Solvation of praseodymium and cerium chlorides in anhydrous methanol and *iso*-propanol from ultrasonic velocity measurements

Jacek Gliñski,* Barbara Keller and Janina Legendziewicz

Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland.
Fax: +48 71 328 2348; E-mail: glin@wchuwr.chem.uni.wroc.pl

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Ultrasonic velocities and densities were measured, and the isentropic compressibility coefficients and solvation numbers for $CeCl_3$ and $PrCl_3$ (anhydrous and hydrated) solutions in methanol and *iso*-propanol at 25 °C were calculated. The results were interpreted in terms of inner-sphere coordination of chloride anions by lanthanide cations, as well as changing dissociation degree of the solutes with concentration. The steric effect of the solvent molecules on modelling the structure and coordination number of metal ions was considered and compared with the X-ray diffraction of solid solvates. The above studies were correlated with our earlier optical investigations[1] and confirmed by conductivity measurements. For comparison, the same methods were also applied to cesium, calcium and tetraethylammonium chlorides.

For over twenty years we have reported the application of spectroscopy to study equilibria in non-aqueous solutions of anhydrous and hydrated chlorides of lanthanides.[2–6] Very recently, we have investigated the structure and emission properties of hydrated and anhydrous cerium and praseodymium chlorides dissolved in different alcohols.[1] The aim of this work was to explain how the steric factor (namely the branch chain of the alcohol) affects the optical properties of the solution (absorption, excitation and emission), how the equilibrium of different metal oxidation states coexisting in the solution (M^{3+} and M^{4+}) influences the emission intensity, and how the concentration of active ions affects the electronic transition probabilities, emission and M^{3+}/M^{4+} equilibrium. The results show that the solutes under investigation are weak electrolytes in both methanol and *iso*-propanol: even at low concentrations there are two chloride anions incorporated in the inner solvation spheres, while the third Cl^- anion dissociates, but not fully. The inner-sphere coordination of lanthanide cations in ethanol was reported as early as 1966 by Ryan and Jorgensen.[7] These results are in accord with our earlier ones in which, on the basis of europium charge-transfer bands, the inner-sphere coordination of halide ions (Cl^- and Br^-) was shown to occur and their number depends on the amount of water present in the solution.[5,6] The above means that water influences the equilibrium between different halogenocomplexes in solutions.[1,2,5,6]

In light of the above, it seemed interesting to apply ultrasonic methods, which are very useful for the study of liquid mixtures, especially in determining the solvation numbers. While the results obtained for chlorides of lanthanides were a typical, solutions of chlorides of cesium, calcium and tetraethylammonium were also investigated for comparison and to observe the influence of cation size and/or charge density on the solvation. Moreover, the coordinating abilities of these cations are much lower (or non-existent) than those of lanthanide ones, which should also be reflected in the observed phenomena.

Experimental

Chemicals and solutions

Cerium and praseodymium hydrated and anhydrous chlorides were obtained by the technique described earlier in detail for lanthanide perchlorates.[1,8] IR spectra were used to detect water in the anhydrous salts. Cesium chloride (Aldrich 99%) and calcium chloride (Ubichem Ltd., pure for analysis) were dried in vacuum at elevated temperature for a few days. Tetraethylammonium chloride (Fluka, pure) was crystallized from a water–methanol mixture and dried and stored in a vacuum desiccator under P_2O_5. Purification of solvents was as reported before.[2,9,10]

Initial solutions (the most concentrated ones) were obtained by weighing. Other solutions were prepared by gradual dilution of the initial ones by volume. All manipulations and measurements were performed in a dry nitrogen atmosphere to avoid any contact of humid air with the solutions.

Density and ultrasonic velocity measurements

All these measurements were performed at 298.15 K (controlled with an accuracy of ± 0.02 K). Density was measured with an accuracy of ± 0.1 kg m^{-3} using a MG-2 (Ecolab, Poland) vibrating tube microprocessor apparatus. Sound velocity was measured using a SA-1000 "sing-around" type device with an accuracy of ± 0.1 m s^{-1}. The details are given elsewhere.[11,12] Conductivity measurements were performed using a MP2 Energopionier (Poland) conductivity meter (accuracy ± 0.2 μS). For calibration, a 0.01 M aqueous solution of KCl was used (specific conductivity 1.4138×10^{-3} ohm^{-1} m^{-1}).

Results and discussion

From the primary sound velocity (v) and density (ρ) data, collected in Table 1, we calculated the adiabatic compressibility coefficients (β) of solutions, also included in Table 1, using the Laplace formula $\beta = (v^2\rho)^{-1}$. Figs. 1 and 2 show the concentration dependences of the compressibility coefficient of the systems tested. For comparison, Figs. 1 and 2 also show the results obtained for CsCl, $(C_2H_5)_4Cl$ and $CaCl_2$ solutes. Note, however, that solubilities of CsCl, anhydrous $CeCl_3$ and anhydrous $PrCl_3$ in *iso*-propanol were too low and the data for these systems are not included in Fig. 2.

In both methanol and *iso*-propanol, all the solutes cause a gradual decrease in the compressibility with increasing salt

Table 1 The experimental results

Molarity c/mol l^{-1}	Density ρ/kg m^{-3}	Sound velocity v/m s^{-1}	Adiabatic compressibility coefficient $\beta/10^{-9}$ m^2 N^{-1}	Molar conductivity Λ_{mol}/m^2 mol^{-1} Ω^{-1}
CsCl in methanol				
0.000000	787.67	1081.12	1.0862	—
0.000500	787.78	1081.12	1.0860	0.0245
0.001000	787.89	1081.05	1.0860	0.0154
0.002000	787.94	1081.21	1.0856	0.0139
0.005000	788.42	1081.37	1.0847	0.0123
0.010000	789.28	1081.60	1.0830	0.0107
0.020000	790.63	1081.85	1.0807	0.0100
0.050000	795.30	1082.93	1.0722	0.00894
0.100000	802.97	1084.01	1.0598	0.00787
$(C_2H_5)_4NCl$ in methanol				
0.000000	787.67	1081.12	1.0862	—
0.001000	787.65	1081.40	1.0857	0.0150
0.002000	787.73	1081.66	1.0850	0.0136
0.005000	787.90	1082.14	1.0838	0.0124
0.010000	788.31	1082.93	1.0817	0.0111
0.020000	788.72	1084.59	1.0778	0.0102
0.050000	790.48	1089.39	1.0660	0.00930
0.100000	792.82	1095.86	1.0503	0.00787
$CaCl_2$ in methanol				
0.000000	787.67	1081.12	1.0862	—
0.002000	787.81	1081.34	1.0856	0.0159
0.006000	788.45	1082.23	1.0829	0.0128
0.010000	789.08	1082.77	1.0809	0.0114
0.020000	790.53	1084.33	1.0759	0.00956
0.050000	794.27	1088.53	1.0625	0.00822
0.100000	800.93	1093.37	1.0444	—
$CeCl_3$ (anhydr.) in methanol				
0.000000	787.67	1081.12	1.0862	—
0.000768	788.29	1081.28	1.0850	0.0116
0.001920	788.33	1081.34	1.0848	0.00959
0.002855	788.79	1081.53	1.0838	0.00839
0.004800	789.26	1081.66	1.0829	0.00715
0.028550	795.45	1084.27	1.0693	0.00495
0.048000	800.15	1085.41	1.0608	0.00439
$PrCl_3$ (anhydr.) in methanol				
0.000000	787.67	1081.12	1.0862	—
0.000726	788.30	1081.47	1.0846	0.0143
0.001814	788.53	1081.56	1.0841	0.0103
0.002702	788.96	1081.66	1.0833	0.0106
0.004535	789.37	1081.75	1.0826	0.00709
0.027020	795.06	1083.57	1.0712	0.00582
0.045350	799.78	1084.78	1.0625	0.00512
$CeCl_3 \cdot 7H_2O$ in methanol				
0.000000	787.67	1081.12	1.0862	—
0.000500	787.81	1081.28	1.0857	0.0179
0.001000	788.20	1081.53	1.0846	—
0.002000	788.50	1081.34	1.0846	0.0111
0.005000	789.45	1082.52	1.0809	0.00894
0.010000	790.94	1084.17	1.0756	0.00787
0.020000	793.73	1085.35	1.0695	0.00697
0.050000	802.97	1092.00	1.0444	0.00572
0.100000	817.43	1100.73	1.0097	—
$PrCl_3 \cdot 6H_2O$ in methanol				
0.000000	787.67	1081.12	1.0862	—
0.000050	787.80	1081.63	1.0850	0.100
0.000500	787.87	1081.75	1.0846	0.0161
0.001000	787.98	1081.95	1.0841	0.0127
0.002500	788.48	1082.36	1.0826	0.00994
0.005000	789.32	1083.12	1.0799	0.00822
0.010000	790.70	1084.17	1.0759	0.00712
0.050000	802.36	1091.40	1.0463	0.00472
$(C_2H_5)_4NCl$ in *iso*-propanol				
0.000000	782.03	1118.50	1.0221	—
0.000500	781.90	1118.31	1.0226	0.00211
0.001000	781.90	1118.28	1.0227	0.00182
0.002000	781.98	1118.82	1.0216	0.00147
0.005000	782.20	1119.11	1.0208	0.00111
0.010000	782.45	1120.10	1.0187	0.00091
0.020000	782.89	1121.41	1.0157	0.00072
0.050000	784.55	1124.70	1.0076	0.00058
0.100000	787.25	1131.09	0.9929	—

Table 1 (*Continued*)

Molarity c/mol l^{-1}	Density ρ/kg m^{-3}	Sound velocity v/m s^{-1}	Adiabatic compressibility coefficient β/10^{-9} m^2 N^{-1}	Molar conductivity Λ_{mol}/m^2 mol^{-1} Ω^{-1}
$CaCl_2$ in *iso*-propanol				
0.000000	782.03	1118.50	1.0221	—
0.001875	782.67	1119.52	1.0194	0.00012
0.003750	782.78	1119.59	1.0192	0.000072
0.007500	783.09	1119.65	1.0186	0.000054
0.015000	783.81	1119.62	1.0178	0.000041
0.030000	784.98	1119.52	1.0164	0.000029
$CeCl_3 \cdot 7H_2O$ in *iso*-propanol				
0.000000	782.03	1118.50	1.0221	—
0.000938	782.27	1119.14	1.0206	0.00019
0.001875	782.54	1118.88	1.0208	0.00015
0.003750	783.04	1119.62	1.0188	0.00015
0.007500	784.16	1119.78	1.0170	0.00012
0.015000	785.86	1119.90	1.0146	0.00011
0.030000	789.90	1116.33	1.0159	0.00010
$PrCl_3 \cdot 6H_2O$ in *iso*-propanol				
0.000000	782.03	1118.50	1.0221	—
0.001875	782.36	1118.98	1.0208	0.00019
0.003750	782.86	1118.60	1.0209	0.00013
0.007500	783.77	1119.20	1.0186	0.00012
0.015000	785.53	1118.56	1.0175	0.00010
0.030000	789.31	1115.12	1.0189	0.00089

concentration. In methanol this compressibility decrease is roughly proportional to the number of ions that could dissociate and/or to their charges; thus, 1 : 1 electrolytes [CsCl and $(C_2H_5)NCl$] cause the smallest, and $LnCl_3$ (1 : 3 electrolytes), the strongest compressibility changes. This behaviour is consistent with the electrostrictive character of the interactions of electrolytes with solvent (see below). It seems interesting that the effect of hydrated lanthanide chlorides on the compressibility of methanol is much stronger than that of anhydrous ones, suggesting higher solvation numbers of the former.

Generally, decreasing compressibility of an ionic solution can be attributed to the increased number of solvent molecules that experience the electric field of the ions. While solvent molecules become incompressible in strong electric fields (electrostriction), increasing concentration of ions results in the engagement of more solvent molecules in incompressible solvation spheres. However, both chloride ions and water molecules (when hydrated salt is used) can replace solvent molecules in the primary, as well as secondary, spheres. It is possible that, even at low concentrations of lanthanide chlorides in alcohol, chloride ions are present in close vicinity to the lanthanide cations. As a result, the lanthanide cation, together with its sphere (containing negatively charged chlorides), has a lower charge density, which means much fewer electrostrictive interactions with its surroundings. This

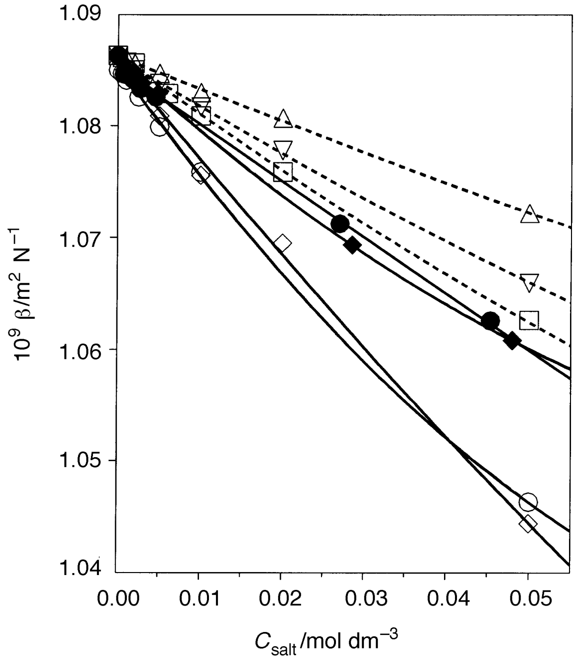

Fig. 1 Adiabatic compressibility *vs.* salt concentration in methanol. (△) CsCl, (▽) $N(C_2H_5)_4Cl$, (□) $CaCl_2$, (◆) $CeCl_3$(anhydr.), (◇) $CeCl_3 \cdot 7H_2O$, (●) $PrCl_3$(anhydr.), (○) $PrCl_3 \cdot 6H_2O$.

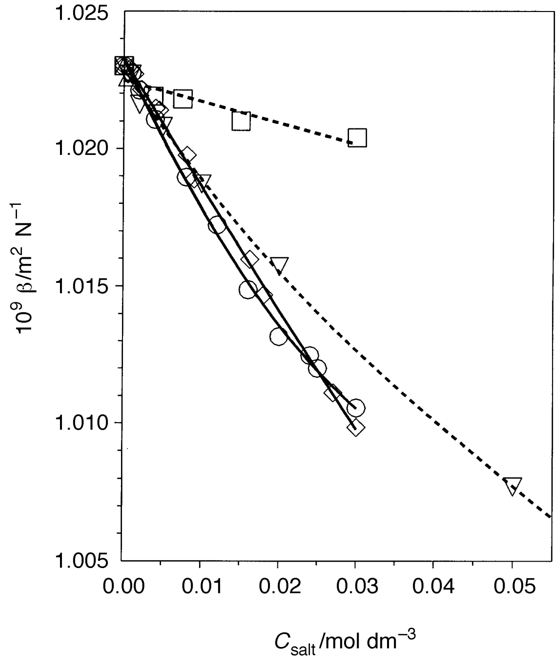

Fig. 2 Adiabatic compressibility *vs.* salt concentration in *iso*-propanol. For symbols see Fig. 1. Solubilities of CsCl and anhydrous lanthanide chlorides in *iso*-propanol are very low and determination of the dependence of compressibility on concentration was impossible in these systems.

process should increase the observed compressibility of the solution with increasing salt content.

Two questions remain: how many chloride ions are engaged in the solvation sphere of the lanthanide cation at a given concentration, and what is the composition of the solvation sphere of this cation at infinite dilution of the salt. The results of spectroscopic investigations (see Introduction) suggest that there are two Cl^- anions in the first solvation sphere in *iso*-C_3H_7OH solutions.[1,2,5] Thus, the observed nonproportionality between the charge of the cation and the decrease in compressibility in *iso*-propanol (Fig. 2) seems to be caused by replacement of *iso*-propanol molecules in the outer solvation sphere by the third chloride anion. The resulting complex is not charged and, consequently, affects the neighbouring alcohol molecules only weakly. These observations were confirmed by our conductivity measurements described below.

The above is in contrast with the behaviour of aqueous solutions of chlorides. Choppin reported that very weakly basic ligands (like chlorides) favour outer-sphere complexation.[13] However, as proved below, in the case of alcoholic solutions the lanthanide chlorides apparently are not strong electrolytes and the chloride ligands may be present in the inner solvation sphere even at infinite dilution, that is, they do not dissociate during salt dissolution.

In light of this explanation, the methanolic solutions must not exhibit a similar characteristic. Methanol is a somewhat better solvating agent than *iso*-propanol, mainly because it is small and its dielectric constant is higher. It is possible, however, that addition of chloride to the solvation shell also occurs in methanolic solutions of lanthanide chlorides. Since CH_3OH is small, the interaction of M^{3+} ions reaches more easily the second coordination sphere and the observed CN (coordination number) is higher. This is confirmed by the X-ray structural data, where CN of Nd^{3+} ions decreases in its solvates with *iso*-propanol down to 7.[14,15] Additionally, the exchange of H_2O molecules in the initial solvation sphere of hydrated lanthanide chlorides can occur. As a result, the effect of the above processes is reflected in the observed changes of adiabatic compressibility of the systems under investigation.

Cations affect the solvent structure much more strongly than anions, mainly because the ionic radii of cations are smaller than those of anions. Assuming a purely electrostrictive mechanism of solvation of ions by alcohol molecules, decreasing compressibility can be attributed mainly to the formation of solvation shells of cations. The solvent molecules forming the shell are compressed enough that we can assume their incompressibility. This assumption allowed Pasynski to calculate solvation numbers of cations according to the formula:[17]

$$n_s = -\frac{\Phi_2}{V_1^0 \beta_1^0} \cong \frac{n_1}{n_2}\left(1 - \frac{\beta}{\beta_1^0}\right) \tag{1}$$

where n_s is the solvation number, n_1 and n_2 are the number of moles of solvent and solute, respectively, V_1^0 is the molar volume of the solvent, Φ_2 is the apparent molar compressibility of the electrolyte, and β and β_1^0 are the compressibility coefficients of the solution and the pure solvent, respectively. Both Φ_2 and β_1^0 can be easily calculated from sound velocity and density data.

Another method to calculate the solvation number, although based on similar assumptions, that is, formation of an incompressible solvation shell around ions, was derived by Ernst and coworkers.[18,19] Purely electrostrictive solvation should lead to the following relation between the composition of the electrolytic solution and its compressibility:

$$\frac{10^3 \beta}{c_1} = V_1^0 \beta_1^0 - n_s \frac{V_1^0 \beta_1^0 M_1}{10^3} m_2 \tag{2}$$

Table 2 The solvation numbers n_s of the salts in two alcohols

	Equation (1)		Equation (2)	
Solute	CH_3OH	*i*-C_3H_7OH	CH_3OH	*i*-C_3H_7OH
CsCl	6.4 ± 0.8	—	5.8 ± 0.6	—
$N(C_2H_5)_4Cl$	8.8 ± 0.6	3.7 ± 0.6	5.8 ± 1.2	2.0 ± 0.5
$CaCl_2$	10.1 ± 1.5	1.3 ± 0.3	13.5 ± 1.6	1.2 ± 0.9
$CeCl_3 \cdot 7H_2O$	18.6 ± 2.5	7 ± 0.5[a]	16.5 ± 1.6	4.3 ± 1.2
$CeCl_3$ (anhydr.)	12.1 ± 1.0	—	12.0 ± 1.5	—
$PrCl_3 \cdot 6H_2O$	21.3 ± 3.0	8 ± 0.5[a]	16.5 ± 1.6	5.0 ± 0.8
$PrCl_3$ (anhydr.)	11.7 ± 1.5	—	11.5 ± 1.2	—

[a] At infinite dilution, see text.

where c_1 is the molar concentration of the solvent in the solution, M_1 is the molar mass of the solvent, and m_2 is the molality of the solute (concentration expressed in moles per kg of the solvent). The solvation numbers of the systems under investigation, calculated using eqn. (1) and (2), are collected in Table 2. Since n_s depends on concentration, Table 2 contains solvation numbers calculated using eqn. (2) by extrapolation to $c = 0$, that is, at infinite dilution.

A (roughly) linear character of $V_1^0 \beta_1^0 M_1 m_2$ *vs.* $10^3 \beta c_1^{-1}$ was observed over the entire concentration range in both alcohols. The solvation numbers determined in this way are very high compared to those of other electrolytic solutions. As an example: the hydration numbers of KCl in water, as well as in water–dioxane mixed solvents, do not exceed 6[11,20] and hardly depend on the experimental method and the method of calculation (for instance, the classical Pasynski method for aqueous solutions of KCl yields the hydration number $n_h = 5.4$).[21] The differences in n_s obtained by the two acoustic methods originates from slightly different assumptions and are a good example of the well-known fact that any comparison of solvation numbers obtained by different methods may be misleading.

The hydration numbers of light lanthanide perchlorates vary from 10 to 13,[10] while those of heavy lanthanides are between 11.7 and 13.[3] These numbers, obtained by the same method for aqueous lanthanide chlorides, vary from 16.8 to 19.4, depending on the lanthanide.[22]

The high solvation numbers obtained by us, sometimes even higher than those observed for aqueous solutions of the solutes under investigation, may indicate either strong electrostriction around the chlorine ions and/or that the range of the cation electrostrictive interaction is longer than the first solvation shell. The first explanation would mean that Pasynski's assumption of negligible effect of solvation of the anion is not true; the second one implies that the acoustic method generally yields too high solvation numbers (not only the inner-shell molecules are compressed). Very high solvation numbers of lanthanide salts in non-aqueous solvents are not surprising: in our recent paper it was about equal to 25 for neodymium perchlorate in methanol.[23] Neutron diffraction studies of lanthanide perchlorates in heavy water also suggest high coordination numbers of the cations (8–9) and the strong radial orientation of water molecules around the ions is interpreted in terms of the high charge of the cations.[24]

Another striking observation is the fact that solvation numbers of hydrated lanthanide chlorides in *iso*-propanol, calculated from eqn. (1), are not concentration independent. The dependences of n_s on salt concentration are shown in Fig. 3. The changing n_s is excellent confirmation of the above assumption that chloride anions enter the solvation sphere of lanthanide cations, lowering the overall charge of the solvated species (and thus causing a slight nonlinearity of the compressibility *vs.* concentration dependences). Recently, in our paper mentioned above, very similar behaviour was found for anhydrous $Nd(ClO_4)_3$ in methanol and interpreted in terms of

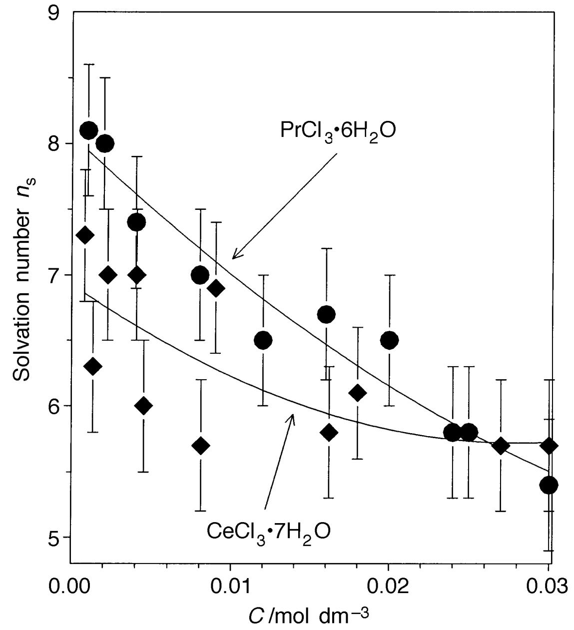

Fig. 3 Solvation numbers *vs.* concentration of hydrated praseodymium and cerium chlorides in *iso*-propanol calculated from eqn. (1).

inclusion of the perchlorate ions into the solvation shell of the lanthanide cation.[23]

Table 2 shows clearly that, in general, the solvation numbers in methanol are higher than in *iso*-propanol. This is easy to understand in terms of steric reasons: molecules of methanol are smaller than these of *iso*-propanol. Another feature, the fact that anhydrous lanthanide chlorides in methanol have much lower n_s than the hydrated ones, is not completely clear and additional studies are needed. It is clear that water molecules interact more strongly than alcohol molecules with ions and should replace the latter in the solvation shells. On the other hand, the statistical effect of the excess of methanol in solution weakens this process. One must also consider the size of water molecules and their role in the easier exchange of chloride ions than by alcohol molecules. As a result, more solvent or water molecules are placed in the first solvation sphere and the M^{3+} ion has also its second and higher shells of solvent molecules. This leads to an increase of the solvation number when compared to anhydrous salts. Moreover, interaction of water molecules with the solvent should also decrease compressibility, leading to increased overall solvation number.

Our conductivity measurements strongly confirm the conclusions drawn from the spectroscopic measurements. The systems under investigation cannot be described in terms of simple Debye–Hückel theory; the reason for this could be changing charge and/or number of ions. This idea is consistent with the model of an equilibrium process in which chloride anions are entering the close environment of the lanthanide cation. Thus, it was necessary to assume that the lanthanide chlorides tested are weak electrolytes and that their dissociation could be described by the reaction

$$LnCl_3 \rightleftharpoons LnCl_{3-n}{}^{+} + nCl^{-}$$

or more precisely by

$$LnCl_3(solvent)_m + solvent \rightleftharpoons LnCl_{3-n}(solvent)_{m+1}{}^{+} + nCl^{-}.$$

In this case, it is easy to derive the equation linking the observed conductivity with molar concentration of the salt:

$$\ln \Lambda = \ln \Lambda_0 + \frac{1}{n+1} \ln K_{diss} - \frac{n}{n+1} \ln c \qquad (3)$$

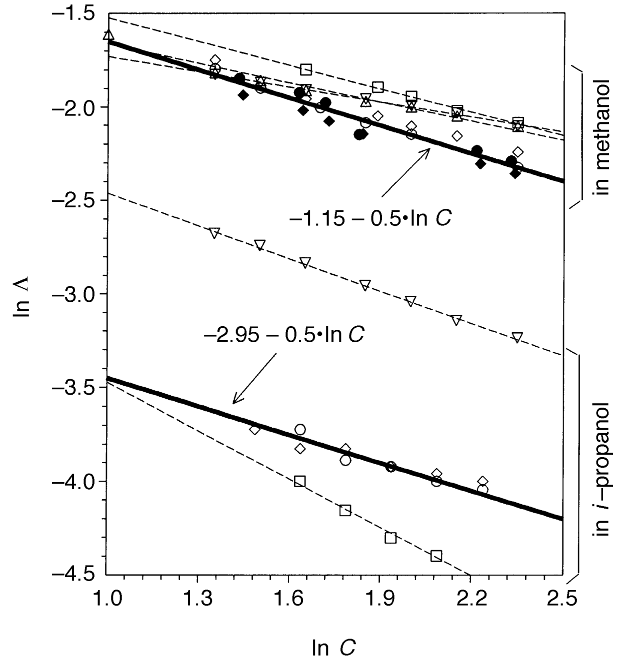

Fig. 4 Plots of ln Λ *vs.* ln *c* for the systems under investigation. For symbols refer to Fig. 1. The thick solid lines are fitted to the data for lanthanide chlorides.

where *c* is the molar concentration of the salt, K_{diss} is the dissociation constant of the salt, Λ_0 is the limiting conductivity of the salt, that is extrapolated to infinite dilution and Λ is the conductivity of a solution of molar concentration *c*. Eqn. (3) is a linear relation between the logarithms of conductivity and concentration, whose slope depends on the number of dissociated chloride ions and the intercept with the ln Λ axis depends on the dissociation constant of the salt.

Fig. 4 presents the corresponding dependences for all the systems measured. It is striking that for lanthanide chlorides, independent of the solvent or crystalline water content, all the slopes are equal to -0.5 (within experimental error). Generally, these results confirm very well our previous conclusions: all the lanthanide chlorides are weak electrolytes and only one chloride anion can be dissociated. The dissociation constants of the chlorides, both hydrated and anhydrous, are of the order of 0.25 in methanol and 6.3×10^{-5} in *iso*-propanol, almost independent of the lanthanide. Other chlorides behave differently, most probably because of the formation of ionic aggregates; it is interesting that lanthanides do not have such a tendency.

Conclusions

It seems evident that lanthanide chlorides are weak electrolytes in alcohols, much weaker in *iso*-propanol than in methanol. Steric effects can lead to the reduction of the coordination numbers of metal ions in *iso*-propanol. At low concentrations the first solvation sphere of lanthanide contains two chloride anions; at higher concentrations replacement of solvent molecule in the outer solvation sphere by a chloride anion is suggested. The conductivity investigations confirm the above results. However, the stronger electrostrictive effect of hydrated lanthanide chlorides compared to the anhydrous ones remains open to question and needs further investigation.

Acknowledgements

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