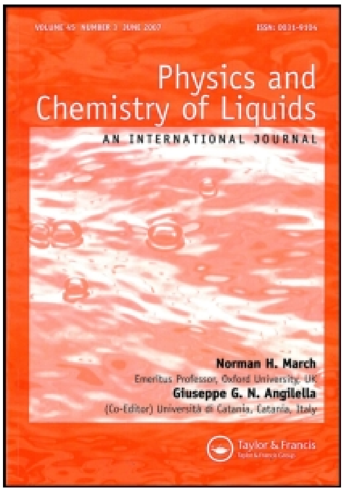

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Partial Structure Factors in $NiCl_2$ Aqueous Solutions in the Long-Wavelength Limit

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The $q = 0$ limits of the partial structure factors in aqueous solutions of $NiCl_2$ are calculated by using experimental data on osmotic coefficients, partial molar volumes and recently available data on the isothermal compressibility. Use has been made of the Beeby formalism, only slightly modified for the case of an AB_2 type salt. The computed values of the structure factors usually not accessible by experiments, are given as a function of the concentration for a temperature $T = 25°C$.

1. INTRODUCTION

During the past few years an increasing deal of investigation has been devoted to the study of the structural properties of liquid systems with more than one component. The problem is stimulating because:

i) of the challenging experimental complexity connected with the derivation of the partial structure factors from neutron or X-rays diffraction data and

ii) in the case of some electrolytic solutions of the appearance of some kind of structural order.[1,2]

Due to the difficulty of obtaining the partial structure factors as a function of the transferred wave-vector q, most of the theoretical discussions rely on the possibility of linking the $q = 0$ limits of the structure factors to statistical thermodynamics[3,4] and are limited to binary systems, like liquid alloys or solutions in which the solute molecules do not dissociate.

In a previous paper of the present authors[5] an attempt has been made to extend the Bhatia and Thornton formalism to electrolytic solutions, in which the constituents are more than two, and to separate the configurational entropy contribution to the Bhatia and Thornton "structure factors" from the energetic contribution.

The connection between thermodynamics and partial structure factors in aqueous electrolytic solution in the long-wavelength limit has been exploited by Beeby[6] who has explicitly written the linkage between the several partial structure factors in these multiconstituent systems and directly measurable quantities, as the isothermal compressibility, the partial molar volumes and the chemical potentials. Even if restricted to $q = 0$ situations, the Beeby formulae are quite important because they allow for fixing the thermodynamical limits of the structure factors, which are not experimentally valuable in an exact way. It should be noticed that the Beeby treatment forces the two types of ions of the solute to fluctuate together and the same happens for the ions of the solvent, so that in practice the actual components of the system are still two, the salt and the water.

In view of the above-mentioned importance and because data on the compressibility has become available very recently for the $NiCl_2$ solutions,[7] we have used the Beeby formalism modified for the $NiCl_2$ case, to compute all the $q = 0$ partial structure factors for this system. Even if the main interest in this kind of calculations is to obtain data which are complementary to the experimental ones, it is also possible to extract from them some considerations on the short-range situation in the solutions. The Bhatia–Thornton structure factors have also been computed and briefly discussed.

2 THE FORMALISM

In a binary mixture or in a two-components system, even if with more than two constituents, three structure factors can be defined[3]

$$\begin{aligned} S_{NN}(q) &= N^{-1}\langle N(q)N^{+}(q)\rangle \\ S_{CC}(q) &= N\langle C(q)C^{+}(q)\rangle \\ S_{NC}(q) &= \mathrm{Re}\langle N^{+}(q)C(q)\rangle \end{aligned} \qquad (1)$$

where $N(q)$ and $C(q)$ are the Fourier components of the fluctuation of the number of particles and of the concentration, respectively. As $q = 0$, these functions have the simple physical meaning

$$\begin{aligned} S_{NN}(0) &= N^{-1}\langle(\Delta N)^2\rangle \\ S_{CC}(0) &= N\langle(\Delta c)^2\rangle \\ S_{NC}(0) &= \langle \Delta N \Delta c\rangle \end{aligned} \qquad (2)$$

where $\langle(\Delta N)^2\rangle$ is the mean square fluctuation in the number of particles in the volume V of the medium, $\langle(\Delta c)^2\rangle$ the mean square fluctuation in the concentration and $\langle\Delta N\Delta c\rangle$ the correlation between the two fluctuations. Through standard thermodynamical arguments, it is possible to relate the structure factors to some macroscopic properties of the system:

$$
\begin{aligned}
S_{NN} &= \delta^2 S_{CC} + \frac{N}{V} k_B T \chi_T \\
S_{CC} &= N k_B T \Big/ \left(\frac{\partial^2 G}{\partial c^2}\right)_{N,P,T} \\
S_{NC} &= -\delta S_{CC}
\end{aligned}
\tag{3}
$$

where

$$
\begin{aligned}
\delta &= -\frac{1}{V}\left(\frac{\partial V}{\partial c}\right)_{N,P,T} \\
\chi_T &= -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,C}
\end{aligned}
$$

and c is the molar fraction of the solute, G the Gibbs potential and the other symbols have the usual meaning.

In a system with more than one species of atoms or ions, it is possible to define the partial structure factors, which in literature are often defined in different ways. We report here two of these different definitions.

If $g_{ij}(r)$ is the pair correlation function between an i-type ion and a j-type one, one can define the partial structure factors as

$$a_{ij}(q) = 1 + \frac{N}{V}\int_0^\infty [g_{ij}(r) - 1]\frac{\sin(qr)}{qr}4\pi r^2\,\mathrm{d}r \tag{4}$$

or

$$S_{ij}(q) = \delta_{ij} + \frac{\sqrt{N_i N_j}}{V}\int_0^\infty [g_{ij}(r) - 1]\frac{\sin(qr)}{qr}4\pi r^2\,\mathrm{d}r \tag{5}$$

with the obvious relation

$$S_{ij}(q) = \delta_{ij} + \frac{\sqrt{N_i N_j}}{N}[a_{ij}(q) - 1] \tag{6}$$

Here N is the total number of ions, while N_α is the number of the ions of type α.

In the case of $NiCl_2$ aqueous solutions, we have made use of the procedure developed by Beeby in order to get expressions for the $a_{ij}(q = 0)$ with the obvious modifications of the Beeby formulae required for our case of a solute of the type AB_2, which dissociates into one A ion and two B ions. In this case one gets the following expressions where, as in the following of the paper, the values of the structure factors are considered for $q = 0$,

$$a_{\mathrm{Ni-Cl}} = 1 + \frac{N}{V}k_B T\left[\chi_T - \frac{N}{V}\frac{v_a^2}{3c\mu_a^1}\right]$$

$$a_{\mathrm{Ni-Ni}} = a_{\mathrm{Ni-Cl}} - \frac{3}{c}$$

$$a_{\mathrm{Cl-Cl}} = a_{\mathrm{Ni-Cl}} - \frac{3}{2c} \tag{7}$$

$$a_{\mathrm{O-H}} = 1 + \frac{N}{V}k_B T\left[\chi_T - \frac{N}{V}\frac{cv_s^2}{3(1-c)^2\mu_a^1}\right]$$

$$a_{\mathrm{O-O}} = a_{\mathrm{O-H}} - \frac{3}{1-c}$$

$$a_{\mathrm{H-H}} = a_{\mathrm{O-H}} - \frac{3}{2(1-c)} \tag{8}$$

$$a_{\mathrm{Ni-O}} = a_{\mathrm{Cl-O}} = a_{\mathrm{Ni-H}} = a_{\mathrm{Cl-H}} = 1 + \frac{N}{V}k_B T\left[\chi_T + \frac{N}{V}\frac{v_a v_s}{3(1-c)\mu_a^1}\right] \tag{9}$$

where v_a and v_s are the partial molar volume of the water and the solute, respectively, and

$$\mu_a^1 = \left(\frac{\partial\mu_a}{\partial c}\right)_P$$

where μ_a is the chemical potential of the solvent. c is defined as

$$c = \frac{n_s}{n_s + n_a} = \frac{n_s}{n} \tag{10}$$

where n_s and n_a are the number of molecules of the salt and the water, respectively. In our case each molecule of water or salt produces three ions, so that $N = 3(n_s + n_a)$.

Because the actual components of the solutions are still two, it is possible to use the Bhatia–Thornton structure factors in their original definition, if use is made of the number of molecules n instead of the number of ions N. As already pointed out by Bhatia and Thornton there is a direct correlation between their structure factors and the S_{ij} and a_{ij}.

Because in our case these relations are somewhat different from those of Bhatia and Thornton, we give them in the following

$$\begin{aligned} S_{nn} &= \tfrac{1}{3}[c^2 a_{\mathrm{Ni-Ni}} + (1-c)^2 a_{\mathrm{O-O}} + 2(1-c)c a_{\mathrm{Ni-O}} + 2] \\ &= cS_{\mathrm{Ni-Ni}} + (1-c)S_{\mathrm{O-O}} + 2\sqrt{c(1-c)}S_{\mathrm{Ni-O}} \end{aligned} \tag{11}$$

$$S_{cc} = \frac{c^2(1-c)^2}{3}\left[a_{\mathrm{Ni-Ni}} + a_{\mathrm{O-O}} - 2a_{\mathrm{Ni-O}} + \frac{3}{c(1-c)}\right]$$

$$= c(1-c)[(1-c)S_{\mathrm{Ni-Ni}} + cS_{\mathrm{O-O}} - 2\sqrt{c(1-c)}\,S_{\mathrm{Ni-O}}] \qquad (12)$$

$$S_{nc} = c(1-c)\left[\frac{c}{3}(a_{\mathrm{Ni-Ni}} - a_{\mathrm{Ni-O}}) - \frac{1-c}{3}(a_{\mathrm{O-O}} - a_{\mathrm{Ni-O}})\right]$$

$$= c(1-c)\left[S_{\mathrm{Ni-Ni}} - S_{\mathrm{O-O}} + \frac{1-2c}{\sqrt{c(1-c)}}S_{\mathrm{Ni-O}}\right] \qquad (13)$$

It has to be noticed that the quantities

$$\Delta N_j = \frac{c_j}{3}(a_{ij} - a_{jj}) \qquad (14)$$

which enter into the expression (13) for S_{nc}, are of relevant interest. In fact, from the definition (4), of the partial structure factors, it is clear that ΔN_j gives the difference between the total number of j ions surrounding an i ion and the total number of j ions surrounding a j ion. Because $g_{ij}(r) \to 1$ within a few interionic distances, ΔN_j provides an integrated measure of the short-range ordering in the system.

It can also be seen from (4) and (13) that

$$\frac{S_{nc}}{c(1-c)} = \Delta N_0 - \Delta N_{\mathrm{Ni}}$$

is given by the average of the difference between the probability of finding any ion, without respect to its kind, around a Ni ion and the probability of finding any ion around an O ion. So it is clear, as it was from (3), that in case the partial molar volume of the constituents are equal, i.e. the different kinds of ions are not distinguishable, S_{nc} vanishes.[3]

3 RESULTS AND DISCUSSION

By using the relations given in the preceeding section, the quantities of interest have been computed for a temperature $T = 25°\mathrm{C}$. The experimental data on the density and the partial molar volumes have been taken from Pearce and Eckstrom[8] and the data on the osmotic coefficient used to get the chemical potential have been taken from Stokes.[9] The data on the isothermal compressibility are from Maisano *et al.*[7]

In Figure 1 the Bhatia–Thornton structure factors are reported, as a function of the solute molar fraction c, up to the saturation concentration. The

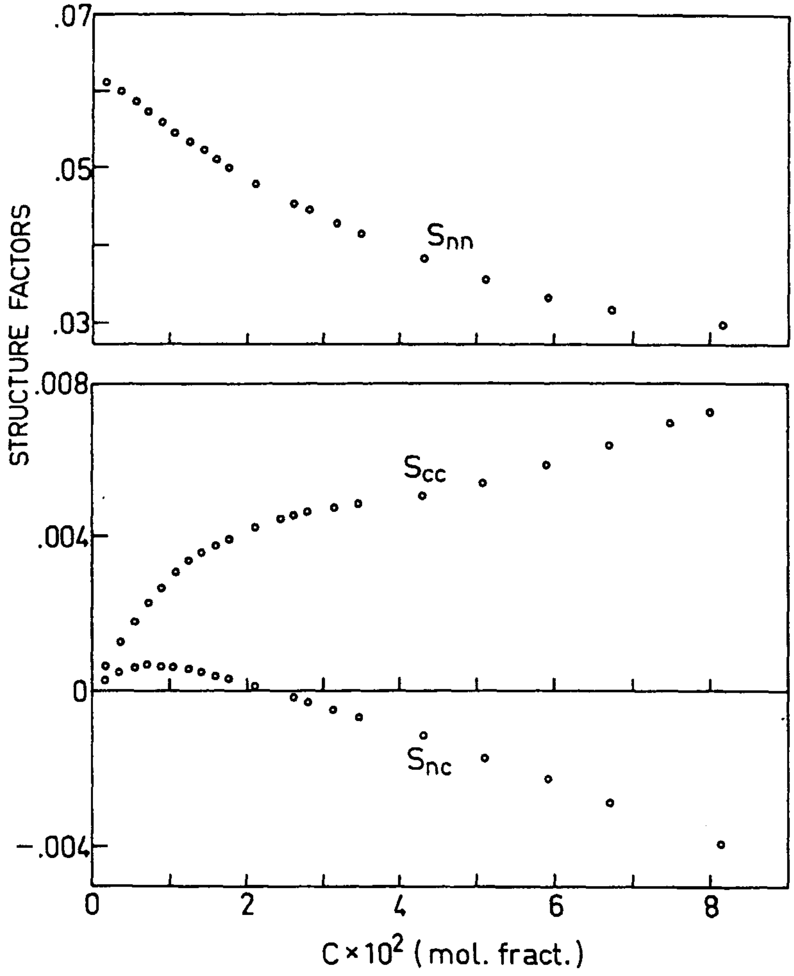

FIGURE 1 The Bhatia–Thornton structure factors are reported as a function of the solute molar fraction *c*.

S_{cc} data have already been reported in Ref. 5, where they have been discussed with regard to the formation of complexes into the solution. The S_{nc} curve shows a maximum at the concentration at which saturation of the relative concentration of complex ions takes place, and then it decreases. The zero value corresponds to the concentration at which $v_a = v_s$ and, if the considerations of Bhatia and Thornton are still valid for the solution, one might expect that $S_{nc} = 0$ for all q and only two structure factors are sufficient to describe the system completely at that concentration.

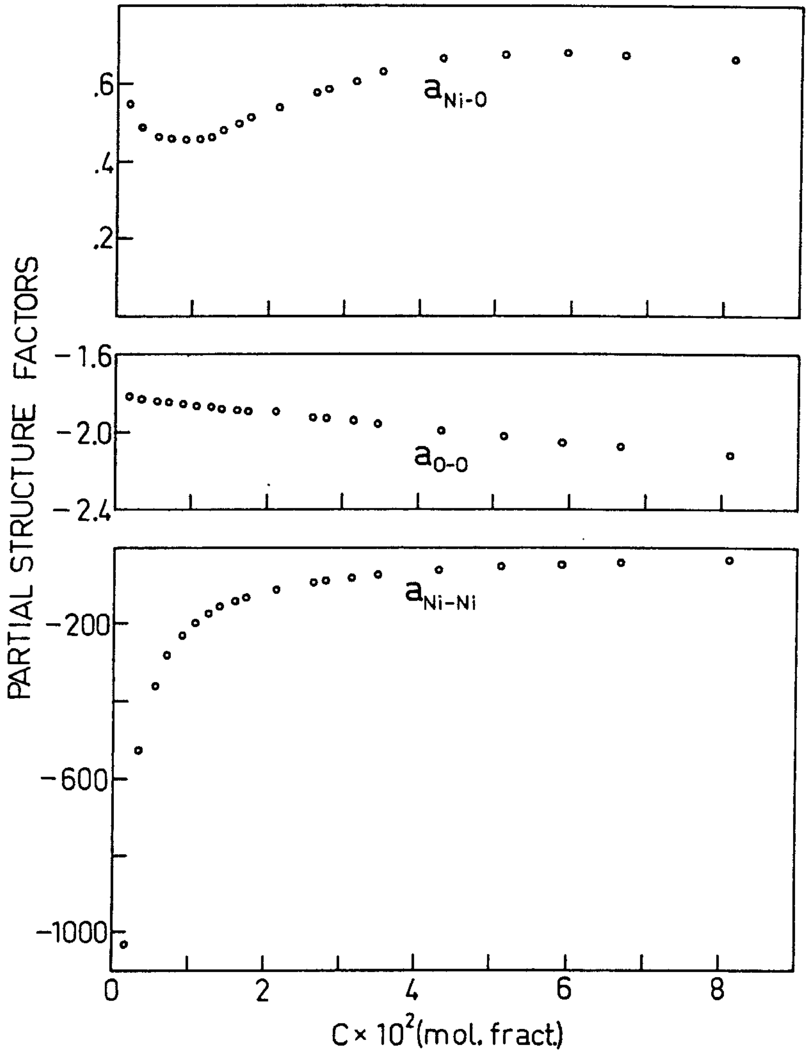

FIGURE 2 The partial structure factors are reported as a function of the solute molar fraction c.

Because of the sum rule which S_{nc} obeys to:

$$\int_0^\infty S_{nc}(q)q^2\,dq = 0$$

it is possible to deduce that, if S_{nc} goes down with increasing concentration at $q = 0$, correspondingly the same function has to become more positive in some region of the q-space.

With some caution, a similar consideration could be drawn from the si rule for S_{nn}

$$\frac{1}{2\pi^2}\int_0^\infty [S_{nn}(q) - 1]q^2\,\mathrm{d}q = -\frac{n}{V}$$

because n/V does not vary appreciably with concentration. Here to which goes down with concentration should correspond some increase of function in q space above the value 1.

TABLE I

Some relevant data used in the computations and the computed S_{ij} partial structure fac m is the molality of the solution, c the $NiCl_2$ molar fraction, N/V is the total number densi the ions in units of Avogadro number and χ_T is the isothermal compressibility.

m	c	N/V (cm^{-3})	χ_T (10^{-11} cm^2/dyne)	$S_{\mathrm{Ni-Ni}}$	$S_{\mathrm{O-O}}$	$S_{\mathrm{Ni-O}}$
0.1	0.00179	0.16616	4.450	0.383	0.0613	−0.006
0.2	0.00359	0.16627	4.352	0.371	0.0600	−0.010
0.3	0.00537	0.16637	4.255	0.351	0.0591	−0.013
0.4	0.00715	0.16647	4.158	0.329	0.0581	−0.015
0.5	0.00892	0.16655	4.065	0.309	0.0571	−0.017
0.6	0.01069	0.16661	3.974	0.293	0.0562	−0.018
0.7	0.01245	0.16668	3.887	0.277	0.0552	−0.019
0.8	0.01421	0.16671	3.808	0.259	0.0543	−0.020
0.9	0.01595	0.16671	3.731	0.242	0.0537	−0.020
1.0	0.01770	0.16678	3.652	0.228	0.0527	−0.021
1.2	0.02116	0.16681	3.508	0.205	0.0515	−0.021
1.5	0.02631	0.16683	3.318	0.176	0.0497	−0.022
1.6	0.02802	0.16675	3.258	0.169	0.0491	−0.022
1.8	0.03141	0.16670	3.137	0.154	0.0479	−0.022
2.0	0.03478	0.16667	3.029	0.141	0.0457	−0.022
2.5	0.04310	0.16642	2.791	0.118	0.0447	−0.022
3.0	0.05128	0.16608	2.582	0.105	0.0437	−0.023
3.5	0.05932	0.16542	2.400	0.097	0.0423	−0.025
4.0	0.06723	0.16528	2.254	0.092	0.0424	−0.027
4.91 (sat.)	0.08130	0.16449	2.035	0.085	0.0433	−0.030

In Figure 2 we report the three independent partial structure fac $a_{\mathrm{Ni-O}}$ $a_{\mathrm{O-O}}$ and $a_{\mathrm{Ni-Ni}}$, from which all the a_{ij} can be deduced by relati (7)–(9), while the corresponding S_{ij} are listed in Table I. As previously noti these a_{ij} or S_{ij} values are just the ones not accessible by a diffraction exp ment and the present data are, to our knowledge, the first which are publis for the case of electrolytic solutions. It is now possible to fix the value of a_{N} for the experiment by Hove *et al.* (1974) as −32.7 at the saturation c centration.

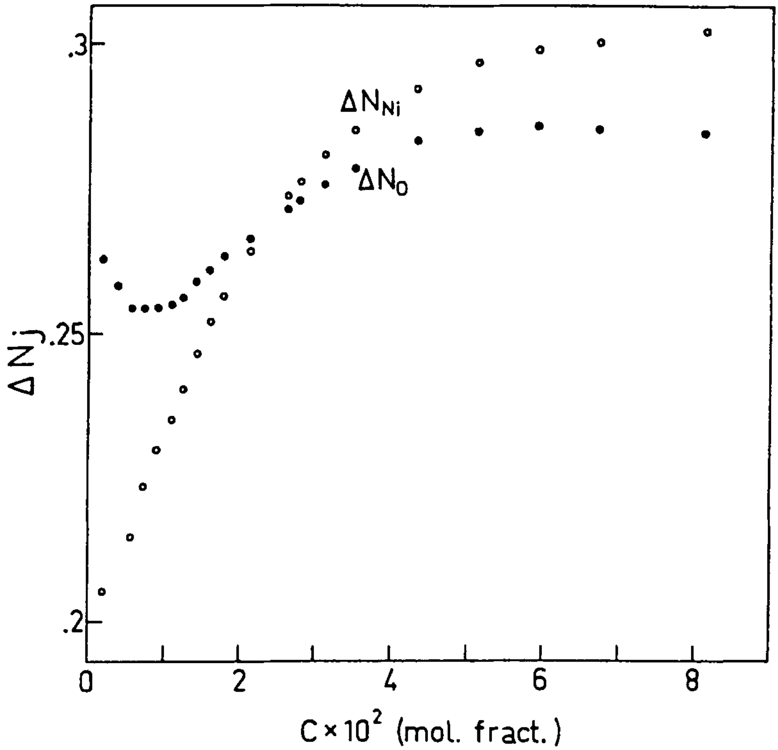

FIGURE 3 The quantities ΔN_O and ΔN_{Ni} (see text) are reported as a function of solute molar fraction c.

It should be noticed the behaviour of a_{Ni-O}, which is consistent with the hypothesis of paper I on the existence of complex ion of the type $(NiCl)_4^{-\,-}$. In fact, up to the concentration at which the relative number of the complexes saturates ($c \sim 0.01$) the correlation between Ni and O ions goes down. Once the relative number of complexes is fixed and with increasing c the interaction between complexes begins to be significant, the correlation becomes stronger.

Once one has the a_{ij}, it is possible to compute the quantities ΔN_j mentioned in Section 2. In Figure 3 we report ΔN_{Ni} and ΔN_O, which in the case of uniform ion distribution should take both the value 1. It can be seen how, especially for the lower concentrations, the N_i ions prefer to stay around a Ni ion rather than around an O ion, and the O ions prefer to stay around an O ion rather than a Ni ion. For a concentration $c \sim 0.024$, $\Delta N_O \equiv \Delta N_{Ni}$. We have already seen how it depends on the equality between the partial molar volumes which in a sense make the particle indistinguishable.

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