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STUDY OF Ni²⁺ SOLVATION DYNAMICS IN METHANOL AND DIMETHYL SULPHOXIDE BY QUASI-ELASTIC NEUTRON SCATTERING

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The high-resolution quasi-elastic neutron scattering (QENS) technique has been applied to study the translational diffusion of methanol (MeOH) and dimethyl sulphoxide (DMSO) protons in neat solvents and NiCl₂ solutions of different concentrations at 223, 297 K and 323 K. Obtained results clearly indicate that the diffusion coefficient of the solvents decrease with (*i*) decrease in temperature, and (*ii*) increase in the concentration of NiCl₂. It is established that electrostatic interaction defined by ion subsystem govern mainly the dynamic behaviour of solvent molecules in its electrolyte solutions irrespective of a solvent nature.

Introduction

Our ability to understand and predict the properties of disordered materials continues to be a challenge for the condensed matter theory. Within this area the non-aqueous electrolyte solutions (NAES) perhaps remain the severest test. The ion-solvation and ion-association are the two phenomena, which mainly govern the macroscopic properties of NAES and, hence, their technological applications. A deeper understanding of these phenomena requires detailed information of ion-solvent and ion-ion interactions at a molecular level.
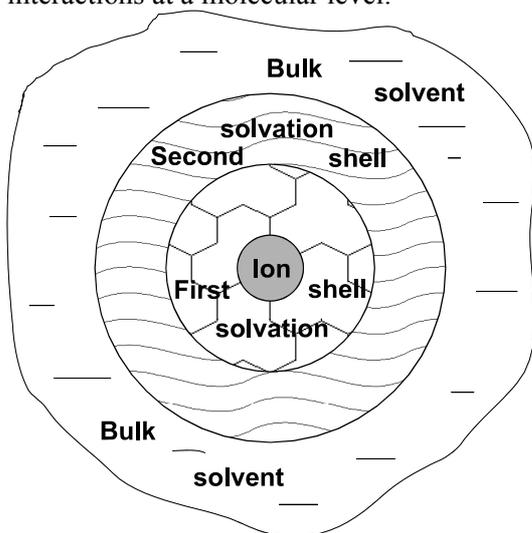

Fig. 1. Model of ion-solvation in solution with three regions of a solvent defined according to Frank & Wen [1] as first solvation shell (FSS), second solvation shell (SSS), and bulk solvent (Bulk).

The solvation of ions in a liquid solvent embodies primarily the interactions between the ions and solvent molecules that alter the solvent structure and its microdynamics in solution. According to the Frank and Wen model of the ion solvation [1] the space around an ion can be divided into three regions, *viz*. first solvation shell (FSS), second solvation shell (SSS), and bulk solvent (Fig. 1). In bulk solvent its properties correspond to those in neat solvent. In the FSS solvent properties are modified significantly by an ion, while SSS is intermediate region between bulk solvent and FSS. It is now entirely clear that the problems associated with the interactions of various types in solution, the structure of the solution, and the thermal movement of its particles are intimately related to each other.

Among the various direct experimental methods (*i.e.*, those methods for which the space and time dimensions are comparable to the molecular dimensions and characteristic times of molecular processes, respectively), neutron diffraction with isotopic substitution (NDIS) [2-5] and quasi-elastic neutron scattering (QENS) [6-10] offer the most powerful techniques for analysing the microscopic structure and ion/molecule dynamics in ion-molecular systems. These methods allow us to derive structural information of nearest-neighbour ion environment in terms of pair radial distribution functions, interatomic distances and co-ordination numbers, and molecular dynamics in terms of dynamic structure factors and diffusion coefficients.

Recently, we demonstrated [11,12] the use of NDIS technique to isolate the ion-ion, ion-H and ion-O partial radial distribution functions (RDFs), and to resolve the co-ordination/solvation structures of the isotopically substituted ions (cation and anion) in NiCl₂-MeOH solutions. Analyses of these RDFs demonstrated that Ni²⁺ is co-ordinated octahedrally by five methanol molecules and one chloride anion. The solvation number of Cl⁻ was determined to be ≅ 2. The joint analysis of the pair RDFs,

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$g_{NiCl}(r)$ and $g_{ClCl}(r)$, revealed that the electrolyte in its 1.4 molal methanolic solution mainly exists in the form of solvated contact ion pairs, $[NiCl]_s^+$, with a very small content of solvated $[NiCl_2]_s^0$ ion-triples.

From this point of view there is a special interest in the study of dynamic aspects of ion-solvation phenomena in NiCl$_2$ – methanol (MeOH) solutions at different temperatures and salt concentrations by using quasi-elastic neutron scattering technique. Another aim of this work is to elucidate a role of solvent nature in dynamics of ion solvation in concentrated solutions. For this purpose the NiCl$_2$ – dimethyl sulphoxide (DMSO) solutions were also investigated by using QENS technique.

Experimental

The aqueous solution of NiCl$_2$ was obtained by dissolving crystalline NiCl$_2$·xH$_2$O (Alfa, Puratronic®, 99.995%) in very dilute HCl (BDH, Aristar®) solution to remove any residual products of hydrolysis. The solutions of NiCl$_2$ were then evaporated to a solid form of NiCl$_2$·6H$_2$O and further dried in a vacuum line under 1-100 Pa at gradually increasing temperatures from 25 °C to 70 °C during one month period. Such procedure provided the water content less than 0.01%, which was monitored by weighting with correspondent accuracy. Anhydrous salt, as expected, [13] was yellow-brownish powder.

The solutions of NiCl$_2$ in MeOH (Analar, 99.8%, < 0.001% H$_2$O) and DMSO (Fluka Chemika, 99.5 %, < 0.01% H$_2$O) of required concentrations were made by weighing in a dried nitrogen-filled glove box. Prior to this, however, the solvents were distilled (DMSO under reduced pressure of 3 mbar at 33° C) and dried under the 0.4 nm molecular sieves during one week.

The sample densities were measured by using Anton Paar DMA 58 densimeter. The compositions and densities of the samples are listed in the Table 1.

Table 1. The diffusion coefficients (D) of the solvent molecules in neat methanol and dimethyl sulphoxide and its NiCl$_2$ solutions. For the solutions these values correspond to the average diffusion coefficient ($\bar{D}$) defined by Eq. (5)

T	d, g/cm^3	m, mol/kg	c, mol/dm^3	x	D·10^9, m^2/s
MeOH and NiCl$_2$ in MeOH
223	0.857	0.0	0.0	0.0	0.39±0.03, 0.498* [10]
297	0.788	0.0	0.0	0.0	2.16±0.07, 2.567* [10], 2.50 [14]
297	0.828	0.2971	0.2369	9.430·10^{-3}	1.40±0.05
297	0.947	1.3004	1.0539	0.0400	0.69±0.07
DMSO and NiCl$_2$ in DMSO
297	1.095	0.0	0.0	0.0	0.65±0.03, 0.72 [15], 0.84 [16]
297	1.106	0.1219	0.1327	9.434·10^{-3}	0.59±0.03
297	1.139	0.5330	0.5679	0.0400	0.31 ± 0.06
323	1.115	0.5330	0.5559	0.0400	0.66 ± 0.02

* Data refer to CD$_3$OH at 300 K and 230 K.

The quasielastic neutron scattering experiments were performed on the backscattering spectrometer IN10 at the ILL, Grenoble, France. Spectra were measured at five equally spaced q-values in the range 0.9 nm^{-1} ≤ q ≤ 3.8 nm^{-1} with an energy window of about ± 15 µeV. The incident wavelength of 0.6271 nm with the resolution in momentum transfer of 0.4 nm^{-1} was used. The monochromator was standard Si(111) and the experimental energy resolution function of ≈1.5 µeV (HWHM) was obtained from incoherent scattering from a sample of vanadium.

The complete experiment required measurements to be taken of the liquid sample (solvents or NiCl$_2$ solutions) in its container, the empty container, the background, and a vanadium slab of 1 mm thickness to give the energy resolution function.

The samples were held in a 40 mm × 40 mm flat container specially made from PTFE material with a sample thickness of 1 mm, providing a sample volume of 1.6 cm^3. All the measurements were performed at three temperatures, 223 K (neat methanol), 323 K (0.53 molal solution of NiCl$_2$ in DMSO) and 297 K (all other samples). The temperature was held constant within 1 K.

The raw data were converted to the dynamic structure factors $S(q,\omega)$ and corrected for background and container scattering using the INX program at the ILL. No multiple scattering corrections were applied to the data. The examples of the experimental QENS spectra are shown in Figs. 2-3.
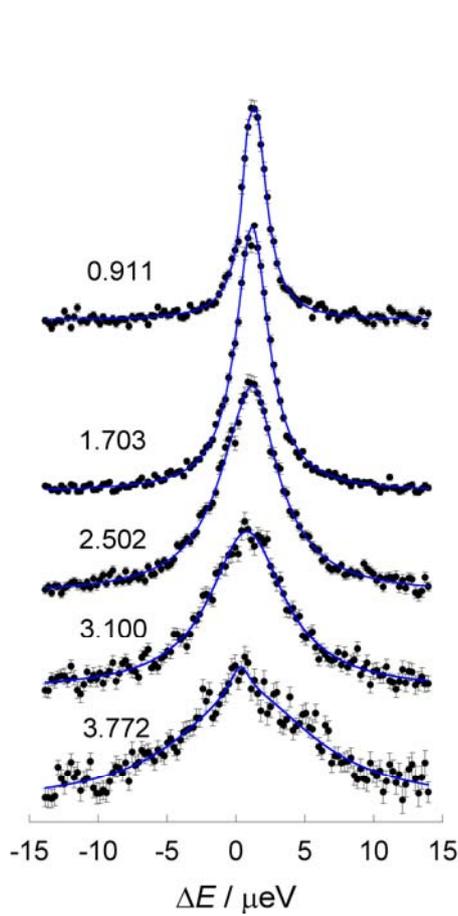

Fig. 2. The experimental quasi-elastic neutron spectra (points) and fitted Lorentzian (solid line) for neat MeOH at 223 K at five different *q*-values in nm^{-1} indicated in the figure, with arbitrary scale on the ordinate.
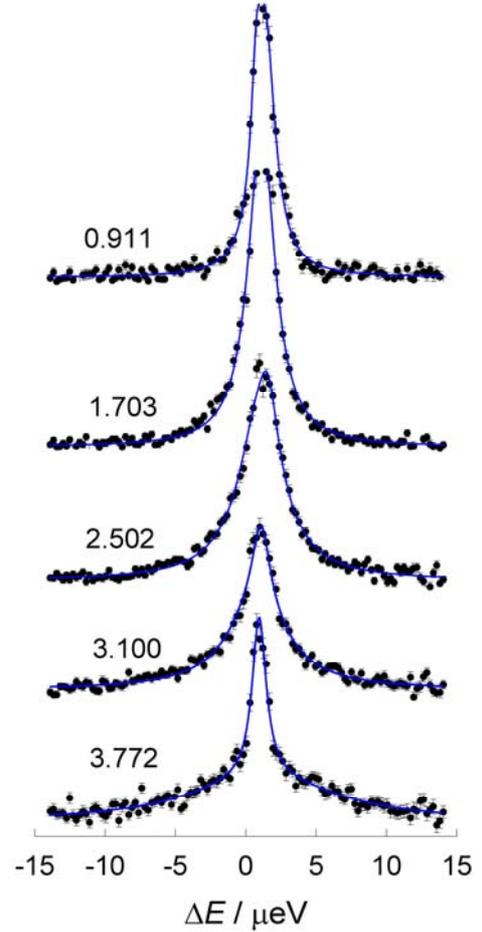
Fig. 3. The experimental quasi-elastic neutron spectra (points) and fitted Lorentzian (solid line) 0.53 molal solution of NiCl$_2$ in DMSO at 297 K at five different *q*-values in nm^{-1} indicated in the figure, with arbitrary scale on the ordinate.

Results and Discussion

The scattering of neutrons from a solution comprising of *n* atomic species is dependent on the double differential cross section $\dfrac{d^2\sigma}{d\Omega d\omega}$ defined by [6,8]

$$\frac{d^2\sigma}{d\Omega d\omega} = \sum_i^n \sum_j^n b_i b_j \left(x_i x_j\right)^{1/2} S_{ij}(q,\omega) + \sum_i^n b_{inc,i}^2 x_i S_i^s(q,\omega), \qquad (1)$$

where x_i, b_i and $b_{inc,i}$ are the atomic fraction, coherent scattering length and incoherent scattering length of species i, $S_i^s(q,\omega)$ is self-part of the scattering law, and $\hbar q = \Delta p$ and $\hbar\omega = \Delta E$ are the momentum and energy transfers, respectively. The incoherent scattering cross-section of the hydrogen (H) nucleus present in all the non-aqueous solvents, including MeOH and DMSO, is so large that $\dfrac{d^2\sigma}{d\Omega d\omega}$ is dominated by the self-term, $S_H^s(q,\omega)$; the other terms being sufficiently small that they

may be neglected in the data analysis. The knowledge of $\dfrac{d^2\sigma}{d\Omega d\omega}$ should thus lead directly to the proton dynamics, which can be identified with that of the solvent molecule itself.

For a proton obeying the diffusion equation, $S_H^s(q,\omega)$ is a Lorentzian of the form

$$S_H^s(q,\omega) = (1/\hbar)Dq^2 \left/ \left[\left(Dq^2\right)^2 + \omega^2\right]\right. , \tag{2}$$

with translational diffusion coefficient, D. This is the form to be expected when the longest ionic binding time, τ_b, present is short relative to the observation time, τ_{ob}, so that during this observation time any proton can sample the entire range of environments present in the solution. Usually this situation is described as the "fast-exchange limit" [6].

For the case when the solvent molecule's binding time (usually to a cation) is longer than the observation time, i.e., when $\tau_b > \tau_{ob}$, the so called "slow-exchange regime", $S_H^s(q,\omega)$ takes the form,

$$S_H^s(q,\omega) = (1/\hbar)\left\{x_1 D_1 q^2 \left/ \left[\left(D_1 q^2\right)^2 + \omega^2\right]\right. + x_2 D_2 q^2 \left/ \left[\left(D_2 q^2\right)^2 + \omega^2\right]\right.\right\} , \tag{3}$$

which is a sum of two weighted Lorentzians with two different diffusion coefficients, D_1 and D_2 in the FSS and SSS (or bulk solvent), respectively. Here x_i ($i=1,2$) denote the atomic fractions of the two proton populations.

Bearing in mind the results of aqueous NiCl$_2$ solutions [6], one can expect the non-aqueous solutions of this salt also to obey the "slow-exchange regime". Accordingly, two separate translational diffusion coefficients of solvent molecules, one originating from the Ni^{2+} FSS and the other from the rest of the solution can, in principle, be evaluated. But, due to the relatively high statistical noise (Figs. 2-3) and narrow energy window available, the fitting procedure did not allow us to resolve more than a single Lorentzian (see solid lines in Figs. 2-3). The experimental neutron spectra of NiCl$_2$ solutions could thus be described by the scattering law in the form,

$$S(q,\omega) = (1/\hbar)\bar{D}q^2 \left/ \left[\left(\bar{D}q^2\right)^2 + \omega^2\right]\right. , \tag{4}$$

where

$$\bar{D} = x_1 D_1 + x_2 D_2 \tag{5}$$

is the average translational diffusion coefficient of solvent molecules throughout the whole solution. Clearly, the experimental spectra for neat solvents were fitted by a single Lorentzian each in the form of Eq. (2). Then, the slopes of the plots of the half-width at half-maximum (HWHM) of the fitted Lorentzians *vs.* the square of wave number (q^2 in nm^{-2}) were used to calculate the corresponding diffusion coefficients (Figs. 4,5). It should be noted, however, that for 0.3 molal NiCl$_2$-MeOH solution, only the first four points could be used because of large statistical errors in HWHM values at high q-values.

The experimental diffusion coefficients, D (for neat solvents) and $\bar{D}$ (for NiCl$_2$ solutions) are listed in Table 1 along with the available literature [10,14-16] data. The analysis of Table 1 firstly shows that D values for neat solvents agree well with the literature data. Secondly, as the temperature decreases the diffusion of MeOH molecules in the neat solvent and DMSO molecules in 0.53 molal solution of NiCl$_2$ slows down drastically. Thirdly, our results clearly indicate that the diffusion coefficient of solvents decreases with increase in the concentration of NiCl$_2$.

To understand the influence of electrolyte concentration on translational diffusion of the solvent molecules we have plotted the reduced diffusion coefficients (D/D_0, where D_0 refers to the neat solvent) for the NiCl$_2$ solutions in MeOH and DMSO as function of electrolyte composition expressed in molar fraction (x) (Fig. 6) and molarity (c) (Fig. 7). The inspection of these figures shows that both the curves, for MeOH and DMSO, more or less coincide only when the solution composition is expressed in molar scale. It is implies that electrostatic interaction defined by ion subsystem govern mainly the dynamic behaviour of solvent molecules in its electrolyte solutions irrespective of a solvent nature. It is interesting to note that both sets of solutions, in MeOH and DMSO, have the same molar

ratios of solute to solvent: (*i*) 1:105 for 0.3 molal solution of $NiCl_2$ in MeOH and 0.12 molal solution of $NiCl_2$ in DMSO, and (*ii*) 1:24 for 1.3 molal solution of $NiCl_2$ in MeOH and 0.53 molal solution of $NiCl_2$ in DMSO. Therefore, the contribution of the solvent molecules from FSS can not provide so significant concentration decrease in translation diffusion coefficients averaged over the whole solutions in accordance with Eq. (5). Clearly, electrostatic interactions affect dynamics of the solvent molecules not only from FSS of Ni^{2+}, but also from bulk.
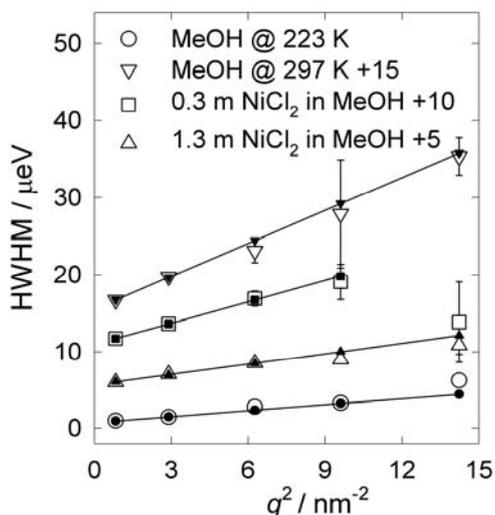
Fig. 4. The half-width at half-maximum (HWHM) of the fitted Lorentzian plotted as a function of the square of wave number for neat MeOH and solutions of $NiCl_2$ in it.
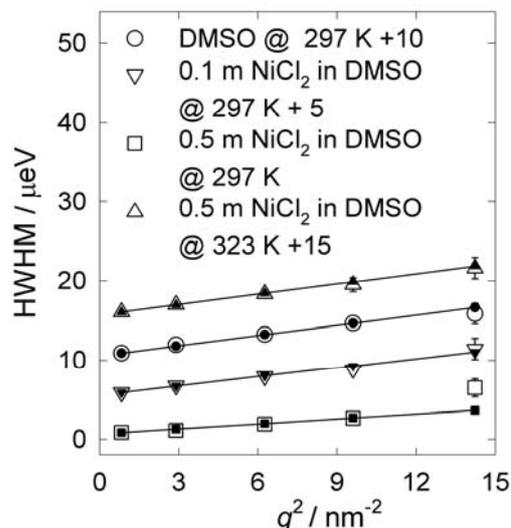
Fig. 5. The half-width at half-maximum (HWHM) of the fitted Lorentzian plotted as a function of the square of wave number for neat DMSO and solutions of $NiCl_2$ in it.

Unfortunately, as our the results of present investigation show, the QENS technique does not allow on its own to separate translational diffusion of the solvent molecules within the cation's solvation shell and bulk phase. However, if the ratio of signal to noise can be increased significantly by using more powerful source of a neutron flux, one would be able to obtain separately the diffusion coefficients of the solvent molecules from the different regions of a solution. Alternatively, some of complementary computer modelling technique such as molecular dynamics simulation should be used to elucidate all the details of ion solvation dynamics.
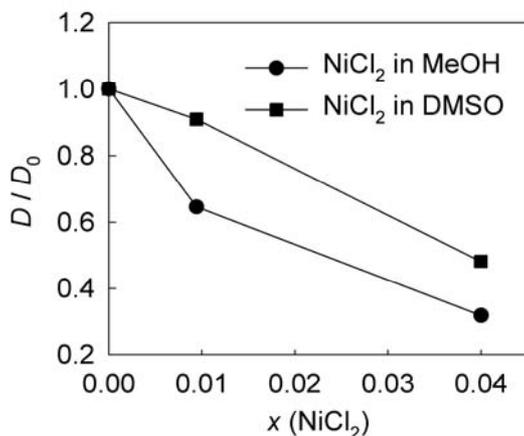

Fig. 6. Reduced translational diffusion coefficient of the solvent molecules at 297 K as a function of the molar fraction (*x*) of the solute.


Fig. 7. Reduced translational diffusion coefficient of the solvent molecules at 297 K as a function of the molarity (*c*).

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Вестник Харьковского национального университета. 2006. №731. Химия. Вып.14(37). О. Н. Калугин, А. К. Адйа. Исследование динамики сольватации Ni^{2+} в метаноле и диметилсульфоксиде методом квази-упругого рассеяния нейтронов.

С использованием метода квазиупругого рассеяния нейтронов (КУРН, QENS) высокого разрешения исследована трансляционная динамика атомов водорода молекул метанола (MeOH) и диметилсудьфоксида (DMSO) в чистых растворителях и в растворах NiCl$_2$ различной концентрации при 223, 297 K and 323 K. Полученные результаты однозначно указывают на уменьшение коэффициентов диффузии молекул растворителей а) с уменьшением температуры, б) с увеличением концентрации NiCl$_2$. Показано, что динамика молекул растворителей в электролитных растворах определяется главным образом электростатическими взаимодействиями, задаваемыми ионной подсистемой, независимо от природы растворителя.