Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

An improved theory of the electric conductance of ionic solutions based on the concept of the ion-atmosphere's smaller-ion shell

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Table S1 lists the co-ion ISP values – b_+ and b_- – of the ions of the electrolytes of this study, along with the corresponding limiting ionic equivalent conductivity values (λ^0_i's; i = +.–).

Table S1 Ion size and limiting ionic equivalent conductivity[a]

Cation	b_+	λ_+^0	Anion	b_-	λ_-^0
H^+	1.16	349.65	Cl^-	3.62	76.31
Li^+	1.36	38.66	Br^-	3.92	78.1
Na^+	1.94	50.08	I^-	4.40	76.8
K^+	2.66	73.48	ClO_4^-	4.80	67.3
Tl^+	2.94	74.7	SO_4^{2-}	4.60	80.0
Mg^{2+}	2.12	53.0	$Fe(CN)_6^{3-}$	5.20	100.9
Ca^{2+}	2.26	59.47	$Fe(CN)_6^{4-}$	5.60	110.4
Cu^{2+}	2.3	53.6			
Sr^{2+}	2.24	59.4			
Zn^{2+}	2.3	52.8			
La^{3+}	2.12	69.7			

[a] in water at 25 °C; b's are in Å; λ^0_i's in S cm^2 g-eq, as those of $(1/z_+)C^{(z+)+}$ or $(1/z_-)A^{(z-)-}$; b data are from Refs. 18 (salts) and 22 (acids), and λ^0_i data, from Ref. 23, **5**-95–**5**-97.

Table S2 lists values of $\omega^\dagger$ computed at different concentrations (c, mol/lit), for six representative electrolytes, all in water at 25 °C, along with the limiting values of I and κa for the conductivity model, as used in the current work.

Table S2 Change of $\omega^{\dagger}$ as a function of concentration and the assumed maximum c-range (and maximum κa, a in Å) of applicability of DHO–SiS, for different aqueous electrolytes at 25 °C

c, mol/liter	HCl	LiCl	KCl	$SrCl_2$	$ZnSO_4$	$K_3Fe(CN)_6$
0.001	1.0175	1.0030	1.00001	1.00057	1.0033	1.00201
0.005	1.0392	1.0067	1.00002	1.00127	1.0074	1.00449
0.01	1.0554	1.0095	1.00003	1.00180	1.0105	1.00635
0.05	1.1239	1.0213	1.00006	1.00402	1.0234	1.01419
0.1	1.1752	1.0301	1.00008	1.00569	1.0332	1.02007
0.2	1.2478	1.0426	1.00012	1.00805	1.0469	1.02839
c_{max}	0.105	0.105	0.101	0.0343	0.022	0.0187
$(\kappa a)_{max}$	0.385	0.385	0.358	0.371	0.266	0.433

Figures S1 to S6 are supplementary Figures, as discussed in the main text.

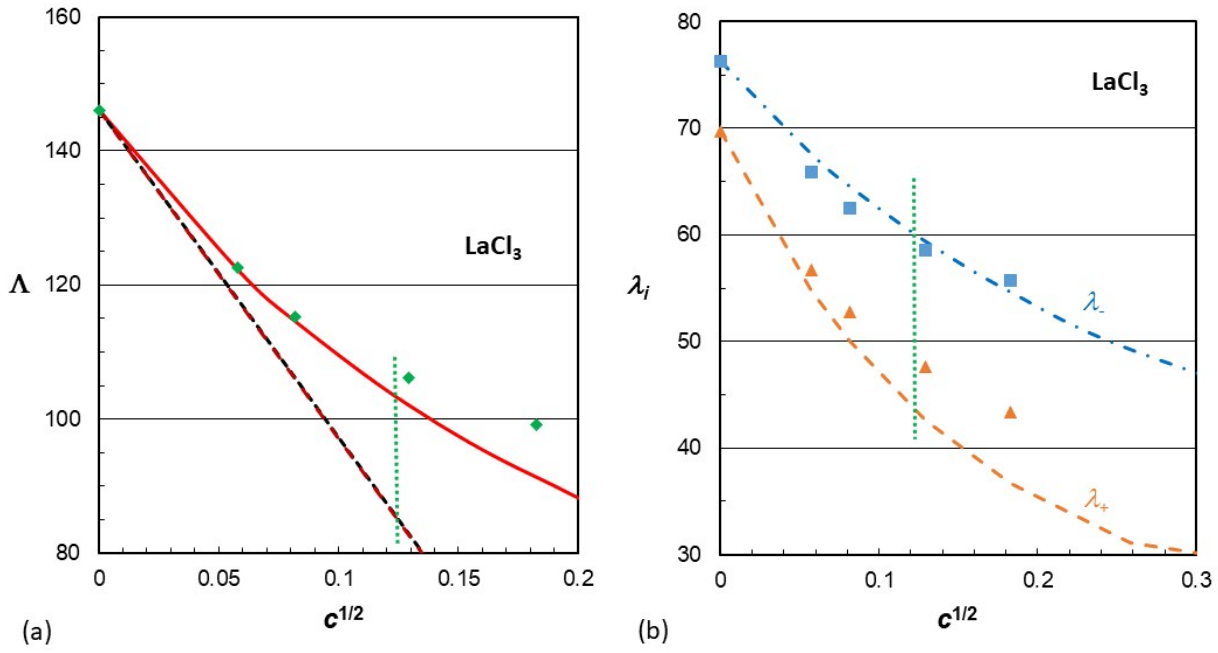

Fig. S1 Equivalent conductivities (Λ, λ_i) of $LaCl_3$ and its ions in H_2O at 25 °C, as functions of concentration, c, as mole electrolyte solute per liter solution (M); vertical bars (dotted lines) indicate the expected limit of the DHO model validity (Table 2): (a) Comparison between the proposed DHO–SiS theory, "Λclc" (solid line); the DHO–SiS limiting law "ΛLL" (hyphenated line), and the "DHOLL" limiting law, eqn (1) (broken line), here the two lines merge with each other; and experimental data (full diamond symbols). (b) Theory–experiment comparison of the single-ion equivalent conductivity of Na^+ (λ_+) and of Cl^- (λ_-); broken line (λ_+) and broken-dotted line (λ_-) are calculated, symbols (full triangles for λ_+, full squares for λ_-) are data based on measured Λ and t_i. Experimental data are in references listed in Table 3.

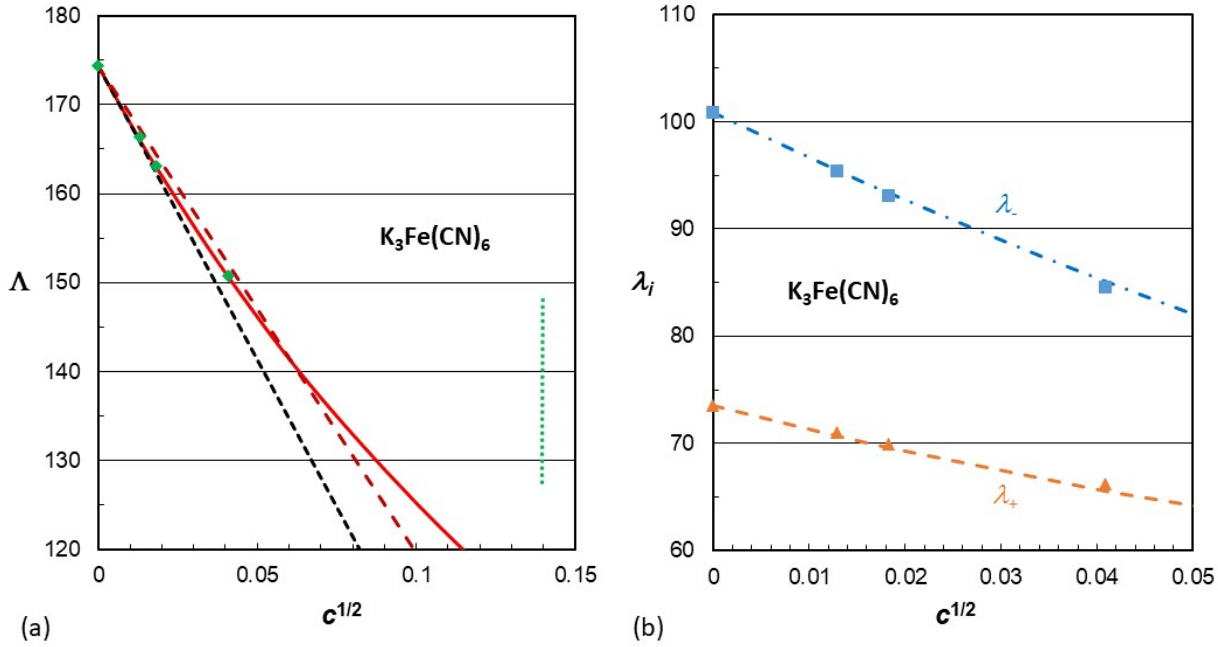

Fig. S2 As Fig. S1, but for $K_3Fe(CN)_6$.

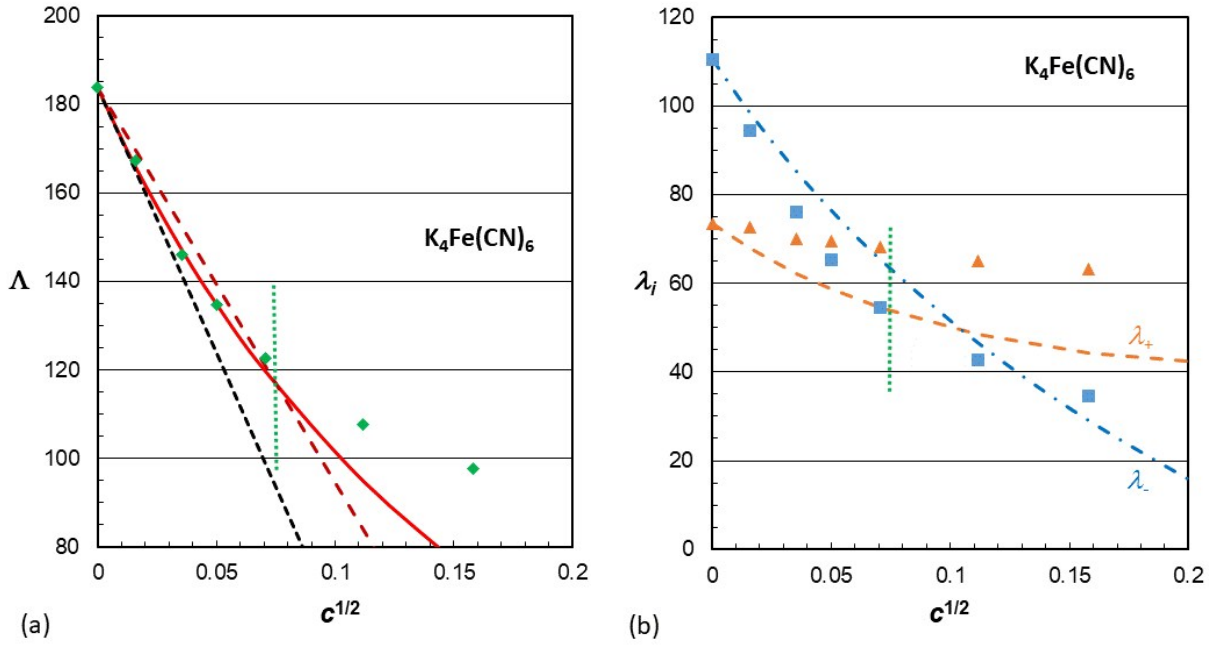

Fig. S3 As Fig. S1, but for $K_4Fe(CN)_6$.

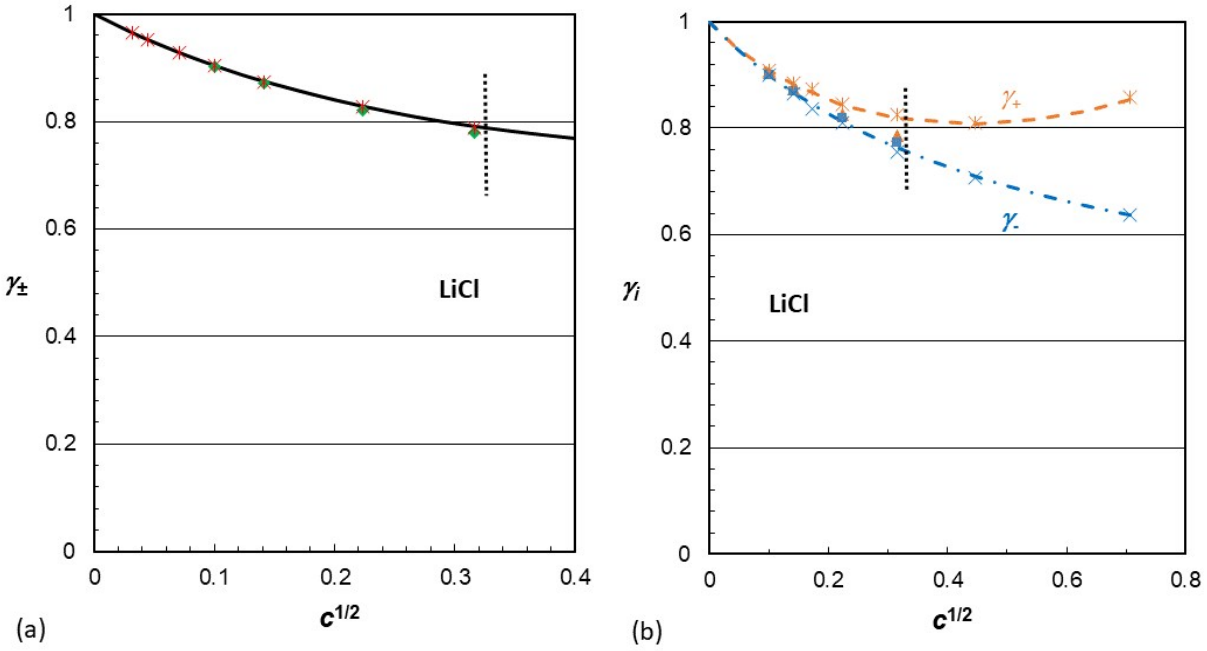

Fig. S4 Activity coefficients of LiCl in H_2O at 25 °C; vertical bars (dotted lines) indicate the expected limit of the DHO model validity (Table 2). (a) $\gamma_\pm$ vs. $c^{1/2}$; the line is the theoretical function computed from the DH–SiS expression using the ISPs of Tables S1 and 3, the star symbols are experimental values (Table 3), and the full diamond symbols are values calculated from conductivity, eqn (16) – (18). (b) γ_i vs. $c^{1/2}$, $i = +,-$; the lines are the theoretical functions (of DH–SiS); the dashed line is of γ_+, the dashed-dotted line is of γ_-; the full triangle and full square symbols are γ_i values calculated from conductivity, for Li^+ and Cl^-, respectively; and the * and × symbols are, respectively, experimental data of Vera's group, Ref. 27.

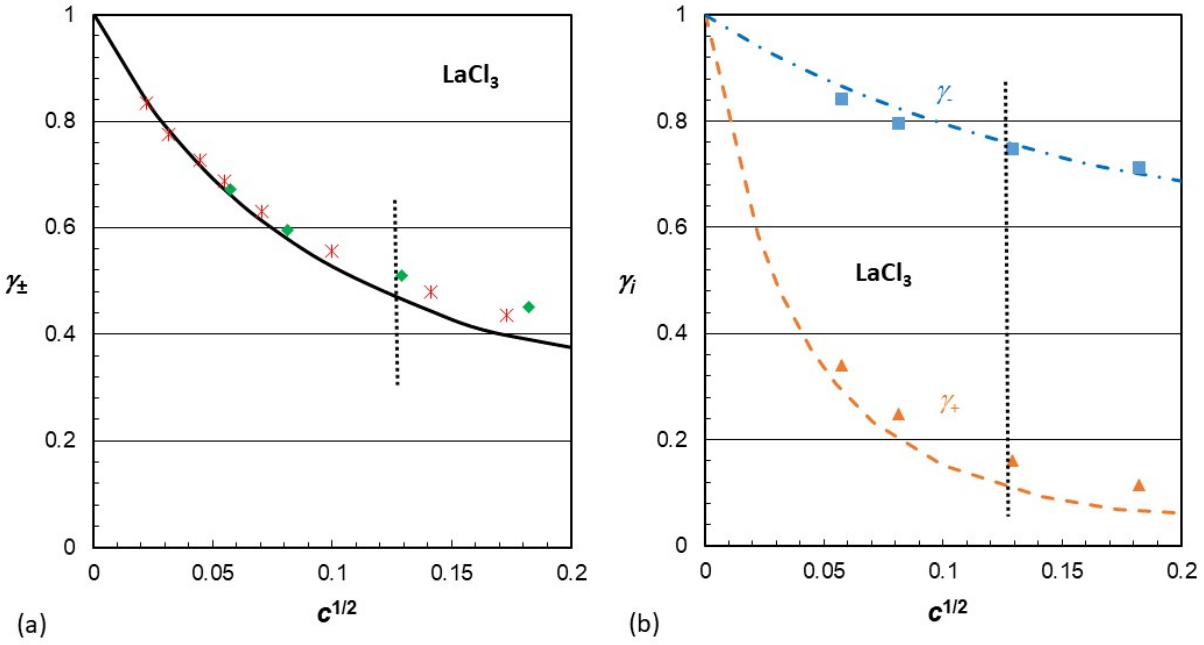

Fig. S5 Activity coefficients of $LaCl_3$ in H_2O at 25 °C; vertical bars (dotted lines) indicate the expected limit of the DHO model validity (Table 2). (a) $\gamma_{\pm}$ vs. $c^{1/2}$; the line is the theoretical function computed from the DH–SiS expression using the ISPs of Tables S1 and 3, the star symbols are experimental values (Table 3), and the full diamond symbols are values calculated from conductivity, eqn (16) – (18). (b) γ_i vs. $c^{1/2}$, $i = +,-$; the dashed and dashed-dotted lines are the theoretical functions (of DH–SiS) for γ_+ and γ_-, respectively; and the full triangle and full square symbols are, respectively, values calculated from conductivity.

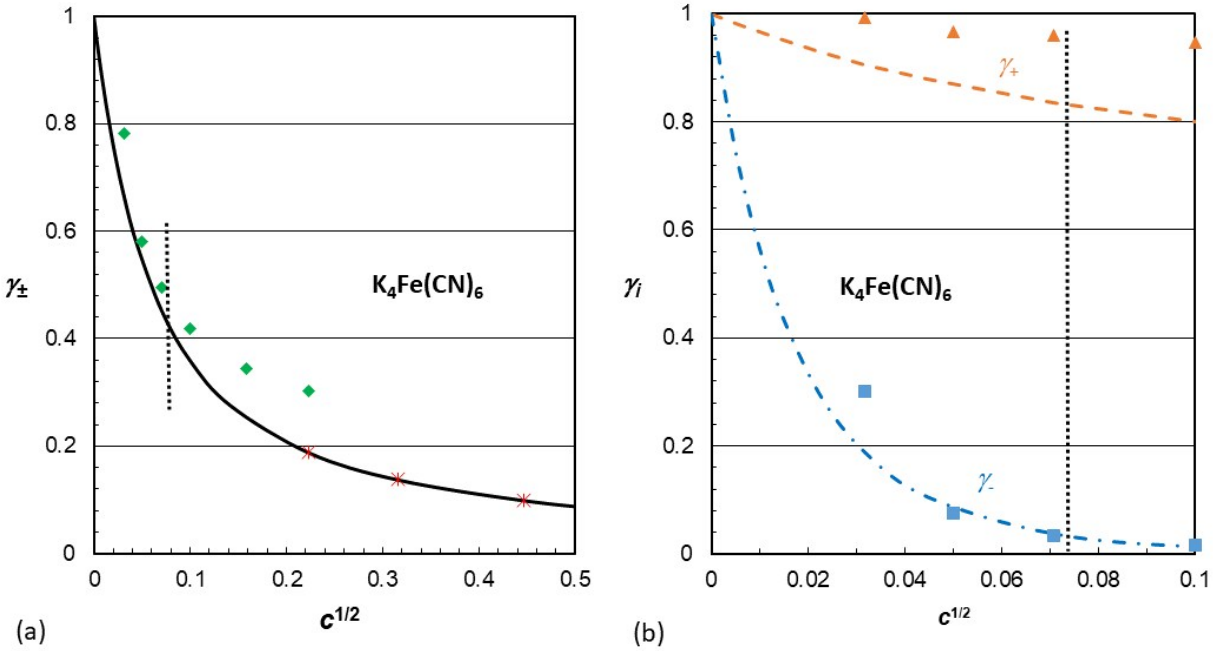

Fig. S6 As Fig. S5, but for $K_4Fe(CN)_6$.