Composition of Ni^{2+} cation solvation shell in $NiCl_2$–methanol solution by multinuclear NMR

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^1H, ^2H and ^{13}C NMR spectra have been used to test the Ni^{2+} solvation shell composition in the 1.1 molal methanol solution of $NiCl_2$. It has been confirmed that Cl- anion takes part in the nearest environment of Ni^{2+} cation at all the temperatures investigated. Using ^2H NMR allowed us to detect for the first time OD-signal of methanol in the primary solvation shell of Ni^{2+} cation. Both ^2H and ^{13}C NMR spectra show that the composition of the cation solvation shell becomes more complicated at temperatures lower than 220 K.

Keywords: nickel chloride, methanol, NMR, solvation

1. Introduction

Recently, $NiCl_2$ solutions in methanol were studied by neutron diffraction with isotopic substitution (NDIS) [1, 2] and quasi-elastic neutron scattering (QENS) [3] techniques, and it was found that the electrolyte exists as an admixture of $[Ni(MeOH)_6]^{2+}$ and $[Ni(MeOH)_5Cl]^+$ ion pairs and partly $[Ni(MeOH)_4Cl_2]^0$ triple associates as the solute components. The molecular dynamics (MD) simulations, in agreement with experimental findings, confirmed these results [3]. It is well known that NMR is one of the most effective techniques employed for investigating the first solvation shells of paramagnetic cations due to strong increase in chemical shifts of the solvated molecules and enhancement of their relaxation rates, see e.g. [4, 5]. In particular, in the *slow exchange* regime i.e. under $\tau_m \delta_m \omega_0 >> 1$ condition[1], it is possible to observe separate signals of bulk solvent and the solvent in the first solvation shell of the cation. Using integral intensity of (area under) the latter peak, one can evaluate in this case the mean number of solvent molecules bound with the cation, n_L. Consequently one can obtain direct information on the composition of the cation first solvation shell. It would, thus, be interesting to compare the data of NDIS and QENS experiments, MD simulations, and NMR measurements in the same systems by using the powerful capabilities of modern multinuclear NMR technique.

^{1}H NMR spectrum of methanol molecules in the primary solvation shell of Ni^{2+} cation was detected for the first time by Luz and Meiboom in 1964 [6] in the methanol solution of $Ni(ClO_4)_2$. It was found that only $[Ni(CH_3OH)_6]^{2+}$ solvate existed in dry methanol, and no complex with the anion was detected[2]. On the other hand in the $NiCl_2$ methanol solution [7], both $[Ni(CH_3OH)_6]^{2+}$ and $[Ni(CH_3OH)_5Cl]^+$ complex ions were found to be present. In both the solutions, however, the ^{1}H spectrum of the coordinated methanol contained only CH_3-group signal and no signal of OH-group was detected in contrast to the corresponding cobalt (II) salt solutions [8].

2. Experimental procedures

The solutions of $NiCl_2$ in MeOH of molality, $m = 1.1311$ mol/kg, and in MeOD, $m = 1.0782$ mol/kg were prepared by weight in a dried (RH < 2 %) nitrogen filled glovebag. The anhydrous $NiCl_2$ (Aldrich, 99.99%) in the form of brownish powder

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[1] Here τ_m is the ligand lifetime and $\delta_m \omega_0 / 2\pi$, in Hertz, is the chemical shift difference between the bulk and coordinated ligand positions.

[2] Methanol solutions in the presence of water impurities showed the existence of some mixtures of aqua-methanol solvation shells of nickel cation.

was used without any additional treatment. The anhydrous solvents, MeOH (Aldrich, 99.8%) and MeOD (Aldrich, 99.8 atom % D) were preliminary dried under the 4Å molecular sieves (Aldrich) during several days, and then after filtration through a 1µ glass fiber (Acrodisc® GF Syringe Filter) were used without further purification.

The MeOD was tested by ^{2}H NMR and no signal of CD_3 group was detected at least up to a level of 0.1% of the OD-group signal intensity. Experiments were carried out with the Bruker AVANCE 400 pulsed NMR spectrometer.

3. Experimental results

First, we obtained ^{1}H spectra of the $NiCl_2$ solutions in both MeOH and MeOD in the temperature range 183–300 K. A few typical spectra centred at zero position with respect to the ^{1}H signal of CH_3 group of the bulk methanol are shown in Fig. 1. It is evident from the Fig. 1(b) that the spectrum in MeOH contains signal of CH_3-group of solvated methanol and two signals of bulk CH_3- and OH-groups. It agrees completely with the results of [6, 7] namely, (*i*) only one signal is observed for coordinated CH_3-group, and (*ii*) no signal is detected for coordinated OH-protons. The same spectrum for MeOD solution contains only two peaks due to absence of bulk OH-group signal. Due to the advantage of modern 400 MHz spectrometer compared with the equipment used in [7] it became possible to detect simultaneously the signals of both the bulk and solvated methanol, and to calculate directly the mean number of methanol molecules in the solvation shell of the cation (solvation number), n_L.

Temperature dependence of this value is shown in Fig. 2. Its right part agrees well with data of [7] namely, n_L displays fast decrease with *increasing* temperature. This decrease was explained in [7] as a consequence of strong difference between methanol lifetimes in $[Ni(CH_3OH)_6]^{2+}$ and $[Ni(CH_3OH)_5Cl]^+$ solvates which results in vanishing of the contribution from the latter solvate at higher temperatures, while for the former one the "slow exchange" regime remains still valid. In our case, the signal of bound methanol in $[Ni(CH_3OH)_6]^{2+}$ solvate is observed up to 300 K, *i.e.* the solutions are in "slow exchange" regime even at room temperature.

Temperature dependence of shift-in-complex, δ_m, shown in Fig. 3 follows $1/T$ curve in the whole temperature range, and it also confirms the validity of "slow exchange" conditions for all the investigated temperatures. The absolute values of δ_m reduced to the temperature of 298 K are listed in the Table 1. These values demonstrate a significant influence of nickel cation on positions of NMR signals of all the nucleus of the methanol in solutions. It should be noted that for the ^{2}H and ^{13}C nucleus two separate signals are observed, that is clear indication of a presence of two kinds of nickel cation complexes in concentrated methanol solutions, namely $[Ni(CH_3OH)_6]^{2+}$ and $[Ni(CH_3OH)_5Cl]^+$.

One feature worth noticing is that below *ca.* 220 K, the n_L *vs.* T dependence changes its type and the fraction of bound methanol molecules starts to decrease with decreasing temperature (Fig. 2). It needs to be emphasized that this temperature range was not investigated in [7], and we could find no other work reported in literature at these temperatures. Hence, we decided to use ^{2}H and ^{13}C spectra, in addition, to clarify the situation at these temperatures. The spectra are shown in Figs. 4 and 5, respectively.

^{2}H spectrum of the MeOD solution at room temperature shows two peaks (Fig. 4). It agrees well with the picture predicted above and the peaks could be attributed to bulk and coordinated -OD groups of the solvent. Once more the latter peak remains even at room temperature *i.e.* the solution is still at "slow exchange" conditions as well as for ^{1}H spectrum. However, at low temperature ^{2}H spectra depict a different picture, namely two separate peaks for coordinated methanol are observed. The same picture is observed for ^{13}C spectra at 200 K (Fig. 5). Once more two peaks of coordinated methanol appeared, and in addition it looks like that the line with larger chemical shift consists, in turn, of at least two components with significantly different line widths. Thus, both ^{2}H and ^{13}C spectra show that the composition of the cation solvation shell at low temperatures is more complicated than what is known before. The exact picture is not clear at the moment and requires special further investigation.

In conclusion, we investigated the composition of Ni^{2+} cation solvation shell in methanol solutions using ^{1}H, ^{2}H, and ^{13}C NMR. We have confirmed that the solutions contain $[Ni(CH_3OH)_6]^{2+}$ solvate and $[Ni(CH_3OH)_5Cl]^+$ complex, both at low and room temperature. Using ^{2}H NMR in CH_3OD solution we have detected for the first time a signal corresponding to OD-group of methanol in the first solvation shell of nickel cation. Using ^{13}C spectra at low temperature we have found carbon signals of solvated methanol and shown that the composition of the cation solvation shell becomes more complicated at temperatures lower than 220 K.

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Table 1. Shift-in-complex magnitudes, δ_m, in NMR spectra of the $NiCl_2$ solution in methanol at 298 K calculated according to the expression $\delta_m \cdot T$ = constant with accuracy ±0.5 ppm if not specified.

Nucleus	δ_m^{298}, ppm	
	CH_3-	-OH (MeOH) / -OD (MeOD)
^1H	48.9 (MeOH) 48.0 (MeOD)	not observed
^2H	– –	– 20.7, 49.8
^{13}C	– 38 ±3, 104 ± 3	– –

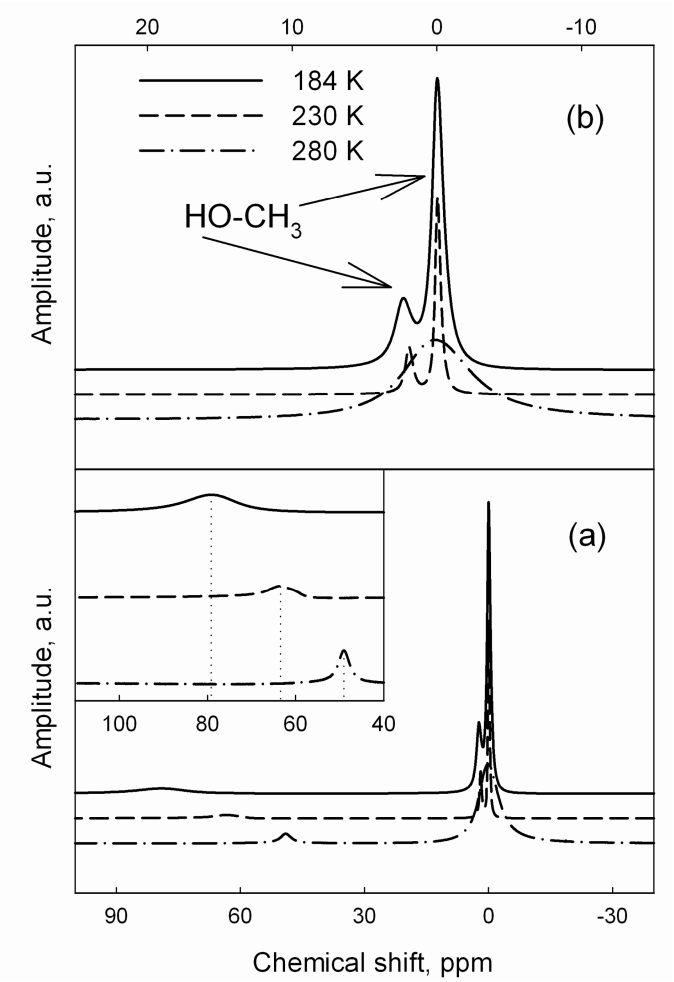

Figure 1. ^1H NMR spectra of $NiCl_2$ solutions in MeOH (m = 1.1311 mol/kg) centred at zero position with respect to the ^1H signal of CH_3-group of the bulk methanol: (a) overall view at three temperatures; insert shows a shift of the ^1H signal (CH_3) of the methanol from the first coordination shell of Ni^{2+} towards those of the bulk solvent with temperature increase; (b) designation of the ^1H peaks for the bulk methanol. At 280 K the ^1H signal of methyl and hydroxyl group cannot be resolved separately due to “fast exchange” regime.

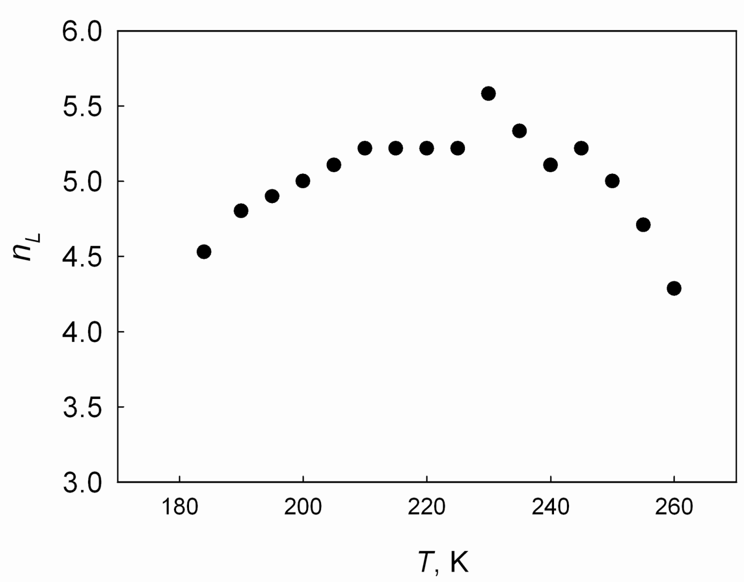

Figure 2. The temperature dependence of the solvation number of solvent molecules in the first solvation shell of nickel cation, n_L, evaluated from the line area analysis of ^{1}H NMR spectra of $NiCl_2$ solutions in MeOH (m = 1.1311 mol/kg).

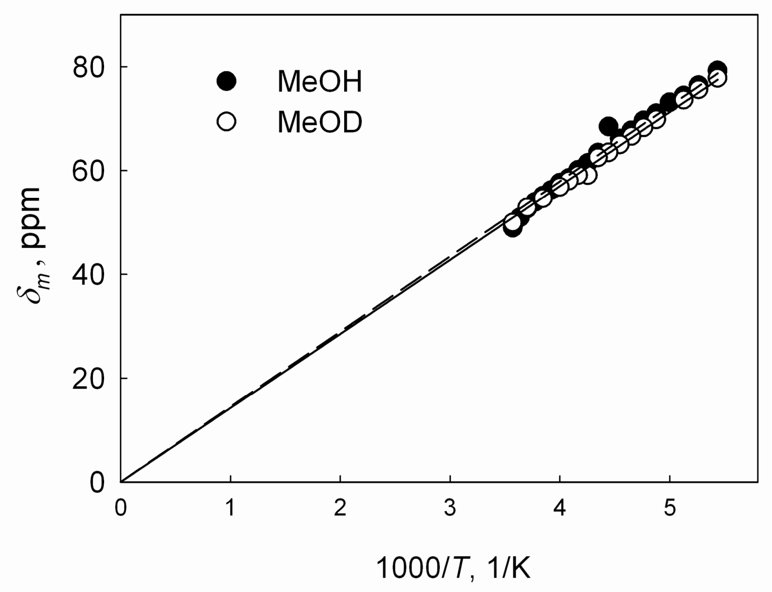

Figure 3. Temperature dependence of the ^{1}H shift-in-complex value, δ_m, for $NiCl_2$ solution in MeOH (solid circles, dashed line, m = 1.1311 mol/kg) and MeOD (hollow circles, solid line, m = 1.0782 mol/kg). These dependences confirm "slow exchange" regime up to room temperature.

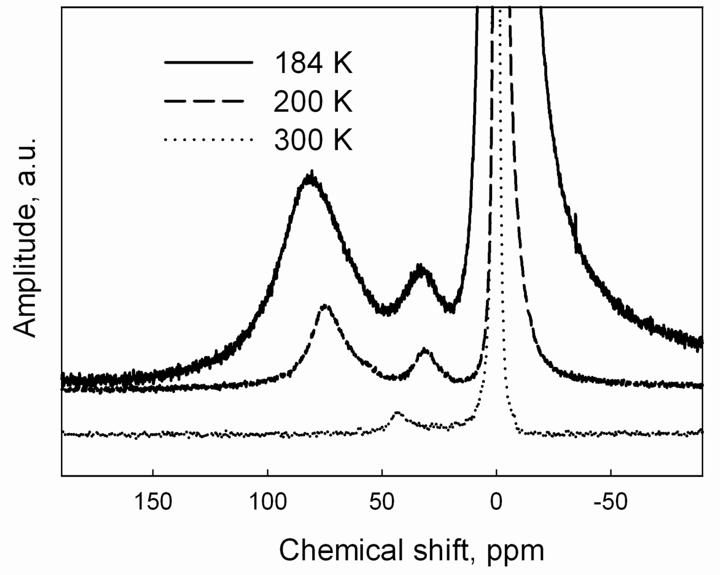

Figure 4. ^{2}H NMR spectra of $NiCl_2$ solutions in MeOD (m = 1.0782 mol/kg) centred at zero position with respect to the ^{2}H signal of OD-group of the bulk methanol.

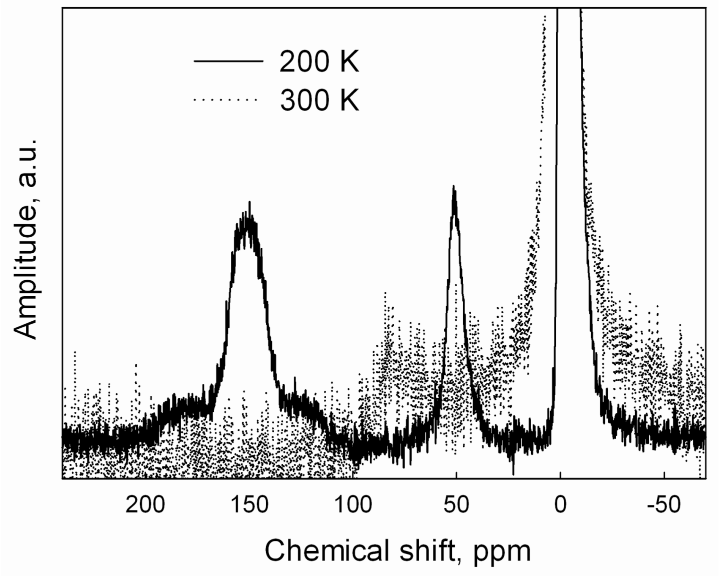

Figure 5. ^{13}C NMR spectra of $NiCl_2$ solutions in MeOD (m = 1.0782 mol/kg) centred at zero position with respect to the ^{13}C signal of CH_3-group of the bulk methanol. The spectra obtained under the most possible acquisition time for the spectrometer (the most available number of repetitions). For the solution in MeOH the spectra are similar.