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Representation of Electrical Conductances for Polyvalent Electrolytes by the Quint-Viallard Conductivity Equation.

Part 2. Symmetrical 3:3 Type Electrolytes. Dilute Aqueous Solutions of Rare Earth Hexacyanoferrates(III) and Hexacyanocobaltates(III)

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Abstract Literature values of the electrical conductivities of dilute aqueous solutions of trivalent rare earth hexacyanoferrates(III) (La, Pr, Nd, Sm, Gd) and of rare earth hexacyanocobaltates(III) (La, Nd, Sm, Y) were reexamined within the framework of the Quint-Viallard conductivity equation in order to obtain a uniform representation of their conductivities. It was observed that the limiting conductances of electrolytes at infinite dilution depend weakly on the applied conductivity equation, whereas the derived ion association equilibrium constants vary considerably and therefore should be treated rather as fitting parameters.

Keywords Electrical conductances · Rare earth hexacyanoferrates(III) · Rare earth hexacyanocobaltates(III) · Limiting conductances · Ion association constants

1 Introduction

Due to the solubility limitations, studies of electrical conductivities of 3:3 type electrolytes in aqueous solutions have been mainly restricted to the rare earth metal ferricyanides [5, 7, 10–13, 15] and cobalticyanides [4, 12, 17, 23]. From this group of salts, most of the attention was directed at dilute solutions of $La[Fe(CN)_6]$ and $La[Co(CN)_6]$. Usually, the conductances were measured at 298.15 K and, less frequently, at other temperatures. The prevailing opinion in the interpretation of conductivity data of rare earth metal hexacyanoferrates(III) and hexacyanocobaltates(III) is that they are strongly associated compared with the behavior that is observed for comparatively weak electrolytes [4, 5, 7, 10–13, 15, 17, 23, 25]. Based on the determination of activity coefficients from the emf of liquid membrane cells in very dilute solutions, this view was challenged by Malatesta [20–22] who postulated that, for example, $La[Fe(CN)_6]$ behaves as a regular non-associated strong electrolyte. However, dielectric relaxation spectroscopy, which is a suitable experimental technique to investigate ion association phenomena, was applied by Buchner et al.

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[7] to lanthanum ferricyanide solutions and their interpretation of the results once again supported the old idea that the ion association constant is very large.

When these electrical conductivity experiments were performed, no suitable conductivity equation existed for 3:3 type electrolytes. Electrical conductances in the literature were examined in terms of various available conductivity equations (Onsager, Fuoss-Onsager (FO), Shedlovsky, Davies and Fuoss-Kraus (FK), see also [6] for other conductivity equations) and by using the Debye-Hückel equations for activity coefficients [9, 16, 24, 30]. This permitted the determination of the limiting conductances at infinite dilution Λ^0, the association constant K_{A}, and the distance of closest approach parameter a. To obtain a uniform representation of conductivities of 3:3 electrolytes, re-evaluation of the determined Λ^0 and K_{A} values based on the Quint-Viallard (QV) [26–29] conductivity equation, which is valid for any charge type of electrolyte, was performed.

2 Results and Discussion

2.1 Conductivity Equations

The molar conductance of an electrolyte $\Lambda(c,T)$ is an additive quantity with regard to the ionic contributions $\lambda_j(c,T)$:

$$\begin{gathered}\Lambda(c,T)=\frac{1000\kappa}{c}=\sum_j\frac{|z_j|c_j\lambda_j(c,T)}{c}\\ j=\mathrm{Me}^{3+},\ \mathrm{Y}^{3-}=[\mathrm{Fe(CN)}_6]^{3-},\ [\mathrm{Co(CN)}_6]^{3-}\end{gathered}\tag{1}$$

where κ is the measured specific conductance and $c_j=c\alpha$ with $|z_j|=3$. The ionic conductances $\lambda_j(c,T)$ are represented by:

$$\begin{gathered}\lambda_j(c,T)=\lambda_j^0(T)-S_j(T)\sqrt{I}+E_j(T)I\ln I+J_{1j}(T)I-J_{2j}(T)I^{3/2}\\ I=9c\alpha\end{gathered}\tag{2}$$

where α is the fraction of "free" ions in the solution and the coefficients S_j, E_j, J_{1j} and J_{2j} are complex functions of the limiting equivalent ionic conductances λ_j^0, the distance of closest approach parameters a_j and the physical properties of water (dielectric constant $D(T)$ and viscosity $\eta(T)$). These coefficients are available from the Quint-Viallard theory [26–29] (for explicit expressions of these coefficients also see [1–3, 26, 35]).

If it is accepted that 3:3 electrolytes are partially associated, then the formal analytical concentration of the solution c is replaced in the conductivity equations by $c\alpha$, where α is the fraction of "free" ions and $c(1-\alpha)$ denotes the concentration of nonconducting (uncharged) particles. Usually, it is assumed that at a given c the values of $c\alpha$ and $c(1-\alpha)$ represent the final result of all processes in solution without going into explicit details about the steps and mechanism of ion pairing. Thus, knowledge of the α fractions (so-called chemical problem) leads to the overall association constants K_{A}, which evidently represent some kind of apparent thermodynamic equilibrium constant. In the literature dealing with conductances of 3:3 electrolytes, ion association was expressed in terms of "incomplete dissociation" with corresponding dissociation constant K rather than the ion-association constant K_{A}.

The overall ion association process is represented by a chemical equilibrium equation in the form:

$$K_{\mathrm{A}}(T)=\frac{\{1-\alpha(c,T)\}F(c,T)}{c(T)\alpha^{2}(c,T)},\tag{3a}$$

$$F(c,T)=\frac{f_{\mathrm{MeY}}(c,T,x)}{f_{\mathrm{Me}^{3+}}(c,T)f_{\mathrm{Y}^{3-}}(c,T)}\tag{3b}$$

where the f_j are the activity coefficients of individual ions (f_{MeY} is assumed to be unity) and they are approximated in dilute solutions by the Debye-Hückel expressions:

$$\log_{10}[f_j(c,T)]=-\frac{z_j^2A(T)\sqrt{I}}{1+a_jB(T)\sqrt{I}}\tag{4}$$

where the constants $A(T)$ and $B(T)$ depend on the dielectric constant of pure water:

$$A(T)=\frac{1.8246\times10^{6}}{\{D(T)T\}^{3/2}},\tag{5a}$$

$$B(T)=\frac{5.029\times10^{9}}{\{D(T)T\}^{3/2}}\tag{5b}$$

The ion size parameters a_j in Eq. 4 were taken as recommended by Kielland [8, 18] for activity coefficients $\{a(\mathrm{La}^{3+})=a(\mathrm{Pr}^{3+})=a(\mathrm{Nd}^{3+})=a(\mathrm{Gd}^{3+})=a(\mathrm{Sm}^{3+})=a(\mathrm{Y}^{3+})=9$ Å and $a([\mathrm{Fe(CN)}_6]^{3-})=a([\mathrm{Co(CN)}_6]^{3-})=4$ Å$\}$ and were assumed to be independent of the temperature T (in the conductivity equations the distance of closest approach parameters were fixed at half of the sum of the cation and anion sizes).

If the value of the association constant $K_{\mathrm{A}}(T)$ is assumed and values of a_j are fixed, then evaluation of the fraction α for any given c from Eqs. 3–5 can be performed. By combining the chemical and conductance problems, then, at each temperature T, the experimental sets of conductivities can formally be written as $(\Lambda,c)=f(K_{\mathrm{A}},\Lambda^0,a_j,D,\eta,c)$ and solved by an optimization procedure to give values of K_{A} and Λ^0, which will assure the best agreement between the experimental and calculated conductivities. The iteration process starts with $\alpha=1$ as the initial value in solving the quadratic equation:

$$\alpha(c,T)=(1/2)\left[-\frac{F(c,T)}{K_{\mathrm{A}}(T)c(T)}+\sqrt{\left(\frac{F(c,T)}{K_{\mathrm{A}}(T)c(T)}\right)^{2}+\frac{4F(c,T)}{K_{\mathrm{A}}(T)c(T)}}\right]\tag{6}$$

Interactions are stopped when the average standard deviation $\sigma(\Lambda)$ is minimized:

$$\sigma(\Lambda)=\sqrt{\frac{\sum_{i=1}^{N}(\Lambda_{i,\mathrm{expt.}}-\Lambda_{i,\mathrm{calc.}})^{2}}{N-1}}\tag{7}$$

where N denotes the number of experimental points.

2.2 Rare Earth Hexacyanoferrates(III)

Conductivities of lanthanum hexacyanoferrate(III), La[Fe(CN)$_6$], in dilute aqueous solutions ($c>0.00003$ mol·dm^{-3}) were determined by Davies and James [10] at 291.15 K and

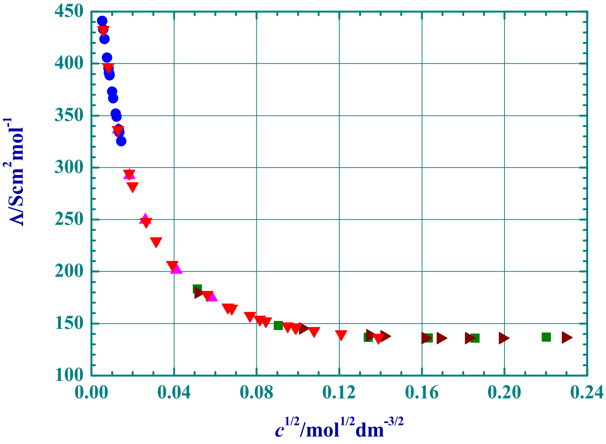


Fig. 1 Molar conductances of lanthanum hexacyanoferrate(III) aqueous solutions at 298.15 K, $\Lambda(c)$ as a function of the square root of concentration c: ▼ [10]; ● [12]; ▲ [15]; ▶ [5]; ■ [17]

303.15 K, and by Dunsmore et al. [12] at 298.15 K (for water + organic solvent mixtures see [11, 12]). In more concentrated solutions, conductance measurements [5, 15, 17] were supplemented by the determination of the pressure effect (Hamann et al. [15]) and solubilities in water (Bhat et al. [5]), and by Buchner et al.'s [7] detailed dielectric relaxation study of lanthanum hexacyanoferrate(III) solutions. The (Λ, c) sets of data at 298.15 K are plotted in Fig. 1. For the purpose of determining the limiting conductances, only those sets dealing with very dilute solutions [10, 12] are of interest. The applied numerical procedures (the Shedlovsky and the Davies conductivity equations) produced $\Lambda^0(\mathrm{La[Fe(CN)_6]}, T)$ values that are systematically larger than those determined from the Quint-Viallard conductivity equation, but the difference is relatively small, by a factor of about 1.03 (Table 3). Calculated ion association constants K_A, however, differ considerably by a factor of 1.6–1.8 (Table 3) which means that the QV treatment predicts much smaller extents of ion association than older numerical procedures. Evidently, differences in K_A come from large differences in calculated values of the free ion fractions α, which to some extent are caused by the different form of the activity coefficient expressions used (different number of terms in the extended Debye-Hückel limiting law). However, K_A values continue to be at least one order of magnitude higher than those observed for 2:2 electrolytes.

There is no doubt that an excellent fitting of the experimental conductivities is achieved when the Quint-Viallard conductivity equation is applied to 3:3 electrolytes (Tables 1 and 2). Molar conductances of lanthanum hexacyanoferrate(III), $\Lambda(c)$, are plotted in Fig. 2 as a function of the square root of the concentration c at three temperatures (291.15 K, 298.15 K and 303.15 K) together with the limiting Onsager slopes derived from [30]:

$$\Lambda_e(c;T) = \Lambda_e^0(T) - \left[\frac{2.801\cdot 10^6|z_+z_-|q\Lambda_e^0(T)}{[D(T)T]^{3/2}(1+\sqrt{q})} + \frac{41.25(|z_+|+|z_-|)}{\eta[D(T)T]^{1/2}}\right]\sqrt{I}$$
$$q = \frac{|z_+||z_-|}{(|z_+|+|z_-|)}\,\frac{[\lambda_+^0(T)+\lambda_-^0(T)]}{[|z_-|\lambda_+^0(T)+|z_+|\lambda_-^0(T)]} \tag{8}$$

where $\Lambda_e(c,T)$ is the equivalent conductance. For symmetrical electrolytes $q = 1/2$, the ionic strength for 3:3 type electrolyte is $I = 9\alpha c$, and the dielectric constants $D(T)$ and viscosities $\eta(T)$ of water are known in the literature [30]. As can be seen, in spite of measurements being performed in very dilute solutions, the concentration region covered by the limiting Onsager law is inaccessible in usual conductivity experiments with 3:3 electrolytes.

Table 1 Experimental molar conductances $\Lambda_{\text{exp.}}$ of rare earth hexacyanoferrates(III) in aqueous solutions as a function of the concentration c and calculated molar conductances $\Lambda_{\text{calc.}}$ from the Quint-Viallard conductivity equation

$c \times 10^4$	$\Lambda_{\text{expt.}}$	$\Lambda_{\text{calc.}}$	$C \times 10^4$	$\Lambda_{\text{exppt.}}$	$\Lambda_{\text{calc.}}$	$c \times 10^4$	$\Lambda_{\text{expt.}}$	$\Lambda_{\text{calc.}}$
La[Fe(CN)$_6$]								
0.50[b]	353.97	353.73	0.27[c]	440.97	440.34	0.30[d]	480.48	480.11
0.51	353.49	353.01	0.33	432.99	432.74	0.38	468.96	468.27
0.63	343.53	344.19	0.40	423.54	423.66	0.44	460.71	460.95
0.82	331.29	331.38	0.57	405.66	405.54	0.57	447.18	447.06
0.86	329.13	329.34	0.68	395.43	395.79	0.81	424.11	424.98
0.93	324.57	325.30	0.72	391.23	392.88	0.88	419.40	419.51
1.13	314.67	314.50	0.75	390.21	389.92	1.01	408.06	409.86
1.13	315.03	314.40	0.77	388.74	388.71	1.11	402.27	402.53
1.22	310.59	310.40	1.00	373.02	372.26	1.46	383.94	381.80
1.27	308.91	307.99	1.11	366.60	364.87	1.47	381.48	381.14
1.53	298.50	296.72	1.40	351.99	348.73	1.61	375.78	373.41
1.58	297.63	294.86	1.48	348.99	344.72	2.07	357.60	352.31
$\sigma(\Lambda)$		1.00			1.62			1.85
Nd[Fe(CN)$_6$]			Gd[Fe(CN)$_6$]					
0.11[c]	470.07	469.54	0.10[c]	464.97	463.33			
0.23	448.11	447.98	0.12	460.98	459.71			
0.30	436.23	436.97	0.18	446.40	447.34			
0.40	423.96	423.56	0.20	444.96	445.30			
0.43	419.94	420.26	0.46	408.24	410.76			
0.48	414.63	414.69	0.80	377.97	380.12			
0.52	408.96	410.81	0.87	373.11	374.49			
0.58	405.15	404.38	1.39	345.24	343.20			
0.62	401.43	400.28	1.44	342.84	340.25			
0.72	391.38	391.48	$\sigma(\Lambda)$		1.90			
0.82	384.87	382.99						
0.89	372.42	377.87						
$\sigma(\Lambda)$		1.87						

[a] Units: c, mol·dm^{-3}; Λ and $\sigma(\Lambda)$, S·cm^2·mol^{-1}

[b] Davies and James [10], $T = 291.15$ K

[c] Dunswore et al. [12], $T = 298.15$ K

[d] Davies and James [10], $T = 303.15$ K

The limiting conductances of the hexacyanoferrate(III) ion from the literature were compiled by Lemire and Lister [19] and they can be expressed as $\lambda^0(1/3[\text{Fe(CN)}_6]^{3-}$, 298.15 K) = (100.1 ± 0.7) S·cm^2·equiv^{-1}. From conductivity determinations analyzed by the Fuoss-Onsager equation and transference number measurements performed by the Spedding group [31–34] with rare earth halides, perchlorates and nitrates it is possible to obtain the average values at 298.15 K for trivalent lanthanide ions considered in this work: $\lambda^0(1/3\text{La}^{3+}) = (69.1 \pm 0.3)$ S·cm^2·equiv^{-1}, $\lambda^0(1/3\text{Pr}^{3+}) = (69.4 \pm 0.1)$ S·cm^2·equiv^{-1},

Table 2 Experimental molar conductances $\Lambda_{\text{exp.}}$ of yttrium and rare earth hexacyanocobaltates(III) in aqueous solutions as a function of the concentration c and calculated molar conductances $\Lambda_{\text{calc.}}$ from the Quint-Viallard conductivity equation

$c \times 10^4$	$\Lambda_{\text{expt.}}$	$\Lambda_{\text{calc.}}$	$c \times 10^4$	$\Lambda_{\text{expt.}}$	$\Lambda_{\text{calc.}}$	$c \times 10^4$	$\Lambda_{\text{expt.}}$	$\Lambda_{\text{calc.}}$
$La[Co(CN)_6]$								
0.41[b]	355.89	354.69	0.20[c]	446.58	446.55	0.08[d]	466.86	463.62
0.54	344.49	344.96	0.29	432.93	432.69	0.33	425.64	427.34
0.71	332.61	332.81	0.30	431.55	431.92	0.75	384.45	389.13
1.00	315.45	316.70	0.33	426.57	427.03	1.33	349.59	353.19
1.10	311.37	311.80	0.48	409.65	408.83	2.08	323.10	320.51
1.39	298.41	298.83	0.54	401.49	402.51	3.00	295.86	290.96
1.41	297.36	297.86	0.57	399.96	398.92	$\sigma(\Lambda)$		3.97
1.42	297.84	297.47	0.57	399.36	398.84			
1.92	281.22	279.45	0.63	392.73	393.53			
1.96	281.22	277.96	0.65	391.59	391.85			
2.65	263.85	258.14	0.82	379.86	377.71			
$\sigma(\Lambda)$		2.07	0.83	379.32	376.82			
			$\sigma(\Lambda)$		1.11			
$Nd[Co(CN)_6]$			$Sm[Co(CN)_6]$			$Y[Co(CN)_6]$		
0.08[d]	421.98	417.94	0.08[d]	372.15	368.18	0.08[d]	380.91	376.96
0.33	358.41	363.35	0.33	315.90	320.56	0.33	325.77	330.15
0.75	310.14	314.55	0.75	271.68	277.70	0.75	283.35	287.34
1.33	272.25	275.01	1.33	239.46	242.74	1.33	247.92	252.02
2.08	245.16	243.13	2.08	217.29	214.41	2.08	224.37	223.12
3.00	224.88	217.04	3.00	200.55	191.10	3.00	208.20	199.18
$\sigma(\Lambda)$		5.16			6.02			5.48

[a] Units: c, mol·dm^{-3}; Λ and $\sigma(\Lambda)$, S·cm^2·mol^{-1}

[b] Davies and James [10], $T = 291.15$ K

[c] Dunswore et al. [12], $T = 298.15$ K

[d] Atkinson [4], $T = 298.15$ K

$\lambda^0(1/3\text{Nd}^{3+}) = (69.5 \pm 0.2)$ S·cm^2·equiv^{-1}, $\lambda^0(1/3\text{Sm}^{3+}) = (68.7 \pm 0.3)$ S·cm^2·equiv^{-1}, $\lambda^0(1/3\text{Gd}^{3+}) = (67.7 \pm 0.4)$ S·cm^2·equiv^{-1} and $\lambda^0(1/3\text{Y}^{3+}) = 64.7$ S·cm^2·equiv^{-1} If the above value of $\lambda^0(1/3[\text{Fe(CN)}_6]^{3-}) = 100.1$ S·cm^2·equiv^{-1} is assumed, then the Quint-Viallard conductivity equation gives for lanthanum ion $\lambda^0(1/3\text{La}^{3+}) = 66.0$ S·cm^2·equiv^{-1}.

Other measurements of the conductivities of hexacyanoferrates of lanthanide metals include Dunsmore et al.'s [12] of aqueous solutions of neodymium and gadolinium and Fidler's [14] measurements of praseodymium, neodymium and samarium (the FK conductivity equation). As can be seen in Fig. 3, the Fidler conductances Λ($Nd[Fe(CN)_6]$, 298.15 K) cover more concentrated solutions, but they are also shifted by about factor 1.035 with regard to the Dunsmore et al. [12] results. If, during the calculations, the original $\Lambda(c)$ values are preserved, then the limiting molar conductances coming from the Fidler conductivities are considerably smaller than those observed for other lanthanides (also K_A values are much higher, Table 3). In a rather arbitrary way, conductivities of aqueous solutions of $Pr[Fe(CN)_6]$, $Nd[Fe(CN)_6]$ and $Sm[Fe(CN)_6]$ were multiplied by the same numerical fac-

Fig. 2 Molar conductances of lanthanum hexacyanoferrate(III) aqueous solutions $\Lambda(c)$ as a function of the square root of concentration c. Experimental results from: 291.15 K. ● [10]; 298.15 K, ▲ [12]; 303.15 K, ■ [10]; *dotted lines* $\Lambda(c)$ calculated using the Onsager conductivity equation, Eq. 8, for 3:3 type electrolyte; *continuous lines* $\Lambda(c)$ calculated using the Quint-Viallard conductivity equation, this work

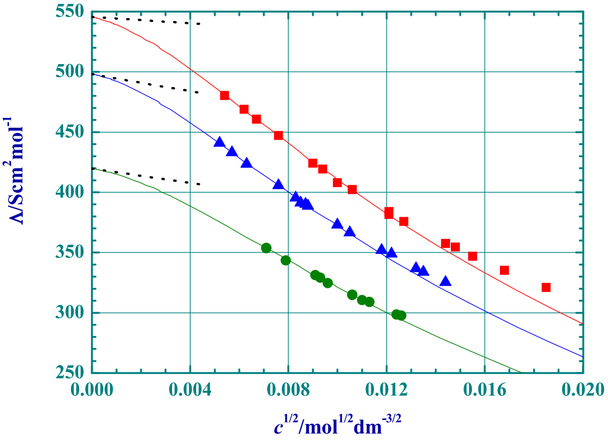
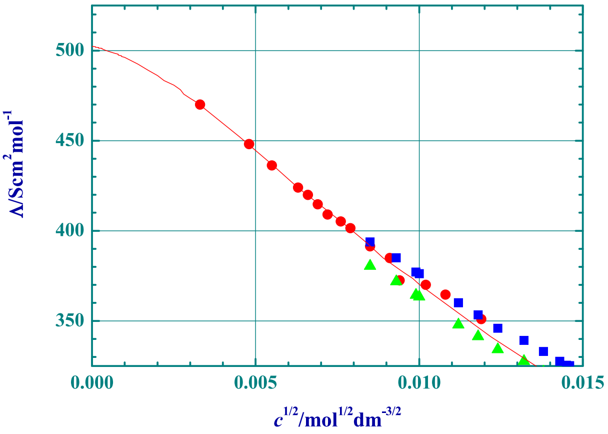


Fig. 3 Molar conductances of neodymium hexacyanoferrate(III) aqueous solutions at 298.15 K, $\Lambda(c)$ as a function of the square root of concentration c. Experimental results from: ● [12]; ▲ [14]; ■ [14] shifted by factor 1.035, see text; *continuous line* $\Lambda(c)$ calculated using the Quint-Viallard conductivity equation, this work



tor. It is evident that the final results of calculations of Λ^0 and K_A for these lanthanides, as presented in Table 3, are to the some degree uncertain.

Using $\lambda^0(1/3[\mathrm{Fe(CN)_6}]^{3-}) = 100.1\ \mathrm{S{\cdot}cm^2{\cdot}equiv^{-1}}$, from the QV equation the limiting ionic conductances based on the Dunsmore et al. [12] results are $\lambda^0(1/3\mathrm{Nd}^{3+}) = 67.4\ \mathrm{S{\cdot}cm^2{\cdot}equiv^{-1}}$ and $\lambda^0(1/3\mathrm{Gd}^{3+}) = 64.0\ \mathrm{S{\cdot}cm^2{\cdot}equiv^{-1}}$ whereas the corresponding Robinson and Stokes [30] values are $\lambda^0(1/3\mathrm{Nd}^{3+}) = 69.4\ \mathrm{S{\cdot}cm^2{\cdot}equiv^{-1}}$ and $\lambda^0(1/3\mathrm{Gd}^{3+}) = 68.5\ \mathrm{S{\cdot}cm^2{\cdot}equiv^{-1}}$. Thus, a systematic trend of limiting conductances is observed in the case of 3:3 type electrolytes, namely that limiting conductances using the Quint-Viallard conductivity equation are lower than values determined by the other methods.

2.3 Rare Earth Hexacyanocobaltates(III)

Conductivities of $\mathrm{La[Co(CN)_6]}$ in dilute aqueous solutions were measured by Davies and James [10] at 291.15 K and by Dunsmore et al. [12] at 298.15 K (Fig. 4). At the same temperature, Atkinson [4] determined the conductances of lanthanum, neodymium, samarium and yttrium hexacyanocobaltates(III), but they are less detailed and are probably less accurate than those determined by the others. It is evident that conductivities of $\mathrm{Nd[Co(CN)_6]}$ reported by Atkinson differ considerably from those of $\mathrm{Sm[Co(CN)_6]}$ and $\mathrm{Y[Fe(CN)_6]}$ whose

Table 3 The limiting molar conductances of rare earth hexacyanoferrates(III) and hexacyanocobaltates(III) Λ^0 and the ion association constants K_A as a function of temperature T[a] derived from the Quint-Viallard and from other conductivity equations

Salt	T/K	Λ^0	$K_A \times 10^3$	Λ^0	$K_A \times 10^3$	$100\sigma(\Lambda)/\Lambda^0$
La[Fe(CN)$_6$]	291.15	432.30[d]	5.05[d]	419.76[b]	2.79	0.24
	298.15	508.71[e]	5.49[e]	498.18	3.45	0.33
	303.15	564.00[d]	5.80[d]	545.64	3.17	0.34
Pr[Fe(CN)$_6$][c]	298.15	514.50[h]	6.67[h]	476.16	1.79	0.20
Nd[Fe(CN)$_6$]	298.15	508.50[e]	6.67[e]	502.41	3.86	0.37
Nd[Fe(CN)$_6$][c]	298.15	508.26[e]	6.25[e]	486.54	2.46	0.22
Sm[Fe(CN)$_6$][c]	298.15	504.30[e]	5.43[e]	486.12	2.57	0.45
Gd[Fe(CN)$_6$]	298.15	498.99[e]	5.52[e]	492.42	3.60	0.39
La[Co(CN)$_6$]	291.15	431.10[f]	5.48[f]	409.02	2.45	0.51
	298.15	505.20[f]	5.79[f]	488.73	3.24	0.33
	298.15	500.94[e]	5.46[e]	495.78	3.92	0.22
	298.15	505.14[g]	2.61[g]	486.93	2.77	0.82
Nd[Co(CN)$_6$]	298.15	504.75[g]	4.93[g]	454.08	8.26	1.14
Sm[Co(CN)$_6$]	298.15	502.44[g]	5.65[g]	399.66	8.00	1.51
Y[Co(CN)$_6$]	298.15	504.24[g]	6.72[g]	407.64	7.38	1.34

[a] Units: Λ^0, S·cm^2·mol^{-1}; K_A, dm^3·mol^{-1}

[b] The Quint-Viallard conductivity equation

[c] Original conductivities multiplied by factor 1.035, see text

[d] [10]

[e] [12]

[f] [17]

[g] [4]

[h] [14]

values are similar (Fig. 5). However, using the Shedlovsky approach, Atkinson derived nearly the same values of the limiting conductances 502–505 S·cm^2·mol^{-1} (Table 3) for all Nd, Sm and Y hexacyanocobaltates(III).

Similarly to rare earth hexacyanoferrates(III), $\Lambda(c)$ of hexacyanocobaltates(III) are represented very well by the Quint-Viallard conductivity equation (Table 2, Figs. 4 and 5). The limiting conductances at infinite dilution from the QV equation are somewhat lower than those determined by other treatments. The ion association constants are smaller by about a factor of 2. The only exceptions are Nd, Sm and Y hexacyanocobaltates(III) where the K_A value are unusually large (Table 3), but, as pointed out above, it seems that additional measurements are desired for these lanthanides.

The average value of the limiting molar conductance of lanthanum hexacyanocobaltate(III) is $\Lambda^0(\text{La}[\text{Co(CN)}_6]) = (490.5 \pm 4.7)$ S·cm^2·mol^{-1}(QV) which, together with the previously derived value $\lambda^0(1/3\text{La}^{3+}) = 66.0$ S·cm^2·equiv^{-1} gives, for the $\lambda^0(1/3[\text{Co(CN)}_6]^{3-}) = (97.5 \pm 1.6)$ S·cm^2·equiv^{-1}, and this value is close to that expected for the hexacyanoferrate anion. Similar estimations based on the QV result for Nd[Co(CN)$_6$] provides a value which is far different, once again raising into question Atkinson's measurements for Nd, Sm and Y hexacyanocobaltates(III).

Fig. 4 Molar conductances of lanthanum hexacyanocobaltate(III) aqueous solutions $\Lambda(c)$ as a function of the square root of concentration c. Experimental results from: 291.15 K, ● [17]; 298.15 K, ■ [12]; ▲ [17]; ▼ [4]; *continuous lines* $\Lambda(c)$ calculated using the Quint-Viallard conductivity equation, this work

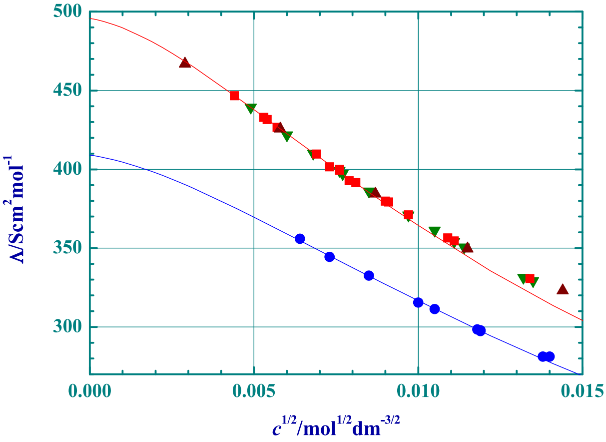
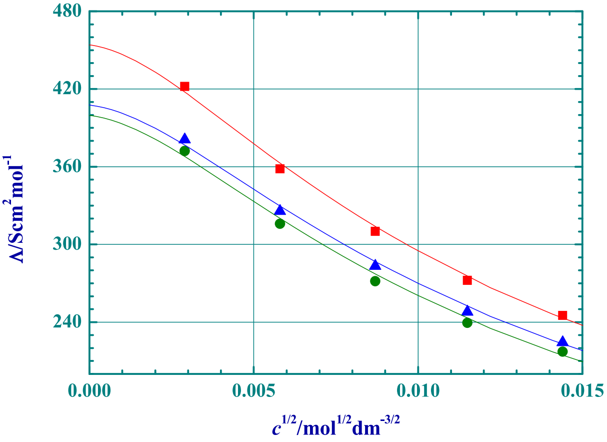


Fig. 5 Molar conductances of neodymium, samarium and yttrium hexacyanocobaltates(III) aqueous solutions at 298.15 K, $\Lambda(c)$ as a function of the square root of concentration c. Experimental results from [4]: ■ Nd[Co(CN)$_6$]; ● Sm[Co(CN)$_6$]; ▲ Y[Co(CN)$_6$]; continuous lines $\Lambda(c)$ calculated using the Quint-Viallard conductivity equation, this work



3 Conclusions and Remarks

Symmetrical electrolytes of the 3:3 type (rare earth hexacyanoferrates(III) and hexacyanocobaltates(III)) were analyzed for the first time in terms of the Quint-Viallard conductivity equation, also taking into account the effect of ion association. Excellent representations of (Λ, c) sets in dilute aqueous solutions are available by applying this conductivity equation. The limiting molar conductances Λ^0 derived from the optimization problem $(\Lambda, c) = f(K_A, \Lambda^0, a_j, D, \eta, c)$ are consistent with those determined by other approaches but, if the values of λ^0 are considered, they are systematically smaller by 2–3 S·cm^2·equiv^{-1}. On the other hand, differences in the ion association constants K_A, which depend very strongly on the chosen model, are very significant, being lower by a factor of 1.6–1.8. Evidently, K_A evaluations based on "integral" type measurements such as electrical conductivities or activity coefficients are inconclusive and the ion association constants should rather be treated as adjustable parameters in the fitting of (Λ, c) curves.

Considering the similarity in physical properties, the limiting equivalent conductances of trivalent lanthanide ions lie within a narrow range. Their temperature dependence is practically unknown because almost all measurements were performed at 298.15 K and at other temperatures they can only be estimated from the Walden rule.

With the exception of lanthanum, the conductivities other rare earth solutions are considerably less documented in the literature and all of them were investigated 50 to 60 years ago. Unfortunately, there are no modern conductivity measurements dealing with dilute aqueous solutions of 3:3 electrolytes. Yet, it appears that the confirmation of a number of important parameters is still necessary for these systems.

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