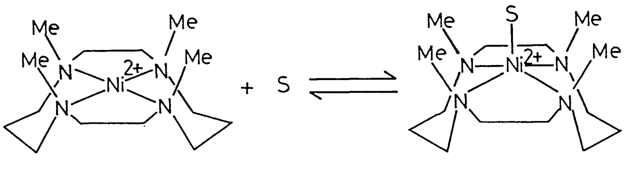
1198 © *1991 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 64, 1198—1204 (1991)* [Vol. 64, No. 4

Solvation and Ionic Association of (1*R*,4*S*,8*R*,11*S*)-1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) Perchlorate in Mixed Solvents of *N,N*-Dimethylformamide and *N,N*-Dimethylacetamide with Nitrobenzene and 1,2-Dichloroethane

Takashi Yokoyama, Etsuro Iwamoto, and Takahiro Kumamaru*
Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima 730
(Received November 30, 1990)

The conductances of $[NiL]^{2+}$ ($[NiL]^{2+}$=(1*R*,4*S*,8*R*,11*S*)-1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecanenickel(II)) have been measured in *N,N*-dimethylformamide (DMF)-1,2-dichloroethane (DCE), and *N,N*-dimethylacetamide (DMA)-DCE, and iso-relative permittivity mixtures DMF-nitrobenzene (NB), DMA-NB, and DMF-DMA at 25 °C. The first ionic association constant of $[NiL]^{2+}$ with the perchlorate ion in the mixtures with NB decreases with increasing fraction of both DMF and DMA, although DMF is coordinated to $[NiL]^{2+}$ and DMA is not, this showing that DMA as well as DMF in NB selectively solvates the axial coordination site of $[NiL]^{2+}$ to change from contact ion pairs to solvent-separated ion pairs. Bulky and delocalized negative pole of NB of which the dipole moment is larger than that of DMF and DMA results in a weak ion-dipole interaction, leading to a larger degree of ionic association. Ionic association was discussed from the viewpoint of steric hindrance and ion-dipole interactions.

The title metal chelate ($[NiL]^{2+}$=(1*R*,4*S*,8*R*,11*S*)-1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecanenickel(II)) cation exists in solutions as an equilibrium mixture of a red, square species and a green, square-pyramidal species according to the reaction



Reaction (1)

where S is a basic solvent.[1–6] In our previous work,[7] it was found that although *N,N*-dimethylformamide (DMF), *N,N*-diethylformamide, formamide, and *N*-methylformamide were coordinated to $[NiL]^{2+}$, *N,N*-dimethylacetamide (DMA), *N,N*-dimethylpropionamide, and *N,N*-diethylacetamide were not coordinated to the square complex, in spite of these solvents having nearly the same basicity. This was explained by steric hindrance between -CO-Me of the DMA, and four -N-Me and methylene groups of L. This led us to inquire as to whether solvation effects of non-coordinating DMA molecules on ionic association of $[NiL]^{2+}$ is different from that of coordinating DMF. 1,2-Dichloroethane (DCE) of a low relative permittivity (10.36) and nitrobenzene (NB) which has nearly the same relative permittivity (34.82) as the amides were used as diluents.

Experimental

NB, DMF, and DMA were purified as described previously.[7] DCE (reagent grade, Wako Pure Chemical Industries Ltd.) was purified by fractional distillation under reduced pressure through a 1.2-m column and left into molecular sieves 4A for a week.

$[NiL](ClO_4)_2$, $[NiL(N_3)]ClO_4$, where N_3 is the azide ion, butyltriisopentylammonium tetraphenylborate $(i\text{-Pent})_3BuNBPh_4$, and butyltriisopentylammonium perchlorate $(i\text{-Pent})_3BuNClO_4$ were prepared by the published method.[1,8,9] The purities of all the complexes were confirmed by the elemental analysis.

The instrumentation and the procedure used for measurements of conductances, viscosities, relative permittivities,

Table 1. Solvent Properties of Mixed Solvents of DMA and DMF with DCE at 25 °C

X_{DMA}	ε	η / cp	d / g cm^{-3}	X_{DMF}	ε	η / cp	d / g cm^{-3}
0.000	10.36	0.787	1.2458	0.000	10.36	0.787	1.2458
0.228	17.8	0.858	1.1642				
0.368	22.0	0.900	1.1184				
0.431	23.7	0.914	1.0981	0.443	24.4	0.854	1.1122
0.526	27.0	0.932	1.0696	0.576	28.3	0.858	1.0722
0.630	29.5	0.944	1.0380				
0.728	32.6	0.949	1.0098	0.759	32.6	0.845	1.0170
1.000	37.78	0.919	0.9366	1.000	36.71	0.802	0.9433

Table 2. Solvent Properties of Mixed Solvents of DMA and DMF with NB at 25 °C

X_{DMA}	ε	η	d	X_{DMF}	ε	η	d
		cp	g cm^{-3}			cp	g cm^{-3}
0.000	34.82	1.8415	1.1986	0.000	34.82	1.8415	1.1986
0.139	35.7	1.722	1.1651	0.158	35.5	1.675	1.1669
0.319	36.2	1.562	1.1206	0.360	36.0	1.462	1.1231
0.586	36.7	1.312	1.0516	0.627	36.8	1.175	1.0567
0.809	37.3	1.093	0.9900	0.837	37.1	0.959	0.9968
0.926	37.7	0.993	0.9574	0.938	37.1	0.908	0.9644
1.000	37.78	0.919	0.9366	1.000	36.71	0.802	0.9433

Table 3. Solvent Properties of Mixed Solvents of DMA with DMF at 25 °C

X_{DMF}	ε	η	d
		cp	g cm^{-3}
0.000	37.78	0.919	0.9365
0.340	36.6	0.890	0.9387
0.544	36.6	0.864	0.9403
0.735	36.6	0.838	0.9418
0.873	36.6	0.817	0.9428
0.955	36.6	0.807	0.9435
1.000	36.71	0.802	0.9439

and spectra were described previously.[7] The relative permittivities (ε), viscosities (η), and densities (d) of the solvent mixtures used for analyses were given in Tables 1 to 3. The specific conductances (S cm^{-1}) of the solvents are 2.2×10^{-8}—2.9×10^{-7} for NB-DMA mixtures, 2.1×10^{-8}—3.4×10^{-7} for NB-DMF, 1.8×10^{-7}—9.3×10^{-7} for DCE-DMA, 2.0×10^{-7}—9.2×10^{-7} for DCE-DMF, and 1.2×10^{-7}—4.0×10^{-7} for DMF-DMA. All solutions were prepared by weight. Densities were measured by using an Anton Paar model DMA 02D digital density meter at 25±0.002 °C.

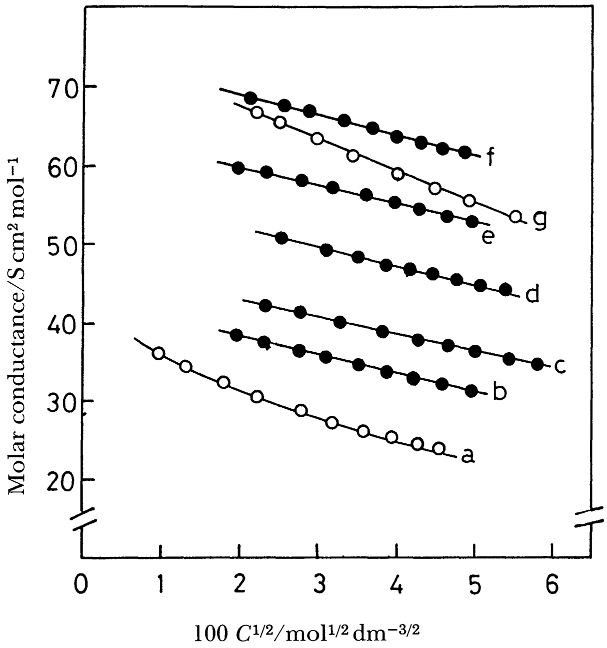


Fig. 1. Plots of molar conductivities of 1/2$[NiL](ClO_4)_2$ against the square root of the concentration in DMA-NB mixtures at 25 °C. DMA fraction: a, 0.00; b, 0.14; c, 0.32; d, 0.59; e, 0.81; f, 0.93; g, 1.00.

Results and Discussion

Conductances for $[NiL](ClO_4)_2$ and $[NiL(N_3)]ClO_4$ were measured at seven to ten concentrations ranging from 1×10^{-4} to 4×10^{-3} mol dm^{-3} in each system. Typical molar conductances measured in the DMA-NB system which of nearly the same relative permittivity are shown in Fig. 1. To analyze conductance data for the 2-1 type of electrolyte the limiting molar conductance for ClO_4^- must be evaluated. In this work, $(i\text{-Pent})_3BuNBPh_4$ was used as a reference electrolyte (i.e. assuming $\lambda_0[(i\text{-Pent})_3BuN^+]=\lambda_0(BPh_4^-)$].[9] The conductances for $(i\text{-Pent})_3BuNBPh_4$ and $(i\text{-Pent})_3BuNClO_4$ in each mixture were measured at 25 °C and analyzed by the Fuoss-Hsia conductance equation for symmetrical electrolytes in the form[10,11]

$$\Lambda=\Lambda_0-S(C\gamma)^{1/2}+EC\gamma\log C\gamma+JC\gamma+J_2(C\gamma)^{3/2}-K_aC\gamma f^2$$

for associated electrolytes, where the coefficients S, E, J, and J_2 have the usual meanings[12] and the relative permittivity and viscosity of solvents were used to calculate these coefficients. The symbol γ is the fraction of solute present as unpaired ions, Λ_0 and Λ are the limiting molar conductance and molar conductance, respectively, and f is the mean ionic activity coefficient on the molarity scale which was evaluated from molality by using the density of solutions. The equation is the form

$$\Lambda=\Lambda_0-SC^{1/2}+EC\log C+JC+J_2C^{3/2}$$

in the cases where association is negligible. For most of the systems the analyses yielded plots of σ against ion distance parameter a with double minimum where is the standard deviation of the individual N points calculated using the expression

$$\sigma=[\Sigma(\Lambda_{\text{obs}}-\Lambda_{\text{calc}})^2/(N-3)]^{1/2}$$

Tables 4 to 6 give compilation of the values of Λ_0, K_{a1}, and σ corresponding to the minimum at larger a values: Λ_0 and σ are almost the same as those corresponding to the minimum at smaller a values, but K_a is a little larger.

Table 4. Conductance Parameters for (i-Pent)$_3$BuNClO$_4$, [NiL](ClO$_4$)$_2$, and [NiL(N$_3$)]ClO$_4$ in Mixed Solvents of DMA and DMF with DCE at 25 °C

(a) DMA-DCE

X_{DMA}	(i-Pent)$_3$BuNBPh$_4$			(i-Pent)$_3$BuNClO$_4$			λ_0(ClO$_4^-$)	[NiL](ClO$_4$)$_2$		[NiL(N$_3$)]ClO$_4$		
	Λ_0	K_a	σ	Λ_0	K_a	σ		Λ_0	K_{a_1}	Λ_0	K_a	σ
	S cm^2 mol^{-1}	dm^3 mol^{-1}		S cm^2 mol^{-1}	dm^3 mol^{-1}		S cm^2 mol^{-1}	S cm^2 mol^{-1}	dm^3 mol^{-1}	S cm^2 mol^{-1}	dm^3 mol^{-1}	
0.228	44.00±0.04	151±1	0.012	59.46±0.06	226±1	0.013	37.46	59.19±1.50	1120±300			
0.368	41.99±0.04	68±1	0.017	58.36±0.05	97±1	0.018	37.36	65.58±0.08	392±10			
0.431	41.70±0.03	57±1	0.016	58.31±0.08	73±3	0.039	37.46	68.62±0.11	496±12	58.16±0.52	112±2	0.023
0.526	41.02±0.04	34±1	0.010	58.02±0.13	53±2	0.072	37.51	70.44±0.05	247±4			
0.630	40.64±0.03	29±1	0.016	58.59±0.07	37±1	0.014	38.27	70.31±0.02	52±1			
0.728	40.43±0.04	23±1	0.035	59.65±0.03	28±1	0.007	39.43	71.86±0.03	31±1	59.54±0.10	34±1	0.028
1.000	41.50±0.03	14±1	0.027	64.20±0.05	16±2	0.10	43.5[a]	74.79±0.53	0	64.68±0.17[a]	20±2[a]	0.10[a]

(b) DMF-DCE

X_{DMF}	(i-Pent)$_3$BuNBPh$_4$			(i-Pent)$_3$BuNClO$_4$			λ_0(ClO$_4^-$)	[NiL](ClO$_4$)$_2$		[NiL(N$_3$)]ClO$_4$		
	Λ_0	K_a	σ	Λ_0	K_a	σ		Λ_0	K_{a_1}	Λ_0	K_a	σ
	S cm^2 mol^{-1}	dm^3 mol^{-1}		S cm^2 mol^{-1}	dm^3 mol^{-1}		S cm^2 mol^{-1}	S cm^2 mol^{-1}	dm^3 mol^{-1}	S cm^2 mol^{-1}	dm^3 mol^{-1}	
0.443	45.06±0.10	54±2	0.065	64.11±0.07	70±7	0.035	41.58	74.79±0.07	424±7	63.49±0.09	98±2	0.047
0.576	44.93±0.09	31±2	0.053	66.09±0.25	30±4	0.049	43.62	77.11±0.25	78±18			
0.759	46.42±0.03	22±2	0.014	69.71±0.04	23±2	0.024	46.50	83.87±0.06	30±3	69.65±0.06	38±1	0.032
1.000	49.27±0.12	20±1	0.06	76.34±0.15	23±2	0.14	51.7[a]	93.70±0.03	6±1	76.64±0.25	26±3	0.13

[a] Ref. 7.

Table 5. Conductance Parameters for (i-Pent)$_3$BuNBPh$_4$, (i-Pent)$_3$BuNClO$_4$, and [NiL](ClO$_4$)$_2$ in Mixed Solvents of DMA and DMF with NB at 25 °C

(a) DMA-NB

	(i-Pent)$_3$BuNBPh$_4$			(i-Pent)$_3$BuNClO$_4$				[NiL](ClO$_4$)$_2$	
X_{DMA}	Λ_0 S cm^2 mol^{-1}	K_a dm^3 mol^{-1}	σ	Λ_0 S cm^2 mol^{-1}	K_a dm^3 mol^{-1}	σ	λ_0(ClO$_4^-$) S cm^2 mol^{-1}	Λ_0 S cm^2 mol^{-1}	K_{a_1} dm^3 mol^{-1}
0.000	21.25[b)]	0[b)]	0.014[b)]	31.72[b)]	0[b)]	0.030[b)]	21.1[a)]	39.2[a)]	1190[a)]
0.139	22.73±0.03	13±2	0.014	33.91±0.03	31±1	0.014	22.54	42.35±0.04	216±4
0.319	25.21±0.04	17±1	0.028	37.56±0.04	28±2	0.028	24.95	46.59±0.06	99±4
0.586	29.89±0.03	23±1	0.007	44.87±0.02	20±3	0.007	29.92	55.76±0.01	48±1
0.809	35.34±0.06	17±1	0.029	53.79±0.05	22±1	0.020	36.12	66.91±0.04	30±2
0.926	38.68±0.12	15±2	0.065	59.81±0.06	18±9	0.028	40.48	74.19±0.04	17±1
1.000	41.50±0.03	14±1	0.027	64.20±0.05	16±2	0.10	43.5[a)]	74.79±0.53	0

(b) DMF-NB

	(i-Pent)$_3$BuNBPh$_4$			(i-Pent)$_3$BuNClO$_4$				[NiL](ClO$_4$)$_2$	
X_{DMF}	Λ_0 S cm^2 mol^{-1}	K_a dm^3 mol^{-1}	σ	Λ_0 S cm^2 mol^{-1}	K_a dm^3 mol^{-1}	σ	λ_0(ClO$_4^-$) S cm^2 mol^{-1}	Λ_0 S cm^2 mol^{-1}	K_{a_1} dm^3 mol^{-1}
0.000	21.25[b)]	0[b)]	0.014[b)]	31.72[b)]	0[b)]	0.030[b)]	21.1[a)]	39.2[a)]	1190[a)]
0.158	23.82±0.05	21±1	0.025	35.65±0.09	32±5	0.044	23.75	44.26±0.06	218±6
0.360	27.16±0.13	11±7	0.066	41.37±0.02	27±1	0.011	27.80	51.24±0.05	109±3
0.627	34.04±0.03	19±1	0.007	51.92±0.03	24±2	0.013	34.90	64.28±0.02	51±1
0.837	41.91±0.03	18±1	0.014	63.60±0.14	15±5	0.060	42.65	78.37±0.21	28±7
0.938	45.84±0.10	20±1	0.052	71.01±0.09	24±1	0.034	48.09	84.26±0.03	13±1
1.000	49.27±0.12	20±1	0.065	76.34±0.15	23±2	0.14	51.7[a)]	93.70±0.03	6±1

a) Ref. 7. b) Ref. 14.

Conductances for [NiL](ClO$_4$)$_2$ were analyzed using the Fuoss-Edelson technique for unsymmetrical electrolytes.[13)] This method consists of evaluating Λ_0 and the first association constant K_{a1} for 2-1 electrolytes with some approximations, such as $\lambda_0(\mathrm{MX}^+)=0.5\,\lambda_0(1/2\mathrm{M}^{2+})$ and the second association constant $K_{a2}=0$. Typical Fuoss-Edelson plots of Λ^* against X for DMA-NB solution are shown in Fig. 2, where

$$\Lambda^*=\Lambda F,\ X=C'\Lambda^*(\Lambda^*-\Lambda_0/2),\ C'=2Cf$$

and

$$\Lambda^*=\Lambda_0-(K_{a1}/\Lambda_0)X$$

The function F is given as

$$F=[1/(1+\lambda_0(1/2\mathrm{M}^{2+})/2\Lambda_0)][1/\{1-S_{2:1}(2I)^{1/2}/\Lambda_0\}+\lambda_0(1/2\mathrm{M}^{2+})/2\Lambda]\Lambda/\Lambda_0$$

where $S_{2:1}$ is the Onsager conductance coefficient for a 2-1 electrolyte and I is the ionic strength. Good linear relations for the plots were obtained. The first association constant K_{a1} is obtained from the negative product of the slope and intercept of the curve. The results obtained for DMA-DCE, DMF-DCE, DMA-NB, DMF-NB, and DMA-DMF binary mixture systems are given in Tables 4 to 6. The extended Jenkins-Monk method[14)] was also used to evaluate the second association constants K_{a2} and it was found that in most cases the K_{a2} values are negligibly small so that neglecting K_{a2} is not serious for evaluating K_{a1}. For example, in NB, where the salts used are most associative, the extended Jenkins-Monk method gave the values of $K_{a1}=1190$ and $K_{a2}=12$[7)] and the analysis of conductances on neglecting the K_{a2} value gave the

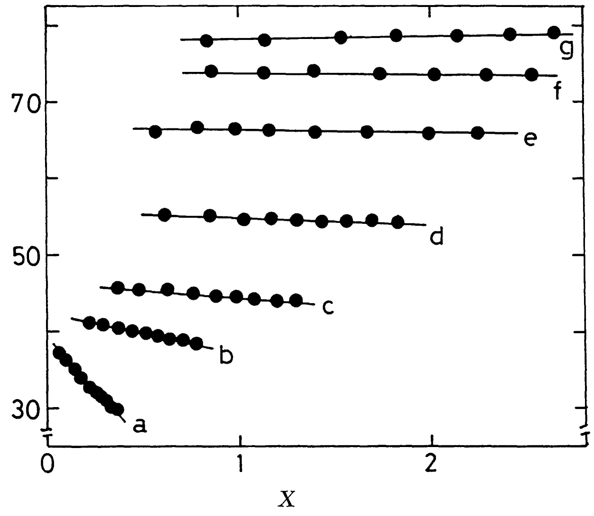


Fig. 2. Fuoss-Edelson plots for [NiL](ClO$_4$)$_2$ in DMA-NB mixtures at 25 °C. DMA fraction: a, 0.00; b, 0.14; c, 0.32; d, 0.59; e, 0.81; f, 0.93; g, 1.00.

Table 6. Conductance Parameters for (i-Pent)$_3$BuNBPh$_4$, (i-Pent)$_3$BuNClO$_4$, [NiL](ClO$_4$)$_2$, and [NiL(N$_3$)]ClO$_4$ in Mixed Solvents of DMA with DMF at 25 °C

DMF-DMA

X_{DMF}	(i-Pent)$_3$BuNBPh$_4$			(i-Pent)$_3$BuNClO$_4$			λ_0(ClO$_4^-$)	[NiL](ClO$_4$)$_2$		[NiL(N$_3$)]ClO$_4$		
	Λ_0	K_a	σ	Λ_0	K_a	σ		Λ_0	K_{a1}	Λ_0	K_a	σ
	S cm^2 mol^{-1}	dm^3 mol^{-1}		S cm^2 mol^{-1}	dm^3 mol^{-1}		S cm^2 mol^{-1}	S cm^2 mol^{-1}	dm^3 mol^{-1}	S cm^2 mol^{-1}	dm^3 mol^{-1}	
0.000	41.50±0.03	14±1	0.027	64.20±0.05	16±2	0.10	43.5	74.79±0.53	0	64.68±0.17[a]	20±2[a]	0.10[a]
0.340	43.52±0.01	19±1	0.0049	66.85±0.04	21±1	0.014	45.08	82.52±0.06	0±1	67.34±0.10	24±1	0.033
0.544	44.91±0.10	16±2	0.048	68.83±0.06	19±1	0.025	46.38	85.24±0.08	1±3			
0.735	46.93±0.31	12±6	0.066	71.85±0.10	11±2	0.016	48.38	88.98±0.04	10±1	72.13±0.13	25±1	0.024
0.873	48.11±0.05	18±3	0.025	73.91±0.10	21±1	0.035	49.86	91.72±0.03	15±2			
0.955	48.56±0.03	16±1	0.011	75.05±0.16	19±3	0.059	50.77	93.21±0.03	13±1			
1.000	49.27±0.12	20±1	0.065	76.34±0.15	23±2	0.14	51.7	93.70±0.03	6±1	76.64±0.25	26±3	0.13

a) Ref. 7.

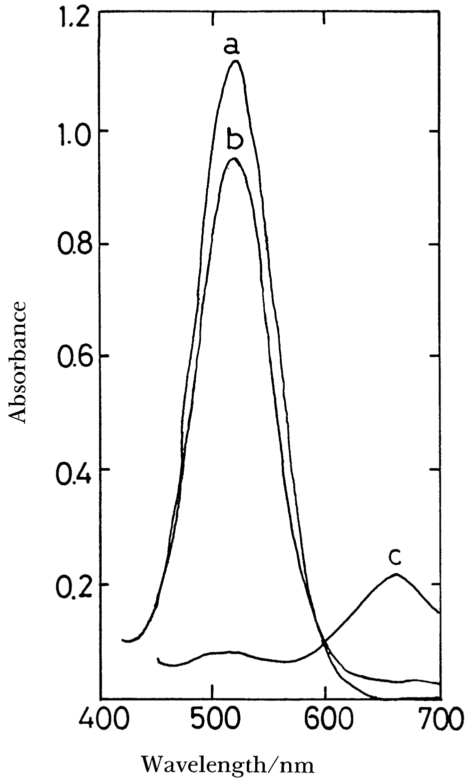


Fig. 3. Visible absorption spectra for [NiL](ClO$_4$)$_2$ (1.0×10^{-3} mol dm^{-3}) in (a) NB, (b) DMA, and (c) DMF at 25 °C.

value of K_{a1}=1200.

The visible spectra of [NiL]$^{2+}$ in NB, DMF, and DMA are shown in Fig. 3. The absorption peaks at 519 nm in DMA and NB, and 503 nm in DMF are assigned to the square species and those at 660 and 400 nm in DMF are assigned to the square pyramidal species. There is no change in spectra of [NiL]$^{2+}$ in those solvents over 40 h at 25 °C. Therefore, the isomerization of [NiL]$^{2+}$ can be neglected. These spectra clearly show that NB and DMA are not coordinated to the [NiL]$^{2+}$ cation but DMF is done. DCE of a very low basicity is not coordinated.

Thus, there is a clear difference in coordination behavior between DMA and DMF, but the K_{a1} values obtained for DMA are almost the same as those for DMF in all the mixed solvents. In the relative permittivity-changing media (DMF- and DMA-DCE) the logarithms of K_{a1} were plotted against the reciprocal of relative permittivity in Fig. 4. Solid and broken lines show the association constants for the 1-1 and 2-1 types of salts, repectively, calculated by the Bjerrum association theory[15] with various ionic size parameters. When the ionic radius of ClO$_4^-$ is 0.236 nm, the Ni-ClO$_4^-$ distance is more than 0.31 nm. The salts of (i-Pent)$_3$BuN$^+$ and [NiL(N$_3$)]$^+$ give the K_a values expected from the electrostatic theory. However, the K_{a1} values for [NiL]$^{2+}$ are much less than those expected from the Bjerrum calculation with a

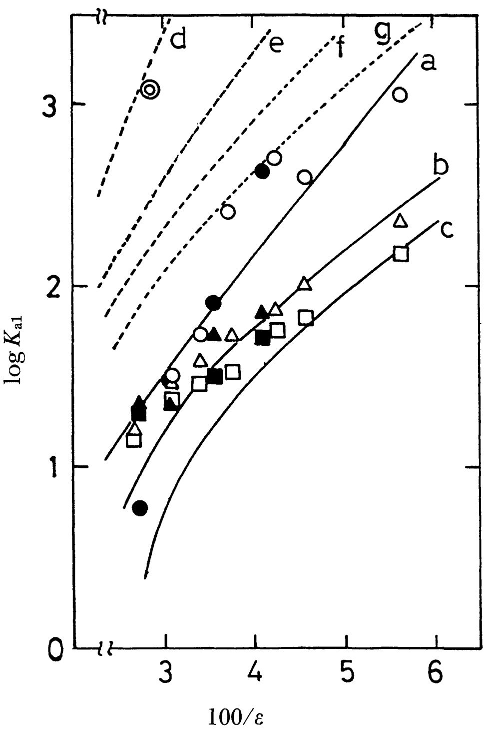


Fig. 4. The dependence of K_{a1} and K_a on the relative permittivity. ●, DMF-DCE; ○, DMA-DCE; ◎, NB for $[NiL](ClO_4)_2$; ▲, DMF-DCE; △, DMA-DCE for $(i\text{-Pent})_3BuNClO_4$; ■, DMF-DCE; □, DMA-DCE for $(i\text{-Pent})_3BuNBPh_4$. Solid and broken lines show the values calculated for 1-1 and 2-1 types of electrolytes, respectively, at 25 °C. Ionic size parameter in nm: a, 0.3; b, 0.5; c, 0.7; d, 0.3; e, 0.5; f, 0.7; g, 1.0.

range of 0.3 to 1.0 nm of *a* parameter which are reasonable for $[NiL]^{2+}$-ClO_4^- association. On the contrary, NB gives a much greater K_{a1} value which corresponds to an ionic distance parameter of 0.32 nm for the Bjerrum equation. It is interesting that when DMF and DMA are added to NB, the K_{a1} value decreases with increasing fraction of DMF and DMA in spite of nearly the same relative permittivity of the mixed solvents. This means that since DMF is bonded to the nickel on the same side as the four methyl groups, the site of ion pairing is mainly the axial pocket in the second coordination sphere surrounded by the four nitrogen substituents, and the axially associated perchlorate ions are easily displaced by the basic solvent. Furthermore, a similar K_{a1}-decreasing effect of non-coordinating DMA indicates that the perchlorate ion associated is easily displaced by DMA through ion-dipole interactions between $[NiL]^{2+}$ and DMA. The large K_{a1} values in NB suggests that the contact ion pair is possibly formed, considering that the K_{a1} value of the octahedral complex, $[Fe(phen)_3](ClO_4)_2$ (phen=1,10-phenanthroline), of the same 2-1 electrolyte as $[NiL](ClO_4)_2$ is only 39 $dm^3\,mol^{-1}$ in NB,[14] although the dipole moment of NB (μ=4.2 Debye) is larger than that of DMF (μ=3.86) and DMA (μ=3.81). This results from a weaker ion-dipole interaction because of the delocalized negative pole on the oxygen atoms and steric hindrance of nitro group for NB, leading to more degree of ionic association. Although the ion-pair formation constants between $[NiL]^{2+}$ and the perchlorate ion in NB is

Table 7. Stokes Radii r_s/nm for ClO_4^-, $[NiL]^{2+}$, and $[NiL(N_3)]^+$ in Various Binary Mixed Solvents at 25 °C

(a) with DCE

X_{DMF}	$r_s(ClO_4^-)$ nm	$r_s([NiL]^{2+})$ nm	$r_s([NiL(N_3)]^+)$ nm	X_{DMA}	$r_s(ClO_4^-)$ nm	$r_s([NiL]^{2+})$ nm	$r_s([NiL(N_3)]^+)$ nm
				0.228	0.26	0.88	
				0.368	0.24	0.65	
0.443	0.23	0.58	0.44	0.431	0.24	0.58	0.43
0.576	0.22	0.57		0.526	0.24	0.53	
				0.630	0.23	0.54	
0.759	0.21	0.52	0.42	0.728	0.22	0.53	0.43
1.000	0.20	0.49	0.41	1.000	0.21	0.57	0.42

(b) with NB

X_{DMF}	$r_s(ClO_4^-)$ nm	$r_s([NiL]^{2+})$ nm	X_{DMA}	$r_s(ClO_4^-)$ nm	$r_s([NiL]^{2+})$ nm
0.000	0.21	0.49	0.000	0.21	0.49
0.158	0.21	0.48	0.139	0.21	0.48
0.360	0.20	0.48	0.319	0.21	0.49
0.627	0.20	0.48	0.586	0.21	0.48
0.837	0.20	0.48	0.809	0.21	0.49
0.938	0.19	0.50	0.926	0.20	0.49
1.000	0.20	0.49	1.000	0.21	0.57

(c) with DMA

X_{DMF}	$r_s(ClO_4^-)$ nm	$r_s([NiL]^{2+})$ nm	$r_s([NiL(N_3)]^+)$ nm
0.000	0.21	0.57	0.42
0.340	0.20	0.49	0.41
0.544	0.21	0.49	
0.735	0.20	0.48	0.41
0.873	0.20	0.48	
0.955	0.20	0.48	
1.000	0.20	0.49	0.41

larger than in DMA, the absorbance of $[NiL]^{2+}$ at 520 nm in NB is larger than that in DMA. This means the outer-sphere interaction of the perchlorate ion with $[NiL]^{2+}$. The localized negative pole on the oxygen atom of DMA[16,17] can be so close to the central nickel that the contact ion-pair cannot be formed.

The K_{a1} values of $[NiL]^{2+}$ in DMF–DMA mixtures are a little less than the K_a values of $[NiL(N_3)]^+$, showing that the double charge for $[NiL]^{2+}$ interacts more strongly with the DMA dipole than with the perchlorate ion, compared with the case for $[NiL(N_3)]^+$.

Table 7 shows the Stokes radii r_s for ClO_4^-, $[NiL]^{2+}$, and $[NiL(N_3)]^+$ ions in all the media used, where

$$r_s = 0.82|z|/\lambda_0\eta$$

and z is the charge of ions. The r_s values in each medium are almost constant except for the DCE systems of a lower relative permittivity, and the r_s values of $[NiL]^{2+}$ are larger than those of $[NiL(N_3)]^+$ in all the mixed solvents. This is compatible with strong solvation by DMA as well as DMF.

Conclusion

The main site of ion pairing for $[NiL]^{2+}$ is the axial pocket surrounded by the four *N*-methyl groups. DMA preferentially solvates the axial pocket by an ion–dipole interaction without a chemical bond between the central nickel and the oxygen atom of DMA, although DMF solvates by the chemical bond. The solvent-separated ion pair is formed in both DMA and DMF, but the contact ion pair is formed in NB.

This work was supported by a Grant-in-Aid for Scientific Research No. 61134043 from the Ministry of Education, Science and Culture.

References

1) E. K. Barefield and F. Wagner, *Inorg. Chem.*, **12**, 2435 (1973).

2) I. S. Crick and P. A. Tregloan, *Inorg. Chim. Acta*, **142**, 291 (1988).

3) A. Anichini, L. Fabbrizzi, P. Paoletti, and R. M. Clay, *Inorg. Chim. Acta Lett.*, **24**, 21 (1977).

4) N. Herron and P. Moore, *Inorg. Chim. Acta*, **36**, 89 (1979).

5) P. Moore, J. Sacchinidis, and G. R. Willey, *J. Chem. Soc., Dalton Trans.*, **1984**, 1323.

6) K. E. Newman, *Inorg. Chim. Acta Lett.*, **89**, 3 (1984).

7) E. Iwamoto, T. Yokoyama, S. Yamasaki, T. Yabe, T. Kumamaru, and Y. Yamamoto, *J. Chem. Soc., Dalton Trans.*, **1988**, 1935.

8) E. K. Barefield, F. Wagner, A. W. Herlinger, and A. R. Dahl, *Inorg. Syn.*, **16**, 220 (1975).

9) M. A. Coplan and R. M. Fuoss, *J. Phys. Chem.*, **68**, 1177 (1964).

10) R. M. Fuoss and K. L. Hsia, *Proc. Natl. Acad. Sci., U.S.A.*, **57**, 1550 (1967).

11) R. Fernández-Prini, *Trans. Faraday Soc.*, **65**, 3311 (1969).

12) R. M. Fuoss and F. Accasina, "Electrolytic Conductance," Interscience Publishers, Inc., New York (1959).

13) R. M. Fuoss and D. Edelson, *J. Am. Chem. Soc.*, **73**, 269 (1951).

14) E. Iwamoto, S. Monya, and Y. Yamamoto, *J. Chem. Soc., Faraday Trans. 1*, **79**, 625 (1983).

15) N. K. Bjerrum, *Danske Vidensk. Selk*, No. 9, 7 (1926).

16) J. F. Yan, F. A. Momany, R. Hoffmann, and H. A. Scheraga, *J. Phys. Chem.*, **74**, 420 (1970).

17) S. Itoh and H. Ohtaki, *Z. Naturforsch., A*, **42**, 858 (1987).