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Combining Diffusion NMR and Conductometric Measurements to Evaluate the Hydrodynamic Volume of Ions and Ion Pairs

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Summary: A simple methodology for rapidly and accurately determining the hydrodynamic volume of single ions and ion pairs, based on the combination of information derived from diffusion NMR spectroscopy and conductometry, is proposed.

In recent years, PGSE (pulsed-field gradient spin−echo) diffusion NMR techniques[1] have been increasingly used to investigate associative processes in solution.[2] Focusing the attention on ion pairing, PGSE experiments were found to be a powerful tool for qualitatively detecting ion association.[3] On the other hand, they do not allow an easy quantification of ion pairing due to the lack of knowledge about the actual hydrodynamic volume of free ions (V_H^{+0} and V_H^{-0}) and ion pairs (V_H^{IP0}) to be compared with the *average* hydrodynamic volume (V_H^+ and V_H^-), derived from the experimentally measured translational self-diffusion coefficients (D_t^+ and D_t^-). For compact species that do not have inlets, the van der Waals volume (V_{vdW}) is a good descriptor of V_H^0.[4] In other cases, a reasonable value of V_H^0 can be found by time-consuming PGSE experiments as a function of salt concentration (C), extrapolating V_H^{+0} and V_H^{-0} at infinite dilution.[5] This procedure usually requires at least two PGSE measurements at $C < 10^{-4}$ M.[5,6]

In principle, V_H^{+0} and V_H^{-0} could also be determined by V_H^+ and V_H^- if the equilibrium constant for ion association (K_{IP}) were known. For symmetrical electrolytes in conditions where equilibria other than ion pairing are negligible, K_{IP} can be directly evaluated by means of conductometric measurements.[7,8] On the other hand, conductometry does not afford structural information easily since the ion-distance parameter sometimes assumes unrealistic values.[9,10] In a certain sense, diffusion NMR and conductometry are complementary, and it has been experimentally demonstrated that they afford consistent results.[11]

We here show how it is possible to take advantage of the complementarity of conductometry and NMR diffusometry[12] to rapidly and accurately determine the hydrodynamic dimensions of single species. The basic idea is simple. K_{IP} and the dissociation degree (α) of the ion pairs (corrected for the activity coefficients) are evaluated from conductometric measurements. The average hydrodynamic volume for the cation and the anion, V_H^+ and V_H^-, respectively, are derived from PGSE NMR measurements. The latter can be expressed as

$$\begin{cases} V_H^+ = \alpha V_H^{+0} + (1-\alpha)V_H^{IP0} \\ V_H^- = \alpha V_H^{-0} + (1-\alpha)V_H^{IP0} \end{cases} \qquad (1)$$

V_H^{+0} and V_H^{-0} are the unknown quantities of the system of eqs 1 and are obtained in the assumption that V_H^{IP0} is equal to the sum of V_H^{+0} and V_H^{-0}.

In order to test the reliability of the methodology, PGSE NMR and conductometric measurements were carried out in methylene chloride for [Ru(η^6-cymene)(N−N)Cl]X salts (**1**, N−N = PhN═C(Me)−C(Me)═NPh, $X^- = PF_6^-$, BPh_4^-, and $BArF^-$ [B(3,5-$(CF_3)_2$-$C_6H_3)_4^-$]; **2**, N−N = $Me_2NCH_2CH_2NMe_2$, $X^- = PF_6^-$, BPh_4^-, and $BArF^-$), for which extensive diffusion NMR results have been reported.[6,13] V_H^+ and V_H^- were derived from the translational self-diffusion coefficients for cation and anion (D_t^+ and D_t^-), measured by means of ^{1}H- and ^{19}F-PGSE NMR experiments (Table 1).[14] From the conductivity measurements[15] K_{IP}, α, and the equivalent conductance at infinite dilution (Λ_0) were obtained (Table 1) according to the method developed by Fuoss and Kraus[16] (Supporting Information).

By applying the system of eqs 1 to the experimental data of Table 1, V_H^{+0}, V_H^{-0}, and V_H^{IP0} shown in Table 2 were obtained.

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(14) All the PGSE NMR measurements were performed by using the standard stimulated echo pulse sequence on a Bruker AVANCE DRX 400 spectrometer, equipped with a GREAT 1/10 gradient unit and a QNP probe with a Z-gradient coil, at 296 K without spinning. D_t was determined exploiting its proportionality to the slope of the regression line obtained by plotting log(I/I_o) vs G^2 (Supporting Information). The proportionality constant was measured by using a sample of HDO (5%) in D_2O (known diffusion coefficient in the range 274−318 K). According to the Stokes−Einstein equation $D_t = kT/c\pi\eta r_H$ (where k is the Boltzman constant, T is the temperature, c is a numerical factor, and η is the fluid viscosity), $c^{st}r_H^{st}/c^{sa}r_H^{sa}$ was obtained by measuring the D_t^{sa}/D_t^{st} ratio of the sample (sa) and TMSS (internal standard, st). Knowing $c^{st}r_H^{st}$ from previous measurements,[13] $c^{sa}r_H^{sa}$ was obtained and finally r_H^{sa} determined by graphically solving the dependence of cr_H on r_H (Chen, H.-C.; Chen, S.-H. *J. Phys. Chem.* **1984**, *88*, 5118). V_H^{sa} was simply derived by assuming a spherical shape of ions and ion pairs.

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Table 1. Diffusion Coefficients ($10^{10}D_t$, $m^2\ s^{-1}$), Average Hydrodynamic Volumes (V_H, Å^3), Equivalent Conductance at Infinite Dilution (Λ_0, S cm^2 mol^{-1}), Equilibrium Constant for Ion Association ($10^{-3}K_{IP}$, M^{-1}), Dissociation Degree (α), and Concentrations (C, mM) for 1X and 2X Salts in Methylene Chloride

	NMR					conductometry		
	D_t^+	D_t^-	V_H^+	V_H^-	C	Λ_0	K_{IP}	α
1PF$_6$	10.4	11.4	565	460	0.12	190	160	0.24
1BPh$_4$	9.79	10.0	693	659	0.29	101	7.10	0.64
1BArF	10.4	8.56	577	927	0.14	82	2.16	0.88
2PF$_6$	11.5	12.8	443	352	0.32	156	680	0.28
2BPh$_4$	10.5	10.5	549	569	0.54	73	3.10	0.73
2BArF	10.8	8.27	511	970	0.59	80	1.26	0.86

Table 2. Hydrodynamic Volume (V_H^0, Å^3), Radius (r_H^0, Å), and Percentage Divergence (%) from Reference Values for Ions and Ion Pairs Derived from Salts 1X and 2X in Methylene Chloride

		V_H^{+0}	r_H^{+0}	V_H^{-0}	r_H^{-0}	V_H^{IP0}	r_H^{IP0}
1	**1**PF$_6$	509	4.95	74	2.60	583	5.18
		+1	+0.4	+23	+7.0	+3	+1
2	**1**BPh$_4$	522	4.99	469	4.82	991	6.18
		+4	+1.2	+9	+2.8	+6	+1.8
3	**1**BArF	472	4.83	870	5.92	1342	6.8
		−6	−2.0	+8	+2.4	+2	+0.7
4	**2**PF$_6$	394	4.55	69	2.54	463	4.80
		+2.6	+0.9	+14	+4.5	+4.2	+1.5
5	**2**BPh$_4$	426	4.67	453	4.76	879	5.94
		+10.9	+3.5	+5	+1.5	+7.7	+2.4
6	**2**BArF	384	4.51	917	6.03	1301	6.77
		0	0	+13	+4.3	+9.1	+2.9

The corresponding hydrodynamic radii (r_H^0), calculated on the assumption that ions and ion pairs have a spherical shape, are also reported in Table 2.

The self-consistency of the methodology can be appreciated by noting that V_H^0 and r_H^0 are the same, within the experimental error (3−5% and 10−15% for r_H^0 and V_H^0, respectively), when the same cation with different counterions (Table 2, entries 1−3 for **1**$^+$, entries 4−6 for **2**$^+$) is considered and vice versa (Table 2, entries 1 and 4 for PF_6^-, entries 2 and 5 for BPh_4^-; entries 3 and 6 for BArF$^-$).

To understand the level of accuracy of the determined V_H^0 and r_H^0 values, they were contrasted with V_{vdW} and r_{vdW} for PF_6^- or with the hydrodynamic volume and radius obtained from PGSE NMR experiments carried out on very diluted solutions for all other ions.[17] The percentage divergence is reported in Table 2. There is a excellent agreement between the hydrodynamic volume and radius determined through the methodology here proposed and the reference ones. For example, V_H^{+0} and r_H^{+0} previously determined[6] from PGSE experiments for **1**$^+$ are 504 Å^3 and 4.93 Å, respectively, while the values obtained here (Table 2, entries 1−3) span from 472 to 522 Å^3 and from 4.83 to 4.99 Å, respectively. Only the V_H^{-0} and r_H^{-0} of **1**PF$_6$ (Table 2, entry 1) shows a percentage deviation higher than the experimental error. This is probably due to the small size of the anion that makes the difference of only 13.6 Å^3 ($V_H^{+0} - V_{vdW}$, 74−60.4 Å^3) particularly relevant in percentage terms. As a confirmation, V_H^{IP0} and r_H^{IP0} for **1**PF$_6$ differ by only 3% and 1%, respectively, from those determined through PGSE experiments on diluted solutions.

It is worth noticing that, since the determined V_H^{-0} or V_H^{+0} refers to a single ion, they can be used to evaluate V_H^{+0} or V_H^{-0} of another salt with the same ion even without carrying out conductometric measurements. In fact, if V_H^{-0} or V_H^{+0} is known and V_H^+ and V_H^- are measured by means of PGSE experiments, the unknown quantities in the system of eqs 1 become V_H^{+0} or V_H^{-0} and α. To verify the reliability of this procedure, a PGSE measurement was carried out for a 0.26 mM solution of [Ru-(η^6-cymene)(2-Et-(C_6H_4))N=C(Me)−C(Me)=N(2-Et-(C_6H_4))-Cl]BPh$_4$ in CD_2Cl_2 obtaining $V_H^+ = 776$ Å^3 and $V_H^- = 697$ Å^3. Imposing $V_H^{-0} = 461$ Å^3, i.e., the average value obtained by mixed conductometric and diffusion NMR measurements, V_H^{+0} and V_H^{IP0} were 592 Å^3 and 1024 Å^3, respectively, in remarkable agreement with the values determined by PGSE experiments as a function of concentration ($V_H^{+0} = 574$ Å^3, $V_H^{IP0} = 1006$ Å^3).[6]

Preliminary PGSE experiments were carried out for NR_4PF_6 salts (R = Et and *n*-Bu) in CD_2Cl_2, acetone-d_6, and DMSO-d_6 in order to determine if V_H^0 values depend on solvent (Supporting Information).[18] By imposing V_H^{-0} equal to our average value (71.5 Å^3), the following values were obtained for V_H^{+0}: R = Et, 227 (CD_2Cl_2), 221 (acetone-d_6), and 225 Å^3 (DMSO-d_6); R = Bu, 461 (CD_2Cl_2) and 486 Å^3 (acetone-d_6). V_H^{+0} is the same within the experimental error, at least for these aprotic solvents.

Applying our methodology to the exhaustively studied tetraalkylammonium salts also leads to a better understanding of which volume best resembles V_H.[19] The latter is considerably higher than V_{vdW} (ca. 1.4 times), but it is very similar to the partial molar volume (V_{PM}).[20] The following V_{PM} values in methylene chloride have been reported:[21] NEt_4^+, 134 cm^3 mol^{-1} (223 Å^3); NBu_4^+, 271 cm^3 mol^{-1} (450 Å^3); and BPh_4^-, 261 cm^3 mol^{-1} (433 Å^3). They are in excellent agreement with the V_H^0 determined here (Table 2).

In conclusion, the above-illustrated methodology allows the hydrodynamic volume of ions to be readily and reliably determined by measuring the dependence of conductance on concentration and a single PGSE NMR measurement at a concentration where ions and ion pairs are present. The methodology appears to be of general applicability, since the nature of the salt is not considered and is useful because ion pairing plays a key role in several branches of chemistry (reactivity and structure of organic compounds[22] and transition metal complexes,[23] anion receptors,[24] materials with nonlinear

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(15) Conductivity measurements were carried out at 40 Hz and 1 kHz using a digital bridge-type conductivity meter (Amel srl, model 160) with a microprobe (model 401/S111) having a cell constant of 0.203 ± 0.001 cm (measured using standard KCl solutions of known specific conductivity). The microprobe was specifically manufactured for our aims in order to fit perfectly into a typical NMR tube (diameter of 5 mm and length of 228.6 mm). It has a diameter of 3.0 mm and a length of 157 mm (Supporting Information) and allowed measurements to be carried out on 0.6 mL of solution. The temperature was held constant at 25.00 ± 0.01 °C using a ThermoHaake C75P thermostat.

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optical properties,[25] lithium-based batteries,[26] etc.). The limitations are essentially dictated by the requirements for conductometric and PGSE NMR experiments. As mentioned before, conductometric measurements require symmetrical electrolytes that do not afford any aggregation process other than ion pairing. As far as PGSE experiments are concerned, NMR-active nuclei with rather high receptivity have to be present in both the anion and cation.

Measurements in other solvents and for salts of a different nature, shape, and dimensions are in progress to determine the scope of the methodology herein reported.

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Supporting Information Available: Experimental details; methodology for treating conductance and diffusional data; conductance data; diffusional data for NR_4PF_6 salts (R = Et and *n*-Bu). This material is available free of charge via the Internet at http://pubs.acs.org.

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