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ION PAIRING IN H_2O AND D_2O SOLUTIONS OF LEAD NITRATE, AS DETERMINED WITH ^{207}Pb NMR SPECTROSCOPY

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The temperature and concentration dependences of ^{207}Pb NMR chemical shifts of $Pb(NO_3)_2$ in D_2O are reported. The results are analyzed in terms of exchange between a solvated lead ion and the $Pb(NO_3)^+$ contact-ion pair. Predictions of the chemical shift difference between the aquated ion and contact-ion pair are carried out for the gas-phase entities and for the solvated species with a DFT calculation. Previously reported data on ^{207}Pb NMR chemical shifts of $Pb(NO_3)_2$ in H_2O are reevaluated. From the analysis, the enthalpy of dissociation of the contact-ion pair is found to be –42.3±1.0 kJ/mol.

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INTRODUCTION

Electrochemical and spectroscopic measurements have demonstrated that dissolution of certain salts in water leads to the formation of contact-ion pairs in equilibrium with fully aquated ions [1—11]. Systems showing this behavior frequently contain divalent cations such as Ca^{2+}, Cd^{2+}, Hg^{2+}, Cu^{2+}, and Pb^{2+}. Recent calculations of the free energies of various configurations of dications and anions indicate the strong preference for ion pairing by cations such as Ca^{2+}, Sr^{2+}, and Pb^{2+} [11]. In aqueous solutions of the nitrates, it is found that Pb^{2+} has the strongest proclivity for the formation of contact ion pairs [11].

The strong temperature variation of the ^{207}Pb NMR chemical shift of solid $Pb(NO_3)_2$ is consistent with a significant sensitivity of the electronic state of the lead ion to small structural changes such as variations of interionic distances induced by thermal expansion [12—16]. Studies of the variation of the ^{207}Pb NMR chemical shift of lead-containing solids with applied pressure also point to the significant variation of electronic state with structural change [15, 16].

The electrochemical and spectroscopic properties of ion pairs in solution are more complex than those of the solid, in part because of the dynamics of exchange in solution, as well as the interaction of the ions with the solvent [1—10]. For example, Nancollas interpreted changes in conductivity of aqueous lead nitrate solutions as evidence for rapid exchange between contact-ion pairs and solvated ions by the mechanism of Eq. (1) [2]:

$$Pb(NO_3)^+_{(aq)} \leftrightarrow Pb^{2+}_{(aq)} + NO^-_{3(aq)}. \qquad (1)$$

From the temperature and concentration dependences of the conductivity of lead nitrate solutions, he determined an equilibrium constant, K_{diss}, of 0.065 at 298.15 K, and $\Delta H_{diss} = 2.38$ kJ/mol and $\Delta S_{diss} = -14.6\ J\cdot K^{-1}\cdot mol^{-1}$ for the process of Eq. (1). A number of Raman and spectroscopic studies of ionic solutions have been interpreted in terms of the effects of concentration and temperature on the equilib-

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rium of Eq. (1), as reflected in the spectroscopic properties [3, 7, 8, 11]. At 298.15 K, the equilibrium constant for 1, as determined by this method, is reported to be 0.071±0.009 [3].

The NMR chemical shifts of nuclei such as ^{207}Pb in solution, which are rapidly interchanging among sites by processes such as those described in Eq. (1), depend strongly on temperature and concentration [4—6, 10]. Harrison et al. analyzed room-temperature concentration-dependent ^{207}Pb chemical-shift data for aqueous lead nitrate solutions to determine an equilibrium constant for the process in Eq. (1) of 0.812 at 298.15 K [4]. Altounian et al. measured the temperature and concentration dependences of the NMR chemical shift to determine the variation of the equilibrium constant for the same process in solutions of $Pb(NO_3)_2$ in H_2O. They report $K_{\text{diss}} = 0.200$ at 295 K and $\Delta H_{\text{diss}} = -12.6$ kJ/mol [10]. Several groups have observed concentration-dependent NMR spin-lattice relaxation, which has been attributed to the effects of the process in Eq. (1) [5, 6, 9].

In unpublished work, Niessen noted the interesting effect that the ^{207}Pb NMR chemical shift of lead nitrate dissolved in a mixed solvent of H_2O and deuterium oxide, D_2O, is linear in the mole fraction of D_2O in the solvent [17]. This observation, which we have confirmed, suggests that the exchange process in Eq. (1) is affected by the solvent molecule.

In this report we focus on NMR chemical shifts of solutions of $Pb(NO_3)_2$ in D_2O. We also re-evaluate data reported in reference [10] on the same salt in H_2O, to provide a self-consistent view of the exchange process resulting from contact-ion-pair formation and dissociation in solutions of $Pb(NO_3)_2$ in H_2O and D_2O, as detected with NMR spectroscopy.

EXPERIMENTAL AND COMPUTATIONAL DETAILS

$Pb(NO_3)_2$ was purchased from Sigma Aldrich. Sodium chloride was purchased from Fisher Chemical Company. Deuterium oxide was purchased from Cambridge Isotopic Laboratories, Inc. The salts were used as received. H_2O and D_2O were deionized and doubly distilled in glass before use.

Solutions of lead nitrate in D_2O were prepared in the range from 0.025 molal to 1.100 molal. Solutions of NaCl in mixtures of H_2O and D_2O were made gravimetrically to be examined by ^{23}Na NMR spectroscopy.

^{207}Pb and ^{23}Na NMR spectra were obtained with a Bruker AMX360 spectrometer at 75.35 MHz and 95.27 MHz, respectively. The $\pi/2$ pulse length was 20 μs, and a relaxation delay of one second was used. The number of co-added transients varied from 64 to 1024, depending on concentration and temperature. Data were recorded at temperatures of 293, 310, 325 and 340 K, with an accuracy of ±0.5 K. Relative shifts could be measured with a precision of ±0.01 ppm. The lead nitrate solutions are referenced against the resonance frequency of tetramethyllead through the resonance of a 1.100 molal solution at 295 K of –2965.72 ppm [13]. The ^{23}Na NMR spectra are referenced to the position of the NaCl resonance in pure D_2O at 1.000 molal.

All computations were performed with the suite of Amsterdam Density Functional (ADF) programs [18]. Geometry optimizations were carried out with and without solvent effects. Solvent effects are included by employing the Conductor-like Screening Method (COSMO) as implemented in the ADF programs [19—21]. Calculations employed the local density approximation (LDA) of Vosko, Wilk and Nusair (VWN) [22] or the Becke88-Perdew86 generalized gradient approximation (BP86) [23, 24], and the TZ2P basis set. To incorporate relativistic effects, the zeroth order regular approximation (ZORA) with spin-orbit coupling [25, 26] was employed in all computations. NMR chemical shieldings were calculated with the NMR module [27] associated with the ADF program package.

RESULTS

Not all salts form ion pairs in aqueous solution. In Fig. 1 are shown ^{23}Na spectra of aqueous solutions of NaCl made with mixed solvents of H_2O and D_2O. There is essentially no dependence of the ^{23}Na resonance frequency on the solvent composition. This result suggests that the local structure around the ^{23}Na nucleus that affects the NMR properties of the ion remains essentially unchanged as the composition is changed. Thus, the NMR shift does not distinguish sodium ions coordinated to protonated or deuterated water ligands.

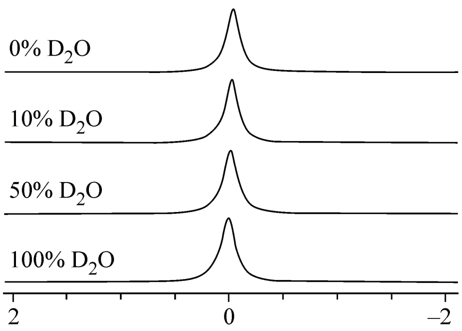

Fig. 1. The ^{23}Na spectra of saturated solutions of NaCl in mixtures of D_2O and H_2O. The chemical shifts are defined relative to the position of the resonance in 100 % D_2O

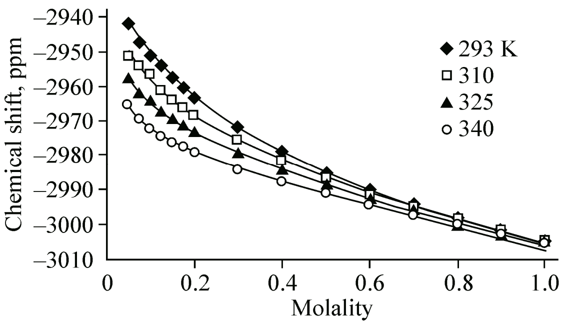

Fig. 2. Variation of the ^{207}Pb NMR shift of lead nitrate in deuterium oxide with concentration at 293 K (◆), 310 K (■), 325 K (▲) and 340 K (●). The solid lines are fits to Eq. (3), with α determined from apparent equilibrium constants, as explained in the text

In solutions of $Pb(NO_3)_2$, on the other hand, the ^{207}Pb shift is a strong function of the solvent composition, with a linear dependence of the shift on the mole fraction of D_2O in the solvent [17]. Our analysis of Niessen's data, and our own, indicates that, in a mixed H_2O/D_2O solvent, the linear variation of the shift with D_2O concentration is characterized by a concentration coefficient at 293 K of

$$\frac{d\delta}{dX_D} = -29.9 \text{ ppm}. \tag{2}$$

As with H_2O, the ^{207}Pb NMR spectrum of lead nitrate dissolved in D_2O is a single sharp resonance, the shift of which is also strongly dependent on temperature and concentration (Fig. 2). We attribute these dependencies to the effects of rapid exchange according to Eq. (1). In a model in which the lead ion is exchanging rapidly between a solvated ion and a solvated contact-ion pair, the average chemical shift at a specific concentration and temperature is given by Eq. (3)

$$\delta = \alpha\delta_A + (1-\alpha)\delta_B , \tag{3}$$

where α is the fraction of time a ^{207}Pb nucleus spends in the environment with chemical shift δ_A, and δ_B is the chemical shift for a ^{207}Pb nucleus at site *B*.

Eq. (3) implies knowledge of the chemical shifts for the lead nucleus when it is in the solvated form (*A*) and in the solvated contact-ion pair (*B*). In our experiments, we have not been able to access conditions of sufficiently slow exchange to observe chemical shifts of either the solvated lead ion or the ion pair. To analyze the data by this method, we have taken the chemical shifts of the solvated lead ion and of the ion pair as adjustable parameters. A rearrangement of Eq. (3) provides a value of α for any concentration and temperature from Eq. (4)

$$\alpha = \frac{\delta - \delta_B}{\delta_A - \delta_B} . \tag{4}$$

From this parameter, one may calculate the apparent dissociation constant at each concentration and temperature (Eq. (5)).

$$K' = \frac{\alpha(1+\alpha)}{1-\alpha} m, \tag{5}$$

where *m* is the molality of the solution.

Extrapolation of the apparent equilibrium constant to $m = 0$ gives the thermodynamic equilibrium constant, K_{diss}. In the analysis of lead ion in H_2O solutions [10], extrapolation was carried out using the Debye—Hueckel limiting law. However, the higher-concentration solutions are in a range where the limiting law is of limited utility. To be consistent, in the present analysis, we have analyzed the D_2O data with the Davies equation [28], which is valid over a wider range of concentrations, and we re-evaluated the data [10] on lead nitrate in H_2O solution in the same manner.

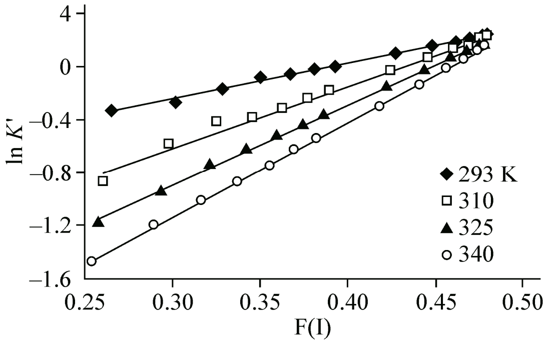

Fig. 3. ln K' versus F(I) at temperatures of 293 K (◆), 310 K (■), 325 K (▲) and 340 K (●) for solutions of $Pb(NO_3)_2$ in D_2O. Extrapolation to infinite dilution gives the thermodynamic equilibrium constant, K_{diss} at each temperature

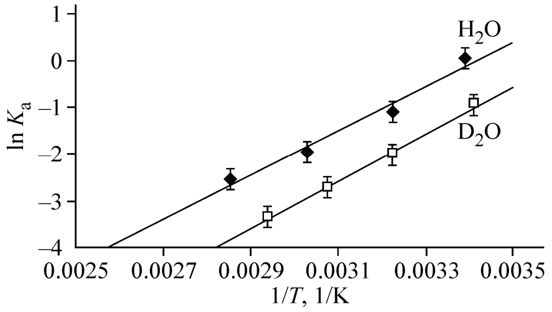

Fig. 4. ln K_{diss} versus $1/T$ for solutions of lead nitrate in pure D_2O (■) and lead nitrate in pure H_2O (◆) [10], determined with ^{207}Pb NMR spectroscopy

Plots of the logarithm of K' versus $F(I) = \sqrt{I}/(1+\sqrt{I}) - 0.1m$, where I is the ionic strength, for the D_2O solutions are shown in Fig. 3. The equilibrium constant for dissociation, obtained by extrapolation of these linear plots, is reported for each temperature in Table 1. From the van′t Hoff plot of Fig. 4, we obtain the enthalpy of dissociation, $\Delta H = -42.3 \pm 1.0$ kJ/mol for the D_2O solutions. Similarly, for the H_2O solutions, $\Delta H = -40 \pm 2$ kJ/mol.

Before continuing, we comment on the data for the H_2O solutions. The re-evaluation of the data for solutions of lead nitrate in H_2O resulted in equilibrium constants for particular sets of conditions that are different from those reported in reference [10]. In addition, the value of the predicted enthalpy of dissociation of the contact-ion pair in H_2O is more negative, when evaluated with the Davies equation. The agreement of the enthalpy of dissociation for ionic solutions in H_2O and in D_2O solution suggests that the Davies equation gives a consistent analysis, whereas the Debye—Hueckel limiting law does not.

The fitting of NMR chemical shifts as a function of concentration involves guesses for the chemical shifts of the isolated contact-ion pair and for the aquated lead ion. To check on the reasonableness of the chemical shifts determined by fitting of these experimental data, we undertook DFT calculations of the ^{207}Pb chemical shifts in clusters that represent the expected local structures in solution. The optimized solution structures of the two species are shown in Fig. 5, and the structures of the isolated

Table 1

K_{diss} for the dissociation of $Pb(NO_3)^+$ *in aqueous solutions*

T, K	K_{diss} (H_2O)	K_{diss} (D_2O)
293[a]	1.037	0.391
310	0.334	0.131
330	0.140	0.066
340	0.079	0.035

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[a] The data for ions in H_2O were carried out at 295 K, and the data for ions in D_2O were at $T = 293$ K.

Table 2

Calculated chemical shielding and chemical shift data for $Pb(H_2O)_6^{2+}$ *and* $Pb(H_2O)_5(NO_3)^+$

Fragment	Chemical shielding, ppm	Chemical shift[a], ppm
$Pb(H_2O)_6^{2+}$ (gas phase)	10698	–3355
$Pb(H_2O)_5(NO_3)^+$ (gas phase)	9726	–2383
$Pb(H_2O)_6^{2+}$ (sol. phase)	9919	–2526
$Pb(H_2O)_5(NO_3)^+$ (sol. phase)	10233	–2840

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[a] Chemical shifts are given relative to the chemical shift of tetramethyllead (TML), calculated at the corresponding level of theory.

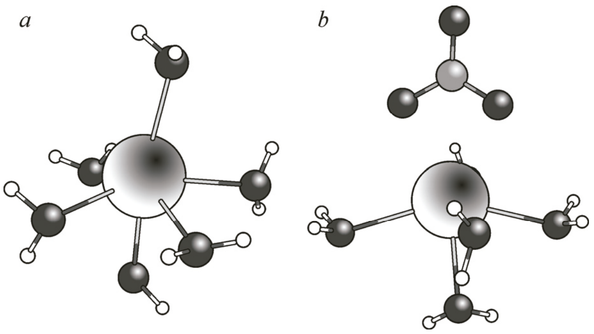

Fig. 5. Solution-state structure of $Pb(H_2O)_6^{2+}$ (*a*); solution-state structure of $Pb(H_2O)_5(NO_3)^+$ (*b*). The difference in the chemical shielding of these two structures is predicted to be 314 ppm

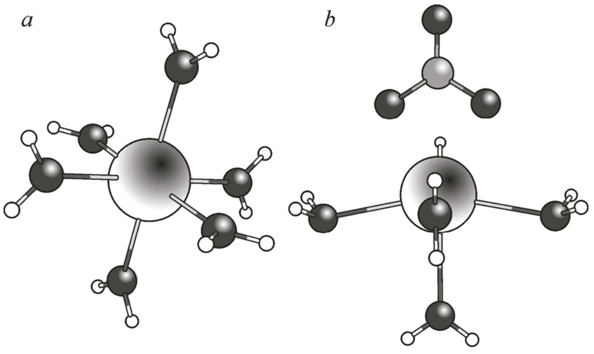

Fig. 6. Gas phase structure of $Pb(H_2O)_6^{2+}$ (*a*); gas phase structure of $Pb(H_2O)_5(NO_3)^+$ (*b*). The difference in the chemical shielding of these two structures is predicted to be 962 ppm. The prediction is opposite to the experimentally observed difference determined from the analysis of the current data

molecules in the gas phase are shown in Fig. 6. In Table 2 are shown the chemical shieldings, as well as the chemical shifts relative to tetramethyllead (TML), for these four species. Calculations for the species isolated in the gas phase overestimate the chemical-shift difference. In addition, the shift of the aquated lead ion from the aquated contact-ion pair is opposite to what is observed experimentally.

To model the local structure more accurately, the calculation including the effects of the solvent predicts the chemical shifts reasonably well. More importantly, the predicted chemical-shift difference between these two species (314 ppm) is only slightly larger than the value of 150 ppm obtained from the experimental data, with the contact-ion pair being more shielded than the aquated ion. In previous calculations, we have shown that the accuracy of calculations of chemical-shift differences is approximately ±200 ppm [15]. The predicted difference between the two species is in qualitative, if not quantitative, agreement with the experimentally derived value. The relative shielding of the two species when the solution effects are included is also correct. It has been suggested by recent experimental and computational work that the $Pb(H_2O)_6^{2+}$ complex exhibits hemi-directed geometry [29, 30]. This suggestion is consistent with these calculations and our experimental NMR data.

DISCUSSION

In analyzing the NMR data, we have assumed that the aquated uncharged complex $Pb(NO_3)_2$ makes no significant contribution; this neglect is consistent with other analyses and the fact that the water is present in excess [4, 5, 9, 10]. The enthalpy of dissociation for the D_2O solutions, given in Table 3, is essentially the same as that reevaluated from the data of Altounian et al. [10]. The variations of the equilibrium constant with temperature for H_2O and D_2O solutions are quite similar, indicating similar processes occur in these two solutions. However, the slight difference in the magnitudes of the equilibrium constants between the D_2O and H_2O solutions at any temperature are consistent with the trends of the chemical shift as a function of the solvent composition as it is varied from pure H_2O to pure D_2O [17]. It appears that the difference in equilibrium constants in the two solutions is a result of a slight difference in the chemical shift of the complex due to isotope effects, rather than a result of the exchange process itself. Given the known sensitivity of the lead chemical shift to slight structural changes, these results are consistent with slight differences in the structure of the complex in H_2O compared to D_2O, probably due to the effects of vibrational motion on the average structure.

The enthalpy of dissociation of the ion pairs formed from lead nitrate in D_2O solution is $\Delta H = -42.3$ kJ/mol, and the re-evaluated data on lead nitrate in H_2O give a value that is, within experimental error, the same. At 293 K (295 K), the Gibbs energy differences are 2.33 kJ/mol and –95.6 J/mol, respectively. At 293 K (295 K), these values give entropy differences $\Delta S = -150\ (\pm 5)\ J \cdot K^{-1} \cdot mol^{-1}$ and

Table 3

Enthalpy of dissociation of $Pb(NO_3)_2$ $[Pb(NO)_3^+ \rightarrow Pb^{2+} + NO_3^-]$ *in aqueous solutions, as determined by various methods*

Solvent	K_{diss} (298.15 K)	ΔH, kJ/mol	Reference
H_2O	0.065	2.38	Nancollas [2], conductivity
H_2O	0.357	—	Hershensohn [31], polarography
H_2O	0.33	—	Mironov [32]
H_2O	0.303	—	Hershensohn [31], potentiometry
H_2O	0.071	—	Bale et al. [3], spectroscopy
H_2O	0.625	—	Hershensohn [31], spectroscopy
H_2O	0.278	—	Owens [9], ^{14}N NMR
H_2O	0.812	—	Harrison [4], ^{207}Pb NMR
H_2O	1.04 (295 K)	–40±2	Altounian [10], ^{207}Pb NMR reevaluated, this report
D_2O	0.391 (293 K)	–42.3±1.0	^{207}Pb NMR, this report

–140 (±5) $J{\cdot}K^{-1}{\cdot}mol^{-1}$, respectively, for the D_2O-solvated and the H_2O-solvated lead nitrate. The differences in Gibbs energies for the two systems indicate that, in D_2O, the contact-ion-pair is the more stable state at these conditions, but in H_2O, the two states are energetically virtually identical.

The only other report of NMR-derived temperature dependence of ionic equilibrium in these lead-containing systems is a report of the equilibrium in the lead acetate system, for which Harrison et al. report $\Delta H = -14.2$ kJ/mol and $\Delta S = -82.9$ $J{\cdot}K^{-1}{\cdot}mol^{-1}$ [4]. The enthalpy of dissociation for the lead acetate system in H_2O is lower than for the lead nitrate system, and the entropy change is also lower.

NMR analyses and a number of spectroscopic and electrochemical methods seem to produce dissociation equilibrium constants that cluster around an average of 0.36 (Table 3), although three results put it higher by a factor of 2—3, including the re-evaluation of the work from our laboratory on solutions of $Pb(NO_3)_2$ in H_2O [10]. The equilibrium constants from the spectroscopic work of Bales et al. [3] and the conductivity data of Nancollas [2] particularly give smaller equilibrium constants than many of the other reports.

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