Study on an Estimation of the Contributed Energy to the Transfer Free Energies of Complex Ions. Part I. $[Fe(CN)_{2n}(phen)_{(3-n)}]^{(2-2n)+}$ from Water to a Water–ethanol Mixed Solvent

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The solubilities of $[Fe(phen)_3](ClO_4)_2 \cdot H_2O$, $[Fe(CN)_2(phen)_2] \cdot 0.5H_2O$, $[Fe(phen)_3][Fe(CN)_4phen] \cdot 8H_2O$, and $[Fe(phen)_3]_2[Fe(CN)_6] \cdot 3.5H_2O$ in ethanol–water mixed solvents were measured at 25.0±0.1 °C, and the transfer free energy of each complex ion from water to water–ethanol mixed solvent was calculated. From the obtained data, the transfer free energies were split into contributions from 1,10-phenanthroline–solvent, cyano ligand–solvent interaction energies, and electrostatic energies. The ratio of the contributed energy from 1,10-phenanthroline vs. transfer free energy of free (non-coordinated) 1,10-phenanthroline is almost constant at about 0.6—0.7 over the whole mole-fraction range. There is thus a possibility to estimate the contributed energy from the transfer free energy of the free ligand in the future. On the other hand, the contributed energy from the cyano ligand can not be obtained by multiplying a certain coefficient to the transfer free energy of the free cyanide ion. The contributed energy from electrostatic energy changes in a somewhat different manner, as expected by the Born equation. However, the estimated transfer free energy as the sum of each contributed energy obtained by a least-squares method is in fair agreement with the observed transfer free energy of each complex ion. It has been confirmed that the proposed conception of the contributed energy to the transfer free energy is a useful means to predict the unknown transfer free energy of complex ions.

The great significance of ion solvation and solubility in physical chemistry has challenged a great many studies. Born theory[1] has provided a useful and intuitively simple method for estimating the solvation energy of ions. The dependence of the solvation energy on the ionic radius and dielectric constant of solvents can be well explained by using 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 a solvent by a strong electric field near the ion, and also using the crystallographic radii as ionic radii are the main reasons for the inconsistency. Hence, the Born equation has been modified for the ionic radii and dielectric constant of a solvent near inorganic ions.[2] However, a determinative view as to ionic solvation, which can be the principle to modify the ionic radii and dielectric constant, has not yet been suggested.

On the other hand, it is considered that for complexes with bulky ligands around a metal ion, a strong electric field of central ions is reduced, so that a correction for dielectric saturation is not needed. Besides, the nonelectrostatic interaction, which is much smaller than the electrostatic interaction and is not easy to estimate for inorganic ions, becomes appreciable between bulky ligands and solvent molecules. In practice, the solubility of some metal complexes show the maximum value at a certain mole fraction of the organic component, rather than reducing monotonically with a decrease in the dielectric constant of the solvent. Hence, in a complex with bulky ligands, it is considered that the solvation energy can be divided into contributions from the electrostatic energy and that from the ligand–solvent interaction energy.[3] Similarly, the transfer free energy, the difference between the solvation energies in two solvents, may also be divided into the same contributed energies.

The additive property of the contributed energy to transfer free energy in complex ions makes it possible to anticipate the solubilities of complexes with various ligands in many solvents quantitatively.

In the present work, iron(II)–cyano–phenanthroline complexes were chosen as an example, and the applicability of the above-mentioned conception was tested.

Experimental

Reagents and Solvents. Ethanol was purified by distillation after a treatment with magnesium activated with iodine. Mixed solvents were made up by weight. All other chemicals were obtaind commercially and used as supplied.

Syntheses of Complexes. $[Fe(phen)_3](ClO_4)_2 \cdot H_2O$ and $[Fe(CN)_2(phen)_2] \cdot 0.5H_2O$ were synthesized according to the cited procedures.[4] Found: C, 65.57; H, 3.53; N, 17.64%. Calcd for $[Fe(CN)_2(phen)_2] \cdot 0.5H_2O$: C, 65.43; H, 3.59; N, 17.61%. $[Fe(phen)_3][Fe(CN)_4phen] \cdot 8H_2O$ was synthesised by mixing $[Fe(phen)_3]Cl_2 \cdot 7H_2O$ and $K_2[Fe(CN)_4phen] \cdot 4H_2O$ obtained from cited procedure,[4] and recrystalized from water and dried. Found: C, 57.08; H, 4.39; N, 15.35%. Calcd for [Fe(phen)₃][Fe-

$(CN)_4phen]\cdot 8H_2O$: C, 56.84; H, 4.59; N, 15.30%. $[Fe(phen)_3]_2[Fe(CN)_6]\cdot 3.5H_2O$ was synthesized from $[Fe(phen)_3]Cl_2\cdot 7H_2O$ and $K_4[Fe(CN)_6]$, then recrystallized from water and dried. Found: C, 63.84; H, 3.53; N, 17.31%. Calcd for $[Fe(phen)_3]_2[Fe(CN)_6]\cdot 3.5H_2O$: C, 63.82; H, 3.78; N, 17.17%.

Measurements. 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 $[Fe(CN)_2(phen)_2]$ and $[Fe(CN)_4phen]^{2-}$ showed solvatochromism, the saturated solution was diluted at least one hundred times.

Treatment of Data

In order for the solubility studies to be meaningful, the solid in equilibrium with the saturated solution must be identical. In the case of $[Fe(phen)_3](ClO_4)_2$, the solid in equilibrium in each solvent was anhydrous.[3] The three other crystals have 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, $[Fe(phen)_3](ClO_4)_2$ was not changed throughout the entire mole-fraction range. The other crystals ($[Fe(CN)_2(phen)_2]\cdot 0.5H_2O$, $[Fe(phen)_3][Fe(CN)_4(phen)]\cdot 8H_2O$, $[Fe(phen)_3]_2[Fe(CN)_6]\cdot 3H_2O$) showed minimum solubility at ethanol mole fraction $x_{EtOH} = 0.8$, 0.9, 0.8, respectively (see Tables 2, 3, and 4). Thus, at higher mole fractions of ethanol, the solid phases in equilibrium with saturated solutions must be changed. Hence, the results in the range of x_{EtOH} 0.8—1.0 are rather suspicious. However, the change in the solid phase may not be like the formation of nitrobenzene solvate, in which nitrobenzene is strongly attracted to $[Fe(phen)_3]^{2+}$, and even at 1.17×10^{-3} mol dm^{-3} of the nitrobenzene concentration, the nitrobenzene solvate begins to precipitate.[5] The lattice constant of the precipitate greatly differs from the original crystal,[6] resulting in a large change in the lattice energy. On the other hand, the interaction of ethanol with $[Fe(phen)_3]^{2+}$ is not as strong as nitrobenezene, and the change in the lattice energy is considered to be small. Accordingly, in this treatment of the data, the change in the solid phase is neglected.

From the solubility data in water and water-ethanol mixtures, the transfer free energies of each salt were calculated as follows. According to the simplest form of the Fuoss model,[7] the equilibrium constant for ion-pair formation is given by

$$K_{ip} = (4\pi Na^3/3000)e^b,$$

where $b = |Z^+Z^-|e^2/a\varepsilon kT$ and a is the distance of closest approach of the two ions of charge Z^+ and Z^-; ε is the dielectric constant of the solvent. When the values of K_{ip} were calculated, the value for a was taken as 5.68 Å for the $[Fe(phen)_3](ClO_4)_2$ system,[8,9] and 7.5 Å for the $[Fe(phen)_3][Fe(CN)_4phen]$ and $[Fe(phen)_3]_2[Fe(CN)_6]$ systems.[10] From the calculated values of K_{ip} and the measured solubilities, the concentrations of free ions were calculated; then the values of K_{sp} and the transfer free energy of the salts were calculated. The values of K_{sp} for each systems are listed in Tables 1, 3, and 4. The activity coefficient in each saturated solution was calculated from the Debye-Hückel formula,

$$\mathrm{Log} f = -A|Z^+Z^-|I^{1/2}/(1+BaI^{1/2}),$$

where $A = 1.8246\times 10^6/(\varepsilon T)^{3/2}$ and $B = 50.29\times 10^8/(\varepsilon T)^{1/2}$.

At first, the transfer free energy of $[Fe(phen)_3]^{2+}$ ($\Delta G_t([Fe(phen)_3]^{2+})$) from water to a mixed solvent was calculated by subtracting the transfer free energy of the perchlorate ion[11]

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

x_{EtOH}	Solubility mol dm^{-3}	$\Delta G_t([Fe(CN)_2(phen)_2])$ kJ mol^{-1}
0.0	0.0000256	0.00
0.1	0.0003376	−6.39
0.2	0.0010526	−9.21
0.3	0.0015531	−10.17
0.4	0.0015905	−10.23
0.5	0.0014703	−10.04
0.6	0.0012750	−9.68
0.7	0.0011452	−9.42
0.8	0.0009412	−8.93
0.9	0.0010654	−9.24
1.0	0.0018309	−10.58

x_{EtOH}; mole fraction of ethanol.

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

x_{EtOH}	Solubility mol dm^{-3}	ε	$1/\varepsilon - 1/\varepsilon_w$	$b(1)$	$K_{ip}(1)$ (mol dm^{-3})$^{-1}$	$b(2)$	$K_{ip}(2)$ (mol dm^{-3})$^{-1}$	K_{sp} (mol dm^{-3})^3	ΔG_t(salt) kJ mol^{-1}	$\Delta G_t(ClO_4^-)$ kJ mol^{-1}	$\Delta G_t([Fe(phen)_3]^{2+})$ kJ mol^{-1}
0	0.000826	78.54	0.0000	2.513	5.703	1.256	1.62	1.608*E*-09	0.00	0	0.00
0.1	0.00299	65.7	0.0025	3.004	9.323	1.502	2.08	4.686*E*-08	−8.36	0.3	−8.96
0.2	0.00706	55.6	0.0052	3.547	16.053	1.774	2.72	2.806*E*-07	−12.80	1.4	−15.60
0.3	0.00832	47.8	0.0082	4.129	28.710	2.064	3.64	2.455*E*-07	−12.46	2.9	−18.26
0.4	0.00732	41.7	0.0113	4.733	52.529	2.366	4.93	1.073*E*-07	−10.41	3.4	−17.21
0.5	0.00569	36.9	0.0144	5.346	96.983	2.673	6.70	3.677*E*-08	−7.76	3.9	−15.56
0.6	0.00378	33.1	0.0175	5.958	178.878	2.979	9.09	9.819*E*-09	−4.48	4.6	−13.68
0.7	0.00225	30.1	0.0205	6.562	327.160	3.281	12.30	2.255*E*-09	−0.84	5.3	−11.44
0.8	0.00144	27.6	0.0235	7.147	587.332	3.574	16.48	6.056*E*-10	2.42	6.5	−10.58
0.9	0.00082	25.7	0.0262	7.691	1011.805	3.846	21.63	1.388*E*-10	6.07	8.2	−10.33
1	0.00022	24.3	0.0285	8.146	1595.449	4.073	27.16	7.671*E*-12	13.25	9.9	−6.55

$\Delta G_t(ClO_4^-)$; from Ref. 11, estimated by interpolation. x_{EtOH}; mole fraction of ethanol.

Table 3. Solubility of $[Fe(phen)_3][Fe(CN)_4(phen)]$ at 25.0±0.1 °C

x_{EtOH}	Solubility	b	K_{ip}	K_{sp}	ΔG_t(salt)	$\Delta G_t([Fe(CN)_4(phen)]^{2-})$
	$mol\ dm^{-3}$		$(mol\ dm^{-3})^{-1}$	$(mol\ dm^{-3})^2$	$kJ\ mol^{-1}$	$kJ\ mol^{-1}$
0.0	0.000662	3.805	48	2.701E−07	0.00	0.00
0.1	0.003891	4.550	101	3.174E−06	−6.11	2.85
0.2	0.015744	5.373	229	7.355E−06	−8.19	7.42
0.3	0.014321	6.254	553	2.926E−06	−5.91	12.39
0.4	0.008552	7.169	1382	8.357E−07	−2.80	14.47
0.5	0.005050	8.098	3498	2.441E−07	0.25	15.88
0.6	0.001766	9.025	8840	4.762E−08	4.30	18.06
0.7	0.000784	9.939	22061	1.105E−08	7.92	19.42
0.8	0.000432	10.826	53522	3.085E−09	11.09	21.72
0.9	0.000265	11.649	121988	9.804E−10	13.93	24.30
1.0	0.000287	12.339	243163	5.795E−10	15.23	21.79

x_{EtOH}; mole fraction of ethanol.

Table 4. Solubility of $[Fe(phen)_3]_2[Fe(CN)_6]$ at 25.0±0.1 °C

x_{EtOH}	Solubility	$b(1)$	$K_{ip}(1)$	$b(2)$	$K_{ip}(2)$	K_{sp}	ΔG_t(salt)	$\Delta G_t([Fe(CN)_6]^{4-})$
	$mol\ dm^{-3}$		$(mol\ dm^{-3})^{-1}$		$(mol\ dm^{-3})^{-1}$	$(mol\ dm^{-3})^3$	$kJ\ mol^{-1}$	$kJ\ mol^{-1}$
0	4.51E-03	7.612	2.15.E+03	3.806	48	8.178E−10	0.00	0.00
0.1	7.53E-03	9.100	9.53.E+03	4.550	101	1.415E−10	4.35	22.27
0.2	8.39E-03	10.746	4.95.E+04	5.373	229	1.177E−11	10.51	41.73
0.3	4.69E-03	12.508	2.88.E+05	6.254	553	6.397E−13	17.73	54.32
0.4	9.86E-04	14.338	1.79.E+06	7.169	1382	1.951E−14	26.38	60.91
0.5	3.55E-04	16.195	1.15.E+07	8.098	3498	7.083E−16	34.60	65.85
0.6	1.22E-04	18.050	7.34.E+07	9.025	8840	2.259E−17	43.14	70.65
0.7	3.86E-05	19.879	4.57.E+08	9.939	22061	6.025E−19	52.12	75.12
0.8	8.43E-06	21.651	2.69.E+09	10.826	53522	9.225E−21	62.48	83.75
0.9	2.71E-05	23.299	1.40.E+10	11.649	121988	4.565E−21	64.23	84.97
1	3.46E-06	24.678	5.56.E+10	12.339	143163	6.397E−23	74.81	87.93

x_{EtOH}; mole fraction of ethanol.

from that of corresponding salts. The transfer free energies for $[Fe(CN)_4phen]^{2-}$ and $[Fe(CN)_6]^{4-}$ were obtained by subtracting $\Delta G_t([Fe(phen)_3]^{2+})$ from the values of each salt. The resulting transfer free energies of the complex ions were divided into the contributions from the electrostatic energy and each ligand–solvent interaction energy according to the following procedure.

From the Born equation, the transfer free energy of an ion is represented as

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

where ε and ε_w represent the dielectric constant of a mixed solvent and water, respectively. Hence, the change in the electrostatic energy is proportional to the valence of the ion squared:

$$\Delta G_t([Fe(phen)_3]^{2+}) = 4 \times EL + 3 \times \Delta G_t^*(\text{phen}), \quad (1)$$

$$\Delta G_t([Fe(CN)_2(phen)_2]) = 2 \times \Delta G_t^*(\text{phen}) + 2 \times \Delta G_t^*(CN^-), \quad (2)$$

$$\Delta G_t([Fe(CN)_4phen]^{2-}) = 4 \times EL + \Delta G_t^*(\text{phen}) + 4 \times \Delta G_t^*(CN^-), \quad (3)$$

$$\Delta G_t([Fe(CN)_6]^{4-}) = 16 \times EL + 6 \times \Delta G_t^*(CN^-), \quad (4)$$

where EL represents the electrostatic energy change per univalent charge (corresponding to $e^2(1/\varepsilon - 1/\varepsilon_w)/8\pi r$ in the Born equation); $\Delta G_t^*(\text{phen})$ and $\Delta G_t^*(CN^-)$ represent the contributions from phenanthroline and the cyano ligand to the transfer free energy, respectively. Strictly speaking, although the radius of four complexes may be different from each other, in this treatment the difference is neglected. The left-hand terms of the four equations are the experimentally obtained transfer free energies in this work. There are now three unknowns (EL, $\Delta G_t^*(\text{phen})$, and $\Delta G_t^*(CN^-)$) and four equations; thus, four set of solutions are obtained from each combination of the three equations.

Discussion

Tables 1, 2, 3, and 4 give the measured values for the solubilities of $[Fe(phen)_3](ClO_4)_2$, $[Fe(CN)_2(phen)_2]$, $[Fe(phen)_3][Fe(CN)_4phen]$, and $[Fe(phen)_3]_2[Fe(CN)_6]$ for various mole fractions of aqueous ethanol. The results for the calculation of the contributions from each ligands and the electrostatic energy to the transfer free energy are shown in Fig. 1. As can be seen from Fig. 1, they depend on the combination of the data series used for the calculation. The scatters for each contributed energy are the maximum at $x_{EtOH} = 0.2$ and about 0.9, 2.1, and 1.7 kJ mol^{-1} for EL, $\Delta G_t^*(\text{phen})$, and $\Delta G_t^*(CN^-)$, respectively. The esimated transfer free ener-

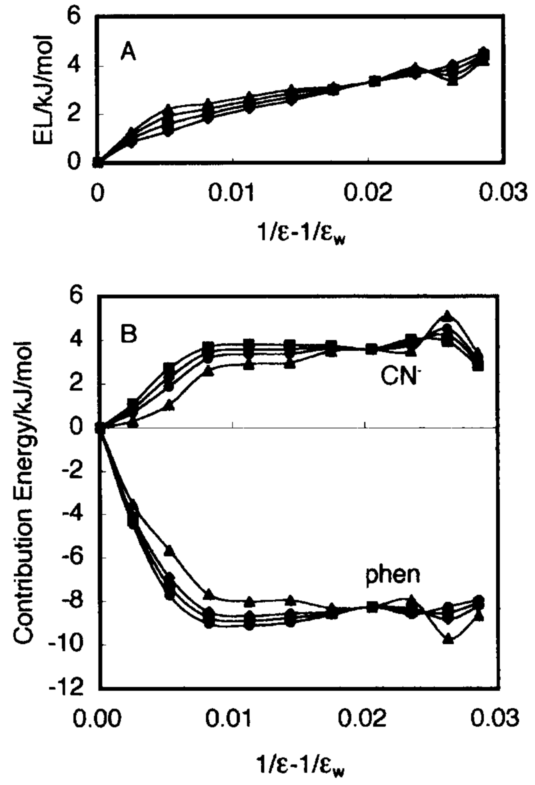

Fig. 1. Contributed energies from (A) *EL*, and (B) 1,10-phenanthroline and $\mathrm{CN^-}$ to transfer free energy. Each contributed energy was calculated from combination of three equations in text. ◆ : (1,2,3), ■ : (1,2,4), ● : (1,3,4), ▲ : (2, 3,4).

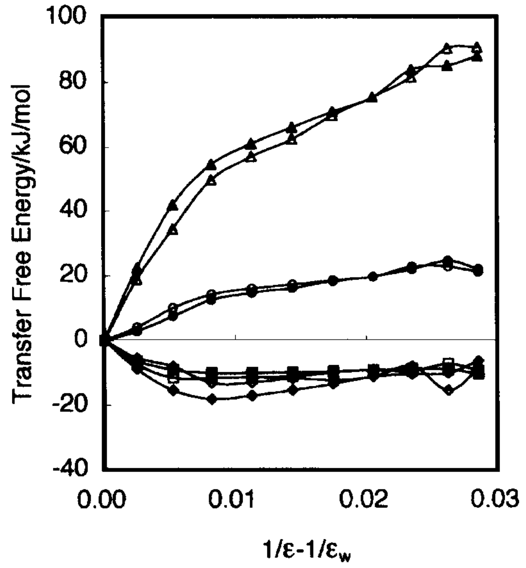

Fig. 2. Transfer free energies of complexes ◆ : $[\mathrm{Fe(phen)_3}]^{2+}$, ■ : $[\mathrm{Fe(CN)_2(phen)_2}]$, ● : $[\mathrm{Fe(CN)_4phen}]^{2-}$, ▲ : $[\mathrm{Fe(CN)_6}]^{4-}$. Open and closed symbols refer to estimated and observed value.

gies calculated from the above results are shown in Fig. 2, together with the observed data. (Each estimated value was calculated from the data series of the three residual complexes). Although each contribution energy series bears some resemblance to each other, the differences are rather large to estimate all four transfer free energies from any one of the results set within permissible errors. There are large deviations from the observed data, especially for $[\mathrm{Fe(phen)_3}]^{2+}$ and $[\mathrm{Fe(CN)_6}]^{4-}$. A small deviation in the observed transfer free energy of $[\mathrm{Fe(CN)_2(phen)_2}]$ or $[\mathrm{Fe(CN)_4phen}]^{2-}$ remarkablly affects the results. The estimated values of the transfer free energies for $[\mathrm{Fe(CN)_2(phen)_2}]$ and $[\mathrm{Fe(CN)_4phen}]^{2-}$ agreed rather well with those of the observed values. The observed and calculated values for $[\mathrm{Fe(phen)_3}]^{2+}$ are almost pararell to each other, but the observed values have more negative values than the calculated values, except for $x_{\mathrm{EtOH}} = 0.9$ and 1.0. $\Delta G_{\mathrm{t}}([\mathrm{Fe(phen)_3}]^{2+})$ is calculated from data series of complexes with fewer coordinated phenanthroline($[\mathrm{Fe(CN)_2(phen)_2}]$, $[\mathrm{Fe(CN)_4phen}]^{2-}$, and $[\mathrm{Fe(CN)_6}]^{4-}$); therefore, the errors in calculating $\Delta G_{\mathrm{t}}^*(\mathrm{phen})$ greatly affect $\Delta G_{\mathrm{t}}([\mathrm{Fe(phen)_3}]^{2+})$. In fact, the calculated $\Delta G_{\mathrm{t}}^*(\mathrm{phen})$ from equations 2, 3, and 4 are negatively smallest of the four sets of results. In a similar manner, the errors for $\Delta G_{\mathrm{t}}^*(\mathrm{CN^-})$ must greatly affect $\Delta G_{\mathrm{t}}([\mathrm{Fe(CN)_6}]^{4-})$. The observed values for $[\mathrm{Fe(CN)_6}]^{4-}$ have more positive values than the calculated values by about 5 $\mathrm{kJ\,mol^{-1}}$ in low mole fraction of ethanol range, and do not increase linearly with $(1/\varepsilon - 1/\varepsilon_{\mathrm{w}})$, contrary to a prediction of the Born equation. As can be seen from Fig. 1, the interaction energy between the cyano ligand and the solvent becomes more positive along with an increase in the mole fraction of ethanol. However, it is not linear with $(1/\varepsilon - 1/\varepsilon_{\mathrm{w}})$, and the change becomes smaller over $x_{\mathrm{EtOH}} = 0.3$. Thus, the values for $[\mathrm{Fe(CN)_6}]^{4-}$ do not increase linearly.

Thus, for all four data series, the least-squares method was applied, and *EL*, $\Delta G_{\mathrm{t}}^*(\mathrm{phen})$, and $\Delta G_{\mathrm{t}}^*(\mathrm{CN^-})$ were calculated. The obtained results are given in Table 5 and Fig. 3. Also, the calculated most probable values of the transfer free energies are given in Fig. 4. The calculated values are in fair agreement with the observed values.

The values for *EL* correspond to $e^2(1/\varepsilon - 1/\varepsilon_{\mathrm{w}})/8\pi r$ in the Born equation, and Born equation predicts that *EL* increases linearly with $(1/\varepsilon - 1/\varepsilon_{\mathrm{w}})$; however, the obtained *EL* increases rather steeply to 1.75 $\mathrm{kJ\,mol^{-1}}$ at $x_{\mathrm{EtOH}} = 0.2$, then

Table 5. Contributed Energies to Transfer Free Energies

x_{EtOH}	*EL* $\mathrm{kJ\,mol^{-1}}$	$\Delta G_{\mathrm{t}}^*(\mathrm{phen})$ $\mathrm{kJ\,mol^{-1}}$	$\Delta G_{\mathrm{t}}^*(\mathrm{CN^-})$ $\mathrm{kJ\,mol^{-1}}$
0.1	1.05(0.07)	−4.33(0.15)	0.87(0.15)
0.2	0.75(0.14)	−7.40(0.31)	2.24(0.32)
0.3	2.21(0.09)	−8.83(0.21)	3.37(0.21)
0.4	2.47(0.08)	−8.96(0.17)	3.54(0.17)
0.5	2.78(0.07)	−8.83(0.15)	3.54(0.16)
0.6	3.04(0.02)	−8.59(0.05)	3.67(0.05)
0.7	3.35(0.00)	−8.29(0.00)	3.57(0.00)
0.8	3.77(0.04)	−8.52(0.10)	3.87(0.10)
0.9	3.72(0.00)	−8.50(0.22)	4.28(0.23)
1.0	4.39(0.05)	−8.07(0.11)	2.98(0.11)

Values in parentheses are probable errors calculated from least-squares method. x_{EtOH}; mole fraction of ethanol.

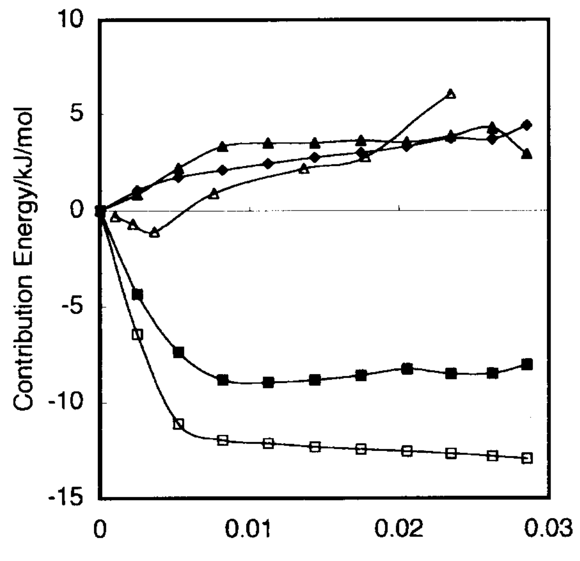

Fig. 3. Contributed energies from *EL* 1,10-phenanthroline, and cyano ligand to transfer free energy calculated by least-squares method. ◆ : *EL*, ■ : ΔG_t^*(phen), □ : ΔG_t(phen), ▲ : $\Delta G_t^*(CN^-)$, △: $\Delta G_t(CN^-)$.[11]

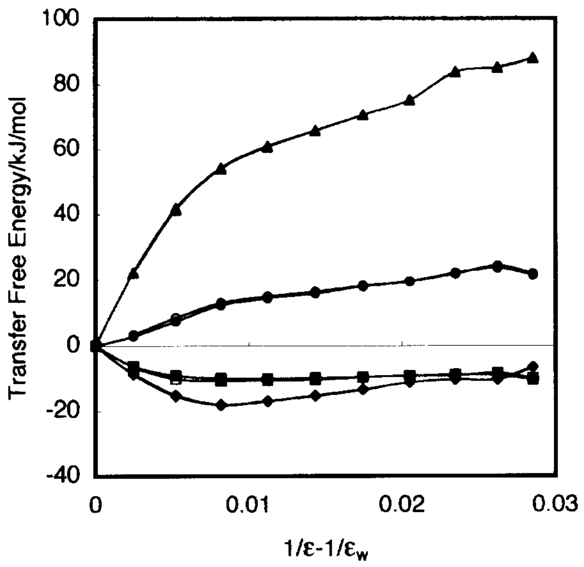

Fig. 4. Transfer free energies of complexes. ◆ : $[Fe(phen)_3]^{2+}$, ■ : $[Fe(CN)_2(phen)_2]$, ● : $[Fe(CN)_4phen]^{2-}$, ▲ : $[Fe(CN)_6]^{4-}$, Open and closed symbols refer to estimated and observed values.

keeps almost constant increment about 1.1 kJ mol^{-1} per 0.01 of $(1/\varepsilon - 1/\varepsilon_w)$. The constant increment of the *EL* values correspond to *r* 6.3 Å, which is comparable to the distance between Fe and a hydrogen atom bonded to a carbon atom at the 5 or 6 position in 1,10-phenanthroline.[12] It is larger than 4.5 Å, the distance between the iron and nitrogen atom of the cyano ligand in $[Fe(CN)_6]^{4-}$ plus the van der Waals radius of the nitrogen atom.

Because contribution from 1,10-phenanthroline to transfer free energy is very similar to the transfer free energy of free 1,10-phenanthroline, it is considered that selective solvation by ethanol is also similar between free and coordinated 1,10-phenanthroline. When ethanol preferentially solvates to non-coordinated 1,10-phenanthroline, the ethyl group side in the ethanol molecule probably faces to the 1,10-phenanthroline molecule; but when it solvates to coordinated 1,10-phenanthroline, the charge on the central iron(II) ion affects the orientation of the ethanol as a dipole, and the direction is opposite to the case of non-coordinated 1,10-phenanthroline. Thus, for the coordinated 1,10-phenanthroline, the orientation due to solvation is weakened, and the resulting contribution of 1,10-phenanthroline to transfer free energy is ca. 70% of free 1,10-phenanthroline. As can be seen from Fig. 5, because the ratio ΔG_t^*(phen)/ΔG_t(phen) is almost constant over whole mole-fraction range, in the future it may be possible to estimate the contribution energy from the transfer free energy of the ligand.

The contribution of the cyano ligand to transfer free energy is somewhat different from the case of 1,10-phenanthroline. Because cyanide anion is much smaller than the 1,10-phenanthroline molecule, it is considered that the surface area participating in the solvation is widely decreased by coordination to the iron(II) ion. Moreover, negative charge on the cyanide anion may undergo an ion–dipole interaction with the solvent; but with respect to the solvent dipole it is in the reverse direction against electrostatic solvation to the iron(II) cation. Hence, the contribution energy of the cyano ligand to transfer free energy is not similar to the transfer free energy of a free cyanide anion, and it may not be estimated from the transfer free energy of the cyanide anion. Nevertheless, $\Delta G_t^*(CN^-)$ is always more positive than $\Delta G_t(CN^-)$, and the difference is almost constant, about 2.5 kJ mol^{-1}, except at x_{EtOH} 0.8, as can be seen from Fig. 3.

Both contributed energies, ΔG_t^*(phen) and $\Delta G_t^*(CN^-)$, are less negative or more positive than ΔG_t(phen) or $\Delta G_t(CN^-)$, respectively. If the origin of destabilization is a decrease in the contact surface area between the ligand and the solvent by coordination, the magnitude of the destabilization must depend on the contact surface area; therefore, it is estimated as the ratio of the contact surface area. On the other hand, if the origin of destabilization is an ion–dipole interaction between the central metal ion and the solvent,

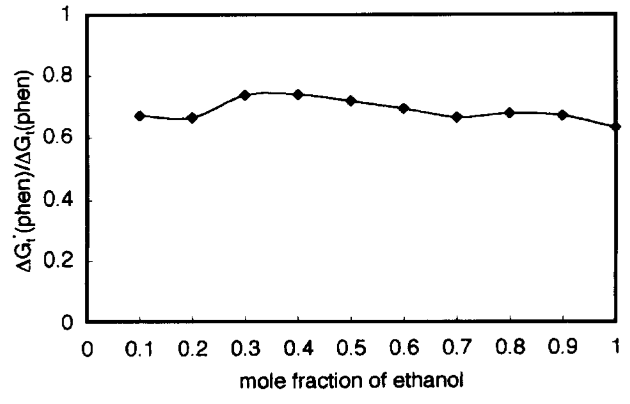

Fig. 5. The ratio of contributed energy of 1,10-phenanthroline vs. transfer free energy of free 1,10-phenanthroline.

the destabilization has a positive value, rather than the ratio. About 2—5 kJ mol^{-1} for ΔG_t^*(phen) and 2.5 kJ mol^{-1} for ΔG_t^*(CN$^-$) of destabilization energy are shown. It is considered that for 1,10-phenanthroline, the destabilization is mainly attributed to a decrease in the contact surface, and for CN$^-$ to a disturbance of the ion-dipole interaction from the charge on the central metal ion. Although the use of ratio ΔG_t^*(phen)/ΔG_t(phen) is very convenient, for cyano ligand ratio cannot be applicable.

$[Fe(phen)_3]^{2+}$ and $[Fe(CN)_6]^{4-}$ have no dipole moment as an ion. However, $[Fe(CN)_2(phen)_2]$ or $[Fe(CN)_4phen]^{2-}$ has a dipole moment. This must affect the transfer free energy, and cosequently the contributed energies to the transfer free energy. Hence, a more exact estimation may be needed by considering the effect of dipolemoment. Unfortunately, there are no data for the solubility or transfer free energy concerning with the difference between the *cis*- and *trans*-configurations. Accordingly, to correct for the effect of the dipole moment, Onsager's equation[13] for the solvation energy of a dipole ($\Delta A_{sol} = (1-\varepsilon)/(1+2\varepsilon)\times\mu^2/a^3$) was applied; the energy was subtracted from the observed free energy and recalculation was carried out. However, the results concerning the contributed energies were not very different. Probably, in this case that the differences in the transfer free energies between complexes are very large, the correction from the dipole moment, at most 2.5 kJ mol^{-1}, may not have much effect. It is considered that in the case of complexes with less different transfer free energies, the effect of the dipole would be more remarkable.

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