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Solubility of Potassium Cyanide in Mixed Aqueous and Non-aqueous Media; Gibbs Free Energies of Transfer of the Cyanide Ion

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Solubilities of potassium cyanide in a variety of non-aqueous solvents and binary aqueous solvent mixtures are reported. From these results and from published data on Gibbs free energies of transfer of the potassium ion, Gibbs free energies have been estimated for transfer of the cyanide ion from water into a selection of mixed aqueous and non-aqueous media. With the aid of these transfer parameters, reactivity trends for the reaction of the $[Fe(bipy)_3]^{2+}$ cation (bipy = 2,2′-bipyridyl) with cyanide ion in mixed aqueous solvents are analysed for initial-state and transition-state contributions.

THERE is little information published on the solubilities of cyanides in aqueous, mixed aqueous, or non-aqueous media. Potassium cyanide is freely soluble in water, soluble in glycerol, and sparingly soluble in methanol and in ethanol.[1] The solubility of potassium cyanide in water is known at 298.2 K (and at other temperatures),[2] but published solubility data for methanol,[3] ethanol,[3] and glycerol [4] refer to the somewhat lower temperatures 292.7 or 288.7 K. We have therefore measured solubilities of potassium cyanide in several non-aqueous solvents and in several ranges of binary aqueous mixtures at 298.2 K. In this paper we describe the observed solubility trends for this salt, estimate Gibbs free energies of transfer for the cyanide ion, and compare trends with those for other anions, particularly the chloride ion. We also consider the relevance of these results to our earlier analysis of kinetic studies involving cyanide ion in binary aqueous solvent mixtures.

EXPERIMENTAL

Potassium cyanide was AnalaR material (B.D.H.), and was used as supplied. Several batches of material were used in the course of this investigation; all gave solubility results consistent with each other. Organic solvents were purified by published methods.[5] Binary aqueous solvent mixtures were made up, by volume before mixing or by weight as specified below, using deionised water.

Saturated solutions were generated by stirring or agitating the respective solvents or solvent mixtures with a large excess of potassium cyanide in sealed thermostatted vessels. Aliquots were removed at intervals for analysis, until it was evident that equilibrium had been attained. Samples were appropriately diluted as soon as they had been obtained, and analysed for potassium and/or cyanide ions. Potassium analysis was carried out using an EEL flame photometer, calibrated over the whole concentration range used (the calibration is non-linear) against standard solutions made up from AnalaR potassium sulphate. Cyanide analysis was performed by titration against standard silver nitrate solution.[6]

RESULTS AND DISCUSSION

Solubilities of potassium cyanide in a range of non-aqueous solvents and binary aqueous mixtures, in all cases at 298.2 K, are reported in Table 1. No direct checks with previously published values are possible, since other data are either in weight units, inconvertible in the absence of density data, or at somewhat different temperatures (see above). However our results compare satisfactorily, in a qualitative sense, with these values.

Solubility of Potassium Cyanide.—The solubility of potassium cyanide decreases as the proportion of organic co-solvent increases (Table 1), which is the normal and expected behaviour for a salt consisting of simple, predominantly hydrophilic, ions. Some solubility trends are illustrated in Figure 1. The shapes of the curves indicate preferential solvation by water, but of course do not indicate whether this may be attributed to favourable hydration of the K^+, the CN^-, or both ions. Acetone–dimethylformamide (curves 5 and 4 in Figure 1) comparisons suggest stronger preferential solvation by water in mixtures containing the former co-solvent than in those containing the latter. The overall solubility pattern for potassium cyanide bears a close resemblance to that for potassium chloride, although for the three co-solvents methanol, ethanol, and dioxan, stronger preferential hydration for potassium cyanide, *i.e.* for cyanide in comparison with chloride, is indicated.

TABLE 1

Solubilities of potassium cyanide, in g dm^{-3}, in binary aqueous solvent mixtures [a] at 298.2 K

	% v/v co-solvent											
	5	10	20	30	40	50	60	70	80	90	95	100
Methanol		810	760	700	600	450	340	230	110	51		21
Ethanol		740	640	580	460	350	273	180	99	24		8.4
t-Butyl alcohol	794	700	*b*	*b*	*b*	*b*	*b*	*b*	*b*	*b*	13	0.1
Ethylene glycol				520		350		235				180
Acetone			700	580		360		100	5.8	1.9		0.03
Dioxan		750		580	490	*b*	*b*	*b*	*b*	7.2		0.9
Formamide			720		540		420		310			250
Dimethylformamide			612		310		180		44			4.0
Dimethyl sulphoxide		820	730	550	400	300	210	110	64	34		7.8
Acetonitrile		814	740	540	*b*	*b*	*b*	*b*	*b*			0.15
Propylene carbonate												0.24

	% w/w co-solvent									
	10	20	22	30	33.3	40	45	50	60	80
Methanol	780	720		610		540				
Glycerol		680			550			420	340	260
Ethylene carbonate			440		320		300			

[a] Solubility in water 845 g dm^{-3} at 298.2 K. [b] Phase separation occurs at these solvent compositions.

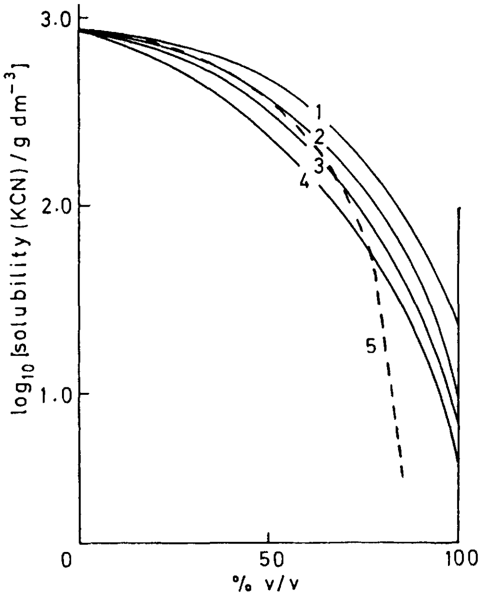

FIGURE 1 Variation of the solubility of potassium cyanide with solvent composition for binary aqueous solvent mixtures. Co-solvents: (1) methanol; (2) ethanol; (3) dimethyl sulphoxide; (4) dimethylformamide; (5) acetone

Cyanide Transfer Parameters.—The main purpose of this paper is to present estimates for the Gibbs free energy of transfer of cyanide ion, $\delta_m\mu^\ominus(CN^-)$, from water into non-aqueous and into mixed aqueous solvents. The first stage in estimating $\delta_m\mu^\ominus(CN^-)$ is the estimation of $\delta_m\mu^\ominus(KCN)$ from our solubility results. The solubilities of this 1 : 1 electrolyte in water, S_w, and in a mixed aqueous or non-aqueous solvent, S_x, are related by the difference in standard-state chemical potential, $\delta_m\mu^\ominus$(KCN), by equation (1). In this equation $\gamma_\pm$ represents the mean ionic activity coefficient of the salt in either aqueous solution [$\gamma_\pm$(w)] or in the mixture of mol fraction x_2 [$\gamma_\pm$(x)]. We have approached the analysis of our solubility results in a number of ways. If it is assumed

$$\delta_m\mu^\ominus(KCN) = 2RT\ln[S_w\gamma_\pm(w)/S_x\gamma_\pm(x)] \qquad (1)$$

that $\gamma_\pm(w)/\gamma_\pm(x)$ is approximately unity, then an indication of the sign and magnitude of $\delta_m\mu^\ominus$(KCN) is obtained directly from the solubilities of Table 1. It is noteworthy that the above approximation does not imply that the solutions are ideal, but merely that the ratio of activity coefficients is unity. However this may not be a justifiable assumption in view of the striking changes in solubility and in solvent permittivity. Consequently we have examined the impact on the calculated transfer coefficients of using various theoretical equations to calculate $\gamma_\pm$ values. One approach was to use the Debye–Hückel limiting law,[7] but this was rejected on the grounds that the concentrations were well outside the range over which this law is valid. Therefore we used either the full Debye–Hückel equation setting *a*, the distance of closest approach, equal to the sum of the ionic radii,* or the Güntelberg equation.[7] The three values of $\delta_m\mu^\ominus$(KCN) calculated in this way are compared for some of the systems in Table 2. A similar approach to the analysis of solubility data is described by Parker and co-workers [8] who used the Davies equation.[9] However we found that this particular equation produced in many cases $\delta_m\mu^\ominus$ values which were strikingly different and often unrealistic compared to the three methods discerned above. Consequently we did not explore this approach any further.

A comparison of the three values of $\delta_m\mu^\ominus$(KCN) for transfer to a series of pure solvents (Table 2) shows that the assumption $\gamma_\pm(w)/\gamma_\pm(x) = 1.0$ is reasonable. Thus the order of solvents based on the magnitude of $\delta_m\mu^\ominus$ is hardly affected. Moreover comparison of these quanti-

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* This approach has very recently been used in estimating transfer activity coefficients for ions from solubility data for potassium and tetraphenylarsonium picrates and potassium tetraphenylborate (C. Tissier, *Compt. rend.*, 1978, **C286**, 35).

ties for transfer between pure solvents represents the ' worst ' case. For transfer between solutions in water and solutions in water-rich mixtures there is less disagreement between the three values for $\delta_{\rm m}\mu^{\ominus}$(KCN). Finally we note that these differences are much smaller than the uncertainties arising from the various assumptions used in establishing single-ion parameters (see below).

Having obtained values for $\delta_{\rm m}\mu^{\ominus}$(KCN) it is now necessary to assume values for $\delta_{\rm m}\mu^{\ominus}(K^+)$ in order to obtain values for $\delta_{\rm m}\mu^{\ominus}(CN^-)$ [equation (2)]. Several sets

$$\delta_{\rm m}\mu^{\ominus}(KCN) = \delta_{\rm m}\mu^{\ominus}(K^+) + \delta_{\rm m}\mu^{\ominus}(CN^-) \qquad (2)$$

of $\delta_{\rm m}\mu^{\ominus}(K^+)$ values exist, for non-aqueous and for mixed aqueous media. They are based on a variety of assumptions and, unhappily, values for a given medium depend markedly on the assumptions involved. Two main approaches to the obtaining of single-ion $\delta_{\rm m}\mu^{\ominus}$ values are relevant here. One type of approach is based on a consideration of the molecular interactions of the ion with solvent molecules coupled with a Born treatment; the other type depends on assuming that the Gibbs free energy of transfer of a given large cation and of a given large anion (often $AsPh_4^+$ and BPh_4^-) are equal. Wells [10] has used the first approach to estimate $\delta_{\rm m}\mu^{\ominus}(K^+)$ in a variety of water-rich binary mixtures, of which those with co-solvents methanol, t-butyl alcohol, ethylene glycol, glycerol, acetone, and dioxan are relevant here. A different aspect of the first approach has been employed by de Ligny and colleagues for $\delta_{\rm m}\mu^{\ominus}(K^+)$ values in non-aqueous and in mixed solvents, *e.g.* with the organic (co-)solvents methanol,[11] ethanol,[12] acetone,[13] and dioxan.[14] The assumption that $\delta_{\rm m}\mu^{\ominus}(AsPh_4^+) = \delta_{\rm m}\mu^{\ominus}(BPh_4^-)$, currently in favour,[15] has been used for an extensive set of single-ion values in non-aqueous solvents,[16] and for dimethyl sulphoxide–water [17] and acetonitrile–water [17] mixtures. The similar assumption that $\delta_{\rm m}\mu^{\ominus}[NBu(i\text{-}C_5H_{11})_3^+] = \delta_{\rm m}\mu^{\ominus}(BPh_4^-)$ has been used for ethanol–water mixtures,[18] while a related assumption that $\delta_{\rm m}\mu^{\ominus}(NMe_4^+) = 0$ has also been employed [19] to obtain single-ion values for transfer into several non-aqueous solvents. Values for $\delta_{\rm m}\mu^{\ominus}$(ions) in dimethyl sulphoxide–water mixtures have also been obtained [20] from e.m.f. measurements of the autoprotolysis constant for water *via* the electrostatic model calculation method for H^+ of Feakins and Watson.[21] We shall be making use of each of the assumptions and derived $\delta_{\rm m}\mu^{\ominus}(K^+)$ values; often it has proved necessary to interpolate from published values, and sometimes to convert units, for example, from the mol fraction into the molarity scale.[9]

TABLE 2

Gibbs free energies of transfer of potassium cyanide, $\delta_{\rm m}\mu^{\ominus}$ (KCN), from water into non-aqueous solvents at 298.2 K (molar scale), calculated from measured solubilities: for potassium ion, $\delta_{\rm m}\mu^{\ominus}(K^+)$ was assumed as indicated; for cyanide ion, $\delta_{\rm m}\mu^{\ominus}(CN^-)$ was calculated from the foregoing

		$\delta_{\rm m}\mu^{\ominus}$/kJ mol^{-1}								
		K[CN]			de Ligny [b,e]		Cox [b,f]		Abraham [b,g]	
Solvent	*AN* [a]	*b*	*c*	*d*	K^+	CN^-	K^+	CN^-	K^+	CN^-
Methanol	41.3	18.6	20.3	21.6	4.9	13.8	10.0	8.6	2.7	15.9
Ethanol	37.1	22.9	25.7	27.2	13.4	9.5	15.7 [h]	7.2 [h]	4.2	18.8
Acetone	12.5	51.0	47.2	47.1	−15.2	66.2	2.9	48.0	9.6	41.4
Dimethyl sulphoxide	19.3	23.2	21.8	21.9			−12.1	35.3	−6.7	29.9
Dimethylformamide	16.0	26.5	25.4	25.6			−9.6	36.1	−2.1	28.6
Formamide	39.8	6.0	4.1	3.8			−6.3	12.3		
Acetonitrile	18.9	42.8	39.2	39.1			8.0	34.9	10.0	32.8
Propylene carbonate		40.5					3.4	36.1		

[a] *AN* = Acceptor number, see ref. 25. [b] Derived assuming $\gamma_{\pm}(w)/\gamma_{\pm}(x) = 1.0$. [c] $\gamma_{\pm}$ Quantities calculated using the Debye–Hückel equation. [d] $\gamma_{\pm}$ Quantities calculated using the Güntelberg equation. [e] Refs. 11—13. [f] Ref. 16. [g] Ref. 19. [h] Derived *via* the assumption of Popovych and Dill.[18]

Cyanide Transfer to Pure Solvents.—Table 2 shows our estimated values of $\delta_{\rm m}\mu^{\ominus}$(KCN) from water into non-aqueous solvents, the various available estimates of $\delta_{\rm m}\mu^{\ominus}(K^+)$, and our thence-derived values for $\delta_{\rm m}\mu^{\ominus}(CN^-)$. Agreement between $\delta_{\rm m}\mu^{\ominus}(K^+)$ values derived by different routes is not good;[22] obviously our $\delta_{\rm m}\mu^{\ominus}(CN^-)$ values reflect this. The negative values for $\delta_{\rm m}\mu^{\ominus}(K^+)$ for transfer to dioxan and to acetone obtained by the treatment of the de Ligny school are particularly unattractive,[13,14] and we therefore discount the $\delta_{\rm m}\mu^{\ominus}(CN^-)$ values derived therefrom. There is still an uncomfortable measure of disagreement between the $\delta_{\rm m}\mu^{\ominus}(K^+)$, and thus $\delta_{\rm m}\mu^{\ominus}(CN^-)$, values obtained by the ' large-ion ' methods. The assumption of Cox and Parker that $\delta_{\rm m}\mu^{\ominus}(AsPh_4^+) = \delta_{\rm m}\mu^{\ominus}(BPh_4^-)$,[16,23] and the related assumption of Popovych and Dill [18] that $\delta_{\rm m}\mu^{\ominus}[NBu(i\text{-}C_5H_{11})_3^+] = \delta_{\rm m}\mu^{\ominus}(BPh_4^-)$, seem slightly more attractive than that of $\delta_{\rm m}\mu^{\ominus}(NMe_4^+) = 0$.[19] In practice the first-named assumption is of widest use; values derived using this assumption are available for several mixed solvents (see below) as well as for non-aqueous solvents.

Values of $\delta_{\rm m}\mu^{\ominus}(CN^-)$ for transfer of cyanide from water into non-aqueous solvents show some degree of correlation with certain empirical solvent parameters.[24] The most satisfactory correlation is that between $\delta_{\rm m}\mu^{\ominus}(CN^-)$ values derived by Cox's method [16] and Gutmann's acceptor numbers, *AN*;[25] the standard error of such a plot is 8%.

Cyanide Transfer to Mixed Aqueous Solvents.—Table 3 collects together our estimates for $\delta_{\rm m}\mu^{\ominus}(CN^-)$ from water into binary aqueous mixtures, with the sources of $\delta_{\rm m}\mu^{\ominus}(K^+)$ indicated in each case. Again the choice of assumptions used in the single-ion split has a disturb-

TABLE 3

Gibbs free energies of transfer of potassium cyanide (calculated from measured solubilities), potassium ion (assumed as indicated), and cyanide ion (calculated from the foregoing) from water into binary aqueous mixtures at 298.2 K, molar scale. The assumptions used are indicated at the head of each column of single-ion values for each co-solvent; column I entries are all based on Wells's Born-derived model, column II top four entries are differently Born-derived, and column III entries are based on various large-ion splitting assumptions

			$\delta_m\mu^\ominus$/kJ mol^{-1}						
				I		II		III	
Co-solvent	%[a] v/v	x_2	KCN	K^+	CN^-	K^+	CN^-	K^+	CN^-
				Wells [b]		de Ligny [c]			
Methanol	10	0.047	0.21	0.5	−0.3	−0.1	0.3		
	10w	0.059	0.38	0.7	−0.3	−0.2	0.6		
	20	0.100	0.52	0.9	−0.4	−0.3	0.8		
	20w	0.123	0.79	1.1	−0.3	−0.5	1.3		
	30	0.160	0.95	1.3	−0.4	−0.7	1.6		
	30w	0.194	1.61	1.4	−0.2	−0.9	2.5		
	40	0.229	1.70	1.6	0.1	−1.2	2.9		
	40w	0.273	2.22	1.6	0.6	−1.8	4.1		
	50	0.31	3.13	1.4	1.7	−2.2	5.3		
	60	0.34	4.5			−2.4	6.9		
	70	0.41	6.5			−2.9	9.4		
	80	0.49	10.4			−3.5	13.9		
	90	0.58	14.0			−4.2	18.2		
						de Ligny [d]		Popovych [e]	
Ethanol	10	0.033	0.67					0.5	0.2
	20	0.072	1.38					0.4	1.0
	30	0.117	1.90			1.3	0.6	0.4	1.5
	50	0.235	4.4			3.6	0.7	0.5	3.9
	70	0.42	7.7			5.5	2.2	3.4	4.2
	80	0.55	10.7					5.6	5.0
	90	0.73	17.7					9.5	8.2
t-Butyl alcohol	5	0.009	0.30	−0.4	0.7				
	10	0.021	0.86	−1.4	2.3				
Ethylene glycol	30	0.15	2.4	0.1	2.3				
	50	0.24	4.4	1.5	2.9				
	70	0.43	6.4	1.2	5.2				
Glycerol	20w	0.047	1.05	0.5	0.5				
	33.3w	0.089	2.15	0.7	1.5				
	50w	0.164	3.50	1.0[f]	2.5				
	60w	0.227	4.63	1.2	3.4				
						de Ligny [g]			
Acetone	20	0.058	0.92	−3.9	4.8	−1.0	1.9		
	30	0.095	1.90	−5.2	7.1	−1.8	3.7		
	50	0.196	4.2	*ca.* −9	*ca.* 13	−4.0	8.2		
	70	0.36	10.4			−7.9	18.3		
	80	0.49	13.3			−10.3	23.6		
	90	0.69	19.0			−13.1	32.1		
						de Ligny [h]			
Dioxan	10	0.023	0.59	−1.8	2.4	−0.4	1.0		
	30	0.083	1.86	−4.1	6.0	−1.3	3.2		
	40	0.123	2.72	−4.7	7.4	−1.9	4.6		
	90	0.65	23.7	*ca.* 7	*ca.* 17				
						Das and Kundu [i]		Cox [j]	
Dimethyl sulphoxide	10	0.027	0.12			−5.0	5.1	−0.1	0.2
	20	0.060	0.80			−10.9	11.7	−0.3	1.1
	30	0.098	2.1					−0.8	2.9
	40	0.144	3.8			−30.1	33.9	−1.5	5.3
	50	0.202	5.1					−2.0	7.1
	60	0.276	7.0			−60.1	67.1	−3.3	10.3
	70	0.37	10.1					−5.3	15.4
	80	0.50	12.8					−7.3	20.1
	90	0.70	15.9					−9.6	25.5
Acetonitrile	20	0.079	0.68					−0.1	0.8
	30	0.129	2.28					−0.3	2.6

[a] w = Weight percent. [b] Ref. 10. [c] Ref. 11. [d] Ref. 12. [e] Ref. 18. [f] An alternative value of $\delta_m\mu^\ominus(K^+)$ = 0.3 kJ mol^{-1} gives $\delta_m\mu^\ominus(CN^-)$ = 3.2 kJ mol^{-1}. [g] Ref. 13. [h] Ref. 14. [i] Ref. 20. [j] Ref. 17.

ingly large effect. Cyanide normally becomes destabilised as more organic co-solvent is added, but the extent of destabilisation appears markedly different depending on the provenance of the $\delta_m\mu^\ominus(K^+)$ values used. Such differences may be most dramatically illustrated by the case of dimethyl sulphoxide–water mixtures, where Das and Kundu [20] calculate $\delta_m\mu^\ominus(K^+) = -60$ kJ mol^{-1} for transfer from water into 60% dimethyl sulphoxide, whereas Cox *et al.*[17] propose $\delta_m\mu^\ominus(K^+) = -3.3$ kJ mol^{-1} for the same transfer.

TABLE 4

Comparison of $\delta_m\mu^\ominus$(anion) values for anions for transfer from water into aqueous methanol. All values obtained by the use of Wells's values for $\delta_m\mu^\ominus(K^+)$; all on the molar scale, at 298.2 K

Methanol (% v/v)	$\delta_m\mu^\ominus$(anion)/kJ mol^{-1}			
	CN^-	Cl^-	SO_4^{2-}	$S_2O_8^{2-}$
10	−0.3	0.9	4	2
20	−0.4	2.1	9	4
30	−0.4	3.6	13	5
40	0.1		17	9
Source	*a*	*b*	*c*	*d*

[a] This work. [b] From refs. 31 and 32. [c] Estimated from the solubilities of potassium sulphate reported by G. Åkerlöf and H. E. Turck, *J. Amer. Chem. Soc.*, 1935, **57**, 1746. [d] From solubilities of potassium peroxodisulphate (M. J. Blandamer, J. Burgess, and R. I. Haines, *J. Inorg. Nuclear Chem.*, 1979, **41**, 258.

In order to compare $\delta_m\mu^\ominus(CN^-)$ values with analogous parameters for other anions, we have collected together in Table 4 sets of values derived using Wells's method in all cases. They can thus be compared fairly. Table 4 brings out clearly the similarity between cyanide ion and the similar size uninegative chloride ion, and the differences between these and dinegative anions such as sulphate and peroxodisulphate. However a more detailed comparison between the similar but by no means identical cyanide and chloride ions is given in Table 5, in the form of differences between $\delta_m\mu^\ominus(CN^-)$ and $\delta_m\mu^\ominus(Cl^-)$ derived from solubilities of potassium cyanide and of potassium chloride [and thus independent of assumptions made about $\delta_m\mu^\ominus(K^+)$ values]. The intimations of different preferential solvation characteristics in the potassium cyanide–potassium chloride solubility comparisons above are confirmed and amplified by these numbers.

TABLE 5

Differences, Δ, between the Gibbs free energies of transfer of cyanide and of chloride from water into selected binary aqueous solvent mixtures [$\Delta = \delta_m\mu^\ominus(Cl^-) - \delta_m\mu^\ominus(CN^-)$].[a] Values of Δ are in kJ mol^{-1}, on the molar scale, at 298.2 K

	% Co-solvent [b]								
	10	20	30	40	50	60	70	80	90
Methanol	1.5	2.0	3.0	4.0	4.5	5.3	6.4	5.0	3.7
Ethanol	0.7	1.4	2.4	3.0	3.6	4.4	5.3	6.8	5.2
Glycerol		−0.2			−1.1	−1.1		−1.1	

[a] $\Delta = \delta_m\mu^\ominus(KCl) - \delta_m\mu^\ominus(KCN)$, with $\delta_m\mu^\ominus(KCl)$ values calculated from published solubility data and $\delta_m\mu^\ominus(KCN)$ values derived as in the text. [b] Percentages by volume before mixing for methanol and ethanol, by weight for glycerol.

Initial-state and Transition-state Solvation.—We and others have recently attempted to separate solvent effects on reactivity for inorganic reactions into initial-state and transition-state components.[26-29] Such treatment of reactions with cyanide ions [30-33] has been hampered by a lack of knowledge of $\delta_m\mu^\ominus(CN^-)$ values. Our earlier analysis on the intuitively reasonable basis [34] of equivalence of $\delta_m\mu^\ominus(CN^-)$ and $\delta_m\mu^\ominus(Cl^-)$ is now superseded.

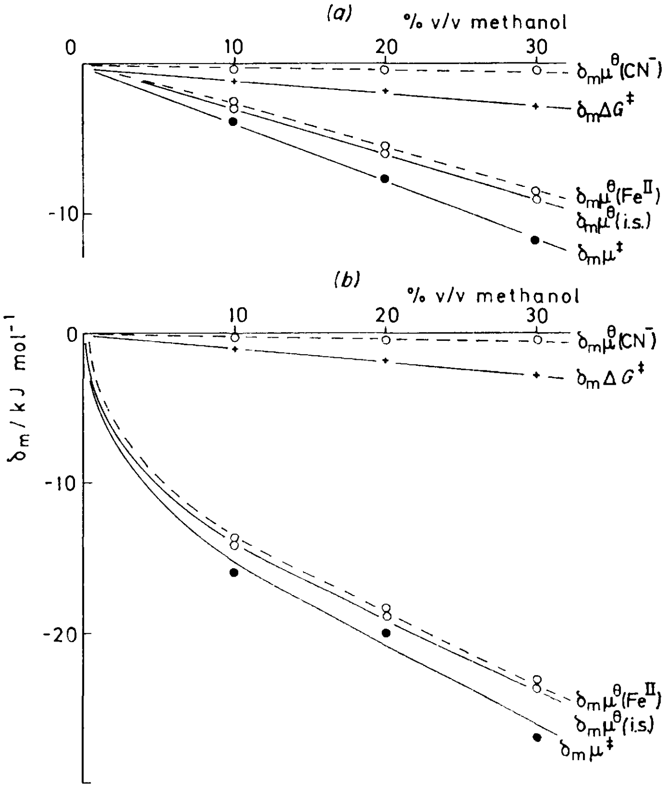

FIGURE 2 Analysis of solvent effects on reactivity separated into initial-state (i.s.) and transition-state contributions for the reaction of the $[Fe(bipy)_3]^{2+}$ cation with cyanide ion; — — ○ — — individual reactants, —— ○ —— initial state, —— + —— Gibbs free energy of activation, —— ● —— transition state

TABLE 6

Derivation of estimates for $\delta_m\mu^\ominus[Fe(bipy)_3{}^{2+}]$ from water into aqueous methanol from measurements of solubilities of its tetraphenylborate

Methanol (% v/v)	$\delta_m\mu^\ominus$(species)/kJ mol^{-1}		
	$[Fe(bipy)_3][BPh_4]_2$ [a]	$[BPh_4]^-$ [b]	$[Fe(bipy)_3]^{2+}$
10	−19.1	−2.7	−13.7
20	−25.9	−3.8	−18.3
30	−36.0	−6.4	−23.2
40	−40.4	−7.5	−25.4

[a] From measured solubilities, estimated *via* spectrophotometric determination of cation concentration. [b] *Via* solubilities of the caesium salt (R. I. Haines, Ph.D. Thesis, University of Leicester, 1977).

Reaction of $[Fe(bipy)_3]^{2+}$ (bipy = 2,2′-*Bipyridyl*) *with Cyanide.*—Figure 2 shows an analysis of solvent effects on this reaction for methanol–water mixtures using our present $\delta_m\mu^\ominus(CN^-)$ values.[31,32] The two parts of Figure 2 use two different sets of estimates for $\delta_m\mu^\ominus[Fe(bipy)_3{}^{2+}]$: graph (*a*) uses van Meter's and Neumann's [35] values and graph (*b*) uses our values for the iron complex derived from solubilities of its tetraphenylborate salt (ref. 36 and Table 6). Despite the obvious differences, the overall conclusion is that solvation changes around the $[Fe(bipy)_3]^{2+}$ moiety dominate, both in the initial and in the transition state, at least in water-rich mixtures. The same conclusion may be reached for acetone–water mixtures, the only other series for which such an analysis is possible.

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REFERENCES

[1] CRC Handbook of Chemistry and Physics, 58th edn., ed. R. C. Weast, CRC Press, Cleveland, Ohio, 1977, p. B144.

[2] H. Bassett and A. S. Corbet, *J. Chem. Soc.*, 1924, 1660; A. S. Corbet, *ibid.*, 1926, 3190.

[3] C. A. L. de Bruyn, *Z. phys. Chem.*, 1892, **10**, 782; *Rec. Trav. chim.*, 1892, **11**, 112.

[4] A. M. Ossendowski, *Pharm. J.* (*London*), 1907, **79**, 575; *J. Pharm. Chim.*, 1907, **26**, 162.

[5] A. J. Gordon and R. A. Ford, 'The Chemist's Companion,' Wiley, New York, 1972.

[6] A. I. Vogel, 'Quantitative Inorganic Analysis,' 2nd edn., Longmans, London, 1951, p. 263.

[7] See, for example, R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' 2nd edn. (revised), Butterworths, London, 1965, ch. 9.

[8] A. J. Parker and W. E. Waghorne, *Austral. J. Chem.*, 1978, **31**, 1181; R. Alexander, A. J. Parker, J. H. Sharp, and W. E. Waghorne, *J. Amer. Chem. Soc.*, 1972, **94**, 1148.

[9] C. W. Davies, 'Ion Association,' Butterworths, London, 1962, p. 39.

[10] C. F. Wells, *J.C.S. Faraday I*, 1973, 984; 1974, 694; 1975, 1868; 1976, 601; 1978, 1569.

[11] C. L. de Ligny and M. Alfenaar, *Rec. Trav. chim.*, 1965, **84**, 81; M. Alfenaar and C. L. de Ligny, *ibid.*, 1967, **86**, 929; D. Bax, C. L. de Ligny, and M. Alfenaar, *ibid.*, 1972, **91**, 452.

[12] D. Bax, C. L. de Ligny, and A. G. Remijnse, *Rec. Trav. chim.*, 1972, **91**, 965.

[13] C. L. de Ligny, D. Bax, M. Alfenaar, and M. G. L. Elferink, *Rev. Trav. chim.*, 1969, **88**, 1183; D. Bax, M. Alfenaar, and C. L. de Ligny, *ibid.*, 1971, **90**, 1002; D. Bax, C. L. de Ligny, and A. G. Remijnse, *ibid.*, 1972, **91**, 1225.

[14] D. Bax, C. L. de Ligny, and A. G. Remijnse, *Rec. Trav. chim.*, 1973, **92**, 374.

[15] H. J. M. Nedermeijer-Denessen, C. L. de Ligny, and A. G. Remijnse, *J. Electroanalyt. Chem.*, 1977, **77**, 153; C. Treiner, *Canad. J. Chem.*, 1977, **55**, 682; J. I. Kim, *J. Phys. Chem.*, 1978, **82**, 191.

[16] B. G. Cox, *Ann. Reports* (*A*), 1974, p. 249.

[17] B. G. Cox, R. Natarajan, and W. E. Waghorne, *J.C.S. Faraday I*, 1979, 86; *ibid.*, submitted for publication.

[18] O. Popovych and A. J. Dill, *Analyt. Chem.*, 1969, **41**, 456.

[19] M. H. Abraham, *J.C.S. Faraday I*, 1973, 1375.

[20] A. K. Das and K. K. Kundu, *J.C.S. Faraday I*, 1973, 730; K. H. Khoo, *J. Chem. Soc.* (*A*), 1971, 2932; *J. Chem. Soc.* (*B*), 1971, 1178.

[21] D. Feakins and P. Watson, *J. Chem. Soc.*, 1963, 4734.

[22] J. Burgess, 'Metal Ions in Solution,' Ellis Horwood, Chichester, 1978, ch. 6.

[23] B. G. Cox, G. W. Hedwig, A. J. Parker, and D. W. Watts, *Austral. J. Chem.*, 1974, **27**, 477.

[24] C. Reichardt, *Angew. Chem. Internat. Edn.*, 1965, **4**, 29.

[25] W. Mayer, V. Gutmann, and W. Gerger, *Monatsh.*, 1975, **106**, 1235.

[26] M. J. Blandamer and J. Burgess, *Pure Appl. Chem.*, 1979, **51**, 2037.

[27] M. H. Abraham, G. F. Johnston, J. F. C. Oliver, and J. A. Richards, *Chem. Comm.*, 1969, 930; M. H. Abraham, *J. Chem. Soc.* (*A*), 1971, 1061.

[28] M. H. Abraham, *Chem. Comm.*, 1969, 1307.

[29] M. J. Blandamer, J. Burgess, and J. G. Chambers, *J.C.S. Dalton*, 1977, 60.

[30] J. Burgess, *J.C.S. Dalton*, 1972, 1061; *Inorg. Chim. Acta*, 1971, **5**, 133.

[31] M. J. Blandamer, J. Burgess, and J. G. Chambers, *J.C.S. Dalton*, 1976, 606.

[32] M. J. Blandamer, J. Burgess, J. G. Chambers, R. I. Haines, and H. E. Marshall, *J.C.S. Dalton*, 1977, 165.

[33] M. J. Blandamer, J. Burgess, S. J. Cartwright, and M. Dupree, *J.C.S. Dalton*, 1976, 1158.

[34] N. N. Greenwood, 'Ionic Crystals, Lattice Defects and Non-Stoichiometry,' Butterworths, London, 1968, pp. 27, 35, 41.

[35] F. M. van Meter and H. M. Neumann, *J. Amer. Chem. Soc.*, 1976, **98**, 1382.

[36] M. J. Blandamer, J. Burgess, and R. I. Haines, unpublished work.