

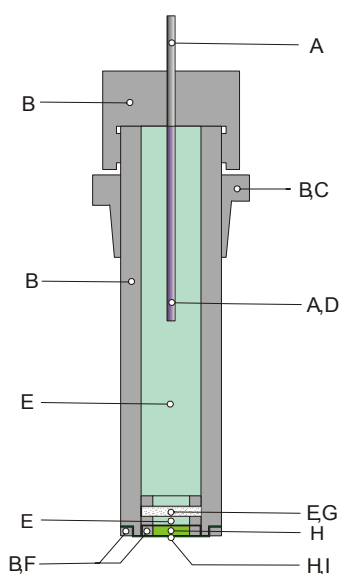
**Electronic Supplementary Information, Part A, to:**

**ACTIVITY COEFFICIENTS IN MIXED ELECTROLYTE SOLUTIONS**

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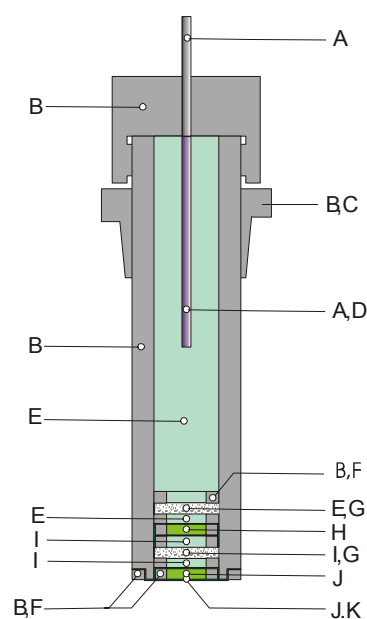
**§1. Apparatus and reagents**



**Figure S1** - The membrane electrode for  $[\text{Co}(\text{en})_3]^{3+}$ ,  $\text{K}^+$ , or  $\text{Cl}^-$ .

For  $[\text{Co}(\text{en})_3]^{3+}$ : A = silver; B = PTFE ; C = sliding ring; D, silver chloride; E =  $5 \times 10^{-3}$  M  $[\text{Co}(\text{en})_3]\text{Cl}_3$ ; F = pressing ring; G, fritted glass; H = membrane oil, ca.12 %  $[\text{Co}(\text{en})_3][\text{TFPB}]_3$  in NPOE; I = one of the two sheets of porous PTFE (held in place by the PTFE pressing rings) which bracket the liquid membrane.

For  $\text{K}^+$  and  $\text{Cl}^-$ : The electrodes are identical to the one for  $[\text{Co}(\text{en})_3]^{3+}$ , except for the aqueous solution in E (KCl 0.01 M or  $\text{CaCl}_2$  0.00667 M respectively) and the membrane oil in H (ca. 17% K[TFPB] in NPOE, or ca. 22 % tetradodecylammonium chloride, [TDA]Cl, in 3, 3, 4, 4, 5, 5, 6, 6, 7, 7, 8, 8, 8 tridecafluoro-1-octanol, respectively).



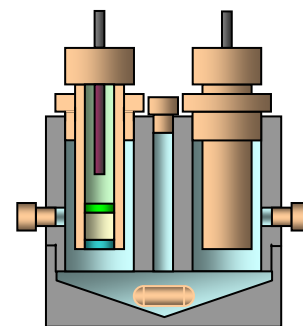
**Figure S2** - The membrane electrode for  $[\text{Co}(\text{CN})_6]^{3-}$  or  $[\text{Fe}(\text{CN})_6]^{3-}$ .

A = silver; B = PTFE ; C = sliding ring; D, silver chloride; E =  $1 \times 10^{-2}$  M KCl; F = pressing ring; G, fritted glass; H = potassium-exchange membrane oil, ~17% K[TFPB] in NPOE; I,  $5 \times 10^{-3}$  M  $\text{K}_3[\text{Co}(\text{CN})_6]$  or  $\text{K}_3[\text{Fe}(\text{CN})_6]$ ; J, the  $[\text{Co}(\text{CN})_6]^{3-}$  or  $[\text{Fe}(\text{CN})_6]^{3-}$  membrane, made of the liquid salt  $[\text{TDA}]_3[\text{Co}(\text{CN})_6]$  or  $[\text{TDA}]_3[\text{Fe}(\text{CN})_6]$  free of solvent; K = one of the four sheets of porous PTFE (held in place by the PTFE pressing rings) which bracket the two liquid membranes.

### Apparatus -

The cell body where the electrodes of Figures S1 and S2 are embedded (side diagram) is the same described for single electrolytes by F. Malatesta, *J. Solution Chem.*, 1995, **24**, 241. It is entirely made of PTFE, and a small magnetic bar (approximately 5×2 mm, with an allowed rotation rate of approximately 1-5 rps) on the bottom ensures moderate stirring conditions when desired. An air bath thermostat (monitored at ±0.001 K with the aid of a platinum resistance thermometer) assures a temperature of 298.15±0.02 K.

The electrical resistance of a typical cell assemblage with 3 liquid membranes ranges from few tens to one - two hundred kΩ. Emf values are measured using a *Digital Adret Electronique 103A DC - Current and Voltage Standard* as a supplier for potentials (±0.001 mV) and a *Keithley 614 Electrometer* (input impedance > 10<sup>14</sup> ohm) as null point (±0.01 mV) detector.



### Membrane salts and membrane oils -

[Co(en)<sub>3</sub>][TFPB]<sub>3</sub> is prepared by pouring a solution of [Co(en)<sub>3</sub>]Cl<sub>3</sub> into a hot aqueous solution of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, Na[TFPB], which contrary to other salts of [TFPB]<sup>-</sup> is soluble in hot water. For preparation of Na[TFPB], see H. Nishida, N. Tanaka, M. Yoshimura, T. Sonoda, and H. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 2600. The precipitate, separated by centrifugation, is repeatedly dissolved in ethanol and precipitated several times by adding an aqueous solution of [Co(en)<sub>3</sub>]Cl<sub>3</sub>, and finally only water. It is then vacuum dried. Other salts for cation membranes, e.g. K[TFPB], are prepared by the same method.

Tetradodecylammonium salts for anion membranes are obtained by dissolving previously purified tetradodecylammonium bromide,<sup>S1</sup> [TDA]Br, in CH<sub>2</sub>Cl<sub>2</sub> + C<sub>5</sub>H<sub>12</sub> or CH<sub>2</sub>Cl<sub>2</sub> + C<sub>6</sub>H<sub>14</sub> as appropriate, and then extracting the organic phase by an aqueous solution of the desired anion, in a separator funnel. The extraction is repeated as many times as requested to eliminate Br<sup>-</sup> –checked by a qualitative test– then several times again as a precautionary measure. One-two extractions (five for safety's sake) suffice for [Co(CN)<sub>6</sub>]<sup>3-</sup> or [Fe(CN)<sub>6</sub>]<sup>3-</sup>, 4 - 5 extractions (ten for safety's sake) for Cl<sup>-</sup>. The organic phase is then evaporated off at reduced pressure and room temperature, either completely (CH<sub>2</sub>Cl<sub>2</sub> + C<sub>5</sub>H<sub>12</sub>) for [TDA]<sub>3</sub>[Co(CN)<sub>6</sub>] and [TDA]<sub>3</sub>[Fe(CN)<sub>6</sub>], two honey-like syrups that do not crystallize, or partially (CH<sub>2</sub>Cl<sub>2</sub> + C<sub>6</sub>H<sub>14</sub>) for [TDA]Cl which separates into crystals when C<sub>6</sub>H<sub>14</sub> (less volatile) becomes predominant. The membrane oils for M<sup>Z+</sup> are prepared by dissolving M[TFPB]<sub>z</sub> in 2-nitrophenyloctyl ether (NPOE). Concerning the [TDA]<sub>z</sub>X salts, [TDA]<sub>3</sub>[Co(CN)<sub>6</sub>] and [TDA]<sub>3</sub>[Fe(CN)<sub>6</sub>] are liquid and do not need any solvent; as to [TDA]Cl, the solvent 3,3,4,4,5,5,6,6,7,7,8,8,8 tridecafluoro-1-octanol proves more appropriate than alternative solvents previously used (1-chloronaphthalene, 3,5-dichlorotoluene, oleyl alcohol) because it dissolves high amounts of the tetradodecylammonium salt and it is very effective in soaking the PTFE porous sheets (detail I of Figure S1) that bracket the membrane.

Membrane oils once prepared were saturated by water and stored in water.

### Other reagents -

K<sub>2</sub>SO<sub>4</sub>, MgCl<sub>2</sub>, [Co(en)<sub>3</sub>]Cl<sub>3</sub>, MgSO<sub>4</sub>, LaCl<sub>3</sub>, La<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, KOH, and HCl were reagent grade commercial products and were used as such, excepting LaCl<sub>3</sub> and [Co(en)<sub>3</sub>]Cl<sub>3</sub> which were further crystallized from conductivity water. K<sub>3</sub>[Co(CN)<sub>6</sub>], [Co(en)<sub>3</sub>][Co(CN)<sub>6</sub>], and [Co(en)<sub>3</sub>][Fe(CN)<sub>6</sub>] were from the same salt stocks already used to study single salts.<sup>S2, S3</sup> K<sub>2</sub>SO<sub>4</sub> was dried in a furnace at 500°C; [Co(en)<sub>3</sub>]Cl<sub>3</sub> was dried in an oven at ca. 1-3 torr, 160-170 °C (the apparent molecular weight of dehydrated [Co(en)<sub>3</sub>]Cl<sub>3</sub> was checked by ion exchange - acidimetric titration and was found to be 347.71±0.09, consistent with 0.118±0.005 residual mol of water per mol of salt). Stock solutions of K<sub>2</sub>SO<sub>4</sub>, [Co(en)<sub>3</sub>]Cl<sub>3</sub>, K<sub>3</sub>[Co(CN)<sub>6</sub>], [Co(en)<sub>3</sub>][Co(CN)<sub>6</sub>] and [Co(en)<sub>3</sub>][Fe(CN)<sub>6</sub>] were directly prepared by weighing the solid salts and water, while the stock solutions of LaCl<sub>3</sub>, La<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, MgCl<sub>2</sub> and MgSO<sub>4</sub> were standardized by EDTA titration, or ion-exchange and acidimetric titration, or both methods. In no case did the relative standard deviations exceed 0.2 %. The hydrochloric acid used as a supporting electrolyte was prepared from 37 wt% in water, 99.999 hydrochloric acid, then standardized with Na<sub>2</sub>CO<sub>3</sub> and adjusted to 0.1000 mol kg<sup>-1</sup> with weighed amounts of water. The KOH supporting electrolyte solution was prepared using a saturated, settled solution of KOH and boiled water. Duplicate titration using phenolphthalein and brom-cresol green indicators revealed that contamination by carbonate was 2.2 ± 0.2 equivalents per cent of the total alkali. Since the substitution of a moderate amount of CO<sub>3</sub><sup>2-</sup> for OH<sup>-</sup> cannot alter the activity coefficients, and since CO<sub>3</sub><sup>2-</sup> (like SO<sub>4</sub><sup>2-</sup> and OH<sup>-</sup>) cannot interfere with the correct response of the anionic membrane, no maniacal care was devoted to preventing further CO<sub>2</sub> by entering. The mixed solutions were all prepared by weighing, and were stored in PTFE bottles.

### §2. Modus operandi.

The measurements take ca. 90 min. per solution, 60 of which as waiting time after loading the cell and 30 for the emf readings –one every five minutes– whose average values and standard deviations are reported in the tables of the experimental results. Readings were made in quiet conditions; however, in several cases one further reading in stirring conditions was performed at the end, as a check for result reliability (an appreciable discrepancy in the E values diagnoses a probable non-equilibrium condition).

The tables of the experimental results provide the data in the same order in which these were determined. The leaching of the membrane surfaces causes some minor shifts of the potential which increase run by run when loading and reloading the cell.<sup>S4</sup> In

<sup>S1</sup> [TDA]Br was purified by dissolving it twice in CH<sub>2</sub>Cl<sub>2</sub> + C<sub>6</sub>H<sub>14</sub>, extracting the solution by water, and crystallizing the salt by a partial evaporation of the solvent and freezing.

<sup>S2</sup> F. Malatesta, F. Bruni, N. Fanelli, S. Trombella, R. Zamboni, *J. Solution Chem.*, 2000, **29**, 449

<sup>S3</sup> F. Malatesta, S. Trombella, A. Giacomelli, M. Onor, *Polyhedron*, 2000, **19**, 2493.

<sup>S4</sup> Immediately after rinsing the cell and loading a new solution, the potential presents perceptible drifts that quickly decrease, yielding (usually, within 20 – 40 min.) a quite flat “definitive” value for E. By loading the cell again and again with the same

order to compensate for such effects, a solution for each system is used as the reference solution, and the corresponding emf,  $E_{\text{ref}}$ , is determined when starting and terminating any series of measurements. The difference between the first and final value of  $E_{\text{ref}}$ , divided by the number of solutions introduced meanwhile in the cell, makes it possible to evaluate the extent of the shift and to introduce a proper correction, by subtracting from any  $E$  the corresponding interpolated value of  $E_{\text{ref}}$ . As a check for the suitability of the corrections, in several cases the same solutions were explored again in a different order.

### §3. Ion selectivity and water-induced ion selectivity

Liquid membrane cells for activity coefficient determinations need particular membranes whose requisites are not the same as those of classic ISE's. An ISE – whose main purpose is to provide sound analytical responses in very complex solutions – requires ion selectivity to be as enhanced as possible; it is not so essential, however, that the electrical response be exactly predictable in theoretical terms (i.e., the slope needs not coincide with Nernst's slope, the diffusion potentials need not necessarily be absent, etc.). On the contrary, the ability to select a specific ion among other ions of the same sign is utterly unimportant for a membrane aimed at determining activity coefficients in single electrolyte solutions. Conversely, such a membrane has to be free from any complications that may cause departure from the ideal behavior of an inert wall in equilibrium with the neighboring phases, and perfectly impermeable to all ions of the wrong sign (a perfect permselective wall). No possibilities may subsist for such a membrane to be the seat of not perfectly understood effects, irreversible transformations, inner diffusion potentials, etc., making the cell no longer reliable for thermodynamic research – even though perhaps preferable for analytical purposes. A "thermodynamically oriented" liquid membrane is therefore made by dissolving – in a liquid phase insoluble in water – a single salt insoluble in water, made of the target ion (e.g.  $K^+$ ) and an extremely hydrophobic counterion (e.g. [TFPB]) which assures an extreme insolubility in water, and no other components.

Neutral carriers and additional components usually introduced in ISE membrane cocktails to increase selectivity may cause complications, causing the membrane to work as a non-equilibrium section of the cell. Consider for instance a membrane made of  $K[TFPB]$  dissolved in NPOE, between two aqueous solutions of e.g.  $KCl$ . While such a membrane is perfectly permselective (the anions are not allowed to pass), it is not ion-selective and, if sodium ions are introduced in the aqueous solutions, a non-equilibrium situation arises between the sodium ions that enter the membrane and potassium ions that go out, giving rise to a mixed potential. The unwanted effect would disappear if  $K^+$  ions were so strongly stabilized in the organic phase as to prevent the reaction  $Na^+_{\text{aq}} + K^+_{\text{org}} \rightarrow Na^+_{\text{org}} + K^+_{\text{aq}}$  from occurring. One can think of taking advantage of a hydrophobic neutral ligand  $R$  that binds  $K^+_{\text{org}}$  (and no  $Na^+_{\text{org}}$ ) forming a complex  $[RK]^+_{\text{org}}$  with a high formation constant and a high exchange rate (the complex must not be kinetically inert). However, it is not easy to fulfill these conditions. Should  $R$  be introduced in sub-stoichiometric amounts, free  $K^+_{\text{org}}$  still reacts with  $Na^+_{\text{aq}}$  and the requisite of selectivity is not fulfilled. Conversely, if the ligand quantity is too great, supernumerary  $K^+$  ions enter the membrane carrying with them an equivalent number of unwanted  $Cl^-$ , and the permselectivity requisite is lost. In theory, one can prepare a membrane made of the perfectly stoichiometric compound  $[RK]^+[TFPB]$ . (Such a compound, with  $R = \text{valinomycin}$ , can be prepared by allowing an excess amount of  $K[TFPB]$  dissolved in methanol to react with valinomycin. After evaporating the solvent,  $[RK][TFPB]$  is extracted with  $CH_2Cl_2 + C_5H_{12}$ , which does not dissolve residual  $K[TFPB]$ .) However, usual ISE membranes employing neutral carriers are built in a different way and work according to a different principle. The typical membrane cocktails for  $K^+$ , for instance, contain  $Na[TFPB]$  or similar sodium salts, the neutral carrier  $R$  (e.g., valinomycin), and the solvent. When introduced in an aqueous solution of  $K^+$ , the potassium ions enter the membrane forming  $[RK]^+_{\text{org}}$  and replacing  $Na^+_{\text{org}}$ . The mechanism is the same widely studied one of  $H_3O^+$  and  $Na^+$  ions in glass electrodes, and yields a stationary kinetic potential, rather than a true equilibrium potential. As a matter of fact, the emf values can be predicted (and are found) to follow the same laws that apply to a true equilibrium potential, provided the ISE is used in the proper conditions. Therefore, it is perfectly conceivable to use a commercial ISE to study activity coefficients in some well-controlled cases, thus extending the number of electrolytes that can be studied in mixed solutions (in particular, there are significant examples of substitution of glass electrodes for hydrogen electrodes, in cells without liquid junctions). However, it seems to be widely preferable to avoid, as far as possible, such devices that are based on non-equilibrium effects, when performing activity coefficient determinations.

Hints for the possible use of "thermodynamically oriented" permselective membranes in mixed solutions –relying on the intrinsic selectivity of the aqueous phase– were implicitly contained in several observations accumulated when studying single electrolytes. We observed, in particular, that the cell responses of several electrolytes seemed perfectly correct, and were not affected by drifts, at dilution levels too high for  $H^+$  and  $OH^-$  to remain negligible. More direct hints came from peculiarities observed when the salts of the anion-exchange membranes were prepared. The  $[TDA]_xX$  salts are obtained by ion exchange, extracting a solution of  $[TDA]Br$  in  $CH_2Cl_2$  and hexane (or pentane) with aqueous solutions of  $Na_xX$  (or  $K_xX$  or similar, as convenient) in a separator funnel, as many times as necessary to eliminate the bromide ions. It was observed that – contrarily to  $ClO_4^-$  or  $[Fe(CN)_6]^{3-}$  or  $[Co(CN)_6]^{3-}$  which were exchanged very quickly, practically with a single extraction –  $Cl^-$  required several extractions, and  $SO_4^{2-}$  and  $C_2O_4^{2-}$  did not enter at all. (The only way to obtain a sulfate or an oxalate membrane is to prepare  $[TDA]HSO_4$  or  $[TDA]HC_2O_4$  using concentrate solutions of sulfuric or oxalic acid:  $HSO_4^-$  and  $HC_2O_4^-$ , whose structure and hindrance and charge recall  $ClO_4^-$ , behave like  $ClO_4^-$  and quickly take the place of  $Br^-$ . The extra-amount of sulfuric or oxalic acid is then extracted by water, or by aqueous solutions of sodium sulfate or sodium oxalate to prevent emulsions, transforming  $[TDA]HSO_4$  and  $[TDA]HC_2O_4$  in  $[TDA]_2SO_4$  and  $[TDA]_2C_2O_4$  respectively). It was clear that the reasons resided in the dissimilar hydrophilic character of the different ions, mainly related to the relevant charge and hindrance. Also, it was clear (although not so immediately) that the different extent of completeness of the exchange reactions  $i_{\text{aq}} + j_{\text{org}} \rightleftharpoons i_{\text{org}} + j_{\text{aq}}$  constituted a sort of water-induced selectivity of the membrane, which opened up a new way to deal with mixed electrolyte solutions.

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solution, such "definitive"  $E$  values are found to differ increasingly (typically, 0.02 to 0.1 mV every new run, depending on the electrodes in use) as if the original composition of membrane surfaces were not perfectly restored (relaxation is slow in the pores of the PTFE filter represented in Figure S1 as the particular I, or K in Figure S2). Usually 12 or 24 hours are needed to restore the original conditions.

Actually, such effects have been known for a long time (the first qualitative scale of the hydrophobic character of anions dates back to 1888).<sup>S5</sup> As a first idea, one could think of making quantitative predictions based on the ion hydration free energies –whose values are generally available.<sup>S6</sup> It is not so, however, since the ions generally do not enter the membranes as bare ions. Potassium, for instance, enters the water-saturated NPOE membranes as  $[\text{K}(\text{H}_2\text{O})]^+$ , lanthanum as  $[\text{La}(\text{H}_2\text{O})_{12}]^{3+}$  (like magnesium), chloride as  $[\text{Cl}(\text{H}_2\text{O})_4]^-$ , etc.<sup>S7</sup>

Therefore, only empirical predictions can be made, needing experimental corroboration.

#### §4. Tests for the ion selectivity.

The systems examined in this section concern the electrolytes containing  $[\text{Co}(\text{CN})_6]^{3-}$  and/or  $[\text{Co}(\text{en})_3]^{3+}$ . We did not perform any further test of this kind for hexacyanoferrate(III) salts (whose activity coefficients were determined, sections §8 and §9, in order to corroborate the strange results observed in the mixtures  $[\text{Co}(\text{en})_3][\text{Co}(\text{CN})_6] + \text{MgSO}_4$ ), because of the complete similarity of behavior of the hexacyanoferrate(III) and hexacyanocobaltate(III) salts observed when studying the respective apparent molal volumes and activity coefficients in single salt solutions.

Tables S1–S5 provide E values measured in a series of solutions of a target electrolyte of low molal concentration  $m_1$ , variable, inside a second electrolyte whose molal concentration  $m_2$  ( $m_2 \gg m_1$ ) is kept constant. The ratio  $m_1/m_2$  is sufficiently low to make all activity coefficients no longer influenced by the change of  $m_1$  and hence constant. The more concentrated solution is taken as the reference solution ( $E = E_{\text{ref}}$ ). Figures S3 – S7 display (with more details than main text's Fig 1) the differences,  $E - E^{\text{id}}$ , between the experimental  $E - E_{\text{ref}}$  and corresponding  $(E - E_{\text{ref}})^{\text{id}}$  ideal values for a theoretical pair of electrodes that are perfectly selective, and the curves  $(E - E^{\text{id}})^{\text{calcd.}}$  that represent equation 3 (main text) for the proper Q. When calculating  $E^{\text{id}}$  we allowed for the slightly different concentration of the ion in common in the different solutions (disregarding the corresponding negligible effect on the activity coefficient values). E.g., for  $\text{K}_3[\text{Co}(\text{CN})_6]$  ( $m$ ) in  $\text{K}_2\text{SO}_4$  ( $m'$ ) the equation for  $E^{\text{id}}$  was  $E^{\text{id}} = E^{*'} + RT/3F \ln m + RT/F \ln [(3m+2m')/(3m_{\text{ref}}+2m')]$ . Likewise, also the theoretical curve reported in Fig S3 uses a modified form of Eqn 3,  $E = E^{*'} + RT/3F \ln (m + Q) + RT/F \ln [(3m+2m')/(3m_{\text{ref}}+2m')]$ . Similar corrections were performed also for  $\text{K}_3[\text{Co}(\text{CN})_6]$  in KOH,  $[\text{Co}(\text{en})_3]\text{Cl}_3$  in HCl,  $[\text{Co}(\text{en})_3]\text{Cl}_3$  in  $\text{MgCl}_2$ ,  $[\text{Co}(\text{en})_3]\text{Cl}_3$  in  $\text{LaCl}_3$ , etc.

**Table S1 - Experimental emf /mV for  $m_1$  /mol kg<sup>-1</sup>  $\text{K}_3[\text{Co}(\text{CN})_6]$  dissolved in  $9.042 \times 10^{-2}$  mol kg<sup>-1</sup>  $\text{K}_2\text{SO}_4$ , compared with the ideal response (superscript <sup>id</sup>) of a pair of perfectly selective electrodes.**

Series	$m_1$	E	$E_{\text{ref}}$	$E - E_{\text{ref}}$	$(E - E_{\text{ref}})^{\text{id}}$	$E - E^{\text{id}}$
1	$8.792 \times 10^{-4}$	46.87 ± 0.07	(46.87)	(0.00)	(0.00)	(0.00)
1	$4.984 \times 10^{-4}$	41.92 ± 0.02	46.88 ± 0.02	-4.96 ± 0.03	-5.02	0.06
1	$2.274 \times 10^{-4}$	34.97 ± 0.03	46.89 ± 0.02	-11.92 ± 0.04	-11.86	-0.06
1	$8.792 \times 10^{-4}$	46.90 ± 0.05				
2	$8.792 \times 10^{-4}$	47.47 ± 0.04				
2	$4.725 \times 10^{-5}$	22.03 ± 0.02	47.41 ± 0.06	-25.38 ± 0.06	-25.39	0.01
2	$5.976 \times 10^{-5}$	24.35 ± 0.05	47.35 ± 0.12	-23.00 ± 0.13	-23.37	0.37
2	$1.526 \times 10^{-4}$	32.01 ± 0.02	47.29 ± 0.18	-15.28 ± 0.18	-15.30	0.02
2	$2.274 \times 10^{-4}$	35.30 ± 0.02	47.23 ± 0.12	-11.93 ± 0.12	-11.86	-0.07
2	$4.984 \times 10^{-4}$	42.21 ± 0.03	47.17 ± 0.06	-4.96 ± 0.07	-5.02	0.06
2	$8.792 \times 10^{-4}$	47.11 ± 0.02				
3	$8.792 \times 10^{-4}$	47.46 ± 0.04				
3	$4.384 \times 10^{-6}$	5.42 ± 0.03	47.41 ± 0.05	-41.69 ± 0.06	-45.77	4.08
3	$1.313 \times 10^{-5}$	10.44 ± 0.04	47.36 ± 0.10	-36.92 ± 0.11	-36.37	-0.55
3	$1.559 \times 10^{-5}$	12.63 ± 0.02	47.31 ± 0.10	-34.68 ± 0.10	-34.90	0.22
3	$4.725 \times 10^{-5}$	21.68 ± 0.01	47.26 ± 0.05	-25.58 ± 0.05	-25.39	-0.19
3	$8.792 \times 10^{-4}$	47.21 ± 0.01				
4	$8.792 \times 10^{-4}$	47.46 ± 0.03				
4	$1.313 \times 10^{-5}$	11.56 ± 0.04	47.40 ± 0.06	-35.84 ± 0.07	-36.37	0.53
4	$4.384 \times 10^{-6}$	4.29 ± 0.05	47.33 ± 0.13	-43.04 ± 0.14	-45.77	2.73
4	$7.256 \times 10^{-6}$	6.75 ± 0.02	47.27 ± 0.13	-40.52 ± 0.13	-41.45	0.93
4	$1.528 \times 10^{-6}$	-5.95 ± 0.13	47.20 ± 0.06	-53.15 ± 0.14	-54.80	1.65
4	$8.792 \times 10^{-4}$	47.14 ± 0.04				

**Table S2 -Experimental emf /mV for  $m_1$  / mol kg<sup>-1</sup>  $\text{K}_3[\text{Co}(\text{CN})_6]$  dissolved in 0.1113 mol kg<sup>-1</sup> KOH, compared with the ideal response (superscript <sup>id</sup>) of a pair of perfect selective electrodes.**

Series	$m_1$	E	$E_{\text{ref}}$	$E - E_{\text{ref}}$	$(E - E_{\text{ref}})^{\text{id}}$	$E - E^{\text{id}}$
1	$1.016 \times 10^{-3}$	44.63 ± 0.02	(44.63)	(0.00)	(0.00)	(0.00)
1	$5.625 \times 10^{-4}$	39.29 ± 0.01	44.56 ± 0.07	-5.27 ± 0.07	-5.37	0.10
1	$3.115 \times 10^{-4}$	34.20 ± 0.01	44.50 ± 0.13	-10.30 ± 0.13	-10.60	0.30
1	$1.745 \times 10^{-4}$	28.99 ± 0.01	44.43 ± 0.13	-15.44 ± 0.13	-15.66	0.22
1	$9.397 \times 10^{-5}$	23.70 ± 0.03	44.37 ± 0.07	-20.67 ± 0.08	-21.02	0.35

<sup>S5</sup> F. Hofmeister, *Arch. Exp. Pathol., Pharmacol.*, **1888**, 247

<sup>S6</sup> Y. Markus, *Ion properties*, Marcel Dekker Inc., New York, **1997** (ISBN: 0-8247-0011-2).

<sup>S7</sup> F. Malatesta and R. Carrara, *J. Solution Chem.*, 1992, **21**, 1251; F. Malatesta, A. Giacomelli, R. Zamboni *J. Solution Chem.*, 1994, **23**, 11; F. Malatesta, A. Giacomelli, R. Zamboni *J. Solution Chem.*, 1996, **25**, 61

1	$1.016 \times 10^{-3}$	$44.30 \pm 0.02$				
2	$1.016 \times 10^{-3}$	$44.70 \pm 0.02$				
2	$5.319 \times 10^{-5}$	$20.04 \pm 0.05$	$44.71 \pm 0.01$	$-24.67 \pm 0.05$	$-25.92$	1.25
2	$2.925 \times 10^{-5}$	$14.73 \pm 0.02$	$44.72 \pm 0.02$	$-29.99 \pm 0.04$	$-31.06$	1.07
2	$1.647 \times 10^{-5}$	$10.35 \pm 0.16$	$44.73 \pm 0.02$	$-34.38 \pm 0.16$	$-35.99$	1.61
2	$9.332 \times 10^{-6}$	$6.08 \pm 0.15$	$44.74 \pm 0.01$	$-38.66 \pm 0.15$	$-40.86$	2.20
2	$1.016 \times 10^{-3}$	$44.75 \pm 0.02$				
1*	$1.016 \times 10^{-3}$	44.63 —			0.00	
1*	$5.625 \times 10^{-4}$	39.31 —	44.57 —	-5.26 —	-5.37	0.11
1*	$3.115 \times 10^{-4}$	34.21 —	44.51 —	-10.30 —	-10.60	0.30
1*	$1.745 \times 10^{-4}$	28.99 —	44.45 —	-15.46 —	-15.66	0.20
1*	$9.397 \times 10^{-5}$	23.71 —	44.39 —	-20.68 —	-21.02	0.34
1*	$1.016 \times 10^{-3}$	44.33 —	—	—		
2*	$1.016 \times 10^{-3}$	44.44 —	—	—		
2*	$5.319 \times 10^{-5}$	19.99 —	44.49 —	-24.50 —	-25.92	1.42
2*	$2.925 \times 10^{-5}$	14.75 —	44.54 —	-29.79 —	-31.06	1.27
2*	$1.647 \times 10^{-5}$	10.70 —	44.58 —	-33.88 —	-35.99	2.11
2*	$9.332 \times 10^{-6}$	6.31 —	44.63 —	-38.32 —	-40.86	2.54
2*	$1.016 \times 10^{-3}$	44.68 —				

\* Duplicated value measured in stirring conditions (5 minutes at ca. 2-4 rps. immediately after the readings in quiet solution; one single reading).

**Table S3 -Experimental emf /mV for  $m_1$  / mol kg<sup>-1</sup> [Co(en)<sub>3</sub>]Cl<sub>3</sub> dissolved in 0.1000 mol kg<sup>-1</sup> HCl, compared with the ideal response (superscript<sup>id</sup>) of a pair of perfectly selective electrodes.**

Series	$m_1$	E	$E_{ref}$	$E - E_{ref}$	$(E - E_{ref})^{id}$	$E - E^{id}$
1	$8.553 \times 10^{-4}$	$15.42 \pm 0.16$	(15.42)	(0.00)	(0.00)	(0.00)
1	$4.680 \times 10^{-4}$	$9.75 \pm 0.13$	$15.36 \pm 0.06$	$-5.61 \pm 0.14$	-5.46	-0.15
1	$2.387 \times 10^{-4}$	$4.38 \pm 0.02$	$15.30 \pm 0.12$	$-10.92 \pm 0.12$	-11.40	0.48
1	$1.232 \times 10^{-4}$	$-0.87 \pm 0.02$	$15.24 \pm 0.06$	$-16.11 \pm 0.06$	-17.15	1.04
1	$8.553 \times 10^{-4}$	$15.18 \pm 0.04$				
2	$8.553 \times 10^{-4}$	$15.68 \pm 0.01$				
2	$6.516 \times 10^{-5}$	$-4.94 \pm 0.02$	$15.60 \pm 0.08$	$-20.54 \pm 0.08$	-22.65	2.11
2	$3.552 \times 10^{-5}$	$-10.13 \pm 0.01$	$15.53 \pm 0.16$	$-25.66 \pm 0.16$	-27.87	2.21
2	$1.861 \times 10^{-5}$	$-14.60 \pm 0.03$	$15.45 \pm 0.08$	$-30.05 \pm 0.09$	-33.42	3.37
2	$8.553 \times 10^{-4}$	$15.37 \pm 0.03$				
3	$8.553 \times 10^{-4}$	$15.59 \pm 0.01$				
3	$9.762 \times 10^{-6}$	$-14.91 \pm 0.05$	$15.52 \pm 0.08$	$-30.43 \pm 0.09$	-38.93	8.50
3	$5.102 \times 10^{-6}$	$-19.02 \pm 0.02$	$15.44 \pm 0.15$	$-34.46 \pm 0.15$	-44.51	10.05
3	$2.880 \times 10^{-6}$	$-21.75 \pm 0.07$	$15.37 \pm 0.08$	$-37.12 \pm 0.11$	-49.41	12.29
3	$8.553 \times 10^{-4}$	$15.29 \pm 0.05$				
1*	$8.553 \times 10^{-4}$	15.42 —	(15.42)	(0.00)	(0.00)	(0.00)
1*	$4.680 \times 10^{-4}$	9.95 —	15.36 —	-5.41 —	-5.46	0.05
1*	$2.387 \times 10^{-4}$	4.41 —	15.30 —	-10.89 —	-11.40	0.51
1*	$1.232 \times 10^{-4}$	-1.24 —	15.24 —	-16.48 —	-17.15	0.67
1*	$8.553 \times 10^{-4}$	15.18 —				
2*	$8.553 \times 10^{-4}$	15.70 —				
2*	$6.516 \times 10^{-5}$	-5.49 —	15.64 —	-21.13 —	-22.65	1.52
2*	$3.552 \times 10^{-5}$	-10.90 —	15.58 —	-26.48 —	-27.87	1.39
2*	$1.861 \times 10^{-5}$	-16.02 —	15.51 —	-31.53 —	-33.42	1.89
2*	$8.553 \times 10^{-4}$	15.45 —				
3*	$8.553 \times 10^{-4}$	15.56 —				
3*	$9.762 \times 10^{-6}$	-15.99 —	15.50 —	-31.49 —	-38.93	7.44
3*	$5.102 \times 10^{-6}$	-19.63 —	15.44 —	-35.07 —	-44.51	9.44
3*	$2.880 \times 10^{-6}$	-22.80 —	15.37 —	-38.17 —	-49.41	11.24
3*	$8.553 \times 10^{-4}$	15.31 —				

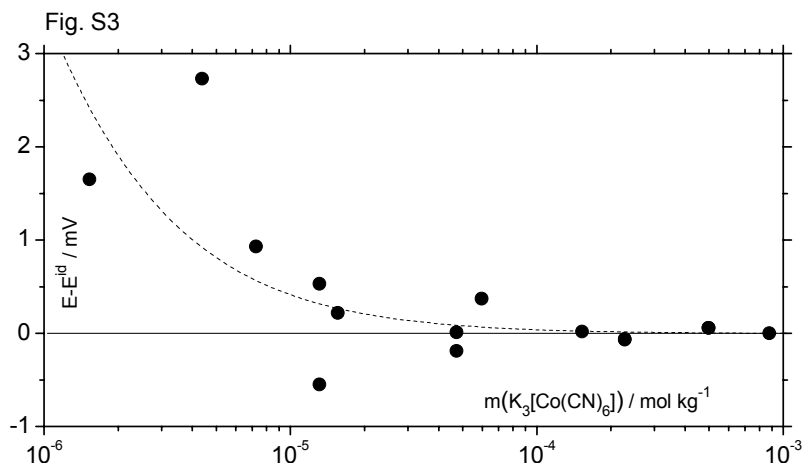
\* Duplicated value measured in stirring conditions (5 minutes at ca. 2-4 rps. immediately after the readings in quiet solution; one single reading).

**Table S4 - Experimental emf /mV for  $m_1$  /mol kg<sup>-1</sup> [Co(en)<sub>3</sub>]Cl<sub>3</sub> dissolved in 0.1054 mol kg<sup>-1</sup> MgCl<sub>2</sub>, compared with the ideal response (superscript <sup>id</sup>) of a pair of perfectly selective electrodes.**

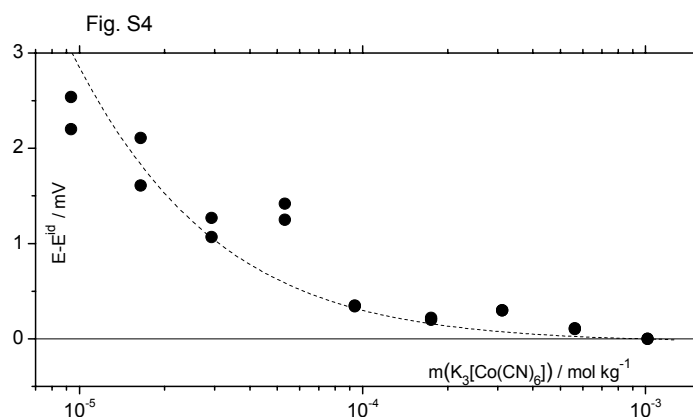
Series	$m_1$	E	$E_{\text{ref}}$	$E - E_{\text{ref}}$	$(E - E_{\text{ref}})^{\text{id}}$	$E - E^{\text{id}}$
1	$5.134 \times 10^{-4}$	19.79 ± 0.01	(19.79)	(0.00)	(0.00)	(0.00)
1	$2.540 \times 10^{-4}$	13.42 ± 0.01	19.73 ± 0.06	-6.31 ± 0.06	-6.12	-0.19
1	$1.279 \times 10^{-4}$	7.58 ± 0.03	19.67 ± 0.12	-12.09 ± 0.12	-12.04	-0.05
1	$6.441 \times 10^{-5}$	1.63 ± 0.06	19.61 ± 0.12	-17.98 ± 0.13	-17.94	-0.04
1	$3.150 \times 10^{-5}$	-4.28 ± 0.05	19.55 ± 0.06	-23.83 ± 0.08	-24.08	0.25
1	$5.134 \times 10^{-4}$	19.49 ± 0.08				
2	$5.134 \times 10^{-4}$	19.79 ± 0.02				
2	$1.579 \times 10^{-5}$	-9.83 ± 0.02	19.77 ± 0.02	-29.60 ± 0.03	-30.00	0.40
2	$7.960 \times 10^{-6}$	-15.82 ± 0.02	19.75 ± 0.04	-35.57 ± 0.04	-35.87	0.30
2	$3.940 \times 10^{-6}$	-20.49 ± 0.09	19.74 ± 0.04	-40.23 ± 0.10	-41.89	1.66
2	$1.981 \times 10^{-6}$	-26.00 ± 0.05	19.72 ± 0.02	-45.72 ± 0.05	-47.78	2.06
2	$5.134 \times 10^{-4}$	19.70 ± 0.03				
3	$5.134 \times 10^{-4}$	19.81 ± 0.01				
3	$2.540 \times 10^{-4}$	13.70 ± 0.01	19.79 ± 0.02	-6.09 ± 0.02	-6.12	0.03
3	$1.279 \times 10^{-4}$	7.90 ± 0.01	19.77 ± 0.04	-11.87 ± 0.04	-12.04	0.17
3	$6.441 \times 10^{-5}$	1.98 ± 0.01	19.74 ± 0.04	-17.76 ± 0.04	-17.94	0.18
3	$3.150 \times 10^{-5}$	-4.32 ± 0.04	19.72 ± 0.02	-24.04 ± 0.04	-24.08	0.04
3	$5.134 \times 10^{-4}$	19.70 ± 0.03				

**Table S5 -Experimental emf /mV for  $m_1$  /mol kg<sup>-1</sup> [Co(en)<sub>3</sub>]Cl<sub>3</sub> dissolved in 0.0646 mol kg<sup>-1</sup> LaCl<sub>3</sub>, compared with the ideal response (superscript <sup>id</sup>) of a pair of perfectly selective electrodes.**

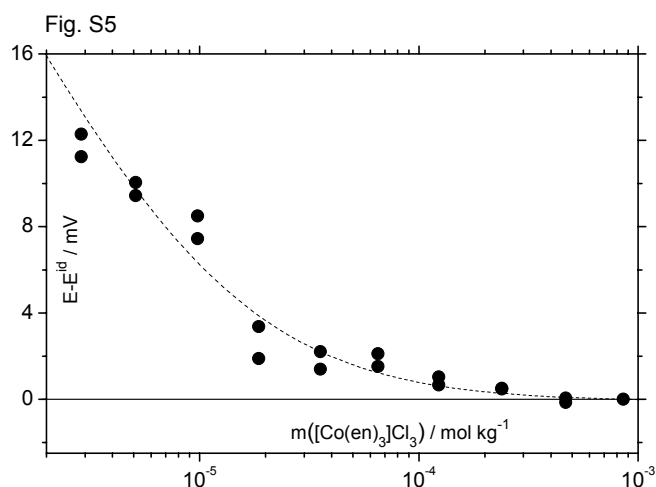
Series	$m_1$	E	$E_{\text{ref}}$	$E - E_{\text{ref}}$	$(E - E_{\text{ref}})^{\text{id}}$	$E - E^{\text{id}}$
1	$4.976 \times 10^{-4}$	17.07 ± 0.02	(17.07)	(0.00)	(0.00)	(0.00)
1	$2.702 \times 10^{-4}$	11.69 ± 0.02	17.04 ± 0.03	-5.35 ± 0.04	-5.32	-0.03
1	$1.372 \times 10^{-4}$	5.82 ± 0.02	17.01 ± 0.06	-11.19 ± 0.06	-11.18	-0.01
1	$6.866 \times 10^{-5}$	-0.02 ± 0.02	16.98 ± 0.06	-17.00 ± 0.06	-17.13	0.13
1	$3.625 \times 10^{-5}$	-5.54 ± 0.02	16.95 ± 0.03	-22.49 ± 0.04	-22.62	0.13
1	$4.976 \times 10^{-4}$	16.92 ± 0.04				
2	$4.976 \times 10^{-4}$	16.86 ± 0.02				
2	$1.838 \times 10^{-5}$	-11.16 ± 0.02	16.83 ± 0.03	-27.99 ± 0.04	-28.44	0.45
2	$9.452 \times 10^{-6}$	-16.79 ± 0.05	16.80 ± 0.06	-33.59 ± 0.08	-34.14	0.55
2	$4.745 \times 10^{-6}$	-22.05 ± 0.08	16.77 ± 0.06	-38.82 ± 0.10	-40.04	1.22
2	$2.444 \times 10^{-6}$	-27.65 ± 0.03	16.74 ± 0.03	-44.39 ± 0.04	-45.73	1.34
2	$4.976 \times 10^{-4}$	16.71 ± 0.05				
3	$4.976 \times 10^{-4}$	16.76 ± 0.02				
3	$2.665 \times 10^{-4}$	10.95 ± 0.07	16.73 ± 0.03	-5.78 ± 0.08	-5.44	-0.34
3	$1.348 \times 10^{-4}$	5.24 ± 0.04	16.71 ± 0.06	-11.47 ± 0.07	-11.33	-0.14
3	$6.866 \times 10^{-5}$	-0.64 ± 0.03	16.68 ± 0.03	-17.32 ± 0.04	-17.13	-0.19
3	$4.976 \times 10^{-4}$	16.65 ± 0.03				
4	$4.976 \times 10^{-4}$	16.95 ± 0.05				
4	$3.625 \times 10^{-5}$	-5.66 ± 0.03	16.85 ± 0.10	-22.51 ± 0.10	-22.62	0.11
4	$1.838 \times 10^{-5}$	-11.42 ± 0.02	16.75 ± 0.20	-28.17 ± 0.20	-28.44	0.27
4	$9.452 \times 10^{-6}$	-17.29 ± 0.03	16.65 ± 0.10	-33.94 ± 0.10	-34.14	0.20
4	$4.976 \times 10^{-4}$	16.55 ± 0.06				



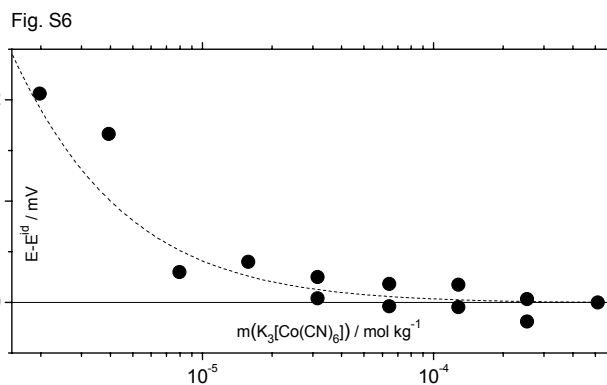
**Figure S3** – Expanded view of the experimental deviation from the ideal response of a pair of perfect selective electrodes,  $E-E^{\text{id}}$ , for  $\text{K}_3[\text{Co}(\text{CN})_6]$  dissolved in  $0.09042 \text{ mol kg}^{-1} \text{ K}_2\text{SO}_4$ . The dashed line represents  $(E-E^{\text{id}})^{\text{calcd.}}$  for  $Q = 8 \times 10^{-7}$ . The results prove that the cell is safely used provided the concentration of  $\text{K}_3[\text{Co}(\text{CN})_6]$  is greater than ca. 0.0003 times the concentration of  $\text{K}_2\text{SO}_4$ .



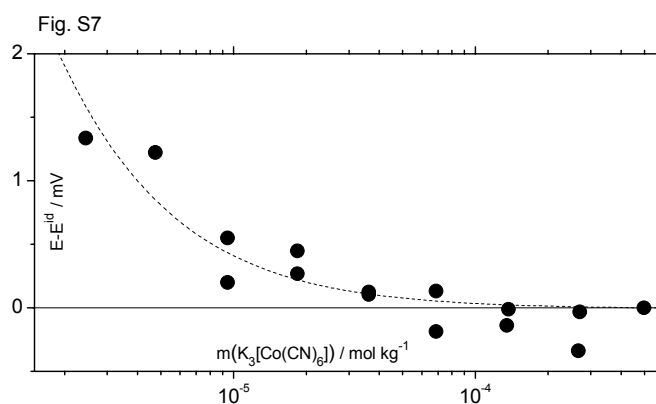
**Figure S4** – Expanded view of the experimental deviation from the ideal response of a pair of perfectly selective electrodes,  $E-E^{\text{id}}$ , for  $\text{K}_3[\text{Co}(\text{CN})_6]$  dissolved in  $0.1113 \text{ mol kg}^{-1} \text{ KOH}$ . The dashed line represents  $(E-E^{\text{id}})^{\text{calcd.}}$  for  $Q = 4 \times 10^{-6}$ . The results prove that the cell is safely used provided the concentration of  $\text{K}_3[\text{Co}(\text{CN})_6]$  is greater than ca. 0.002 times the concentration of  $\text{KOH}$ .



**Figure S5** – Expanded view of the experimental deviation from the ideal response of a pair of perfectly selective electrodes,  $E-E^{\text{id}}$ , for  $[\text{Co}(\text{en})_3]\text{Cl}_3$  dissolved in  $0.1000 \text{ mol kg}^{-1} \text{ HCl}$ . The dashed line represents  $(E-E^{\text{id}})^{\text{calcd.}}$  for  $Q = 1.1 \times 10^{-5}$ . The results prove that the cell is safely used provided the concentration of  $[\text{Co}(\text{en})_3]\text{Cl}_3$  is greater than ca. 0.004 times the concentration of  $\text{HCl}$ .



**Figure S6** – Expanded view of the experimental deviation from the ideal response of a pair of perfectly selective electrodes,  $E-E^{\text{id}}$ , for  $[\text{Co}(\text{en})_3]\text{Cl}_3$  dissolved in  $0.1054 \text{ mol kg}^{-1} \text{ MgCl}_2$ . The dashed line represents  $(E-E^{\text{id}})^{\text{calcd.}}$  for  $Q = 5 \times 10^{-7}$ . The results prove that the cell is safely used provided the concentration of  $[\text{Co}(\text{en})_3]\text{Cl}_3$  is greater than ca. 0.0002 times the concentration of  $\text{MgCl}_2$ .



**Figure S7** – Expanded view of the experimental deviation from the ideal response of a pair of perfectly selective electrodes,  $E-E^{\text{id}}$ , for  $[\text{Co}(\text{en})_3]\text{Cl}_3$  dissolved in  $0.0646 \text{ mol kg}^{-1} \text{ LaCl}_3$ . The dashed line represents  $(E-E^{\text{id}})^{\text{calcd.}}$  for  $Q = 5 \times 10^{-7}$ . The results prove that the cell is safely used provided the concentration of  $[\text{Co}(\text{en})_3]\text{Cl}_3$  is greater than ca. 0.0002 times the concentration of  $\text{LaCl}_3$ .

### §5. Less demanding checks.

So far, we have examined only electrolyte combinations with particularly small  $Q$ , permitting  $m/m'$  ratios as low as  $10^{-2}$  and beyond to be explored. We consider now the less favorable case of electrolytes with which  $Q$  can be neglected only at much higher ratios  $m/m'$ . Yet, if  $m/m' \gg 0.01$  the assumption of the activity coefficients independent of  $m$  no longer holds. Thus, the linearity test of  $E$  vs.  $\log m$  fails, and other criteria have to be applied to decide whether the activity coefficients of the target electrolyte are liable to determination or not. In other words, it is necessary to decide whether the membranes are really working as equilibrium devices, or are a seat of irreversible transformations.

Non-equilibrium situations, when occurring, produce a drifting emf as long as the concentrations vary, before reaching their stationary-state or equilibrium values. In a glass electrode where  $\text{H}_3\text{O}^+$  ions are entering and  $\text{Na}^+$  coming out of the glass, the water / glass interface reaches and maintains a nearly definitive state very quickly, because of the diffusion rates in water which are incomparably faster than in glass. Contrary to glass, the oil phases of our liquid membranes cannot differ too much from water as regards the diffusion rates, and the interface layers (both water-side and oil-side) do not stop quickly to modify their composition when an exchange reaction  $i_{\text{aq}} + j_{\text{oil}} \rightleftharpoons i_{\text{oil}} + j_{\text{aq}}$  is occurring. Besides, if exchange reactions occur to an appreciable extent, the emf values observed in stirred and unstirred solutions display appreciable discrepancies, since stirring modifies the renovation rate in the water-side neighborhoods of the interface. Therefore, as the first check, if no significant drifts are observed and the readings do not differ appreciably between stirred and quiet solutions, there are good reasons for believing that the cell is correctly tracing the activity of the target electrolyte.

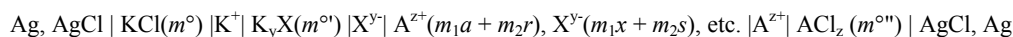
As a second check, an approximate evaluation of the range of the interfering effect can be made. Assuming the Nicolsky equation as approximately valid, the  $Q$  term should be proportional to the activity of the interfering ion, that is to say, approximately proportional to the concentration of the second electrolyte,  $Q \approx K' m'$  ( $K'$ , a sort of approximate selectivity constant). Starting from a rather high ratio  $m/m'$ , one progressively reduces  $m$  at constant  $m'$ . The  $dE/d(\ln m)$  slope will be sub-Nernstian because of the activity coefficients that increase when decreasing  $m$ , and possibly, also because of the increasing influence of the  $Q$  term. However, while the effect of the activity coefficients makes the slope become greater at decreasing  $m$  – to attain the Nernst slope as a limiting value – the  $Q$  term flattens the curve to the asymptotic horizontal limit  $S \ln Q$  ( $S$ , the Nernst slope of the target electrolyte). Accurate determinations of  $Q$  are of course impossible (drifts, or more generally, unstable and stirring-dependent values of the potential, characterize the region where  $Q$  is no longer negligible compared with  $m$ ). However, even a rough estimation – e.g., an approximate



value within half an order or one order of magnitude, obtained by graphical methods – is widely sufficient. Once Q or K' are approximately known, the conditions required for the activity coefficient of the target electrolyte to be reliably measured (e.g.,  $m / m' \geq 100 K'$ ), are easily stated.

### §6. Mixed electrolytes with (or not) ions in common.

Consider a target electrolyte (to which we assign the label 1 and molality  $m_1$ ) made of  $a$  cations  $A^{z+}$  and  $x$  anions  $X^{y-}$ ,  $A_aX_x$ , and a second electrolyte (the “modifier”, to which we assign the label 2 and molality  $m_2$ ) which modifies the composition of the bulk, and therefore, the activity coefficients. As the modifier is allowed to have the cation or the anion in common with the target electrolyte, we will assume for the sake of generality that it contains  $r$  cations  $A^{z+}$  and  $s$  anions  $X^{y-}$  per mol in addition to other ions; of course  $r$ , or  $s$ , or both  $r$  and  $s$ , can be null. We do not display the case of many modifiers present all together (although the extension is straightforward) to avoid too many symbols and unnecessarily cumbersome formulae. The cell structure is



with  $m^\circ$ ,  $m^{\circ\circ}$ ,  $m^{\circ\circ}$  constant,  $m_1$  and  $m_2$  variable;  $|\text{K}^+|$ ,  $|\text{X}^{y-}|$ , and  $|\text{A}^{z+}|$  are the membranes. We are supposing that the other ions of the modifier do not interfere with the correct behaviour of the membranes, i.e., that the membranes  $|\text{A}^{z+}|$  and  $|\text{X}^{y-}|$  be only permeable to  $\text{A}^{z+}$  and  $\text{X}^{y-}$  respectively and no other ions, a preliminary condition to be checked with the aid of the tests described in the previous sections (§4, §5). The virtual net transformations that occur in the cell, for any mol of positive charges traveling left to right at constant composition (we consider an infinitely large cell) are: 1 mol of KCl that goes out of the solution  $\text{KCl}(m^\circ)$ ,  $y^{-1}$  mol  $\text{K}_y\text{X}$  that enter the solution  $\text{K}_y\text{X}(m^\circ)$ ,  $z^{-1}$  mol of  $\text{A}^{z+}$  together with  $y^{-1}$  mol of  $\text{X}^{y-}$  (i.e.,  $1/az$ , the same as  $1/xy$ , mol of  $\text{A}_a\text{X}_x$ ) that go out of the mixed solution, and finally,  $z^{-1}$  mol of  $\text{AgCl}_z$  that enter the solution  $\text{AgCl}_z(m^{\circ\circ})$ . Thus, the virtual change per faraday (F) of the free enthalpy  $\Delta G$  is

$$\Delta G = -\mu[\text{KCl}(m^\circ)] + y^{-1}\mu[\text{K}_y\text{X}(m^\circ)] - z^{-1}[\mu^\circ(\text{A}^{z+}) + \text{RT} \ln(m_A \gamma_A)] - y^{-1}[\mu^\circ(\text{X}^{y-}) + \text{RT} \ln(m_X \gamma_X)] + z^{-1}\mu[\text{AgCl}_z(m^{\circ\circ})]$$

Substituting  $(m_1a + m_2r)$  for  $m_A$ ,  $(xm_1 + sm_2)$  for  $m_X$ , and  $\gamma_\pm^{(y+z)}$  for  $\gamma_A^y \gamma_X^z$ ,<sup>S8</sup> and collecting the constant terms in a single term  $\Delta G^\#$ , one obtains

$$\Delta G = \Delta G^\# - (yz)^{-1}\text{RT} \ln[(a m_1 + r m_2)^y (x m_1 + s m_2)^z] - [(y+z)/(yz)] \text{RT} \ln \gamma_\pm$$

Hence, the emf ( $E = -\Delta G / F$ ) of the cell is

$$E = E^\# + \text{RT}(yzF)^{-1} \ln[(m_1a + m_2r)^y (xm_1 + sm_2)^z] + (\text{RT}/F)[(y+z)/(yz)] \ln \gamma_\pm \quad (\text{Eq. S1})$$

In order to obtain  $E^\#$ , one substitutes a solution containing the salt alone and no modifier ( $m_1 = m'$ ,  $m_2 = 0$ ) for the mixed solution, and reads the corresponding emf,  $E'$ ; equation S1 transforms into the usual relationship that applies to the single electrolytes and to mixed electrolytes with  $x = s = 0$ ,

$$E' = E^\# + \text{RT}(yzF)^{-1} \ln(a^y x^z) + (\text{RT}/F)[(y+z)/(yz)] \ln (m' \gamma_\pm') \quad (\text{Eq. S2})$$

Provided the salt has already been studied alone and thus the activity coefficient  $\gamma_\pm'$  at  $m'$  is known,  $E'$  and equation S2 provide  $E^\#$ , which –through  $E$  and Eq. S1– yields the mean activity coefficient  $\gamma_\pm$  of the salt in the mixed solution.

### §7. Activity coefficients of $[\text{Co}(\text{en})_3][\text{Co}(\text{CN})_6]$ in water at 298.15 K.

The activity coefficients of  $[\text{Co}(\text{en})_3][\text{Co}(\text{CN})_6]$  in water were required in order to determine the activity coefficients of the same salt in the mixed solutions. We realized that the data reported in the original paper<sup>S3</sup> were incorrect – since wrongly copied from a preliminary table whose concentration values were not based on the correct formula weight of the analysis. Moreover the datum at  $5.083 \times 10^{-4} \text{ mol kg}^{-1}$  – not far from the saturation limit – was lacking. (However, the data displayed in the plots of the same paper were the right ones.) The correct values that should have appeared in the cited paper are reported in Table S6.

**Table S6 – Revised activity coefficient of  $[\text{Co}(\text{en})_3][\text{Co}(\text{CN})_6]$  in water.**

Series	$m / \text{mol kg}^{-1}$	$E / \text{mV}$	$E_{\text{ref}} / \text{mV}$	$\ln \gamma_\pm^{(*)}$
1	$4.048 \times 10^{-4}$	$-33.30 \pm 0.02$		$(-1.514 \pm 0.014)$
1	$2.881 \times 10^{-4}$	$-36.71 \pm 0.01$		$-1.372 \pm 0.014$
1	$2.145 \times 10^{-4}$	$-39.78 \pm 0.01$	$-33.32 \pm 0.02$	$-1.255 \pm 0.014$
1	$1.570 \times 10^{-4}$	$-43.08 \pm 0.01$	$-33.34 \pm 0.04$	$-1.134 \pm 0.015$
1	$1.072 \times 10^{-4}$	$-47.09 \pm 0.01$	$-33.36 \pm 0.06$	$-0.985 \pm 0.014$
1	$7.777 \times 10^{-5}$	$-50.65 \pm 0.02$	$-33.38 \pm 0.04$	$-0.871 \pm 0.014$
1	$4.048 \times 10^{-4}$	$-33.41 \pm 0.02$	$-33.40 \pm 0.02$	
2	$4.048 \times 10^{-4}$	$-33.07 \pm 0.01$		
2	$5.309 \times 10^{-5}$	$-54.81 \pm 0.01$	$-33.08 \pm 0.01$	$-0.789 \pm 0.014$

<sup>S8</sup>  $\gamma_\pm$  is the usual definition of the mean activity coefficient of an electrolyte  $\text{A}_a\text{X}_x$  ( $\text{A}^{z+}$ ,  $\text{X}^{y-}$ ) either alone or in a mixed solution with or without ions in common; the product  $\gamma_A^{a/(a+x)} \gamma_X^{x/(a+x)}$  is the same thing as  $\gamma_A^{y/(y+z)} \gamma_X^{z/(y+z)}$  since  $a/(a+x) = y/(y+z)$  and  $x/(a+x) = z/(y+z)$ .

2	$3.846 \times 10^{-5}$	$-58.67 \pm 0.01$	$-33.10 \pm 0.03$	$-0.691 \pm 0.014$
2	$2.500 \times 10^{-5}$	$-64.06 \pm 0.01$	$-33.11 \pm 0.04$	$-0.574 \pm 0.014$
2	$1.763 \times 10^{-5}$	$-68.55 \pm 0.01$	$-33.12 \pm 0.05$	$-0.487 \pm 0.014$
2	$1.224 \times 10^{-5}$	$-73.24 \pm 0.03$	$-33.13 \pm 0.04$	$-0.395 \pm 0.014$
2	$8.331 \times 10^{-6}$	$-78.57 \pm 0.03$	$-33.15 \pm 0.02$	$-0.320 \pm 0.014$
2	$5.784 \times 10^{-6}$	$-83.29 \pm 0.04$	$-33.16 \pm 0.01$	$-0.231 \pm 0.014$
2	$4.048 \times 10^{-4}$	$-33.17 \pm 0.01$		
3	$4.048 \times 10^{-4}$	$-32.68 \pm 0.01$		
3	$1.757 \times 10^{-5}$	$-67.57 \pm 0.05$	$-32.71 \pm 0.03$	$-0.453 \pm 0.014$
3	$3.846 \times 10^{-5}$	$-58.30 \pm 0.03$	$-32.73 \pm 0.06$	$-0.691 \pm 0.015$
3	$7.777 \times 10^{-5}$	$-50.20 \pm 0.01$	$-32.76 \pm 0.09$	$-0.921 \pm 0.015$
3	$1.570 \times 10^{-4}$	$-42.43 \pm 0.01$	$-32.79 \pm 0.06$	$-1.168 \pm 0.014$
3	$2.876 \times 10^{-4}$	$-36.35 \pm 0.01$	$-32.81 \pm 0.03$	$-1.419 \pm 0.014$
3	$4.048 \times 10^{-4}$	$-32.84 \pm 0.01$		
4	$4.048 \times 10^{-4}$	$-32.70 \pm 0.01$		
4	$5.083 \times 10^{-4}$	$-30.81 \pm 0.01$	$-32.79 \pm 0.09$	$-1.626 \pm 0.015$
4	$4.048 \times 10^{-4}$	$-32.88 \pm 0.01$		

(\*) The range of uncertainty is inclusive of the uncertainty of the reference point ( $\ln \gamma_{\pm} = -1.514 \pm 0.014$  at  $m = 4.048 \times 10^{-4}$  mol kg<sup>-1</sup>).

### §8. Activity coefficients of reference mixed solutions.

The determination method relies on the Equations S1 and S2 of §6. Alternate determinations of E and E' are performed, to eliminate the disturbing effects that arise from the leaching of the membrane surface when substituting the solutions in the cell (see footnote S4). The activity coefficients  $\gamma_{\pm}'$  of salt solutions  $m'$  free of modifier salts are interpolated from experimental values reported in the cited papers.

Tables S7– S15 report the data for the reference mixed solutions considered.

**Table S7 - Activity coefficient of  $8.792 \times 10^{-4}$  mol kg<sup>-1</sup> K<sub>3</sub>[Co(CN)<sub>6</sub>] ( $m_1$ ) in  $9.042 \times 10^{-2}$  mol kg<sup>-1</sup> K<sub>2</sub>SO<sub>4</sub> ( $m_2$ ).**

Run	E' <sup>a</sup>	E <sup>b</sup>	E-E'	average E-E'	$\ln \gamma_{\pm}'$ <sup>c</sup>	average $\ln \gamma_{\pm}$ <sup>d</sup>
1	-26.02	—	—	74.17 ± 0.28	-0.251 ± 0.008 <sup>c</sup> in 0.01002 mol kg <sup>-1</sup> K <sub>3</sub> [Co(CN) <sub>6</sub> ]	-1.137 ± 0.011
2	(26.01) <sup>e</sup>	48.26	74.27			
3	-26.01	(47.83) <sup>e</sup>	73.84			
4	(26.57) <sup>e</sup>	47.41	73.98			
5	-27.13	(47.42) <sup>e</sup>	74.55			
6	(26.96) <sup>e</sup>	47.42	74.39			
7	-26.72	(47.41) <sup>e</sup>	74.13			
8	—	47.40	—			

<sup>a</sup> E' /mV measured in the single salt solution,  $1.002 \times 10^{-3}$  mol kg<sup>-1</sup> K<sub>3</sub>[Co(CN)<sub>6</sub>] in water ( $m'$ ). <sup>b</sup> E /mV measured in the mixed solution,  $8.792 \times 10^{-4}$  mol kg<sup>-1</sup> K<sub>3</sub>[Co(CN)<sub>6</sub>] ( $m_1$ ) in  $9.042 \times 10^{-2}$  mol kg<sup>-1</sup> K<sub>2</sub>SO<sub>4</sub> ( $m_2$ ) <sup>c</sup> From the data and interpolating equation reported in ref. S2. <sup>d</sup> Calculated as:  $\ln \gamma_{\pm} = \ln \gamma_{\pm}' + 3F(E-E')/(4RT) - (1/4) \ln \{ [m_1 (2m_2 + 3m_1)^3] / [m' (3m')^3] \}$  <sup>e</sup> Interpolated value.

**Table S8 - Activity coefficient of  $1.016 \times 10^{-3}$  mol kg<sup>-1</sup> K<sub>3</sub>[Co(CN)<sub>6</sub>] ( $m_1$ ) in 0.1113 mol kg<sup>-1</sup> KOH ( $m_2$ ).**

Run	E' <sup>a</sup>	E <sup>b</sup>	E-E'	average E-E'	$\ln \gamma_{\pm}'$ <sup>c</sup>	average $\ln \gamma_{\pm}$ <sup>d</sup>
1		46.73		72.80 ± 0.10	-0.250 ± 0.008 <sup>c</sup> in $9.990 \times 10^{-4}$ mol kg <sup>-1</sup> K <sub>3</sub> [Co(CN) <sub>6</sub> ]	-0.860 ± 0.009
2	-26.40	(46.55)	72.95			
3	(-26.38)	46.36	72.74			
4	-26.37	(46.37)	72.74			
5	(-26.41)	46.37	72.78			
6	-26.44					

<sup>a</sup> E' /mV measured in the single salt solution,  $9.990 \times 10^{-4}$  mol kg<sup>-1</sup> K<sub>3</sub>[Co(CN)<sub>6</sub>] in water ( $m'$ ). <sup>b</sup> E /mV measured in the mixed solution,  $1.016 \times 10^{-3}$  mol kg<sup>-1</sup> K<sub>3</sub>[Co(CN)<sub>6</sub>] ( $m_1$ ) in 0.1113 mol kg<sup>-1</sup> KOH ( $m_2$ ) <sup>c</sup> From the data and interpolating equation reported in ref. S2. <sup>d</sup> Calculated as:  $\ln \gamma_{\pm} = \ln \gamma_{\pm}' + 3F(E-E')/(4RT) - (1/4) \ln \{ [m_1 (m_2 + 3m_1)^3] / [m' (3m')^3] \}$  <sup>e</sup> Interpolated value.

**Table S9 - Activity coefficient of  $8.553 \times 10^{-4}$  mol kg<sup>-1</sup> [Co(en)<sub>3</sub>]Cl<sub>3</sub> (*m*<sub>1</sub>) in 0.1000 mol kg<sup>-1</sup> HCl (*m*<sub>2</sub>).**

Run	E' <sup>a</sup>	E <sup>b</sup>	E-E'	average E-E'	ln $\gamma_{\pm}$ ' <sup>c</sup>	average ln $\gamma_{\pm}$ <sup>d</sup>
1		16.45		65.91±0.14	-0.261 ± 0.005 <sup>c</sup> in 9.996×10 <sup>-4</sup> mol kg <sup>-1</sup> [Co(en) <sub>3</sub> ]Cl <sub>3</sub>	-0.947 ± 0.006
2	-49.34	(16.46) <sup>e</sup>	65.80			
3	(-49.49) <sup>e</sup>	16.47	65.96			
4	-49.63	(16.45) <sup>e</sup>	66.08			
5	(-49.35) <sup>e</sup>	16.43	65.78			
6	-49.07					

<sup>a</sup> E' /mV measured in the single salt solution, 9.996×10<sup>-4</sup> mol kg<sup>-1</sup> [Co(en)<sub>3</sub>]Cl<sub>3</sub> in water (*m*<sub>1</sub>). <sup>b</sup> E /mV measured in the mixed solution, 8.553×10<sup>-4</sup> mol kg<sup>-1</sup> [Co(en)<sub>3</sub>]Cl<sub>3</sub> (*m*<sub>1</sub>) in 0.1000 mol kg<sup>-1</sup> HCl (*m*<sub>2</sub>) <sup>c</sup> From the data and interpolating equation reported in ref. S10. <sup>d</sup> Calculated as:  $\ln \gamma_{\pm} = \ln \gamma_{\pm}' + 3F(E-E')/(4RT) - (1/4) \ln \{ [m_1 (m_2 + 3m_1)^3] / [m' (3m')^3] \}$ ; <sup>e</sup> Interpolated.

**Table S10 - Activity coefficient of  $5.134 \times 10^{-4}$  mol kg<sup>-1</sup> [Co(en)<sub>3</sub>]Cl<sub>3</sub> (*m*<sub>1</sub>) in 0.1047 mol kg<sup>-1</sup> MgCl<sub>2</sub> (*m*<sub>2</sub>).**

Run	E' <sup>a</sup>	E <sup>b</sup>	E-E'	average E-E'	ln $\gamma_{\pm}$ ' <sup>c</sup>	average ln $\gamma_{\pm}$ <sup>d</sup>
1	-49.80			69.53± 0.04	-0.261 ± 0.005 <sup>c</sup> in 1.002×10 <sup>-3</sup> mol kg <sup>-1</sup> [Co(en) <sub>3</sub> ]Cl <sub>3</sub>	-1.253 ± 0.005
2	(-49.82) <sup>e</sup>	19.69	69.51			
3	-49.84	(19.70) <sup>e</sup>	69.54			
4		19.72				

<sup>a</sup> E' /mV measured in the single salt solution, 1.002×10<sup>-3</sup> mol kg<sup>-1</sup> [Co(en)<sub>3</sub>]Cl<sub>3</sub> in water (*m*<sub>1</sub>). <sup>b</sup> E /mV measured in the mixed solution, 5.134×10<sup>-4</sup> mol kg<sup>-1</sup> [Co(en)<sub>3</sub>]Cl<sub>3</sub> (*m*<sub>1</sub>) in 0.1047 mol kg<sup>-1</sup> MgCl<sub>2</sub> (*m*<sub>2</sub>) <sup>c</sup> From the data and interpolating equation reported in ref. S10. <sup>d</sup> Calculated as:  $\ln \gamma_{\pm} = \ln \gamma_{\pm}' + 3F(E-E')/(4RT) - (1/4) \ln \{ [m_1 (2m_2 + 3m_1)^3] / [m' (3m')^3] \}$ ; <sup>e</sup> Interpolated.

**Table S11 - Activity coefficient of  $4.976 \times 10^{-4}$  mol kg<sup>-1</sup> [Co(en)<sub>3</sub>]Cl<sub>3</sub> (*m*<sub>1</sub>) in  $6.46 \times 10^{-2}$  mol kg<sup>-1</sup> LaCl<sub>3</sub> (*m*<sub>2</sub>).**

Run	E' <sup>a</sup>	E <sup>b</sup>	E-E'	average E-E'	ln $\gamma_{\pm}$ ' <sup>c</sup>	average ln $\gamma_{\pm}$ <sup>d</sup>
1		16.33		67.04 ± 0.09	-0.260 ± 0.005 <sup>c</sup> in 9.875×10 <sup>-4</sup> mol kg <sup>-1</sup> [Co(en) <sub>3</sub> ]Cl <sub>3</sub>	-1.273 ± 0.006
2	-50.43	(16.51) <sup>e</sup>	66.94			
3	(-50.43) <sup>e</sup>	16.69	67.12			
4	-50.44	(16.61) <sup>e</sup>	67.05			
5		16.53				

<sup>a</sup> E' /mV measured in the single salt solution, 9.875×10<sup>-4</sup> mol kg<sup>-1</sup> [Co(en)<sub>3</sub>]Cl<sub>3</sub> in water (*m*<sub>1</sub>). <sup>b</sup> E /mV measured in the mixed solution, 4.976×10<sup>-4</sup> mol kg<sup>-1</sup> [Co(en)<sub>3</sub>]Cl<sub>3</sub> (*m*<sub>1</sub>) in 0.06460 mol kg<sup>-1</sup> LaCl<sub>3</sub> (*m*<sub>2</sub>) <sup>c</sup> From the data and interpolating equation reported in ref. S10. <sup>d</sup> Calculated as:  $\ln \gamma_{\pm} = \ln \gamma_{\pm}' + 3F(E-E')/(4RT) - (1/4) \ln \{ [m_1 (3m_2 + 3m_1)^3] / [m' (3m')^3] \}$ ; <sup>e</sup> Interpolated.

**Table S12 - Activity coefficient of  $4.747 \times 10^{-4}$  mol kg<sup>-1</sup> [Co(en)<sub>3</sub>][Co(CN)<sub>6</sub>] (*m*<sub>1</sub>) in  $9.92 \times 10^{-2}$  mol kg<sup>-1</sup> MgSO<sub>4</sub> (*m*<sub>2</sub>).**

Run	E' <sup>a</sup>	E <sup>b</sup>	E-E'	average E-E'	ln $\gamma_{\pm}$ ' <sup>c</sup>	average ln $\gamma_{\pm}$ <sup>d</sup>
1	-35.89			-43.56 ± 0.07	-1.542 ± 0.015 in 4.301×10 <sup>-4</sup> mol kg <sup>-1</sup> [Co(en) <sub>3</sub> ][Co(CN) <sub>6</sub> ]	-4.184± 0.016
2	(-36.00) <sup>e</sup>	-79.55	-43.55			
3	-36.11	(-79.61) <sup>e</sup>	-43.50			
4	(-36.04) <sup>e</sup>	-79.67	-43.63			
5	-35.96					

<sup>a</sup> E' /mV measured in the single salt solution, 4.301×10<sup>-4</sup> mol kg<sup>-1</sup> [Co(en)<sub>3</sub>][Co(CN)<sub>6</sub>] in water (*m*<sub>1</sub>). <sup>b</sup> E /mV measured in the mixed solution, 4.747×10<sup>-4</sup> mol kg<sup>-1</sup> [Co(en)<sub>3</sub>][Co(CN)<sub>6</sub>] (*m*<sub>1</sub>) in 9.92×10<sup>-2</sup> mol kg<sup>-1</sup> MgSO<sub>4</sub> (*m*<sub>2</sub>) <sup>c</sup> Interpolated from the data of ref. S3 (revised, see table S6). <sup>d</sup> Calculated as:  $\ln \gamma_{\pm} = \ln \gamma_{\pm}' + (2RT/3F)^{-1} (E-E') - \ln (m_1 / m')$ ; <sup>e</sup> Interpolated value.

**Table S13 - Activity coefficient of  $4.452 \times 10^{-4}$  mol kg<sup>-1</sup> [Co(en)<sub>3</sub>][Co(CN)<sub>6</sub>] (*m*<sub>1</sub>) in  $1.180 \times 10^{-2}$  mol kg<sup>-1</sup> La<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (*m*<sub>2</sub>).**

Run	E' <sup>a</sup>	E <sup>b</sup>	E-E'	average E-E'	ln $\gamma_{\pm}$ ' <sup>c</sup>	average ln $\gamma_{\pm}$ <sup>d</sup>
1		-60.48		-24.37 ± 0.15	-1.542 ± 0.015 in 4.301×10 <sup>-4</sup> mol kg <sup>-1</sup> [Co(en) <sub>3</sub> ][Co(CN) <sub>6</sub> ]	-2.999 ± 0.017
2	-36.28	(-60.50) <sup>e</sup>	-24.22			
3	(-36.15) <sup>e</sup>	-60.51	-24.36			
4	-36.02	(-60.54) <sup>e</sup>	-24.52			
5		-60.56				

<sup>a</sup> E' /mV measured with the single salt solution, 4.301×10<sup>-4</sup> mol kg<sup>-1</sup> [Co(en)<sub>3</sub>][Co(CN)<sub>6</sub>] in water (*m*<sub>1</sub>). <sup>b</sup> E /mV measured with the mixed solution, 4.452×10<sup>-4</sup> mol kg<sup>-1</sup> [Co(en)<sub>3</sub>][Co(CN)<sub>6</sub>] (*m*<sub>1</sub>) in 1.180×10<sup>-2</sup> mol kg<sup>-1</sup> La<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (*m*<sub>2</sub>) <sup>c</sup> Interpolated from the data of ref. S3 (revised, see table S6) <sup>d</sup> Calculated as:  $\ln \gamma_{\pm} = \ln \gamma_{\pm}' + (2RT/3F)^{-1} (E-E') - \ln (m_1 / m')$ ; <sup>e</sup> Interpolated value.

**Table S14 - Activity coefficient of  $2.243 \times 10^{-4} \text{ mol kg}^{-1} [\text{Co}(\text{en})_3][\text{Fe}(\text{CN})_6]$  ( $m_1$ ) in  $0.0988 \text{ mol kg}^{-1} \text{ MgSO}_4$  ( $m_2$ ).**

Run	E' <sup>a</sup>	E <sup>b</sup>	E-E'	average E-E'	$\ln \gamma_{\pm}$ <sup>c</sup>	average $\ln \gamma_{\pm}$ <sup>d</sup>
1		-189.04		-49.11±0.11	-1.301 ± 0.015 <sup>c</sup> in $2.242 \times 10^{-4} \text{ mol kg}^{-1}$ [Co(en) <sub>3</sub> ][Fe(CN) <sub>6</sub> ]	-4.169± 0.016
2	-139.92	(-189.00) <sup>e</sup>	-49.08			
3	(-139.94) <sup>e</sup>	-188.96	-49.02			
4	-139.95	(-189.01) <sup>e</sup>	-49.06			
5	(-139.78) <sup>e</sup>	-189.05	-49.27			
6	-139.60					

<sup>a</sup> E' /mV measured in the single salt solution,  $2.242 \times 10^{-4} \text{ mol kg}^{-1} [\text{Co}(\text{en})_3][\text{Fe}(\text{CN})_6]$  in water ( $m'$ ). <sup>b</sup> E /mV measured in the mixed solution,  $2.243 \times 10^{-4} \text{ mol kg}^{-1} [\text{Co}(\text{en})_3][\text{Fe}(\text{CN})_6]$  ( $m_1$ ) in  $0.0988 \text{ mol kg}^{-1} \text{ MgSO}_4$  ( $m_2$ ) <sup>c</sup> Ref. S3. <sup>d</sup> Calculated as:  $\ln \gamma_{\pm} = \ln \gamma_{\pm}' + (2RT/3F)^{-1} (E-E') - \ln (m_1 / m')$  <sup>e</sup> Interpolated.

**Table S15 - Activity coefficient of  $2.242 \times 10^{-4} \text{ mol kg}^{-1} [\text{Co}(\text{en})_3][\text{Fe}(\text{CN})_6]$  ( $m_1$ ) in  $1.180 \times 10^{-2} \text{ mol kg}^{-1} \text{ La}_2(\text{SO}_4)_3$  ( $m_2$ ).**

Run	E' <sup>a</sup>	E <sup>b</sup>	E-E'	average E-E'	$\ln \gamma_{\pm}$ <sup>c</sup>	average $\ln \gamma_{\pm}$ <sup>d</sup>
1	-139.15			-29.27 ± 0.14	-1.301 ± 0.015 <sup>c</sup> in $2.242 \times 10^{-4} \text{ mol kg}^{-1}$ [Co(en) <sub>3</sub> ][Fe(CN) <sub>6</sub> ]	-3.017 ± 0.015
2	(-139.38) <sup>e</sup>	-168.76	-29.38			
3	-139.61	(-168.73) <sup>e</sup>	-29.12			
4	(-139.51) <sup>e</sup>	-168.70	-29.19			
5	-139.40	(-168.79) <sup>e</sup>	-29.39			
6		-168.88				

<sup>a</sup> E' /mV measured in the single salt solution,  $2.242 \times 10^{-4} \text{ mol kg}^{-1} [\text{Co}(\text{en})_3][\text{Fe}(\text{CN})_6]$  in water ( $m'$ ). <sup>b</sup> E /mV measured in the mixed solution,  $2.242 \times 10^{-4} \text{ mol kg}^{-1} [\text{Co}(\text{en})_3][\text{Fe}(\text{CN})_6]$  ( $m_1$ ) in  $1.180 \times 10^{-2} \text{ mol kg}^{-1} \text{ La}_2(\text{SO}_4)_3$  ( $m_2$ ) <sup>c</sup> Ref. S3. <sup>d</sup> Calculated as:  $\ln \gamma_{\pm} = \ln \gamma_{\pm}' + (2RT/3F)^{-1} (E-E') - \ln (m_1 / m')$  <sup>e</sup> Interpolated value.

### §9. Activity coefficients of trace electrolytes in supporting electrolytes of variable concentration.

Tables S16 – S24 report the activity coefficients of electrolytes of low concentration dissolved in a supporting electrolyte of a much higher, variable concentration. With the only exception of Tables S18 and S24 (where the concentration ratio between supporting and target electrolyte is lower because of the low solubility of lanthanum sulfate) these activity coefficients can be considered as the practical limiting values to infinite dilution of the target electrolyte in the supporting electrolyte. The different solutions are obtained by progressive dilution of one of the reference mixed solutions already examined in Tables S7 - S15, whose activity coefficients are therefore known. Because of the very low concentration of the target electrolyte compared with the supporting electrolyte, the activity coefficient of the supporting electrolyte cannot differ appreciably from those (all available in literature) of the supporting electrolyte alone at the same ionic strengths.

**Table S16 -Activity coefficients of  $\text{K}_3[\text{Co}(\text{CN})_6]$  ( $m_1 / \text{mol kg}^{-1}$ ) in  $\text{K}_2\text{SO}_4$  ( $m_2 = 102.9 m_1$ )**

Series	$m_1$	$I^a$	E / mV	$E_{\text{ref}} / \text{mV}$	$\ln \gamma_{\pm}$
1	$8.792 \times 10^{-4}$	$2.765 \times 10^{-1}$	47.73 ± 0.03		(-1.137 ± 0.011)
1	$4.763 \times 10^{-4}$	$1.498 \times 10^{-1}$	33.07 ± 0.05	47.62 ± 0.11	-0.949 ± 0.012
1	$2.572 \times 10^{-4}$	$8.089 \times 10^{-2}$	17.24 ± 0.06	47.51 ± 0.22	-0.791 ± 0.013
1	$1.367 \times 10^{-4}$	$4.300 \times 10^{-2}$	0.77 ± 0.02	47.40 ± 0.33	-0.637 ± 0.015
1	$7.311 \times 10^{-5}$	$2.300 \times 10^{-2}$	-16.26 ± 0.02	47.29 ± 0.22	-0.505 ± 0.013
1	$3.890 \times 10^{-5}$	$1.224 \times 10^{-2}$	-33.75 ± 0.04	47.18 ± 0.33	-0.381 ± 0.015
1	$8.792 \times 10^{-4}$	$2.765 \times 10^{-1}$	47.07 ± 0.04		
2	$8.792 \times 10^{-4}$	$2.765 \times 10^{-1}$	47.36 ± 0.03		
2	$5.185 \times 10^{-6}$	$1.631 \times 10^{-3}$	-95.35 ± 0.03	47.26 ± 0.10	-0.167 ± 0.011
2	$1.067 \times 10^{-5}$	$3.357 \times 10^{-3}$	-72.80 ± 0.04	47.16 ± 0.20	-0.228 ± 0.013
2	$3.890 \times 10^{-5}$	$1.224 \times 10^{-2}$	-34.06 ± 0.02	47.06 ± 0.30	-0.387 ± 0.014
2	$7.311 \times 10^{-5}$	$2.300 \times 10^{-2}$	-16.43 ± 0.03	46.96 ± 0.20	-0.500 ± 0.012
2	$1.367 \times 10^{-4}$	$4.300 \times 10^{-2}$	0.71 ± 0.04	46.86 ± 0.10	-0.623 ± 0.011
2	$8.792 \times 10^{-4}$	$2.765 \times 10^{-1}$	46.76 ± 0.02		
2	$8.792 \times 10^{-4}$	$2.765 \times 10^{-1}$	46.13 ± 0.04		
3	$2.128 \times 10^{-5}$	$6.694 \times 10^{-3}$	-50.10 ± 0.03	46.22 ± 0.09	-0.227 ± 0.011
3	$2.576 \times 10^{-6}$	$8.104 \times 10^{-4}$	-117.98 ± 0.03	46.31 ± 0.18	-0.100 ± 0.012
3	$1.383 \times 10^{-6}$	$4.349 \times 10^{-4}$	-136.51 ± 0.02	46.40 ± 0.09	-0.021 ± 0.011
3	$8.792 \times 10^{-4}$	$2.765 \times 10^{-1}$	46.49 ± 0.05		
4	$8.792 \times 10^{-4}$	$2.765 \times 10^{-1}$	46.62 ± 0.02		
4	$2.128 \times 10^{-5}$	$6.694 \times 10^{-3}$	-51.94 ± 0.02	46.63 ± 0.02	-0.293 ± 0.011
4	$1.069 \times 10^{-5}$	$3.362 \times 10^{-3}$	-73.08 ± 0.02	46.64 ± 0.02	-0.222 ± 0.011
4	$8.792 \times 10^{-4}$	$2.765 \times 10^{-1}$	46.65 ± 0.04		
5	$8.792 \times 10^{-4}$	$2.765 \times 10^{-1}$	46.85 ± 0.02		
5	$5.354 \times 10^{-6}$	$1.684 \times 10^{-3}$	-93.25 ± 0.02	46.72 ± 0.13	-0.122 ± 0.012

5,6	$8.792 \times 10^{-4}$	$2.765 \times 10^{-1}$	$46.59 \pm 0.05$		
6	$1.491 \times 10^{-6}$	$4.688 \times 10^{-4}$	$-133.37 \pm 0.05$	$46.46 \pm 0.13$	$-0.007 \pm 0.012$
6	$8.128 \times 10^{-7}$	$2.557 \times 10^{-4}$	$-153.11 \pm 0.02$	$46.33 \pm 0.13$	$0.027 \pm 0.012$
6	$8.792 \times 10^{-4}$	$2.765 \times 10^{-1}$	$46.20 \pm 0.06$		
7	$8.792 \times 10^{-4}$	$2.765 \times 10^{-1}$	$47.06 \pm 0.05$		
7	$2.826 \times 10^{-6}$	$8.890 \times 10^{-4}$	$-113.45 \pm 0.15$	$46.80 \pm 0.26$	$-0.075 \pm 0.014$
7	$8.792 \times 10^{-4}$	$2.765 \times 10^{-1}$	$46.54 \pm 0.05$		

<sup>a</sup> I = molal ionic strength / mol kg<sup>-1</sup>.

**Table S17 - Activity coefficients of K<sub>3</sub>[Co(CN)<sub>6</sub>] ( $m_1$  / mol kg<sup>-1</sup>) in KOH ( $m_2 = 109.6 m_1$ )**

Series	$m_1$	$I^a$	$E / mV$	$E_{ref} / mV$	$\ln \gamma_{\pm}$
1	$1.016 \times 10^{-3}$	$1.174 \times 10^{-1}$	$45.73 \pm 0.01$		$(-0.860 \pm 0.009)$
1	$5.751 \times 10^{-4}$	$6.643 \times 10^{-2}$	$31.19 \pm 0.01$	$45.70 \pm 0.03$	$-0.714 \pm 0.009$
1	$3.151 \times 10^{-4}$	$3.639 \times 10^{-2}$	$15.20 \pm 0.01$	$45.67 \pm 0.06$	$-0.578 \pm 0.009$
1	$1.760 \times 10^{-4}$	$2.033 \times 10^{-2}$	$-0.66 \pm 0.01$	$45.65 \pm 0.06$	$-0.459 \pm 0.009$
1	$1.012 \times 10^{-4}$	$1.169 \times 10^{-2}$	$-16.36 \pm 0.03$	$45.62 \pm 0.03$	$-0.363 \pm 0.009$
1	$1.016 \times 10^{-3}$	$1.174 \times 10^{-1}$	$45.59 \pm 0.02$		
2	$1.016 \times 10^{-3}$	$1.174 \times 10^{-1}$	$45.47 \pm 0.01$		
2	$5.789 \times 10^{-5}$	$6.686 \times 10^{-3}$	$-32.50 \pm 0.04$	$45.21 \pm 0.30$	$-0.263 \pm 0.013$
2	$3.375 \times 10^{-5}$	$3.898 \times 10^{-3}$	$-50.07 \pm 0.01$	$44.95 \pm 0.60$	$-0.229 \pm 0.020$
2	$1.930 \times 10^{-5}$	$2.229 \times 10^{-3}$	$-66.65 \pm 0.04$	$44.69 \pm 0.30$	$-0.146 \pm 0.013$
2	$1.016 \times 10^{-3}$	$1.174 \times 10^{-1}$	$44.43 \pm 0.03$		
3	$1.016 \times 10^{-3}$	$1.174 \times 10^{-1}$	$44.78 \pm 0.04$		
3	$5.789 \times 10^{-5}$	$6.686 \times 10^{-3}$	$-33.49 \pm 0.02$	$44.88 \pm 0.10$	$-0.282 \pm 0.009$
3	$1.113 \times 10^{-5}$	$1.285 \times 10^{-3}$	$-84.29 \pm 0.06$	$44.97 \pm 0.19$	$-0.119 \pm 0.011$
3	$6.258 \times 10^{-6}$	$7.228 \times 10^{-4}$	$-102.91 \pm 0.14$	$45.07 \pm 0.19$	$-0.090 \pm 0.011$
3	$3.531 \times 10^{-6}$	$4.078 \times 10^{-4}$	$-117.36 \pm 0.06$	$45.16 \pm 0.10$	$0.058 \pm 0.010$
3	$1.016 \times 10^{-3}$	$1.174 \times 10^{-1}$	$45.26 \pm 0.02$		
4	$1.016 \times 10^{-3}$	$1.174 \times 10^{-1}$	$45.24 \pm 0.01$		
4	$3.375 \times 10^{-5}$	$3.898 \times 10^{-3}$	$-49.13 \pm 0.06$	$45.18 \pm 0.06$	$-0.208 \pm 0.009$
4	$1.930 \times 10^{-5}$	$2.229 \times 10^{-3}$	$-61.26 \pm 0.30$	$45.11 \pm 0.13$	? <sup>c</sup>
4	$1.113 \times 10^{-5}$	$1.285 \times 10^{-3}$	$-84.47 \pm 0.10$	$45.05 \pm 0.13$	$-0.126 \pm 0.010$
4	$6.258 \times 10^{-6}$	$7.228 \times 10^{-4}$	$-102.25 \pm 0.20$	$44.98 \pm 0.06$	$-0.068 \pm 0.011$
4	$1.016 \times 10^{-3}$	$1.174 \times 10^{-1}$	$44.92 \pm 0.02$		
1 <sup>b</sup>	$1.016 \times 10^{-3}$	$1.174 \times 10^{-1}$	$45.67$		
1 <sup>b</sup>	$5.751 \times 10^{-4}$	$6.643 \times 10^{-2}$	$31.01$	$45.64$	$-0.718$
1 <sup>b</sup>	$3.151 \times 10^{-4}$	$3.639 \times 10^{-2}$	$15.21$	$45.60$	$-0.576$
1 <sup>b</sup>	$1.760 \times 10^{-4}$	$2.033 \times 10^{-2}$	$-0.85$	$45.57$	$-0.462$
1 <sup>b</sup>	$1.012 \times 10^{-4}$	$1.169 \times 10^{-2}$	$-16.49$	$45.53$	$-0.364$
1 <sup>b</sup>	$1.016 \times 10^{-3}$	$1.174 \times 10^{-1}$	$45.50$		
2 <sup>b</sup>	$1.016 \times 10^{-3}$	$1.174 \times 10^{-1}$	$45.47$		
2 <sup>b</sup>	$5.789 \times 10^{-5}$	$6.686 \times 10^{-3}$	$-32.77$	$45.19$	$-0.270$
2 <sup>b</sup>	$3.375 \times 10^{-5}$	$3.898 \times 10^{-3}$	$-50.06$	$44.91$	$-0.227$
2 <sup>b</sup>	$1.930 \times 10^{-5}$	$2.229 \times 10^{-3}$	$-66.65$	$44.63$	$-0.144$
2 <sup>b</sup>	$1.016 \times 10^{-3}$	$1.174 \times 10^{-1}$	$44.35$		
3 <sup>b</sup>	$1.016 \times 10^{-3}$	$1.174 \times 10^{-1}$	$44.75$		
3 <sup>b</sup>	$5.789 \times 10^{-5}$	$6.686 \times 10^{-3}$	$-33.60$	$44.85$	$-0.285$
3 <sup>b</sup>	$1.113 \times 10^{-5}$	$1.285 \times 10^{-3}$	$-84.17$	$44.94$	$-0.114$
3 <sup>b</sup>	$6.258 \times 10^{-6}$	$7.228 \times 10^{-4}$	$-103.30$	$45.04$	$-0.100$
3 <sup>b</sup>	$3.531 \times 10^{-6}$	$4.078 \times 10^{-4}$	$-117.90$	$45.13$	$0.043$
3 <sup>b</sup>	$1.016 \times 10^{-3}$	$1.174 \times 10^{-1}$	$45.23$		
4 <sup>b</sup>	$1.016 \times 10^{-3}$	$1.174 \times 10^{-1}$	$45.21$		
4 <sup>b</sup>	$3.375 \times 10^{-5}$	$3.898 \times 10^{-3}$	$-49.28$	$45.15$	$-0.211$
4 <sup>b</sup>	$1.930 \times 10^{-5}$	$2.229 \times 10^{-3}$	$-63.10$	$45.09$	? <sup>c</sup>
4 <sup>b</sup>	$1.113 \times 10^{-5}$	$1.285 \times 10^{-3}$	$-84.59$	$45.04$	$-0.130$
4 <sup>b</sup>	$6.258 \times 10^{-6}$	$7.228 \times 10^{-4}$	$-102.08$	$44.98$	$-0.063$
4 <sup>b</sup>	$1.016 \times 10^{-3}$	$1.174 \times 10^{-1}$	$44.92$		

<sup>a</sup> I = molal ionic strength / mol kg<sup>-1</sup>.

<sup>b</sup> Duplicated value measured in stirring conditions (5 minutes at ca. 2-4 rps. immediately after the readings in quiet solution, one single reading).

<sup>c</sup> Although the result is an outlier, the run was registered because of the effect on  $E_{ref}$ .

**Table S18 - Activity coefficients of  $[\text{Co}(\text{en})_3]\text{Cl}_3$  ( $m_1$  / mol kg<sup>-1</sup>) in HCl ( $m_2 = 116.9 m_1$ )**

Series	$m_1$	$I^a$	$E / \text{mV}$	$E_{\text{ref}} / \text{mV}$	$\ln \gamma_{\pm}$
1	$8.553 \times 10^{-4}$	$1.051 \times 10^{-1}$	16.30 ±0.02		(-0.947 ±0.011)
1	$4.882 \times 10^{-4}$	$5.999 \times 10^{-2}$	2.67 ±0.04	16.21 ±0.09	-0.781 ±0.011
1	$2.718 \times 10^{-4}$	$3.340 \times 10^{-2}$	-12.03 ±0.01	16.12 ±0.18	-0.622 ±0.012
1	$1.542 \times 10^{-4}$	$1.895 \times 10^{-2}$	-27.05 ±0.02	16.04 ±0.18	-0.492 ±0.012
1	$8.699 \times 10^{-5}$	$1.069 \times 10^{-2}$	-43.12 ±0.01	15.95 ±0.09	-0.386 ±0.011
1	$8.553 \times 10^{-4}$	$1.051 \times 10^{-1}$	15.86 ±0.05		
2	$8.553 \times 10^{-4}$	$1.051 \times 10^{-1}$	16.53 ±0.01		
2	$5.083 \times 10^{-5}$	$6.246 \times 10^{-3}$	-57.50 ±0.04	16.49 ±0.05	-0.283 ±0.011
2	$3.033 \times 10^{-5}$	$3.726 \times 10^{-3}$	-73.57 ±0.02	16.44 ±0.10	-0.235 ±0.011
2	$1.722 \times 10^{-5}$	$2.116 \times 10^{-3}$	-91.24 ±0.02	16.40 ±0.10	-0.184 ±0.011
2	$9.548 \times 10^{-6}$	$1.173 \times 10^{-3}$	-109.08 ±0.03	16.35 ±0.05	-0.113 ±0.011
2	$8.553 \times 10^{-4}$	$1.051 \times 10^{-1}$	16.31 ±0.01		
1 <sup>b</sup>	$8.553 \times 10^{-4}$	$1.051 \times 10^{-1}$	16.30 —		
1 <sup>b</sup>	$4.882 \times 10^{-4}$	$5.999 \times 10^{-2}$	2.73 —	16.23 —	-0.780 —
1 <sup>b</sup>	$2.718 \times 10^{-4}$	$3.340 \times 10^{-2}$	-12.03 —	16.15 —	-0.623 —
1 <sup>b</sup>	$1.542 \times 10^{-4}$	$1.895 \times 10^{-2}$	-27.02 —	16.08 —	-0.492 —
1 <sup>b</sup>	$8.699 \times 10^{-5}$	$1.069 \times 10^{-2}$	-43.11 —	16.00 —	-0.387 —
1 <sup>b</sup>	$8.553 \times 10^{-4}$	$1.051 \times 10^{-1}$	15.93 —		
2 <sup>b</sup>	$8.553 \times 10^{-4}$	$1.051 \times 10^{-1}$	16.53 —		
2 <sup>b</sup>	$5.083 \times 10^{-5}$	$6.246 \times 10^{-3}$	-57.43 —	16.49 —	-0.282 —
2 <sup>b</sup>	$3.033 \times 10^{-5}$	$3.726 \times 10^{-3}$	-73.55 —	16.45 —	-0.235 —
2 <sup>b</sup>	$1.722 \times 10^{-5}$	$2.116 \times 10^{-3}$	-91.22 —	16.42 —	-0.184 —
2 <sup>b</sup>	$9.548 \times 10^{-6}$	$1.173 \times 10^{-3}$	-109.04 —	16.38 —	-0.113 —
2 <sup>b</sup>	$8.553 \times 10^{-4}$	$1.051 \times 10^{-1}$	16.34 —		

<sup>a</sup>  $I$  = molal ionic strength / mol kg<sup>-1</sup>.

<sup>b</sup> Duplicated value measured in stirring conditions (5 minutes at ca. 2-4 rps. immediately after the readings in quiet solution, one single reading).

**Table S19 - Activity coefficients of  $[\text{Co}(\text{en})_3]\text{Cl}_3$  ( $m_1$  / mol kg<sup>-1</sup>) in MgCl<sub>2</sub> ( $m_2 = 203.9 m_1$ )**

Series	$m_1$	$I^a$	$E / \text{mV}$	$E_{\text{ref}} / \text{mV}$	$\ln \gamma_{\pm}$
1	$5.134 \times 10^{-4}$	$3.172 \times 10^{-1}$	19.91 ±0.03		(-1.253 ±0.005)
1	$2.659 \times 10^{-4}$	$1.643 \times 10^{-1}$	5.03 ±0.04	19.86 ±0.05	-1.028 ±0.005
1	$1.317 \times 10^{-4}$	$8.135 \times 10^{-2}$	-11.38 ±0.03	19.80 ±0.11	-0.802 ±0.006
1	$6.588 \times 10^{-5}$	$4.070 \times 10^{-2}$	-28.80 ±0.03	19.75 ±0.05	-0.617 ±0.005
1	$5.134 \times 10^{-4}$	$3.172 \times 10^{-1}$	19.69 ±0.04		
2	$5.134 \times 10^{-4}$	$3.172 \times 10^{-1}$	20.09 ±0.04		
2	$3.244 \times 10^{-5}$	$2.004 \times 10^{-2}$	-47.14 ±0.06	20.04 ±0.05	-0.452 ±0.005
2	$1.635 \times 10^{-5}$	$1.010 \times 10^{-2}$	-66.23 ±0.09	19.99 ±0.10	-0.323 ±0.006
2	$8.169 \times 10^{-6}$	$5.047 \times 10^{-3}$	-85.84 ±0.09	19.93 ±0.10	-0.200 ±0.006
2	$4.042 \times 10^{-6}$	$2.497 \times 10^{-3}$	-108.27 ±0.15	19.88 ±0.05	-0.150 ±0.007
2	$5.134 \times 10^{-4}$	$3.172 \times 10^{-1}$	19.83 ±0.01		
3	$5.134 \times 10^{-4}$	$3.172 \times 10^{-1}$	19.85 ±0.01		
3	$8.169 \times 10^{-6}$	$5.047 \times 10^{-3}$	-85.16 ±0.14	19.86 ±0.01	-0.178 ±0.006
3	$1.635 \times 10^{-5}$	$1.010 \times 10^{-2}$	-65.80 ±0.02	19.87 ±0.02	-0.307 ±0.005
3	$6.588 \times 10^{-5}$	$4.070 \times 10^{-2}$	-28.58 ±0.02	19.88 ±0.02	-0.614 ±0.005
3	$1.317 \times 10^{-4}$	$8.135 \times 10^{-2}$	-11.26 ±0.02	19.89 ±0.01	-0.802 ±0.005
3	$5.134 \times 10^{-4}$	$3.172 \times 10^{-1}$	19.89 ±0.01		
1 <sup>b</sup>	$5.134 \times 10^{-4}$	$3.172 \times 10^{-1}$	19.85 —		(-1.253 ±0.005)
1 <sup>b</sup>	$2.659 \times 10^{-4}$	$1.643 \times 10^{-1}$	5.06 —	19.82 —	-1.026 —
1 <sup>b</sup>	$1.317 \times 10^{-4}$	$8.135 \times 10^{-2}$	-11.35 —	19.80 —	-0.802 —
1 <sup>b</sup>	$6.588 \times 10^{-5}$	$4.070 \times 10^{-2}$	-28.74 —	19.77 —	-0.616 —
1 <sup>b</sup>	$5.134 \times 10^{-4}$	$3.172 \times 10^{-1}$	19.74 —		
2 <sup>b</sup>	$5.134 \times 10^{-4}$	$3.172 \times 10^{-1}$	20.04 —		
2 <sup>b</sup>	$3.244 \times 10^{-5}$	$2.004 \times 10^{-2}$	-47.01 —	19.99 —	-0.447 —
2 <sup>b</sup>	$1.635 \times 10^{-5}$	$1.010 \times 10^{-2}$	-65.95 —	19.93 —	-0.313 —
2 <sup>b</sup>	$8.169 \times 10^{-6}$	$5.047 \times 10^{-3}$	-84.58 —	19.88 —	-0.162 —
2 <sup>b</sup>	$4.042 \times 10^{-6}$	$2.497 \times 10^{-3}$	-107.14 —	19.82 —	-0.115 —
2 <sup>b</sup>	$5.134 \times 10^{-4}$	$3.172 \times 10^{-1}$	19.77 —		
3 <sup>b</sup>	$5.134 \times 10^{-4}$	$3.172 \times 10^{-1}$	19.79 —		
3 <sup>b</sup>	$8.169 \times 10^{-6}$	$5.047 \times 10^{-3}$	-84.76 —	19.80 —	-0.164 —
3 <sup>b</sup>	$1.635 \times 10^{-5}$	$1.010 \times 10^{-2}$	-65.83 —	19.81 —	-0.306 —

3 <sup>b</sup>	6.588×10 <sup>-5</sup>	4.070×10 <sup>-2</sup>	-28.56 —	19.81 —	-0.612 —
3 <sup>b</sup>	1.317×10 <sup>-4</sup>	8.135×10 <sup>-2</sup>	-11.25 —	19.82 —	-0.799 —
3 <sup>b</sup>	5.134×10 <sup>-4</sup>	3.172×10 <sup>-1</sup>	19.83 —		

<sup>a</sup> I = molal ionic strength / mol kg<sup>-1</sup>.

<sup>b</sup> Duplicated value measured in stirring conditions (5 minutes at ca. 2-4 rps. immediately after the readings in quiet solution, one single reading).

**Table S20 - Activity coefficients of [Co(en)<sub>3</sub>]Cl<sub>3</sub> (*m*<sub>1</sub> / mol kg<sup>-1</sup>) in LaCl<sub>3</sub> (*m*<sub>2</sub> = 129.8 *m*<sub>1</sub>).**

Series	<i>m</i> <sub>1</sub>	<i>I</i> <sup>a</sup>	<i>E</i> / mV	<i>E</i> <sub>ref</sub> / mV	ln <i>γ</i> <sub>±</sub>
1	4.968×10 <sup>-4</sup>	3.904×10 <sup>-1</sup>	16.99 ±0.01		(-1.273 ±0.008)
1	2.400×10 <sup>-4</sup>	1.886×10 <sup>-1</sup>	0.61 ±0.02	16.94 ±0.05	-1.022 ±0.008
1	1.186×10 <sup>-4</sup>	9.323×10 <sup>-2</sup>	-16.21 ±0.04	16.89 ±0.10	-0.807 ±0.009
1	6.172×10 <sup>-5</sup>	4.850×10 <sup>-2</sup>	-32.75 ±0.03	16.84 ±0.05	-0.635 ±0.008
1	4.968×10 <sup>-4</sup>	3.904×10 <sup>-1</sup>	16.79 ±0.03		
2	4.968×10 <sup>-4</sup>	3.904×10 <sup>-1</sup>	17.07 ±0.02		
2	3.143×10 <sup>-5</sup>	2.470×10 <sup>-2</sup>	-50.76 ±0.05	16.97 ±0.10	-0.490 ±0.009
2	1.653×10 <sup>-5</sup>	1.299×10 <sup>-2</sup>	-68.35 ±0.05	17.87 ±0.20	-0.387 ±0.010
2	8.881×10 <sup>-6</sup>	6.979×10 <sup>-3</sup>	-86.98 ±0.03	16.76 ±0.10	-0.277 ±0.009
2	4.968×10 <sup>-4</sup>	3.904×10 <sup>-1</sup>	16.66 ±0.03		
1 <sup>b</sup>	4.968×10 <sup>-4</sup>	3.904×10 <sup>-1</sup>	17.00 —		(-1.273 ±0.008)
1 <sup>b</sup>	2.400×10 <sup>-4</sup>	1.886×10 <sup>-1</sup>	0.62 —	16.95 —	-1.022 —
1 <sup>b</sup>	1.186×10 <sup>-4</sup>	9.323×10 <sup>-2</sup>	-16.17 —	16.91 —	-0.806 —
1 <sup>b</sup>	6.172×10 <sup>-5</sup>	4.850×10 <sup>-2</sup>	-32.74 —	16.86 —	-0.635 —
1 <sup>b</sup>	4.968×10 <sup>-4</sup>	3.904×10 <sup>-1</sup>	16.81 —		
2 <sup>b</sup>	4.968×10 <sup>-4</sup>	3.904×10 <sup>-1</sup>	17.00 —		
2 <sup>b</sup>	3.143×10 <sup>-5</sup>	2.470×10 <sup>-2</sup>	-50.63 —	16.92 —	-0.484 —
2 <sup>b</sup>	1.653×10 <sup>-5</sup>	1.299×10 <sup>-2</sup>	-68.10 —	16.84 —	-0.349 —
2 <sup>b</sup>	8.881×10 <sup>-6</sup>	6.979×10 <sup>-3</sup>	-86.97 —	16.75 —	-0.276 —
2 <sup>b</sup>	4.968×10 <sup>-4</sup>	3.904×10 <sup>-1</sup>	16.67 —		

<sup>a</sup> I = molal ionic strength / mol kg<sup>-1</sup>.

<sup>b</sup> Duplicated value measured in stirring conditions (5 minutes at ca. 2-4 rps. immediately after the readings in quiet solution, one single reading).

**Table S21 - Activity coefficients of [Co(en)<sub>3</sub>][Co(CN)<sub>6</sub>] (*m*<sub>1</sub> / mol kg<sup>-1</sup>) in MgSO<sub>4</sub> (*m*<sub>2</sub> = 209.0 *m*<sub>1</sub>).**

Series	<i>m</i> <sub>1</sub>	<i>I</i> <sup>a</sup>	<i>E</i> / mV	<i>E</i> <sub>ref</sub> / mV	ln <i>γ</i> <sub>±</sub>
1	4.747×10 <sup>-4</sup>	4.011×10 <sup>-1</sup>	-79.99 ±0.03		(-4.184 ±0.017)
1	2.078×10 <sup>-4</sup>	1.756×10 <sup>-1</sup>	-82.78 ±0.01	-79.88 ±0.12	-3.527 ±0.017
1	8.949×10 <sup>-5</sup>	7.561×10 <sup>-2</sup>	-86.82 ±0.01	-79.76 ±0.24	-2.928 ±0.021
1	4.277×10 <sup>-5</sup>	3.614×10 <sup>-2</sup>	-90.77 ±0.02	-79.65 ±0.12	-2.426 ±0.018
1	4.747×10 <sup>-4</sup>	4.011×10 <sup>-1</sup>	-79.53 ±0.01		
2	4.747×10 <sup>-4</sup>	4.011×10 <sup>-1</sup>	-79.15 ±0.01		
2	2.142×10 <sup>-5</sup>	1.810×10 <sup>-2</sup>	-94.84 ±0.01	-79.23 ±0.08	-1.997 ±0.017
2	1.059×10 <sup>-5</sup>	8.948×10 <sup>-3</sup>	-100.13 ±0.01	-79.31 ±0.16	-1.597 ±0.019
2	5.379×10 <sup>-6</sup>	4.545×10 <sup>-3</sup>	-105.86 ±0.01	-79.38 ±0.08	-1.250 ±0.017
2	4.747×10 <sup>-4</sup>	4.011×10 <sup>-1</sup>	-79.46 ±0.01		
3	4.747×10 <sup>-4</sup>	4.011×10 <sup>-1</sup>	-79.48 ±0.07		
3	2.911×10 <sup>-6</sup>	2.460×10 <sup>-3</sup>	-109.61 ±0.01	-79.50 ±0.02	-0.848 ±0.016
3	1.504×10 <sup>-6</sup>	1.271×10 <sup>-3</sup>	-115.60 ±0.05	-79.52 ±0.04	-0.536 ±0.016
3	8.203×10 <sup>-7</sup>	6.931×10 <sup>-4</sup>	-123.44 ±0.10	-79.53 ±0.02	-0.387 ±0.017
3	4.747×10 <sup>-4</sup>	4.011×10 <sup>-1</sup>	-79.55 ±0.07		
1 <sup>b</sup>	4.747×10 <sup>-4</sup>	4.011×10 <sup>-1</sup>	-80.08 —		
1 <sup>b</sup>	2.078×10 <sup>-4</sup>	1.756×10 <sup>-1</sup>	-82.81 —	-79.96 —	-3.524 —
1 <sup>b</sup>	8.949×10 <sup>-5</sup>	7.561×10 <sup>-2</sup>	-86.85 —	-79.84 —	-2.925 —
1 <sup>b</sup>	4.277×10 <sup>-5</sup>	3.614×10 <sup>-2</sup>	-90.80 —	-79.72 —	-2.424 —
1 <sup>b</sup>	4.747×10 <sup>-4</sup>	4.011×10 <sup>-1</sup>	-79.60 —		
2 <sup>b</sup>	4.747×10 <sup>-4</sup>	4.011×10 <sup>-1</sup>	-79.17 —		
2 <sup>b</sup>	2.142×10 <sup>-5</sup>	1.810×10 <sup>-2</sup>	-94.90 —	-79.24 —	-2.000 —
2 <sup>b</sup>	1.059×10 <sup>-5</sup>	8.948×10 <sup>-3</sup>	-100.15 —	-79.31 —	-1.598 —
2 <sup>b</sup>	5.379×10 <sup>-6</sup>	4.545×10 <sup>-3</sup>	-106.00 —	-79.38 —	-1.258 —

2 <sup>b</sup>	4.747×10 <sup>-4</sup>	4.011×10 <sup>-1</sup>	-79.45	—		
3 <sup>b</sup>	4.747×10 <sup>-4</sup>	4.011×10 <sup>-1</sup>	-79.57	—		
3 <sup>b</sup>	2.911×10 <sup>-6</sup>	2.460×10 <sup>-3</sup>	-110.50	—	-79.57	-0.896
3 <sup>b</sup>	1.504×10 <sup>-6</sup>	1.271×10 <sup>-3</sup>	-115.57	—	-79.57	-0.531
3 <sup>b</sup>	8.203×10 <sup>-7</sup>	6.931×10 <sup>-4</sup>	-123.95	—	-79.57	-0.414
3 <sup>b</sup>	4.747×10 <sup>-4</sup>	4.011×10 <sup>-1</sup>	-79.57	—		

<sup>a</sup> I = molal ionic strength / mol kg<sup>-1</sup>.

<sup>b</sup> Duplicated value measured in stirring conditions (5 minutes at ca. 2-4 rps. immediately after the readings in quiet solution, one single reading).

**Table S22 - Activity coefficients of [Co(en)<sub>3</sub>][Co(CN)<sub>6</sub>] (*m*<sub>1</sub> / mol kg<sup>-1</sup>) in La<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (*m*<sub>2</sub> = 26.51 *m*<sub>1</sub>).**

Series	<i>m</i> <sub>1</sub>	<i>I</i> <sup>a</sup>	<i>E</i> / mV	<i>E</i> <sub>ref</sub> / mV	ln <i>γ</i> <sub>±</sub>
1	4.452×10 <sup>-4</sup>	1.810×10 <sup>-1</sup>	-60.69 ±0.01		(-2.999 ±0.017)
1	5.864×10 <sup>-5</sup>	2.384×10 <sup>-2</sup>	-75.67 ±0.03	-60.67 ±0.03	-1.848 ±0.017
1	1.142×10 <sup>-4</sup>	4.642×10 <sup>-2</sup>	-70.01 ±0.01	-60.64 ±0.06	-2.185 ±0.017
1	2.244×10 <sup>-4</sup>	9.124×10 <sup>-2</sup>	-65.02 ±0.01	-60.61 ±0.03	-2.571 ±0.017
1	4.452×10 <sup>-4</sup>	1.810×10 <sup>-1</sup>	-60.59 ±0.01		
2	4.452×10 <sup>-4</sup>	1.810×10 <sup>-1</sup>	-60.42 ±0.01		
2	5.587×10 <sup>-6</sup>	2.271×10 <sup>-3</sup>	-98.84 ±0.01	-60.45 ±0.03	-0.862 ±0.017
2	1.137×10 <sup>-5</sup>	4.624×10 <sup>-3</sup>	-91.70 ±0.01	-60.49 ±0.06	-1.154 ±0.017
2	2.442×10 <sup>-5</sup>	9.929×10 <sup>-3</sup>	-83.88 ±0.03	-60.52 ±0.03	-1.460 ±0.017
2	4.452×10 <sup>-4</sup>	1.810×10 <sup>-1</sup>	-60.55 ±0.02		
1 <sup>b</sup>	4.452×10 <sup>-4</sup>	1.810×10 <sup>-1</sup>	-60.68	—	—
1 <sup>b</sup>	5.864×10 <sup>-5</sup>	2.384×10 <sup>-2</sup>	-75.73	—	-1.852
1 <sup>b</sup>	1.142×10 <sup>-4</sup>	4.642×10 <sup>-2</sup>	-70.06	—	-2.188
1 <sup>b</sup>	2.244×10 <sup>-4</sup>	9.124×10 <sup>-2</sup>	-65.05	—	-2.573
1 <sup>b</sup>	4.452×10 <sup>-4</sup>	1.810×10 <sup>-1</sup>	-60.61	—	—
2 <sup>b</sup>	4.452×10 <sup>-4</sup>	1.810×10 <sup>-1</sup>	-60.43	—	—
2 <sup>b</sup>	5.587×10 <sup>-6</sup>	2.271×10 <sup>-3</sup>	-98.83	—	-0.860
2 <sup>b</sup>	1.137×10 <sup>-5</sup>	4.624×10 <sup>-3</sup>	-91.80	—	-1.158
2 <sup>b</sup>	2.442×10 <sup>-5</sup>	9.929×10 <sup>-3</sup>	-83.95	—	-1.462
2 <sup>b</sup>	4.452×10 <sup>-4</sup>	1.810×10 <sup>-1</sup>	-60.59	—	—

<sup>a</sup> I = molal ionic strength / mol kg<sup>-1</sup>.

<sup>b</sup> Duplicated value measured in stirring conditions (5 minutes at ca. 2-4 rps. immediately after the readings in quiet solution, one single reading).

**Table S23 - Activity coefficients of [Co(en)<sub>3</sub>][Fe(CN)<sub>6</sub>] (*m*<sub>1</sub> / mol kg<sup>-1</sup>) in MgSO<sub>4</sub> (*m*<sub>2</sub> = 440.6 *m*<sub>1</sub>).**

Series	<i>m</i> <sub>1</sub>	<i>I</i> <sup>a</sup>	<i>E</i> / mV	<i>E</i> <sub>ref</sub> / mV	ln <i>γ</i> <sub>±</sub>
1	2.243×10 <sup>-4</sup>	3.973×10 <sup>-1</sup>	-189.36 ±0.01		(-4.169 ±0.016)
1	1.249×10 <sup>-4</sup>	2.212×10 <sup>-1</sup>	-191.52 ±0.03	-189.34 ±0.02	-3.711 ±0.016
1	6.945×10 <sup>-5</sup>	1.230×10 <sup>-1</sup>	-194.13 ±0.02	-189.32 ±0.04	-3.277 ±0.016
1	3.952×10 <sup>-5</sup>	7.000×10 <sup>-2</sup>	-196.93 ±0.04	-189.29 ±0.02	-2.879 ±0.016
1	2.243×10 <sup>-4</sup>	3.973×10 <sup>-1</sup>	-189.27 ±0.02		
2	2.243×10 <sup>-4</sup>	3.973×10 <sup>-1</sup>	-189.06 ±0.01		
2	2.254×10 <sup>-5</sup>	3.993×10 <sup>-2</sup>	-200.20 ±0.02	-189.07 ±0.01	-2.521 ±0.016
2	1.250×10 <sup>-5</sup>	2.214×10 <sup>-2</sup>	-203.08 ±0.02	-189.07 ±0.02	-2.099 ±0.016
2	6.856×10 <sup>-6</sup>	1.214×10 <sup>-2</sup>	-207.21 ±0.20	-189.08 ±0.02	-1.740 ±0.020
2	3.636×10 <sup>-6</sup>	6.441×10 <sup>-3</sup>	-211.48 ±0.20	-189.08 ±0.01	-1.355 ±0.020
2	2.243×10 <sup>-4</sup>	3.973×10 <sup>-1</sup>	-189.09 ±0.02		

<sup>a</sup> I = molal ionic strength / mol kg<sup>-1</sup>.

**Table S24 - Activity coefficients of [Co(en)<sub>3</sub>][Fe(CN)<sub>6</sub>] (*m*<sub>1</sub> / mol kg<sup>-1</sup>) in La<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (*m*<sub>2</sub> = 52.7 *m*<sub>1</sub>).**

Series	<i>m</i> <sub>1</sub>	<i>I</i> <sup>a</sup>	<i>E</i> / mV	<i>E</i> <sub>ref</sub> / mV	ln <i>γ</i> <sub>±</sub>
1	2.242×10 <sup>-4</sup>	1.791×10 <sup>-1</sup>	-168.74 ±0.03		-3.017 ±0.015
1	1.298×10 <sup>-4</sup>	1.036×10 <sup>-1</sup>	-172.15 ±0.01	-168.73 ±0.01	-2.670 ±0.015
1	7.231×10 <sup>-5</sup>	5.775×10 <sup>-2</sup>	-176.40 ±0.00	-168.72 ±0.02	-2.334 ±0.015



1	$3.964 \times 10^{-5}$	$3.166 \times 10^{-2}$	$-181.23 \pm 0.01$	$-168.70 \pm 0.02$	$-2.016 \pm 0.015$
1	$2.210 \times 10^{-5}$	$1.766 \times 10^{-2}$	$-186.44 \pm 0.03$	$-168.69 \pm 0.01$	$-1.737 \pm 0.015$
1	$2.242 \times 10^{-4}$	$1.791 \times 10^{-1}$	$-168.68 \pm 0.01$		
2	$2.242 \times 10^{-4}$	$1.791 \times 10^{-1}$	$-168.23 \pm 0.03$		
2	$1.236 \times 10^{-5}$	$9.871 \times 10^{-3}$	$-191.53 \pm 0.02$	$-168.29 \pm 0.06$	$-1.476 \pm 0.015$
2	$6.944 \times 10^{-6}$	$5.546 \times 10^{-3}$	$-197.55 \pm 0.01$	$-168.34 \pm 0.11$	$-1.248 \pm 0.016$
2	$3.851 \times 10^{-6}$	$3.076 \times 10^{-3}$	$-203.90 \pm 0.08$	$-168.40 \pm 0.11$	$-1.025 \pm 0.017$
2	$2.158 \times 10^{-6}$	$1.724 \times 10^{-3}$	$-210.26 \pm 0.10$	$-168.45 \pm 0.06$	$-0.815 \pm 0.016$
2	$2.242 \times 10^{-4}$	$1.791 \times 10^{-1}$	$-168.51 \pm 0.01$		
1 <sup>b</sup>	$2.242 \times 10^{-4}$	$1.791 \times 10^{-1}$	$-168.65$		
1 <sup>b</sup>	$1.298 \times 10^{-4}$	$1.036 \times 10^{-1}$	$-172.14$	$-168.65$	$-2.674$
1 <sup>b</sup>	$7.231 \times 10^{-5}$	$5.775 \times 10^{-2}$	$-176.41$	$-168.66$	$-2.338$
1 <sup>b</sup>	$3.964 \times 10^{-5}$	$3.166 \times 10^{-2}$	$-181.25$	$-168.66$	$-2.019$
1 <sup>b</sup>	$2.210 \times 10^{-5}$	$1.766 \times 10^{-2}$	$-186.50$	$-168.67$	$-1.741$
1 <sup>b</sup>	$2.242 \times 10^{-4}$	$1.791 \times 10^{-1}$	$-168.67$		
2 <sup>b</sup>	$2.242 \times 10^{-4}$	$1.791 \times 10^{-1}$	$-168.29$		
2 <sup>b</sup>	$1.236 \times 10^{-5}$	$9.871 \times 10^{-3}$	$-191.58$	$-168.33$	$-1.476$
2 <sup>b</sup>	$6.944 \times 10^{-6}$	$5.546 \times 10^{-3}$	$-197.62$	$-168.37$	$-1.250$
2 <sup>b</sup>	$3.851 \times 10^{-6}$	$3.076 \times 10^{-3}$	$-203.84$	$-168.41$	$-1.021$
2 <sup>b</sup>	$2.158 \times 10^{-6}$	$1.724 \times 10^{-3}$	$-210.13$	$-168.45$	$-0.807$
2 <sup>b</sup>	$2.242 \times 10^{-4}$	$1.791 \times 10^{-1}$	$-168.49$		

<sup>a</sup> I = molal ionic strength / mol kg<sup>-1</sup>.

<sup>b</sup> Duplicated value measured in stirring conditions (5 minutes at ca. 2-4 rps. immediately after the readings in quiet solution, one single reading).

#### §10. Ion hydration effects.

Equations S1 and S2 (as well as equations 1, 4 and 5 of the main text) neglect the free enthalpy variation arising from the water molecules that the ions of the target electrolyte carry with them when entering the membranes. The problem has already been examined for single electrolytes.<sup>S9</sup> To be exact, the quantities so far represented as  $\ln \gamma_{\pm}$  in the equations and tables of the present paper and SI should be rewritten as  $\ln \gamma_{\pm \text{dir}}$ , where  $\ln \gamma_{\pm \text{dir}} = \ln \gamma_{\pm} + [n_w / (a + x)] \cdot \ln a_w$  ( $\gamma_{\pm}$  the true activity coefficient of  $A_a X_x$ ,  $a_w$  the activity of water in the solution,  $n_w$  = the number of water molecules that the  $a$  cations and  $x$  anions of  $A_a X_x$  carry with them into membranes).<sup>S9</sup> The distinction has not been further emphasized in the present work since the differences were unimportant. The value of  $n_w$  is three for  $K_3[Co(CN)_6]$  (potassium ions enter the NPOE – K[TFPB] membrane as  $[KH_2O]^+$ ) and zero for  $[Co(en)_3][Co(CN)_6]$  ( $[Co(en)_3]^{3+}$  and  $[Co(CN)_6]^{3-}$  do not carry with them water in the relevant membranes). We have not determined so far the hydration number of Cl<sup>-</sup> in the membranes made of [TDA]Cl dissolved in 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanol; possible values are three or four (Cl<sup>-</sup> ions carry with them three molecules of water in membranes made of 1-chloro-naphthalene, and four in membranes made of NPOE), or more probably less than three (the solvent may compete with the water molecules in the coordination shell of Cl<sup>-</sup>). Thus, for  $[Co(en)_3]Cl_3$  it is probable that  $n_w \leq 12$ . The difference between  $\ln \gamma_{\pm \text{dir}}$  and  $\ln \gamma_{\pm}$  is negligible at the concentration levels considered in the present paper, with only two possible exceptions. These possible exceptions are  $5.134 \times 10^{-4}$  mol kg<sup>-1</sup>  $[Co(en)_3]Cl_3$  in 0.1047 mol kg<sup>-1</sup> MgCl<sub>2</sub>, and  $4.976 \times 10^{-4}$  mol kg<sup>-1</sup>  $[Co(en)_3]Cl_3$  in  $6.46 \times 10^{-2}$  mol kg<sup>-1</sup> LaCl<sub>3</sub>. However, also in these two cases the corrections are presumably lower than in e.g. 0.1 mol kg<sup>-1</sup>  $[Co(en)_3](NO_3)_3$  ( $n_w = 12$ ), in which  $\ln \gamma_{\pm \text{dir}} = \ln \gamma_{\pm} - 0.018$ ,<sup>S10</sup> or 0.1 mol kg<sup>-1</sup> La(ClO<sub>4</sub>)<sub>3</sub>,<sup>S9</sup> where  $n_w$  is also 12 and  $\ln \gamma_{\pm \text{dir}}$  is once again equal to  $\ln \gamma_{\pm} - 0.018$  (i.e.,  $\gamma_{\pm \text{dir}}$  differs from  $\gamma_{\pm}$  by only -1.8 % in the most unfavorable hypothesis). In all other solutions, the differences between  $\ln \gamma_{\pm \text{dir}}$  and  $\ln \gamma_{\pm}$  are below the experimental error and can be neglected.

<sup>S9</sup> F. Malatesta, F. Bruni and N. Fanelli, *Phys. Chem. Chem. Phys.*, 2002, **4**, 121.

<sup>S10</sup> F. Malatesta, *J. Solution Chem.*, 2002, **31**, 547.