Supporting Information

Densities and apparent molar volumes of aqueous solutions of $K_4Fe(CN)_6$, $K_3Fe(CN)_6$, $K_3Co(CN)_6$, $K_2Ni(CN)_4$ and $KAg(CN)_2$ at 293 to 343 K

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Table S1. Sample Sources and Purities[a]

chemical name [CASRN]	source	initial mass fraction purity	purification method
Potassium hexacyanoferrate(II) hydrate [14459-95-1]	Chem-Supply	>0.985	recrystallization from water (2×)
Potassium hexacyanoferrate(III) [13746-66-2]	Baker Analyzed	0.999	none
Potassium hexacyanocobaltate(III) [13963-58-1]	Hopkin & Williams	0.995	recrystallization from water (2×)
Potassium tetracyanonickelate(II) hydrate [14220-17-8]	Aldrich	>0.99	recrystallization from water (2×)
Potassium dicyanoargentate(I) [506-61-6]	Aldrich	not stated	none

[a] Note that this table is identical to that published previously[1] (as Table 1).

Table S2. Standard Molar Volumes of Ions, V^o, at Experimental Temperatures, *T*

T/K	V^o / $cm^3 \cdot mol^{-1}$					
	K^{+a}	$[Fe(CN)_6]^{4-}$	$[Fe(CN)_6]^{3-}$	$[Co(CN)_6]^{3-}$	$[Ni(CN)_4]^{2-}$	$[Ag(CN)_2]^{-}$
293.15	3.5	97.6	134.4	131.7	103.8	66.9
298.15	3.5	99.1	135.8	133.0	105.0	68.0
303.15	3.6	99.9	136.7	133.8	105.9	68.8
308.15	3.6	100.8	137.7	134.7	106.7	69.7
313.15	3.6	101.5	138.4	135.4	107.4	70.5
318.15	3.6	101.9	139.0	135.9	108.0	71.2
323.15	3.6	102.1	139.4	136.2	108.4	71.8
328.15	3.6	102.1	139.6	136.3	108.7	72.4
333.15	3.6	101.9	139.6	136.3	108.9	72.9
338.15	3.6	101.5	139.5	136.1	109.0	73.4
343.15	3.6	100.9	139.3	135.8	108.9	73.8

[a] based on the widely accepted value of $V^o(H^+) = -5.5$ $cm^3 \cdot mol^{-1}$ reported by Conway[2]

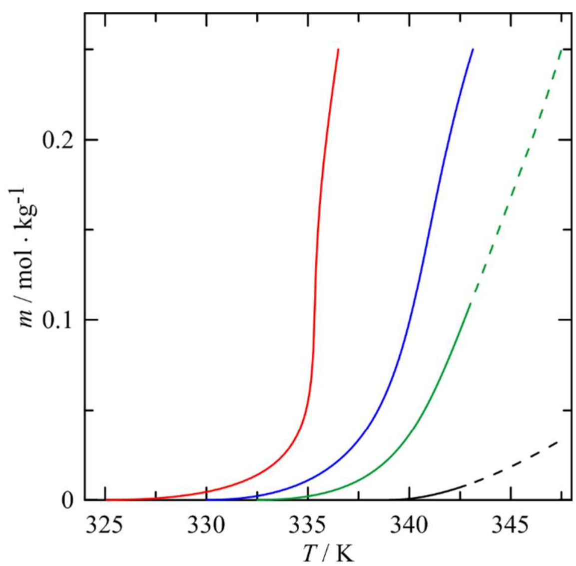

Figure S1. Locations of maxima, $V_\phi^{max}(T, m)$ on the $V_\phi - T$ curves shown in the temperature-molality plane: red – $K_4Fe(CN)_6$, blue – $K_3Co(CN)_6$, green – $K_3Fe(CN)_6$, black – $K_2Ni(CN)_4$. Dashed lines represent extrapolations outside the experimental range.

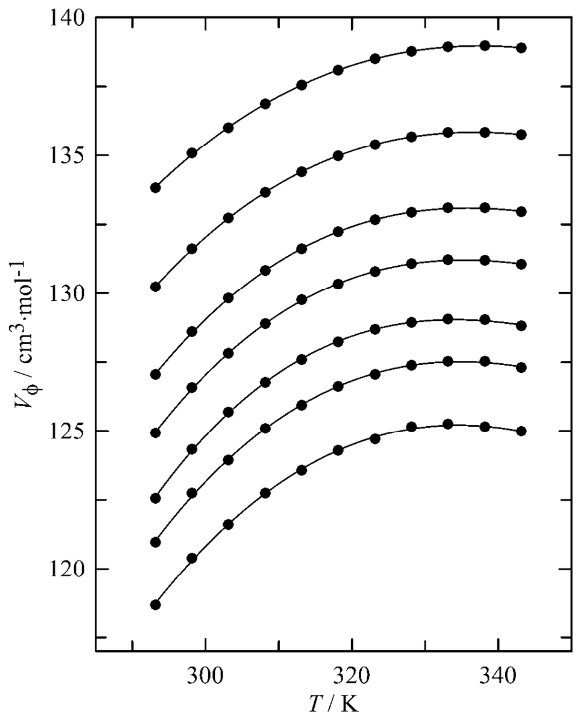

Figure S2. Apparent molar volumes, V_ϕ, of $K_4Fe(CN)_6$(aq) as function of temperature, *T*, at selected molalities, *m*. From bottom to top: m/mol·kg^{-1} = 0.020, 0.040, 0.060, 0.100, 0.150, 0.250, 0.400.

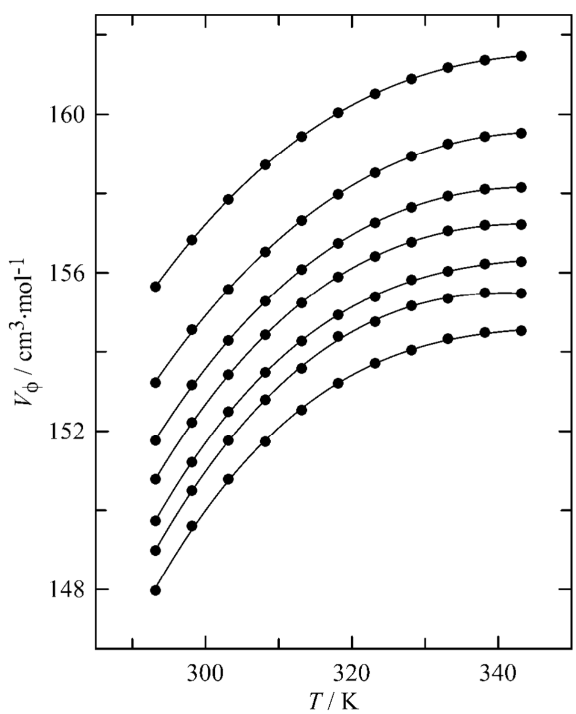

Figure S3. Apparent molar volumes, V_ϕ, of $K_3Fe(CN)_6$(aq) as function of temperature, *T*, at selected molalities, *m*. From bottom to top: m/mol·kg^{-1} = 0.018, 0.037, 0.054, 0.091, 0.135, 0.225, 0.400.

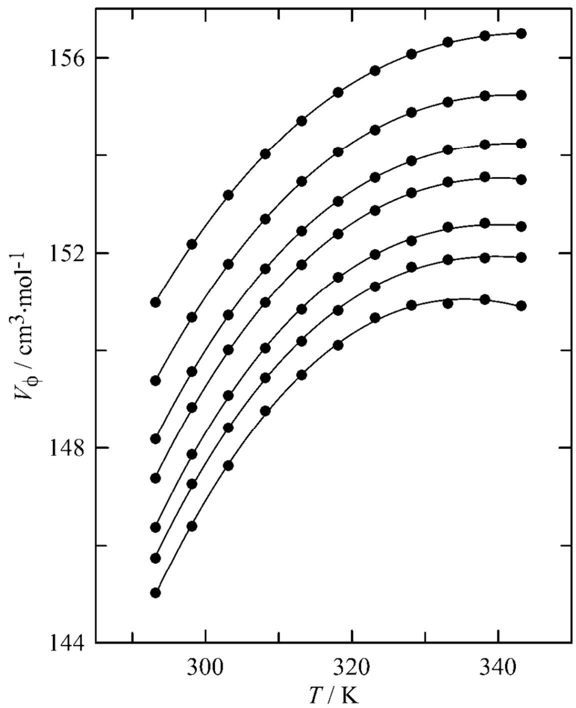

Figure S4. Apparent molar volumes, V_ϕ, of $K_3Co(CN)_6$(aq) as function of temperature, T, at selected molalities, m. From bottom to top: m/mol·kg^{-1} = 0.015, 0.030, 0.050, 0.080, 0.120, 0.201, 0.357.

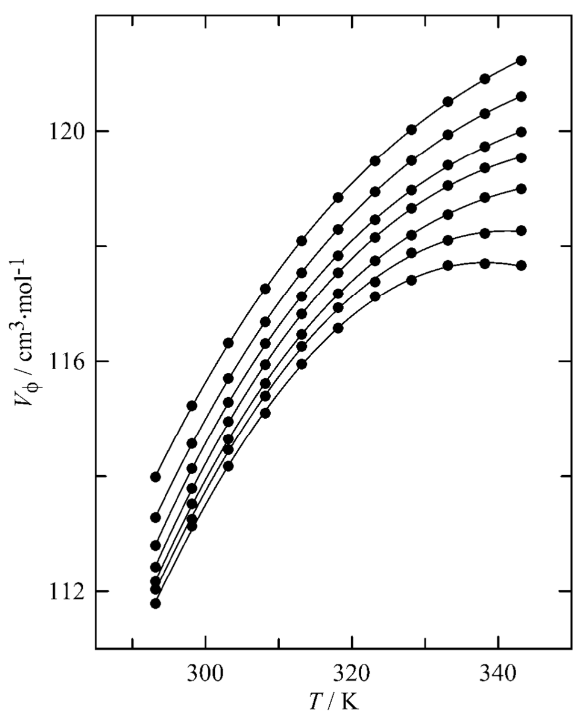

Figure S5. Apparent molar volumes, V_ϕ, of $K_2Ni(CN)_4$(aq) as function of temperature, T, at selected molalities, m. From bottom to top: m/mol·kg^{-1} = 0.020, 0.040, 0.060, 0.101, 0.151, 0.250, 0.348.

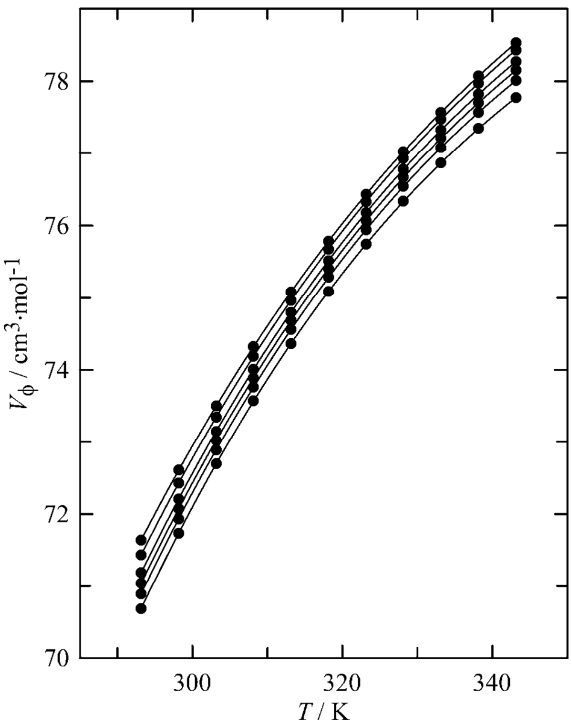

Figure S6. Apparent molar volumes, V_ϕ, of $KAg(CN)_2$(aq) as function of temperature, T, at selected molalities, m. From bottom to top: m/mol·kg^{-1} = 0.020, 0.030, 0.060, 0.101, 0.151, 0.251, 0.350.

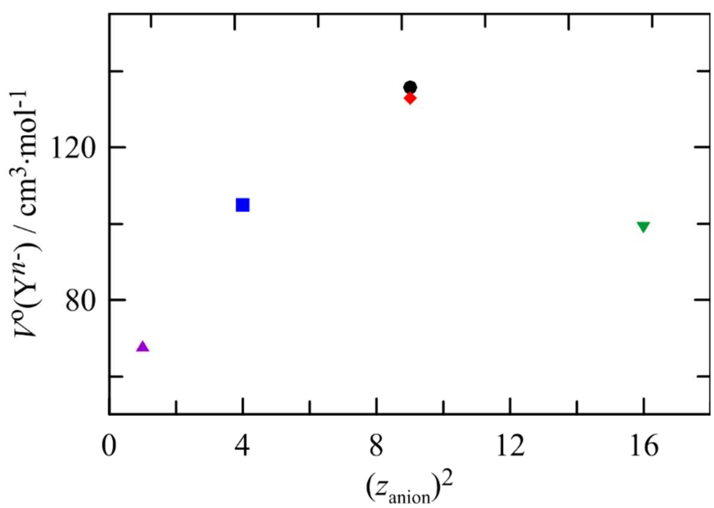

Figure S7. Standard molar volumes of cyanometallate anions, $V^o(Y^{n-})$, at T = 298.15 K as a function of the square of the anion charge, z^2_{anion} : violet ▲ - $Ag(CN)_2^-$; blue ■ - $Ni(CN)_4^{2-}$; red ◆ - $Co(CN)_6^{3-}$; black ● - $Fe(CN)_6^{3-}$; green ▼ - $Fe(CN)_6^{4-}$.

References

(1) Kianinia, Y.; Hnedkovsky L.; Senanayake, G.; Akilan, C.; Khalesi, M. R.; Abdollahy, M.; Darban, A. K.; Hefter, G. Heat capacities of aqueous solutions of $K_4Fe(CN)_6$, $K_3Fe(CN)_6$,

$K_3Co(CN)_6$, $K_2Ni(CN)_4$, and $KAg(CN)_2$ at 298.15 K. *J. Chem. Eng. Data* **2018**, *63*, 1773-1739.

(2) Conway, B. E. The evaluation and use of properties of individual ions in solution. *J. Solution Chem.*, **1978**, *7*, 721-770.