{C}^+$ ,  $\text{A}^-$ ), the total structure functions obtained from scattering experiments have to be regarded as weighted sums of ten partial structure functions. The treatment can be simplified by taking the solvent molecule ( $\text{s}$ ) as a unit thus reducing the number of components to three ( $\text{S}$ ,  $\text{C}^+$ ,  $\text{A}^-$ ) and the number of terms in the total structure function to six. Also, the contributions of the ion-ion interactions to the diffraction pattern of electrolyte solutions can often be neglected [1].

In the past decade numerous attempts have been made to extract the contributions of ion-solvent interactions from the measured total structure functions, either approximately or exactly. For this purpose first neighbour models (FNM) were introduced and difference methods such as isotopic substitution and isomorphic replacement [2, 3, 4, 5] have been developed.

The main object of the present work was to test a certain version of the first neighbour model for describing the ionic hydration in concentrated aqueous alkali chloride solutions. The experimental basis for this investigation was provided by the X-ray diffraction studies of the authors.

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## First Neighbour Models (FNM)

The first version of this model (FNM1) was introduced by Narten, Vaslow, and Levy [2] in their extensive X-ray and neutron diffraction studies on aqueous lithium chloride solutions. The basic assumptions of FNM1 are the following:

- Two states of water are distinguished: water bound in the hydration shells and water outside the hydration shells (“free” water),
- hydration shells comprise only nearest neighbours,
- hydration shells are imbedded in “free” water,
- hydration shells exhibit the highest degree of symmetry (water molecules occupying the vertices of regular polyhedra),
- the structure of “free” water is identical with that of pure water.

In terms of FNM1 the structure function of a solution can be written as

$$H(k) = X_C \mathcal{H}_C(k) + X_A \mathcal{H}_A(k) + X_f \mathcal{H}_f^u(k), \quad (1)$$

where  $X_C$ ,  $X_A$  and  $X_f$  are the mole fractions of the aggregates and “free water”, respectively.  $\mathcal{H}_C(k)$ ,  $\mathcal{H}_A(k)$  are structure functions of ion-water aggregates and  $\mathcal{H}_f(k)$  is the structure function of pure water, where  $k$  denotes the scattering variable  $k = (4\pi/\lambda) \sin(\vartheta/2)$ .  $\lambda$  is the wavelength of the primary and coherently scattered radiation, and  $\vartheta$  the scattering angle.

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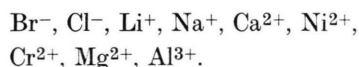
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Once the type of polyhedra is chosen, the independent adjustable parameters of the model are the ion-water first neighbour distances  $r_{IW}$ , their rms variation  $l_{IW}$ , the rms variation of the  $H_2O-H_2O$  distances within the hydration shells  $l_{WW}^I$ , the (even) coordination numbers  $CN_{IW}$  and the parameters of the boundary of the domain of free water around the ions,  $r_{0IW}$ ,  $l_{0IW}$ . The above parameters are determined by fitting the model structure function to the experimental one (least squares refinement method) [2, 3].

In recent years many solutions have been studied by analysing X-ray diffraction patterns with the FNM1 model. From Table 1, where a collection of results is presented [7–13], it can be seen that the structural parameters of given hydrated ions as obtained from different solutions hardly depend on the counter ion and the concentration. Since some systematic differences can be observed between the  $l_{IW}$  parameters, they seem to be a measure for the strength of nearest neighbour ion-solvent interactions. A sequence of increasing stability of the hydration shells can be deduced from these  $l_{IW}$  parameters:



A comparison of the ion-water distances obtained by FNM1 with those obtained by adding the ionic radii (of Pauling) to the radius of the water molecule (1.4 Å) shows agreement for doubly and triply charged ions and deviations for single charged ions. The distances are longer for  $Li^+$  and  $Na^+$  and shorter for  $Cl^-$  and  $Br^-$  than expected from the ionic radii. The coordination numbers presented by FNM1 agree with those accepted in the literature. It has been shown [6] that with FNM1 also partial ion-water pair correlation functions can be derived. To check the adequacy of FNM1, we have calculated the cation-water and anion-water pair correlation functions according to Eq. (12) of Ref. [6] for  $CaCl_2$  solutions at three concentrations. The structural parameters used were those of FNM1 published by Caminiti et al. [3]. The calculated pair correlation functions  $g_{IW}(r)$  and the running coordination number functions

$$I_{IW}(r) = 4\pi \varrho_W \int_0^r r'^2 g_{IW}(r') dr', \quad (2)$$

where  $\varrho_W$  is the number density of water molecules, are shown in Fig. 1 and Fig. 2, respectively. The

Table 1. FNM1 literature data of previous X-ray investigations of some electrolyte solutions.

Ion	$CN_{IW}$	$r_{IW}$ [Å]	$l_{IW}$ [Å]	Solution
$Li^+$	4	2.25	0.25	2.1 M LiBr [7]
	4	2.14	0.25	4.5 M LiBr [7]
	4	2.16	0.25	5.6 M LiBr [7]
	4	1.95	0.25	6.9 M LiCl [2]
	4	2.22	0.21	13.9 M LiCl [2]
	4	2.25	0.25	18.5 M LiCl [2]
$Al^{3+}$	6	1.89	0.04	2 M $AlCl_3^+$ [13]
$Na^+$	6	2.41	0.24	5 M NaCl [8]
$Mg^{2+}$	6	2.044	0.06	2 M $MgCl_2$ - $CaCl_2$ [9]
$Ca^{2+}$	6	2.42	0.14	1 M $CaCl_2$ [3]
	6	2.41	0.15	2 M $CaCl_2$ [3]
	6	2.42	0.13	4 M $CaCl_2$ [3]
	6	2.43	0.14	2 M $MgCl_2$ - $CaCl_2$
	6	2.40	0.12	1.2 M $CaBr_2$ [10]
	6	2.44	0.15	2 M $CaBr_2$ [10]
$Cr^{3+}$	6	1.99	0.07	1 M $CrCl_3^+$ [11]
	6	2.00	0.08	1 M $Cr(NO_3)_3$ [11]
	6	1.99	0.10	2 M $Cr(NO_3)_3$ [11]
$Ni^{2+}$	6	2.05	0.10	2 M $NiCl_2$ [12]
	6	2.06	0.13	4 M $NiCl_2$ [12]
$Cl^-$	6	3.19	0.20	LiCl 3 $H_2O$
	6	3.18	0.19	LiCl 4 $H_2O$
	6	3.10	0.20	LiCl 8 $H_2O$
	6	3.14	0.22	1 M $CaCl_2$
	6	3.14	0.23	2 M $CaCl_2$
	6	3.15	0.21	4 M $CaCl_2$
	6	3.08	0.25	1 M $CrCl_3$
	6	3.13	0.24	2 M $MgCl_2$ - $CaCl_2$
	6	3.13	0.21	2 M $NiCl_2$
	6	3.15	0.28	4 M $NiCl_2$
	6	3.16	0.24	5 M NaCl
	6	3.13	0.21	2 M $AlCl_3$
$Br^-$	6	3.29	0.23	2.1 M LiBr
	6	3.29	0.25	4.5 M LiBr
	6	3.29	0.26	5.6 M LiBr

average number of water molecules in a sphere of radius  $r$  is

$$\bar{I}_W(r) = \frac{4\pi}{3} \varrho_W r^3, \quad (3)$$

marked by the full line in Figure 2.

The partial ion-water correlation functions show three remarkable features.

- 1) the nearest neighbour arrangement around the ions hardly depends on ionic concentration;
- 2) although the coordination numbers for the  $Ca^{2+}$  and  $Cl^-$  ions are the same, the hydration shell of  $Ca^{2+}$  is more pronounced;
- 3) in FNM1 there appears a lack of water molecules ( $\Delta \sim 6$ ) in the surrounding the ions (Figure 2).

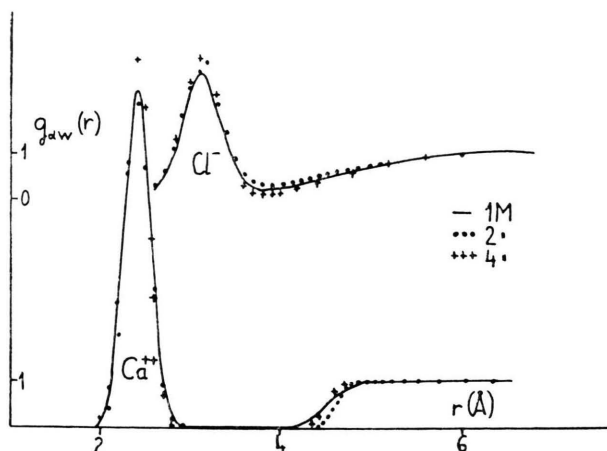


Fig. 1. Cation-water and anion-water pair correlation functions from FNM1 for  $\text{CaCl}_2$  solutions.

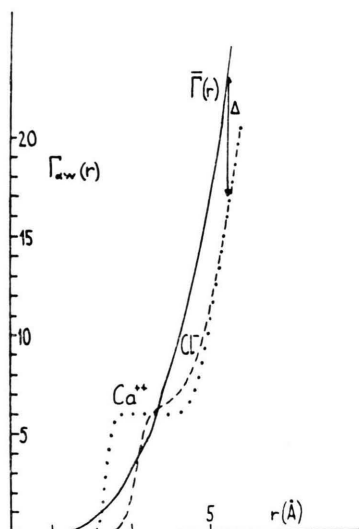


Fig. 2.  $T(r)$  functions from FNM1 for  $\text{CaCl}_2$  solutions.

In FNM1 fittings, model parameters having physically unreasonable values, even when leading to a good agreement with experimental data, must be rejected [3]. The requirement of reasonableness is an additional criterion f) used in the application of FNM1.

It is evident that assumptions d) and e) and criterion f) involve the most serious limitations of the model. Assumption e) on the identity of the structures of free and pure solvent excludes the possibility of studying changes of solvent-solvent interactions under the influence of ions, and it may

also cause an uncertainty of the ion-solvent parameters.

These deficiencies induced us to introduce a new version of the first neighbours model, FNM2, by dropping the assumption e) and the criterion f) of FNM1. Omitting criterion f) means that we accept without discrimination the set of model parameters that yields the best fit. In FNM2 the structure of "free" water is also interpreted in terms of first neighbour interactions, which involves the introduction of the new adjustable parameters  $\text{CN}_{\text{ww}}$ ,  $r_{\text{ww}}$ ,  $l_{\text{ww}}$ ,  $l_{\text{ww}}^{\text{w}}$ ,  $r_{0\text{ww}}$ ,  $l_{0\text{ww}}$ .

Assumptions a) through d) of FNM1 are retained in FNM2.

The expedience of assumption d) of FNM1 is questionable.

Its omission leads to a third version, FNM3, whose adequacy will be tested in a following paper on the same data set.

The use of FNM2 for describing hydration has been checked earlier in a molecular dynamics study [6] pertaining to the calculation of the X-ray structure function of a 2.2 molal  $\text{NaCl}$  solution.

## Experimental and Data Treatment

Our X-ray diffraction measurements were carried out on flat plane-parallel specimens using transmission geometry and  $\text{MoK}\alpha$  radiation monochromated by a flat  $\text{LiF}$  crystal in the primary beam. The plane parallel windows of the thermostated specimen holder have been prepared from 0.1 mm thick plates of quartz single crystal. For details of this technique and data processing cf. [14]. The X-ray scattering of 2 and 4 molal (mole/kg solvent) aqueous  $\text{LiCl}$ ,  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{CsCl}$  solutions was measured in the range of the scattering variable  $0.2 \leq k \leq 14.75 \text{ \AA}^{-1}$  at  $25^\circ\text{C}$ . The measured intensities were corrected for background, polarization, absorption and Compton scattering. Intensity data were collected using a step-scanning facility. The steps of the scan were programmed to be equidistant on the  $k$  scale ( $k = (4\pi/\lambda) \sin(\vartheta/2)$ ) according to the following scheme:

$$\begin{aligned} \Delta k &= 0.05 \text{ \AA}^{-1} & \text{for } 0.2 \leq k < 5 \text{ \AA}^{-1}, \\ \Delta k &= 0.1 \text{ \AA}^{-1} & \text{for } 5 \leq k < 10 \text{ \AA}^{-1}, \text{ and} \\ \Delta k &= 0.25 \text{ \AA}^{-1} & \text{for } 10 \leq k \leq 14.75 \text{ \AA}^{-1}. \end{aligned}$$

The experimental structure functions  $H(k)$ , were constructed according to the equation

$$H(k) = \left[ \alpha I_{\text{cor}}(k) - \sum_{i=1}^3 x_i f_i^2(k) - \sum_{i=1}^3 x_i I_{\text{inc},i}(k) \right] / \left[ \sum_{i=1}^3 x_i f_i(k) \right]^2, \quad (4)$$

where  $I_{\text{cor}}$  is the corrected intensity,  $\alpha$  the normalizing factor (Krogh-Moe),  $x_i$  the mole fraction of component  $i$  (the subscripts 1, 2 and 3 denote cation, anion and water),  $f_i(k)$  the scattering amplitude of component  $i$  and  $I_{\text{inc},i}$  the corresponding Compton intensity. The coherent scattering amplitudes of the ions and the water molecule were computed by use of the formulas of Cromer and Waber [15], and Hajdu [16], respectively. Similarly Compton intensities were calculated with the aid of the analytical formulas of Hajdu [16] for  $\text{Cs}^+$  and  $\text{H}_2\text{O}$ , and Pálkás and Radnai [17] for the other ions. Normalization of the intensities was performed with the method of Krogh-Moe. The Compton intensities were modified by relativistic corrections. The experimental  $kH(k)$  structure functions for all solutions involved in the present study are shown as dotted lines in Figs. 3 and 4.

### Modified First Neighbour Model (FNM2)

In order to examine the usefulness of FNM2, model structure functions have been fitted to the experimental  $kH(k)$  functions by systematically refining the model parameters via a least squares procedure.

#### Model Structure Function

In terms of FNM2, the structure function is given as

$$H^{\text{M}}(k) = \sum_{i=1}^3 X_i \mathcal{H}_i(k). \quad (5)$$

The  $X_i$ 's are the mole fractions of the three types of aggregates (depending on the coordination numbers) and  $\mathcal{H}_i(k)$  is the partial structure function of aggregate  $i$ . Each  $\mathcal{H}_i(k)$  is composed of contributions from the discrete structure and from a continuum:

$$\mathcal{H}_i(k) = \mathcal{H}_i^{\text{D}}(k) + \mathcal{H}_i^{\text{C}}(k), \quad (6)$$

$$\mathcal{H}_i^{\text{D}}(k) = \sum_{m,n \neq i}^{\text{CN}_i+1} e_{mn}(k) \Delta_0(k r_{mn}, l_{mn}), \quad (7)$$

$$\mathcal{H}_i^{\text{C}}(k) = -\frac{4\pi \varrho_0}{k} r_{0i\text{W}}^2 C_{i\text{W}}(k) \Delta_1(k r_{0i\text{W}}, l_{0i\text{W}}) \quad (8)$$

where

$$\Delta_p(k r_{mn}, l_{mn}) = j_p(k r_{mn}) \exp\left(-\frac{l_{mn}^2}{2} k^2\right) \quad (9)$$

and

$$e_{mn}(k) = \frac{f_m(k) f_n(k)}{\left[ \sum_{\alpha=1}^3 x_{\alpha} f_{\alpha}(k) \right]^2} \quad (10)$$

with the  $p$ -th order spherical Bessel function  $j_p$ .

The  $C_{i\text{W}}$  are defined by the relation

$$C_{i\text{W}}(k) = (2 - \delta_{i\text{W}}) x_i x_{\text{W}} e_{i\text{W}}(k) \quad (11)$$

( $\delta_{i\text{W}}$  is the Kronecker symbol). The adjustable parameters of the model are as follows: The even coordination numbers  $\text{CN}_{i\text{W}}$ ; the mean first neighbour distances  $\langle r_{i\text{W}} \rangle$ ; the corresponding root mean square deviations

$$l_{ij}^2 = \langle (\langle r_{ij} \rangle - r_{ij})^2 \rangle$$

and the figures  $r_{0\text{W}}$ ,  $l_{i\text{W}}$  characteristic for the boundary of the structured environment or, in other words, the correlation lengths of the particles. The mole fractions of ions  $x_{\pm}$  and water molecules  $x_{\text{W}}$ , the mole numbers of aggregates  $M_i$  and the corresponding mole fractions  $X_i$  are given in Table 2.  $\varrho_0$  is the averaged number density of particles. The refined model structure functions are presented as solid lines in Figs. 3 and 4. The structural parameters calculated by FNM2 are given in Tables 3–5.

Table 2. Composition of the solutions; molality  $m$ , stoichiometric mol fractions ( $x_{\pm}$ ,  $x_{\text{W}}$ ), coordination number in the aggregates in FNM 2 ( $\text{CN}_{+\text{W}}$ ,  $\text{CN}_{-\text{W}}$ ,  $\text{CN}_{\text{WW}}$ ), mol numbers ( $M_{\pm}$ ,  $M_{\text{W}}$ ) and mol fractions ( $X_{\pm}$ ,  $X_{\text{W}}$ ) of aggregates in the solutions.

$m$	$x_{\pm}$	$x_{\text{W}}$	$\text{CN}_{+\text{W}}$	$\text{CN}_{-\text{W}}$	$\text{CN}_{\text{WW}}$	$M_{\pm}$	$M_{\text{W}}$	$X_{\pm}$	$X_{\text{W}}$
2	0.0336	0.9328	4	6	4	2	7.11	0.18	0.64
			6	6	4	2	6.30	0.19	0.61
			8	6	4	2	5.51	0.21	0.58
4	0.0629	0.8742	4	6	4	4	3.11	0.36	0.28
			6	6	4	4	1.51	0.42	0.16

Table 3. FNM2 parameters for cation-water interactions.

		$r_{+w}$ [Å]	$l_{+w}$ [Å]	$r_{0+w}$ [Å]	CN <sub>+w</sub>	$\Gamma_{+w}^*$
2 m	Li <sup>+</sup>	(2.17)	(0.51)	(5.42)	(4)	(4)
	Na <sup>+</sup>	2.42	0.27	4.52	4	4.7
	K <sup>+</sup>	2.80	0.19	4.02	6	8.1
	Cs <sup>+</sup>	3.15	0.22	3.51	8	9.8
4 m	Li <sup>+</sup>	2.08	0.25	4.58	4	4
	Na <sup>+</sup>	2.42	0.21	2.33	4	7.2
	K <sup>+</sup>	2.80	0.19	2.80	6	8
	Cs <sup>+</sup>	3.15	0.19	3.33	6	9

Table 4. FNM2 parameters for Cl<sup>-</sup>-water interactions.

		$r_{-w}$ [Å]	$l_{-w}$ [Å]	$r_{0-w}$ [Å]	CN <sub>-w</sub>	$\Gamma_{-w}^*$
2 m	LiCl	3.15	0.19	6.00	6.00	6.00
	NaCl	3.14	0.16	6.06	6.00	6.00
	KCl	3.14	0.17	6.10	6.00	6.00
	CsCl	3.09	0.14	6.20	6.00	6.00
4 m	LiCl	3.08	0.19	5.30	6.00	6.00
	NaCl	3.14	0.17	5.80	6.00	6.00
	KCl	3.14	0.17	5.74	6.00	6.00
	CsCl	3.16	0.14	6.00	6.00	6.00

Table 5. FNM2 parameters for solvent-solvent interactions.

		$r_{ww}$ [Å]	$l_{ww}$ [Å]	$r_{0ww}$ [Å]	CN <sub>ww</sub>	$\Gamma_{ww}^*$
2 m	LiCl	2.91	0.042	2.46	4	4.4
	NaCl	2.95	0.065	2.47	4	4.1
	KCl	2.94	0.103	2.61	4	3.7
	CsCl	2.92	0.173	3.2	4	2.8
4 m	LiCl	2.95	0.171	2.59	4	3.3
	NaCl	2.95	0.139	2.50	4	3.4
	KCl	2.94	0.109	2.73	4	2.7
	CsCl	2.93	0.25	3.07	4	(1.6)
	pure water	2.84	0.116	2.71	4	4.5

### The Model Pair Correlation Functions

An advantage of the first neighbour models is that they give a description of the hydration phenomena both in short and long range. This allows the interpretation of the structure function in the whole scattering variable range. This is why FNM's permit to derive approximations for the partial atom pair correlation functions on the basis of diffraction measurements.

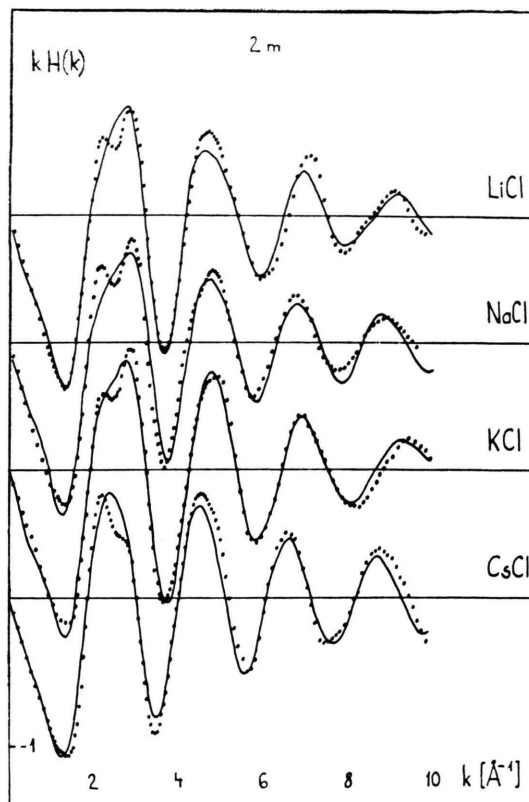


Fig. 3. Experimental (dots) and FNM2 (full line) structure functions for 2 molal solutions.

The relation between the X-ray structure function  $H(k)$  and the partial structure functions  $h_{ij}(k)$  [6] is

$$H(k) = \sum_{i \leq j}^3 c_{ij}(k) h_{ij}(k). \quad (12)$$

With a suitable rearrangement of the terms in equations (5)–(11) relations can be derived between the partial structure functions and the parameters of FNM2 [6]. The partial structure functions determine the partial atom pair-correlation functions through a Fourier transformation:

$$g_{ij}(r) = 1 + \frac{1}{2\pi^2 r \rho_0} \int k h_{ij}(k) \sin k r dk. \quad (13)$$

The cation-water and water-water pair correlation functions (PCF), obtained in this way for 2 and 4 molal alkali chloride solutions are presented in Figs. 5–7. On the basis of PCF's, coordination numbers determined by integration up to the first minimum  $\Gamma_{iw}(r_{\min}) = \Gamma_{iw}^*$  can also be calculated (Tables 3–5). They may differ from the even coordination numbers CN<sub>iw</sub>.



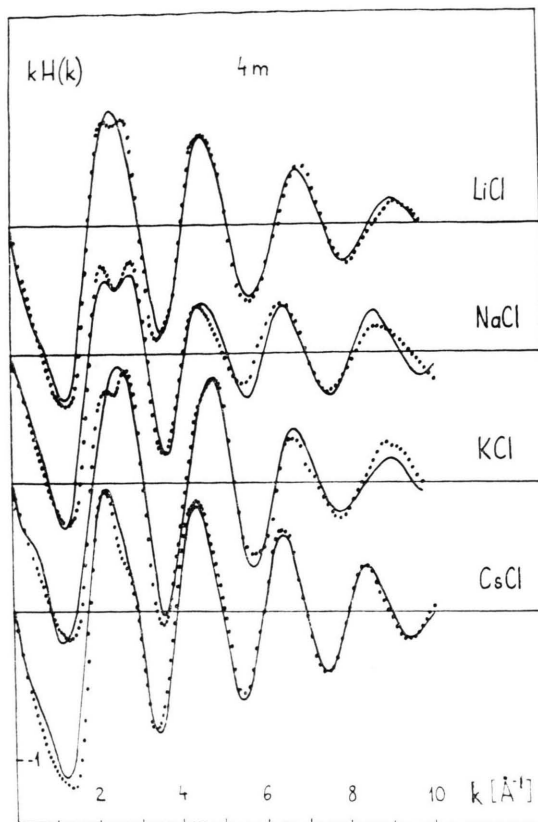


Fig. 4. Experimental (dots) and FNM2 (full line) structure functions for 4 molal solutions.

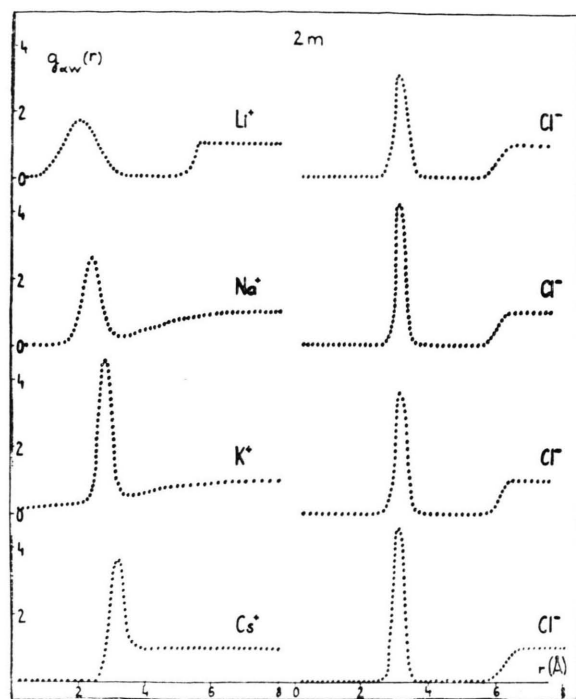


Fig. 5. Pair correlation functions determined by FNM2. Cation-water and anion-water interactions in 2 molal solutions.

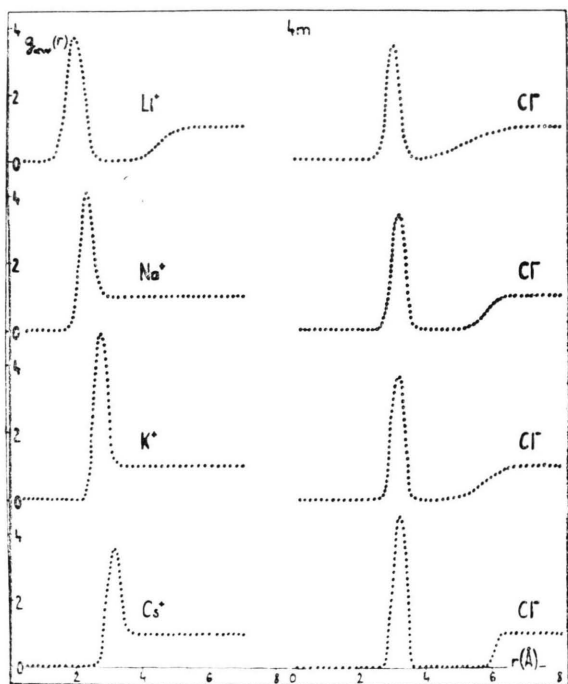


Fig. 6. Pair correlation functions determined by FNM2. Cation-water and anion-water interactions in 4 molal solutions.

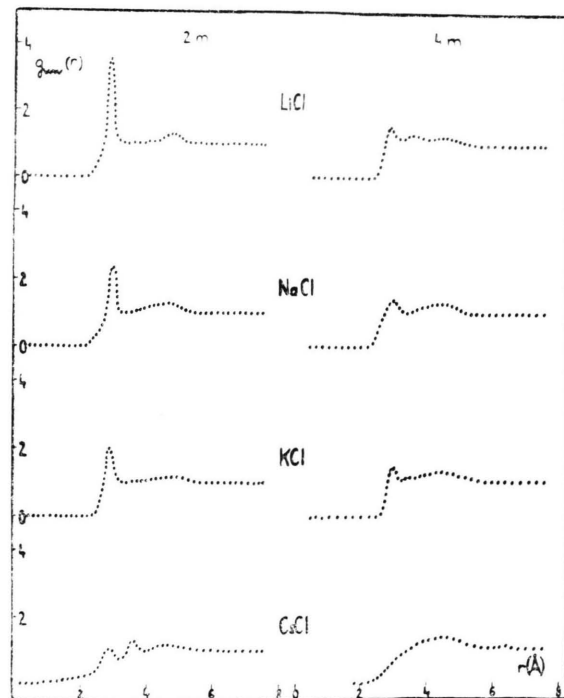


Fig. 7. Pair correlation functions determined by FNM2. Water-water interactions for each solution.

## Results and Discussion

We intend to discuss some general features of the applied model and to draw some conclusions on the ion-solvent and solvent-solvent interactions in alkali chloride solutions. An earlier comparison of FNM2 with molecular dynamics pair correlation functions did show that the model describes the first peaks of the true pair correlation functions quite well and marks correctly the beginning of the homogeneous distribution of the water molecules. It is worth noting that inherent limitations of the model prevent a correct description of  $g_{ij}(r)$  in the intermediate range. It is also to be noted that the PCF's of FNM2 like those of FNM1 do not satisfy the sum rule for particle numbers

$$4\pi\rho_W \int_0^\infty (g_{iW}(r) - 1) r^2 dr = -\delta_{iW},$$

$$i = 1, 2, 3. \quad (14)$$

### *Ion-Water Interaction*

Ion-water PCF's of FNM2 are shown in Figs. 5 and 6, while numerical parameters of the interactions are given in Tables 3–5.

It turns out that the parameters describing the hydration of the  $\text{Cl}^-$  are almost independent of the concentration and the kind of counter ion. Only the rms deviation  $l_{-W}$  exhibits a slight decrease on increasing radius of the cation. This points to a greater effect of the smaller cations on the hydration of the anion.

The  $r_{-W}$  values are found to be identical within the limits of standard errors. The  $r_{0-W}$  parameter, which gives the boundary of the continuum surrounding the anion, is always high,  $r_{0-W} \sim 6 \text{ \AA}$ . This would suggest that the correlation radius of the  $\text{Cl}^-$  ion is greater than that of the cations. But the  $\text{Cl}^-$ -water PCF is the one which strongly violates the sum rule (14), so that the high value of  $r_{0-W}$  could also be due to one of the basic assumptions of the model. It seems probable that the arrangement of the water molecules around a  $\text{Cl}^-$  ion is not symmetrical. This guess is supported by the great rms deviations of the water-water distances within the hydration shells of  $\text{Cl}^-$ , which amount up to  $1.2 \text{ \AA}$  (not given in the Tables). The general features of the hydrated  $\text{Cl}^-$  ion in FNM2 are very close to those in FNM1, although the  $l_{-W}$  values are somewhat smaller in FNM2 than in FNM1. Moreover a slight counter ion dependence of  $l_{-W}$  can be found

in FNM2. The parameters of FNM1 and FNM2 for the hydrated cations (Table 3) differ much more. Data for the 2 molal  $\text{LiCl}$  solution are given in parenthesis in Table 3, because the contribution of  $\text{Li}^+$  ions to the X-ray structure function is very small, which renders the determination of the parameters uncertain. Cation-water distances do not depend on the concentration of the solutions investigated. Between the Pauling radii of the cations  $r_p$  and the cation-water distances  $r_{+W}$  obtained by FNM2, the empirical relation

$$r_{+W} = 1.48 \pm 0.01 + r_p(0.98 \pm 0.01) \quad (15)$$

could be established.

The constant term of Eq. (15) ( $1.48 \text{ \AA}$ ) defines an effective solvent radius. This value is in good agreement with the water-water distance  $r_{WW} = 2.95 \text{ \AA}$  resulting from FNM2 (see Table 5).

In general, the  $l_{+W}$  values are seen to decrease with increasing cationic size and increasing concentration.

The behaviour of the  $r_{0+W}$  values is also remarkable: The larger the ion, the shorter is in general the range  $r_{0+W}$  of its influence on structure formation. For the 4 molal solutions this range does not exceed that of the first neighbours, with the only exception of the  $\text{LiCl}$  solution;  $r_{0+W}$  does also decrease with increasing concentration.

The  $I_{+W}^*$  running coordination numbers are greater than the coordination numbers  $\text{CN}_{+W}$ , again with the only exception of  $\text{Li}^+$  ion.

### *Solvent-Solvent Interactions*

The application of FNM2 on alkali chloride solutions yields clear evidence that the structure of the “free” water differs from that of pure water. The FNM2 parameters for the “free” and pure water interactions are reported in Table 5, while the corresponding PCF's are given in Figure 7. The mean distance of the nearest “free” water molecules has been found significantly greater ( $2.94 \text{ \AA}$ ) than that of molecules in pure water ( $2.84 \text{ \AA}$ ).

On comparing the  $l_{WW}$ -values of free and pure water, one observes more structure for the 2 molal  $\text{LiCl}$  and  $\text{NaCl}$  solutions than for pure water, and less structure for the  $\text{CsCl}$  solution. This can be interpreted as the “structure making” and “structure breaking” effect of the ions, discussed so often in the literature. Accordingly, the  $\text{Li}^+$  and  $\text{Na}^+$  ions

are "structure making" while the  $\text{Cs}^+$  ion is "structure breaking" in 2 molal solutions. The  $l_{\text{WW}}$  parameters for 4 molal solutions do not show the above regularity probably because the high concentration of ions masks the ion size effect, except for the CsCl solution, where effect of the ions on the structure of the solvent seems to be the strongest. All the above effects can clearly be read from the solvent-solvent PCF's in Fig. 6. The solvent-solvent  $l_{\text{WW}}$  parameters are smaller than the  $l_{\text{IW}}$ 's of ion-solvent interactions (excluding CsCl). This means that the model based on X-ray data suggests the solvent-solvent interactions to be more intensive than the ion-solvent interactions. The behaviour of the  $r_{0\text{WW}}$  parameters is also remarkable. These values, characteristic for the boundary of the continuum, are near to the central  $r_{\text{WW}}$  parameters both for solutions and pure solvent. The same result is obtained from FNM interpretation of the neutron structure function of pure water [18].

The low  $r_{0\text{WW}}$  parameters both for the pure solvent and for the solutions suggest that the basic assumption d) of symmetry must be weakened. The  $I_{\text{WW}}^*$  coordination numbers are always smaller than the corresponding  $\text{CN}_{\text{WW}}$  values reflecting only the discrete interaction in free solvent (Table 5). The  $I_{\text{WW}}^*$  parameters decrease

with increasing cation radius for both concentrations. The influence of ions can be recognized in the  $I_{\text{WW}}^*$  parameters also, since these are always smaller than their corresponding values for pure water. A lack or at least a lowered degree of symmetry in the first coordination spheres of water is supported also by the rms deviations of noncentral water-water distances  $l_{\text{WW}}$  in the tetrahedra of the free water (Table 6).

	2 <i>m</i> $l_{\text{WW}}$	4 <i>m</i> $l_{\text{WW}}$
LiCl	0.27	0.42
NaCl	0.42	0.65
KCl	0.46	0.46
CsCl	0.59	0.38
pure water	0.32	

Table 6. RMS deviations for the non-central water-water interactions in the solvent centered aggregates.

Apart from the 2 molal LiCl solution, they are always greater than in pure water. Their values for the 2 molal solutions are increasing together with the increasing size of cations.

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