

## Autocorrelation spectroscopy of nickel chloride aqueous solutions

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1977 J. Phys. C: Solid State Phys. 10 L115

(<http://iopscience.iop.org/0022-3719/10/6/001>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.130.106.65

The article was downloaded on 28/05/2010 at 21:26

Please note that [terms and conditions apply](#).

## LETTER TO THE EDITOR

### Autocorrelation spectroscopy of nickel chloride aqueous solutions†

C M Sorensen and J F Scott§

Department of Physics, University of Colorado, Boulder, Colorado 80309 USA

Received 4 January 1977

**Abstract.** Intensity autocorrelation spectroscopy measurements have been made on aqueous solutions of nickel chloride as a function of wavevector and molarity. No long-range order is observed on a  $10^{-5}$  s time scale. A  $k^2$  dependence is observed, indicating Gaussian diffusion. The particle size is found to be 2 Å; and the correlation time varies linearly with the shear viscosity of the solutions. We interpret the particles as  $\text{NiCl}_2$  molecules, having vibrational energies of  $\sim 200 \text{ cm}^{-1}$ .

The possibility of long-range order in aqueous solutions has been raised for several systems recently. In this note we report light-scattering autocorrelation measurements on aqueous solutions of  $\text{NiCl}_2$ . Our interest in this system was stimulated by recent measurements (Howe *et al* 1974, Fontana 1976) which indicated the possibility of long-range or quasi-crystalline order in these solutions. Neutron-scattering experiments (Howe *et al* 1974) on highly concentrated solutions ( $5.5 \text{ mol l}^{-1}$  in  $\text{D}_2\text{O}$ ) have shown unusually strong peaks in the Ni–Ni correlation function, implying an ordered structure over distances much larger than the average Ni–Ni distance. Raman spectra of these systems (Fontana 1976) showed that a broad peak develops at  $220 \text{ cm}^{-1}$  as the concentrations are increased to  $4 \text{ mol l}^{-1}$ . This broad Raman peak was interpreted as due to the onset of a quasi-crystalline structure in which collective vibrations (phonons) could occur. Both Raman data and luminescence data indicated that long-range order evolved continuously with increasing concentration. A different interpretation of these data is provided in the present paper.

It is well known that the diffusion constant of Brownian particles in a fluid can be measured with light-scattering autocorrelation techniques (Clark *et al* 1970). If the suggested long-range order or quasi-crystalline structure of  $\text{NiCl}_2$  solutions manifests itself in the form of complexes which diffuse in the solution, their average size can be easily measured. This assumes, however, that such complexes have an average lifetime longer than the correlation time of the light scattered due to spatial diffusion (10–30  $\mu\text{s}$  in our experiments).

We prepared a  $4.0 \text{ mol l}^{-1}$  solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in boiled distilled water. This solution was filtered through a sintered glass filter of 'fine' porosity. This  $4.0 \text{ mol l}^{-1}$  solution was our stock solution from which solutions of other concentrations were

† Work supported in part by Energy Research and Development Administration Contract No. E(11-1)-2203.

§ Address for 1977: Clarendon Laboratory, Oxford University, Oxford, UK.

diluted. The beam of an argon ion laser operating at a wavelength of 514.5 nm was directed into a cylindrical scattering cell containing the  $\text{NiCl}_2$  solution. The beam was focused to 1 mm diameter. Light scattered from the solution was detected by a photomultiplier tube and analyzed to obtain the intensity-intensity autocorrelation function of the scattered light (Lyons 1973).

The correlation time for light scattering from Brownian motion is expected to vary as (Clark *et al* 1970)

$$\tau = \frac{1}{2} D^{-1} k^{-2} = \frac{1}{2} (6\pi\eta r / k_B T) k^{-2} \quad (1)$$

where  $k$  is the scattering wavevector, equal to  $4\pi n\lambda^{-1} \sin(\theta/2)$ ;  $n$  is the index of refraction of the scattering medium;  $\lambda$  is the wavelength of the incident light; and  $\theta$  is the scattering angle.  $D$  is the Stokes-Einstein diffusion constant for particles of radius  $r$  diffusing in a fluid at temperature  $T$  and of shear viscosity  $\eta$ .

Our experimental results for the correlation times are given in table 1. Three different scattering angles were used in the 4.0 mol l<sup>-1</sup> solution to test the  $k^2$  dependence. The predicted dependence was verified, indicating that Gaussian diffusion occurs. Table 1 also shows that the correlation time decreases with decreasing  $\text{NiCl}_2$  concentration.

Table 1. Correlation times and diffusion constants for  $\text{NiCl}_2$  aqueous Solutions.

Concentration (mol m <sup>-3</sup> )	Scattering angle (degrees)	Correlation time ( $\mu\text{s}$ )	Diffusion constant ( $\times 10^{-6}$ cm <sup>2</sup> s <sup>-1</sup> )
4.0	31	$24 \pm 2$	2.7
4.0	37.5	$18 \pm 1$	2.5
4.0	43	$12 \pm 1$	2.9
3.4	30	$16 \pm 1$	4.35
2.6	30	$8.5 \pm 2$	8

To determine the size of the diffusing complexes from these correlation-time measurements, we need to know the viscosity of the fluid in which the complexes diffuse. We measured the viscosity of our three solutions with a Pouiselle flow viscometer. Using these viscosity values and the Stokes-Einstein relation for the diffusion constant given in equation (1), we determined the diameter of the diffusing complexes. These results are given in table 2. These values are found to be approximately 2 Å for all concentrations of  $\text{NiCl}_2$  solutions. This is significantly smaller than the average Ni-Ni distance of 6 Å obtained from neutron scattering, which was taken as the *lower bound* of long-range order in these solutions. Indeed, our 2 Å value is typical of an average ionic diameter, and therefore implies no long-range order for periods of time longer than the correlation time ( $10^{-5}$  s).

Objections to our use of the Stokes-Einstein relation might be made. This relation is appropriate for macroscopic particles diffusing in a homogeneous fluid. On the 2 Å size scale of our inferred particles, the fluid is not homogeneous. In reply to this objection, we point out that quasi-crystalline structures of the size ( $\gg 6$  Å) inferred from Raman and neutron scattering should obey the Stokes-Einstein relation and would therefore not yield the observed data. Independent of the exact interpretation of the 2 Å particle size, it is clear that the observed data do not indicate any long-range order.

Whereas the three different solution concentrations yielded three different diffusion constants, the viscosities differed in such a way as to yield the same particle diameter in

each case. This implies that the Stokes-Einstein relation remains valid in this small particle regime, or, at a minimum, that  $D$  remains inversely proportional to viscosity in this regime (although perhaps modified by a numerical factor of order unity). Such an inverse proportionality between diffusion constant and viscosity has been observed previously in self-diffusion (Egelstaff 1967), but not, so far as we know, in the mutual

Table 2. Particle size inferred from the Stokes-Einstein equation for nickel-chloride aqueous solutions of different concentrations.

Concentration (mol m <sup>-3</sup> )	Viscosity (cP)	Particle diameter (Å)
4.0	8.2	1.75
3.4	5.15	1.94
2.6	3.12	1.96

diffusion process which describes our NiCl<sub>2</sub>/H<sub>2</sub>O system. We have compared mutual diffusion data obtained from autocorrelation studies on binary mixtures of simple organic compounds by Czworniak *et al* (1975) to tabulated shear viscosities for these binary systems (*International Critical Tables* 1933). In no case is the Stokes-Einstein relation seen to hold. However, the data of Czworniak *et al* were for systems more concentrated than a 0.1 mole fraction, whereas in our NiCl<sub>2</sub> solutions, the mole fractions were  $\leq 0.07$ , so that perhaps this behaviour is characteristic only of the dilute limit.

Table 3. Raman-active phonon frequencies in NiCl<sub>2</sub>.2H<sub>2</sub>O and related structures. Units are cm<sup>-1</sup>.

FeCl <sub>2</sub> .2H <sub>2</sub> O <sup>a</sup>	NiCl <sub>2</sub> .2H <sub>2</sub> O <sup>b</sup>	CoCl <sub>2</sub> .2H <sub>2</sub> O <sup>c</sup>	CuCl <sub>2</sub> .2H <sub>2</sub> O <sup>d</sup>
36	53	31.5	67
148	146	146	94
198	193	201	112
202	205	209	216
377	242	377 <sup>e</sup>	237
500	264 <sup>e</sup>		249
594			391
644			407
1625			669
1800			693
3392			778
3432			1612
			1622
			3366
			3390

<sup>a</sup> Kinne *et al* 1975.

<sup>b</sup> Helms and Scott 1975.

<sup>c</sup> C A Helms 1976 (private communication).

<sup>d</sup> Beattie *et al* 1969.

<sup>e</sup> No measurements have been made at higher energies in the Ni or Co compounds.

In order to understand Fontana's Raman results in NiCl<sub>2</sub> solutions, we have compared, in table 3, the phonon frequencies in CuCl<sub>2</sub>.2H<sub>2</sub>O, NiCl<sub>2</sub>.2H<sub>2</sub>O, FeCl<sub>2</sub>.2H<sub>2</sub>O, and CoCl<sub>2</sub>.2H<sub>2</sub>O. These values show that in each system, vibrations of strong Raman

intensity lie at about  $200\text{ cm}^{-1}$ , vibrations assigned as the symmetric stretch of the Ni–Cl (or M–Cl) bond (Beattie *et al* 1969). These values, however, would also be characteristic of  $\text{NiCl}_2$  molecules and do not in themselves imply any long-range order. Furthermore, there is strong evidence (Morosin† 1967) that the Ni–Cl bonding in  $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$  is almost perfectly covalent, much more so than in the iron and cobalt isomorphs. Thus, for solutions of  $\text{NiCl}_2$  in water, the Ni–Cl bonds should remain intact, and the  $\text{NiCl}_2$  molecule should function as an entity, even in dilute solutions. Thus, the stretching modes at about  $200\text{ cm}^{-1}$  will be preserved.

Our conclusions concerning the Raman data are in conflict with those of Fontana. Fontana assumes that the Raman data are due to collective vibrational excitations of a quasi-lattice of strongly interacting ionic complexes associated with the  $\text{Ni}^{2+}$  ions. This conclusion relies upon the assumption that  $\text{NiCl}_2$  in water dissociates into  $\text{Ni}^{2+}$  and  $\text{Cl}^-$  ions. This is not expected, however, due to the strong covalent nature of the Ni–Cl bonds discussed above.

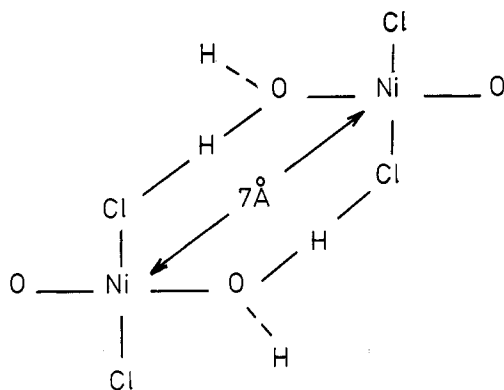


Figure 1. Hydrogen bonding in  $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ .

Why then do the neutron data of Egelstaff (1967) show such sharp peaks in the Ni–Ni correlation function for  $\text{NiCl}_2$  molecules in solution? The answer is that there is strong hydrogen bonding in all  $\text{NiCl}_2$  hydrates, as shown in figure 1. This does not imply that the hydrated  $\text{NiCl}_2$  (e.g.  $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ ) groups diffuse as Brownian particles, only that the distribution of Ni–Ni distances will be peaked much more sharply in aqueous solutions than would be the case for a random distribution of  $\text{NiCl}_2$  molecules. For the  $5.5\text{ mol l}^{-1}$  solution studied by Howe *et al*, the average Ni–Ni distance should be about  $6\text{ \AA}$ ; figure 1 shows that hydrogen bonding will work to prevent Ni–Ni separations much greater than 6 or  $7\text{ \AA}$ , or much less than this characteristic length.

In conclusion, our autocorrelation data support the view that no large complexes ( $\geq 2\text{ \AA}$ ) of  $\text{NiCl}_2$  exist in aqueous solutions for times longer than  $10^{-5}\text{ s}$ .

We thank W J O'Sullivan for helpful discussions.

† The experimental Ni–Cl bond length is  $2.40\text{ \AA}$ , which agrees with the covalent theory ( $2.38\text{ \AA}$ ) and not the ionic ( $2.53\text{ \AA}$ ).

**References**

- Beattie I R, Gilson T R and Ozin G A 1969 *J. Chem. Soc.* **A4** 534  
Clark N A, Lunacek J H and Benedek G B 1970 *Am. J. Phys.* **38** 575  
Czworniak K J, Andersen H C and Pecora R 1975 *Chem. Phys.* **11** 451  
Egelstaff P A 1967 *An Introduction to the Liquid State* (New York: Academic Press)  
Fontana M P 1976 *Solid St. Commun.* **18** 765  
Helms C A and Scott J F 1975 *Bull. Am. Phys. Soc.* **20** 326  
Howe R A, Howells W S and Enderby J E 1974 *J. Phys. C: Solid St. Phys.* **7** L111  
International Critical Tables 1933 (New York: McGraw Hill)  
Kinne R W, O'Sullivan W J, Ryan J F and Scott J F 1960 *Phys. Rev.* **B11** (1975)  
Lyons K B 1973 *PhD Thesis* University of Colorado  
Morosin B 1967 *Acta Crystallogr.* **23** 630