

Study on Estimating the Contribution to the Transfer Free Energies of Complex Ions. Part II. $[Fe(CN)_{2n}(bpy)_{(3-n)}]^{(2-2n)+}$ from Water to a Water–Ethanol Mixed Solvent

Takao Tarui

Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami, Kumamoto 860-8555

(Received June 4, 2001)

The solubilities of $[Fe(bpy)_3](ClO_4)_2$, $[Fe(CN)_2(bpy)_2]$, and $K_2[Fe(CN)_4(bpy)]$ in ethanl–water mixed solvents were measured at 25.0 ± 0.1 °C, and the transfer free energy of each complex from water to a water–ethanol mixed solvent was calculated. From the obtained data, the transfer free energies were split into contributions from 2,2′-bipyridine-solvent, cyano ligand-solvent interaction energies, and electrostatic energies. The ratios of the contributed energy from 2,2′-bipyridine vs transfer free energy of free(non-coordinated) 2,2′-bipyridine are almost constant at about 0.6–0.75 over the whole mole fraction range; this is similar to the case of 1,10-phenanthroline, although 2,2′-bipyridine has a single bond between two pyridine rings and the configuration of non-coordinated 2,2′-bipyridine differs markedly as compared with that of the coordinated one. The contributed energy from the cyano ligand in this work is somewhat smaller than that estimated from an iron(II)–cyano-1,10-phenanthroline mixed-ligand complex system; it is considered that the weaker selective solvation of 2,2′-bipyridine than 1,10-phenanthroline affects the contribution from the neighbouring cyano ligand. That the contribution from the electrostatic energy does not agree with the expected value from the Born equation, is attributed to the difference between the local and bulk dielectric constants resulting from the strong selective solvation of 2,2′-bipyridine by ethanol, where ε and ε_w represent the dielectric constant of a mixed solvent and water, respectively.

The Born theory[1] has provided a useful and simple method for estimating the solvation energy of ions. The dependence of the solvation energy on the ionic radius and the dielectric constant of the solvents can be well explained by the use of the Born equation. However, the calculated values of the solvation energy did not agree with the observed values quantitatively. It is considered that neglecting the dielectric saturation of the solvent by a strong electric field near the ion and also using crystallographic radii as ionic radii are the main reasons for the inconsistency. It is therefore expected that for those complexes with bulky ligands around the metal ion the strong electric field of the central ions is reduced, and thus a correction for dielectric saturation is not needed. Besides, the nonelectrostatic interaction, which is much smaller than the electrostatic interaction, is not easy to estimate for inorganic ions, and becomes appreciable between bulky ligands and solvent molecules. On the other hand, dividing the solvation free energy into electrostatic and non-electrostatic energies has been mainly carried out in pure solvents. Since there is no selective solvation in a pure solvent, the non-electrostatic energy, i.e. the contribution from ligands, is calculated by subtracting the electrostatic energy from the solvation energy. In a mixed solvent, almost the same procedure was carried out. However, when the selective solvation attributed to a ligand–solvent interaction is remarkable, it is considered that the solvent composition near to the complex becomes greatly different from that of the bulk solvent, and the dielectric constant is also changed. Thus, a calculation of the electrostatic energy using the Born equation may not be possible, unless the extent of selective solvation is estimated by another method. Thus, the transfer free energy of complexes is divided into those contributions from the electrostatic energy and ligands by using the differences in the transfer free energies of a series of complexes. In a previous paper, the $[Fe(CN)_{2n}(phen)_{(3-n)}]^{(2-2n)+}$ series was used, and the additive property of contributions was confirmed.[2]

In the present paper, the transfer free energies of $[Fe(CN)_{2n}(bpy)_{(3-n)}]^{(2-2n)+}$ from water to a water–ethanol mixed solvent, and the contributed energies from the electrostatic energy and the ligand-solvent interaction energies estimated from the transfer free energies of the series of complexes are reported.

By using 2,2′-bipyridine instead of 1,10-phenanthroline as one of the ligands, the radii of the complexes become smaller, and also the contact area of a ligand with a solvent decreases. It is expected that the contributed energies reflect the change, and provide any other information. Besides, the possibility of estimating the contributed energy from the transfer free energy of non-coordinated 2,2′-bipyridine has been tested, even if the non-coordinated 2,2′-bipyridine has a different conformation as compared with the coordinated one.

Experimental

$[Fe(bpy)_3](ClO_4)_2$, $[Fe(CN)_2(bpy)_2]\cdot 2.25H_2O$, and $K_2[Fe(CN)_4(bpy)]\cdot 2.5H_2O$ were synthsized according to cited procedures.[3] Found: C,57.36; H,4.44; N,18.10%. Calcd for $[Fe(CN)_2(bpy)_2]\cdot 2.25H_2O$: C,57.35; H,4.48; N,18.24%. The value of $2.25H_2O$ for $[Fe(CN)_2(bpy)_2]\cdot 2.25H_2O$ is abnormal crystallographically, but the calculated values for carbon atom are very sensitive to the number of crystal water as compared with those of nitrogen and

Table 1. Solubility of $[Fe(bpy)_3](ClO_4)_2$ at 25.0 ± 0.1 °C

χ_{EtOH}	Solubility	ε	$\Delta G_t(salt)$	$\Delta G_t(ClO_4^-)$	$\Delta G_t([Fe(bpy)_3]^{2+})$
	mol dm^{-3}		kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
0.0	1.94×10^{-3}	78.54	0.00	0.0	0.00
0.1	4.79×10^{-3}	65.8	−5.42	0.3	−6.02
0.2	8.14×10^{-3}	54.9	−7.61	1.4	−10.41
0.3	9.10×10^{-3}	47.8	−6.97	2.9	−12.77
0.4	7.35×10^{-3}	41.7	−4.50	3.4	−11.30
0.5	4.99×10^{-3}	36.9	−1.25	3.9	−9.05
0.6	3.17×10^{-3}	33.5	2.11	4.6	−7.09
0.7	1.58×10^{-3}	30.1	6.63	5.3	−3.97
0.8	7.31×10^{-4}	27.6	11.42	6.5	−1.58
0.9	3.26×10^{-4}	25.7	16.39	8.2	−0.01
1.0	1.26×10^{-4}	24.3	22.19	9.9	2.39

$\Delta G_t(ClO_4^-)$; from Ref. 10, estimated by interpolation.
χ_{EtOH}: mole fraction of ethanol.

hydrogen; also, because the crystal was recrystallized from water without any other solvent, the value was used as it was. However, this does not mean that the crystal which equilibrated with the solvent was necessarily such a crystal. Found: C,38.50; H,2.92; N,19.20%. Calcd for $K_2[Fe(CN)_4(bpy)]\cdot2.5H_2O$: C,38.27; H,2.98; N,19.13%.

The solubility was measured by a series of operations: the saturation at 25.0 ± 0.1 °C, filtration with a glass filter, dilution with water and a measurement of the absorbance using a Hitachi 3400 spectrophotometer. Because solutions of $[Fe(CN)_2(bpy)_2]$ and $[Fe(CN)_4(bpy)]^{2-}$ showed solvatochromism, the saturated solution was diluted at least one hundred times.

Results and Discussion

In order for the solubility studies to be meaningful, a solid in equilibrium with a saturated solution must be identical. In the case of $[Fe(bpy)_3](ClO_4)_2$, the solid in equilibrium in each solvent was anhydrous. The other crystals had some water of crystallization. In this work, the solid phase in equilibrium with each saturated solution was not identified, but as judged from the smooth curve in solubility, the crystals of $[Fe(CN)_2(bpy)_2]$ and $K_2[Fe(CN)_4(bpy)]$ showed minimum solubility at ethanol mole fractions of 0.7 and 0.9, respectively. Thus, at higher mole fractions of ethanol, the solid phases in equilibrium with saturated solutions must be changed. Hence, the results in the χ_{EtOH} range of 0.8 to 1.0 are rather suspicious; however, because in this work the change in the solid phase was neglected, caution must be needed when referring to the data in this range.

The transfer free energy for each complex, ΔG_t(complex), was calculated as follows. The ion-pair formation constants were calculated according to the simplest form of the Fuoss model;[4,5] then, from the measured solubility data, the concentration of free ions was calculated. The solubility product was calculated using the activity coefficient calculated from the Debye-Hückel formula, and the transfer free energy of the salts, ΔG_t(salt), was also calculated. Then, the transfer free energy of the counter ion calculated by interporation from reference data was subtracted. The detailed procedure is given in a previous paper.[2]

Tables 1, 2, and 3 give the measured values for the solubilities of $[Fe(bpy)_3](ClO_4)_2$, $[Fe(CN)_2(bpy)_2]$, and $K_2[Fe(CN)_4$-(bpy)] for various mole fractions of aqueous ethanol and the calculated transfer free energies.

Table 2. Solubility of $[Fe(CN)_2(bpy)_2]$ at 25.0 ± 0.1 °C

χ_{EtOH}	Solubility	$\Delta G_t([Fe(CN)_2(bpy)_2])$
	mol dm^{-3}	kJ mol^{-1}
0.0	1.34×10^{-4}	0.00
0.1	1.17×10^{-3}	−5.38
0.2	4.17×10^{-3}	−8.52
0.3	6.28×10^{-3}	−9.54
0.4	6.68×10^{-3}	−9.69
0.5	6.16×10^{-3}	−9.49
0.6	5.83×10^{-3}	−9.36
0.7	5.64×10^{-3}	−9.27
0.8	6.16×10^{-3}	−9.49
0.9	6.17×10^{-3}	−9.49
1.0	5.74×10^{-3}	−9.32

According to the Born equation, the transfer free energy of inorganic ions from water to a certain solvent is represented as

$$\Delta G_t(M^{Z+}) = Z^2e^2(1/\varepsilon - 1/\varepsilon_w)/8\pi r,$$

where Z, e, r, ε and ε_w represent the valence of the complex, unit charge, radius of the complex, and dielectric constants of the mixed solvent and water, respectively. For complex ions, a non-electrostatic interaction, which is much smaller than an electrostatic interaction, and is not easy to estimate for inorganic ions, becomes appreciable. Hence, in addition to the electrostatic term, a non-electrostatic interaction between the ligand and the solvent must be taken into account,

$$\Delta G_t(\text{complex ion}) = Z^2EL + \Sigma\Delta G_t^*(\text{ligand}),$$

where ΔG_t^*(ligand) represents the contribution from the ligand (interaction energy between a coordinated ligand and the solvent) and EL correspnds to $e^2(1/\varepsilon - 1/\varepsilon_w)/8\pi r$. The results for a least-squares calculation of the contributions from each ligand and the electrostatic energy to the transfer free energy are given in Table 4. Data for the transfer free energy of $[Fe(CN)_6]^{4-}$ was taken from a reference.[2]

Although the agreement between the observed and calculat-

Table 3. Solubility of $K_2[Fe(CN)_4(bpy)]$ at 25.0 ± 0.1 °C

χ_{EtOH}	Solubility	ΔG_t(salt)	$\Delta G_t((K^+)$	$\Delta G_t(([Fe(CN)_4(bpy)]^{2-})$
	mol dm^{-3}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
0.0	7.04×10^{-1}	0.00	0.0	0.00
0.1	3.39×10^{-1}	4.80	2.7	−0.60
0.2	1.15×10^{-1}	10.81	3.5	3.81
0.3	4.98×10^{-2}	16.06	3.7	8.66
0.4	1.51×10^{-2}	22.53	5.3	12.03
0.5	4.10×10^{-3}	29.68	7.0	15.78
0.6	1.28×10^{-3}	36.51	9.0	18.51
0.7	4.19×10^{-4}	43.44	10.8	21.84
0.8	1.45×10^{-4}	50.33	12.6	25.13
0.9	8.04×10^{-5}	54.43	14.6	25.23
1	1.19×10^{-4}	52.54	16.6	19.34

Table 4. Contributed Energies to Transfer Free Energies

χ_{EtOH}	*EL*	$\Delta G_t^*(CN^-)$	ΔG_t^*(bpy)	ΔG_t^*(bpy)/ΔG_t(bpy)	ΔG_t^*(phen)/ΔG_t(phen)
	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}		
0.1	1.39(0.26)	−0.11(0.60)	−3.63(0.59)	0.64	0.67
0.2	2.25(0.29)	0.82(0.65)	−6.22(0.64)	0.68	0.66
0.3	2.65(0.24)	1.88(0.54)	−7.58(0.53)	0.75	0.74
0.4	2.96(0.13)	2.21(0.30)	−7.59(0.30)	0.72	0.74
0.5	3.16(0.02)	2.56(0.04)	−7.24(0.04)	0.68	0.72
0.6	3.40(0.11)	2.76(0.25)	−6.99(0.25)	0.66	0.69
0.7	3.66(0.27)	2.87(0.62)	−6.44(0.60)	0.61	0.66
0.8	4.16(0.35)	3.02(0.80)	−6.38(0.78)	0.60	0.67
0.9	4.33(0.36)	2.79(0.83)	−6.09(0.81)	0.59	0.66
1	5.02(0.01)	1.28(0.02)	−5.90(0.02)	0.57	0.62

Values in parentheses are deviations calculated from least-squares method.

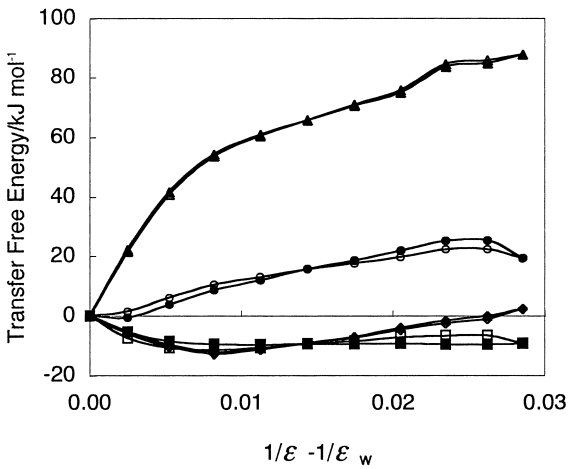

Fig. 1. Transfer free energies of complexes. ◆ $[Fe(bpy)_3]^{2+}$, ■ $[Fe(CN)_2(bpy)_2]$, ● $[Fe(CN)_4(bpy)]^{2-}$, ▲ $[Fe(CN)_6]^{4-}$. Open and closed symbols refer to estimated and observed value.

ed values is not as good as that for the case of $[Fe(CN)_{2n}(phen)_{(3-n)}]^{(2-2n)+}$, as can be seen from Fig. 1, the transfer free energies for each complex calculated as the sum of each contributed energies well reproduce the experimentally observed values; hence, it is considered that the estimated contributed energies are reliable.

1,10-phenanthroline and 2,2′-bipyridine complexes have a nonspherical, three-bladed shape,[6] and solvent molecules can enter between the propeller blades of these chelate complexes.[7] Thus, solvent molecules can solvate to coordinated 1,10-phenanthroline or 2,2′-bipyridine not only from the direction of the phenyl ring plane, but also from above and below the phenyl ring plane. This makes the value of the contribution from 1,10-phenanthroline or 2,2′-bipyridine larger than that expected from a spherical structure, and the contribution from the electrostatic solvation energy to become complex.

The non-coordinated 2,2′-bipyridine is selectively solvated by ethanol as well as 1,10-phenanthroline; as can be seen from Table 4, the ratio of the contribution vs transfer free energy of 2,2′-bipyridine, ΔG_t^*(bpy)/ΔG_t(bpy), is almost constant throughout the whole mole-fraction range. This means that the selective solvation by ethanol to a free ligand is retained when the 2,2′-bipyridine is bonded to the central metal ion. Hence, in the neighbourhood of the central metal ion coordinated by 2,2′-bipyridine, water molecules are replaced by ethanol molecules exclusively, even at a low ethanol mole fraction. Accordingly, the dielectric constant in the neighbourhood of the central metal ion is not equal to that of the bulk solvent, and is lowered locally. As a result, the values of *EL* are estimated to have positively larger values than that expected from the Born equation; also the dependence of *EL* on $(1/\varepsilon-1/\varepsilon_w)$ is not linear as well as the results from the $[Fe(CN)_{2n}(phen)_{(3-n)}]^{(2-2n)+}$ system, as can be seen from Fig. 2. For $[Fe(CN)_6]^{4-}$ without any coordinated 2,2′-bipyridine, although the above discussion cannot be applied, the transfer free energy, itself, changes in a

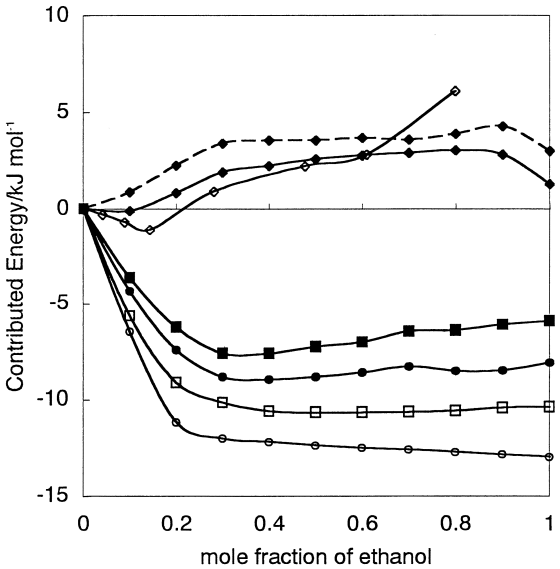

Fig. 2. Contributed energies from ligands. ● 1,10-phenanthroline, ■ 2,2′-bipyridine, ◆ CN^-.
Open and closed symbols refer to transfer free energy of free ligand and contributed energy. Broken line refers to the results from $[Fe(CN)_{2n}(phen)_{(3-n)}]^{(2-2n)+}$.

manner similar to *EL*. It is not clear if there is any common reason applicable for both complexes. The values of *EL* for the 2,2′-bipyridine system are larger than those of the 1,10-phenanthroline system. This is attributable to the smaller radius of the 2,2′-bipyridine complexes.

In Fig. 2, the contribution from 2,2′-bipyridine is negatively smaller than that from 1,10-phenanthroline as well as the transfer free energies of free ligands. This may be result from a decrease in the contact surface area of 2,2′-bipyridine with the solvent due to a lack of the third phenyl ring connected to two pyridine rings, as compared with 1,10-phenanthroline. However, the energy difference between both of the contributed energies is not as large as that expected from the decrease in the number of phenyl rings, from 3 to 2; also, the ratios, $\Delta G_t^*(\text{ligand})/\Delta G_t(\text{ligand})$, have almost the same values for both 1,10-phenanthroline and 2,2′-bipyridine.

The 1,10-phenanthroline molecule is rigid, and all phenyl rings are in the same plane regardless of whether they are coordinated or not to a metal ion; however, a non-coordinated 2,2′-bipyridine molecule has a single bond between two pyridine rings, and the two pyridine rings change angles to one another in various mole fractions of methanol.[8,9] This is attributed to a repulsion between hydrogen atoms at the 3-position. On the other hand, a coordinated 2,2′-bipyridine molecule is forced to align the nitrogen atoms in the same direction to the central metal ion, and two pyridine rings tend to arrange in the same plane. Consequently, the resonance structure or the electron distribution in the molecule is changed. It is expected that this change affects the affinity to the solvent, and that the contribution from 2,2′-bipyridine must be changed. However, the values of the ratio $\Delta G_t^*(\text{bpy})/\Delta G_t(\text{bpy})$ are almost the same as $\Delta G_t^*(\text{phen})/\Delta G_t(\text{phen})$. As can be seen from Table 4, the ratio $\Delta G_t^*(\text{bpy})/\Delta G_t(\text{bpy})$ gradually becomes smaller as χ_{EtOH} increases relative to $\Delta G_t^*(\text{phen})/\Delta G_t(\text{phen})$. This may result from the above conformation change of non-coordinated 2,2′-bipyridine.

As can be seen from Fig. 2, the contributed energy from the cyano ligand, $\Delta G_t^*(CN^-)$, calculated from the $[Fe(CN)_{2n}(bpy)_{(3-n)}]^{(2-2n)+}$ data series, shows more stable values than that from the $[Fe(CN)_{2n}(phen)_{(3-n)}]^{(2-2n)+}$ data series[7] by about 1 kJ mol^{-1}; also, the value is closer to the value of the transfer free energy of the free cyanide anion,[10] $\Delta G_t(CN^-)$. As can be seen from Fig. 2, the values of $\Delta G_t^*(\text{bpy})/\Delta G_t(\text{bpy})$ are not very different from that of $\Delta G_t^*(\text{phen})/\Delta G_t(\text{phen})$, but the absolute value of $\Delta G_t(\text{bpy})$ is somewhat smaller than that of $\Delta G_t(\text{phen})$; thus, the amount of ethanol selectively solvated to 2,2′-bipyridine, which means the local mole fraction of ethanol around the ion in the case of 2,2′-bipyridine, is smaller than in the case of 1,10-phenanthroline, and the mole fraction of water is larger. As a result, it is considered that a hydrophilic cyano ligand has a greater chance to contact with water penetrated into the 2,2′-bipyridine propellar blades, resulting in a somewhat more stable value than in the case of the 1,10-phenanthroline complex. This means that the contributed energy of each ligand must be corrected for the case of a pairing ligand and a solvent when remarkable selective solvation is observed by penetration of the solvent.

It is expected that for those complexes with bulky ligands around the metal ion a strong electric field of the central metal ions is reduced; thus a correction for dielectric saturation is not needed. However, under a condition with very strong selective solvation of the ligand, the dielectric constant in the neighbourhood of the central metal ion differs from the bulk dielectric constant in a different manner to an electrostatic interaction. As a result, it appeared that the metal complexes with 1,10-phenanthroline or 2,2′-bipyridine as ligands are not suitable for estimating the radii of complexes from the Born equation. For the Born equation to be available it is necessary that selective solvation is weak, or neglegible, and that there are no pockets between the ligands in the complexes. However, metal complexes with 1,10-phenanthroline or 2,2′-bipyridine as ligands always show selective solvation in an ethanol–water mixed solvent; accordingly, the contribution from the electrostatic energy estimated in this work is still sufficiently useful, although the values cannot be universally applicable.

References

1 M. Born, *Z. Phys.*, **1**, 45 (1920).
2 T. Tarui, *Bull. Chem. Soc. Jpn.*, **73**, 2481 (2000).
3 A. A. Schilt, *J. Am. Chem. Soc.*, **82**, 3000 (1960).
4 R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).
5 F. M. Van Meter and H. M. Neumann, *J. Am. Chem. Soc.*, **98**, 1382, 1388 (1976).
6 A. Jensen, F. Basolo, and H. M. Neumann, *J. Am. Chem. Soc.*, **80**, 2354 (1958).
7 H. Yokoyama, K. Shinozaki, S. Hattori, and F. Miyazaki, *Bull. Chem. Soc. Jpn.*, **70**, 2357 (1997).
8 S. Castellano, H. Gunther, and S. Ebersole, *J. Phys. Chem.*, **69**, 4166 (1965).
9 F. A. Kramer and R. West, *J. Phys. Chem.*, **69**, 673 (1965).
10 M. J. Blandamer, B. Briggs, John Burgess, Diane Elvidge, Pilar Guardado, Andrew W. Hakin, Stojan Radulovic, and Colin Hubbard, *J. Chem. Soc., Faraday Trans. 1*, **84**, 2703 (1988).