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Preferential Solvation of Ni(II) and Mg(II) Ions in Water-Acetonitrile Mixtures. Enthalpies of Transfer and the Electronic Spectra

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The enthalpies of transfer (ΔH_t°) from water to water-acetonitrile (W–AN) mixtures for Ni^{2+} and Mg^{2+} ions were estimated using the enthalpies of dilution of the concentrated aqueous electrolyte solutions into water and mixtures, and the enthalpies of solution of water in the mixtures. The ΔH_t° values for these ions decreased with an increase in the mole fraction of AN (x_{AN}) in the range of $x_{AN}<$ca. 0.9, however, they increased rapidly in the range $x_{AN}>$ca. 0.9. The values of ΔH_t° for the Ni^{2+} ion were more negative than those for the Mg^{2+} ion throughout the x_{AN} regions, especially in the extremely AN-rich region and in pure AN. The average number of coordinated water molecules, N, for the $[Ni(AN)_{6-N}(W)_N]^{2+}$ ion in the mixtures (x_{AN}=0.2, 0.6, and 0.9), as estimated from the electronic absorption spectra, was always greater than that calculated on the basis of the bulk-solvent composition, indicating that the Ni^{2+} ion was preferentially solvated by water. These results, including the conductance data, were discussed in terms of the principle of hard and soft acid and base.

The preferential solvation of an ion in a mixed solvent has been one of the most fundamentally important problems in solution chemistry, and some phenomena have been applied in chemical technology.[1,2] Although various types of ion–solvent interactions have been noted to contribute to the ionic solvation in pure solvents,[3] in mixed solvents the concept of hard and soft acid (cation) and base (solvent) (i.e., the HSAB principle) is considered to be one of the most important factors. We have studied previously the preferential solvation behavior of ions in water–acetonitrile (W–AN) mixtures by means of the conductance[4,5] and the enthalpies of transfer (ΔH_t°). The majority of papers on ionic solvation so far have been concerned with monovalent ion. A difference in limiting ionic conductances was observed between the Ni^{2+} and Mg^{2+} ions in the mixtures, while they have equal conductance values in both water and acetonitrile.[5] Since the Ni^{2+} and Mg^{2+} ions have similar ionic radii, the electrostatic contributions to the overall ion–solvent interaction for the free ions can be regarded as similar. Therefore, the difference in the solvation property of the Ni^{2+} and Mg^{2+} ions should reflect the difference in the covalency of ion–solvent bonding. The nickel ion is expected to have a stronger affinity for acetonitrile than the Mg^{2+} ion, since the former ion is less hard than the latter. The ΔH_t° method was found to be a powerful tool in studying the preferential solvation of ions in the mixtures,[6,7] so the ΔH_t° values for the Ni^{2+} and Mg^{2+} ions from water to water–acetonitrile mixtures were estimated in this study.

It is not easy to measure directly the enthalpies of solution for highly hygroscopic salts of divalent cations. In such cases, the enthalpic measurements of dilution of a concentrated aqueous electrolyte solution into water and a mixed solvent, as proposed by Valera et al., are very attractive.[9] We have applied this method to estimate the enthalpies of transfer for nickel and magnesium perchlorates from water to the mixtures. The electronic absorption spectra have also been measured for nickel perchlorate solutions.

Experimental

Materials. Hexakis(acetonitrile)nickel perchlorate, $[Ni(CH_3CN)_6](ClO_4)_2$, was prepared from the hexaaqua salt and purified by the method described in the literature.[10] Commercially available magnesium perchlorate, $Mg(ClO_4)_2$ ("Anhydron"), was used without further purification. For the measurement of the enthalpies of solution it was dried in vacuo at 250 °C just before its use. The anhydrous salt was weighed in a glove bag filled with dried nitrogen gas. The other reagents and solvents were purified as described previously.[7,11] The alkali and acid solutions were prepared and standardized by the usual method. The concentrations of aqueous perchlorate solutions were determined by the EDTA titration method.

Enthalpic Measurements. The enthalpies of solution and dilution were measured by a heat-exchange type calorimeter.[12] Liquid samples were introduced continuously into the mixtures via a peristatic pump (LKB 2132) after having been passed through a Teflon heat exchanger at 25±0.02 °C. Aliquots of a solution (0.1—0.5±0.001 ml) were added to ca. 40 ml of the solvent in the reaction vessel. The enthalpies of dilution were determined in series by measuring the enthalpy changes accompanying the successive addition of the concentrated solution in the reaction vessel.

The calorimeter was calibrated by the measurements of the enthalpies of neutralization for NaOH and HCl solutions[12] and also the enthalpies of dilution for aqueous KNO_3 solution.

Spectral Measurements. The electronic absorption spectra were measured with a Hitachi 340 spectrophotometer.

Results and Discussion

Principle of Measurements. The enthalpy change, $\Delta H_R^C(\text{mixt})$, when a small aliquot of a concentrated

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aqueous electrolyte solution is added to a large amount of a mixed solvent can be regarded as involving the enthalpy of dilution for electrolytes to a definite concentration and the enthalpy of solution of the water contained in the original electrolyte solution with the mixed solvent. The latter enthalpy of solution of water in a mixed solvent, $\Delta H^{\mathrm{C}}_{\mathrm{W}}$(mixt), can be measured directly by the use of the present titration calorimeter. The enthalpy of dilution for an electrolyte, $\Delta H^{\mathrm{C}}_{\mathrm{D}}$(mixt) (=$\Delta H^{\mathrm{C}}_{\mathrm{R}}$(mixt)−$\Delta H^{\mathrm{C}}_{\mathrm{W}}$(mixt)), changes with the electrolyte concentration according to the following equation:

$$\Delta H^{\mathrm{C}}_{\mathrm{D}}(\mathrm{mixt}) = \Delta H^{\circ}_{\mathrm{D}}(\mathrm{mixt}) + (2/3)A_{\mathrm{H}}C^{1/2} + BC, \qquad (1)$$

where A_{H} is the Debye-Hückel coefficient (1.48 kJ mol$^{-1/2}$ for a 1:1 electrolyte aqueous solution and 5.12$_9$ kJ mol$^{-3/2}$ dm$^{-3/2}$ for a 2:1 electrolyte aqueous solution)[13] and where B is the experimental parameter.

Defining the enthalpy of solution for preparing a concentrated aqueous electrolyte solution as $\Delta H^{\mathrm{C}}_{\mathrm{S}}$(W),[9] the standard enthalpy of solution for electrolytes in an aqueous solution, $\Delta H^{\circ}_{\mathrm{S}}$(W), and in a mixed solvent, $\Delta H^{\circ}_{\mathrm{S}}$(mixt), can be expressed as follows:

$$\Delta H^{\circ}_{\mathrm{S}}(\mathrm{W}) = \Delta H^{\mathrm{C}}_{\mathrm{S}}(\mathrm{W}) + \Delta H^{\circ}_{\mathrm{D}}(\mathrm{W}) \qquad (2)$$

$$\Delta H^{\circ}_{\mathrm{S}}(\mathrm{mixt}) = \Delta H^{\mathrm{C}}_{\mathrm{S}}(\mathrm{W}) + \Delta H^{\circ}_{\mathrm{D}}(\mathrm{mixt}). \qquad (3)$$

The enthalpy of transfer for an electrolyte from water to a mixed solvent, $\Delta H^{\circ}_{\mathrm{t}}$, can be then obtained as:

$$\Delta H^{\circ}_{\mathrm{t}} = \Delta H^{\circ}_{\mathrm{D}}(\mathrm{mixt}) - \Delta H^{\circ}_{\mathrm{D}}(\mathrm{W}). \qquad (4)$$

Relative Partial Molar Enthalpies for Water in Water-Acetonitrile Mixtures. The enthalpy of solution of water in the mixtures, $\Delta H^{\mathrm{C}}_{\mathrm{W}}$(mixt), was found to vary linearly with the concentration of water added. An extrapolation of the experimental $\Delta H^{\mathrm{C}}_{\mathrm{W}}$ (mixt) values to zero concentration of water will give the relative partial molar enthalpies of water ($\bar{L}_{\mathrm{W}}$) in the mixtures. The values thus obtained are shown in Table 1, together with those values estimated by the method of graphical intercepts[14] on the basis of excess enthalpy data.[15] The values estimated in this experiment are derived from directly measurable quantities and are, therefore, more accurate than those in the literature.[15]

Table 1. Relative Partial Molar Enthalpies of Water in Water-Acetonitrile Mixtures, $\bar{L}_{\mathrm{W}}$/kJ mol^{-1}

x_{AN}	$\bar{L}_{\mathrm{W}}$ This Exper.	$\bar{L}_{\mathrm{W}}$ Lit.[a]
0	0	0
0.1	−0.154±0.002	−0.15±0.14
0.2	−0.049±0.003	−0.04±0.07
0.4	0.276±0.006	0.30±0.05
0.6	0.864±0.001	0.79±0.01
0.8	2.51 ±0.05	2.5 ±0.1
0.9	4.41 ±0.06	4.5 ±0.1

a) From Ref. 15.

As may be seen in Table 1, $\bar{L}_{\mathrm{W}}$ decreases with the addition of a small amount of AN, passes through a minimum at the mole fraction of AN(x_{AN}) (ca. 0.1), and then increases with an increase in x_{AN}. Beyond x_{AN} ca. 0.2, the $\bar{L}_{\mathrm{W}}$ values become positive, increase almost linearly until x_{AN} reaches ca. 0.65. With a further increase in x_{AN}, the $\bar{L}_{\mathrm{W}}$ values increase more rapidly. The x_{AN} dependence of $\bar{L}_{\mathrm{W}}$ appears to reflect the change in the solvent structure of these mixtures: a water-rich region, an intermediate region, and an acetonitrile-rich region.[7]

Enthalpies of Transfer for Nickel and Magnesium Perchlorates. The enthalpies of dilution, $\Delta H^{\mathrm{C}}_{\mathrm{D}}$(mixt), change with the electrolyte concentration in the final electrolyte concentration range from 5×10^{-3} to 0.09 mol dm^{-3}. Examples of the plots for obtaining the $\Delta H^{\circ}_{\mathrm{D}}$(mixt) values are shown in Fig. 1. The $\Delta H^{\circ}_{\mathrm{D}}$(mixt) values were obtained using the A_{H} values for water. There were no significant differences between the $\Delta H^{\circ}_{\mathrm{D}}$(mixt) values calculated using A_{H} value for water and those calculated using the A_{H} value for AN. The enthalpies of transfer obtained on the basis of Eq. 4 for nickel and magnesium perchlorates are given in Table 2. As may be seen in Table 2, the change in the initial concentration of an electrolyte aqueous solution does not seem to cause any significant error in the estimation of the $\Delta H^{\circ}_{\mathrm{t}}$ values.

The enthalpy of transfer for $\mathrm{Mg(ClO_4)_2}$ from water to AN was obtained from the direct measurements of the enthalpies of solution. The enthalpy of solution in water is found to be −157.$_3$±2 kJ mol^{-1} in good agreement with the literature value of −156.6$_1$ kJ mol^{-1}.[16] The enthalpy of solution in AN was difficult to measure because of its high hygroscopicity, but the most careful repeated measurements (more than ten times) gave the enthalpy of solution of −185.$_5$±5 kJ mol^{-1}. The enthalpy of transfer for $\mathrm{Mg(ClO_4)_2}$ from water to AN was taken as −28±5 kJ mol^{-1}. The

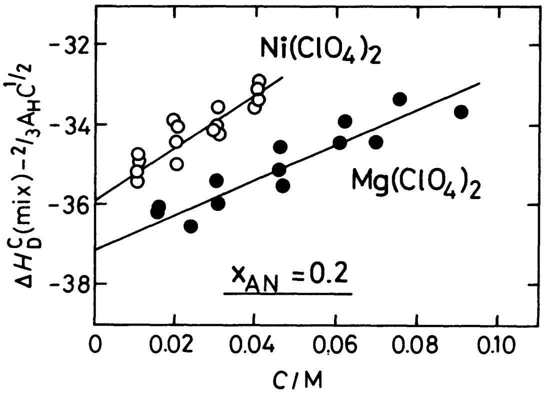

Fig. 1. Plots based on Eq. 1 for the enthalpies of dilution in the mixtures.

Table 2. Enthalpies of Dilution at Infinite Dilution in Water and Water–Acetonitrile Mixtures, ΔH°_D, and Enthalpies of Transfer for Electrolytes, ΔH°_t/kJ mol^{-1}

x_{AN}	Ni(ClO$_4$)$_2$		Mg(ClO$_4$)$_2$	
	$-\Delta H^\circ_D$	$-\Delta H^\circ_t$	$-\Delta H^\circ_D$	$-\Delta H^\circ_t$
0	4.3[a)]	0	10.$_4$	0
0	3.5	0	5.8[b)]	0
0.1	16.$_2$	12.$_7$±0.6	20.$_8$	10.$_4$±0.2
0.2	34.$_6$	31.$_1$±0.5	36.$_8$	26.$_4$±0.3
0.4	54.$_5$[a)]	50.$_2$±1.0[a)]	55.$_7$	45.$_3$±0.3
0.4	54.$_3$	50.$_8$±0.9		
0.6	72.$_4$	68.$_9$±1.1	75.$_1$	64.$_7$±1.3
0.8	90.$_8$	87.$_3$±0.7	93.$_9$	83.$_5$±0.5
0.9	93.$_6$	95.$_1$±0.2	101.$_9$	91.$_5$±0.6
0.9			100.$_4$[b)]	94.$_6$±0.2[b)]

a) The initial concentration of nickel perchlorate solutions is 2.08$_8$ mol dm^{-3} unless otherwise noted in which case it is 2.11$_5$ mol dm^{-3}. b) The initial concentration of magnesium perchlorate solutions is 2.09$_6$ mol dm^{-3} unless otherwise noted in which case it is 3.10$_4$ mol dm^{-3}.

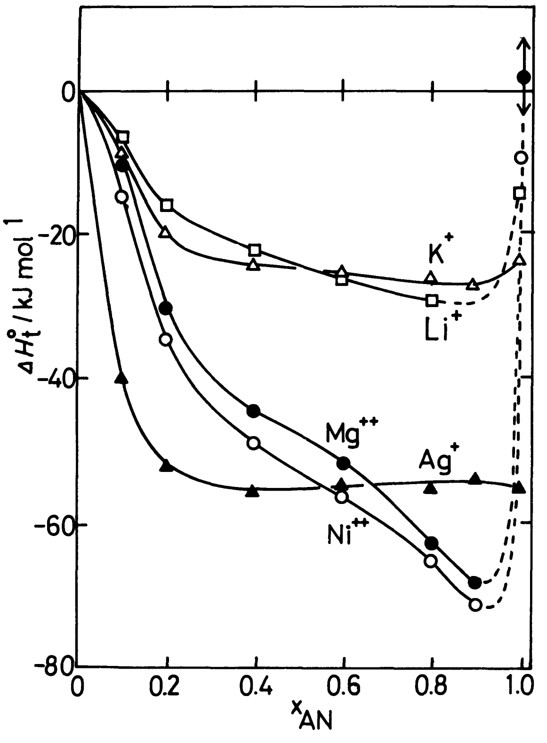

Fig. 2. Plots of the ionic enthalpies of transfer (ΔH°_t) vs. the mole fraction of acetonitrile (x_{AN}). Data for M$^+$ ions were cited from Ref. 6.

enthalpy of transfer for Ni(ClO$_4$)$_2$ from water to AN was cited from the literature.[17)]

The ionic enthalpies of transfer were calculated by using the reported values of the ClO$_4^-$ ion estimated on the basis of the TATB assumption $\{\Delta H^\circ_t(\text{Ph}_4\text{As}^+)=\Delta H^\circ_t(\text{Ph}_4\text{B}^-)\}$.[6)] The estimated ΔH°_t values for the Ni^{2+} and Mg^{2+} ions are plotted as a function of x_{AN} in Fig. 2. For convenience of comparison, the x_{AN} dependences of ΔH°_t for the Li$^+$, K$^+$, and Ag$^+$ ions are also shown in Fig. 2.[6)] It has been established by several kinds of measurements that the Ag$^+$ ion is preferentially solvated by AN in this mixed solvent system.[8)] The ΔH°_t values for the Ag$^+$ ion decrease very rapidly in the water-rich region, but change only slightly in the other regions. The ΔH°_t values for the K$^+$ ion, similar in ionic size to the Ag$^+$ ion, decrease much less rapidly in the water-rich region, and its x_{AN} dependence profile in the other regions is nearly the reverse of that of the Ag$^+$ ion. The values of ΔH°_t for the Li$^+$ ion decrease a little more slowly than that for the K$^+$ ion in the water-rich region, continue to decrease less slowly in the intermediate region, and increase rapidly in the AN-rich region. Such an x_{AN} dependence profile of the Li$^+$ ion is characteristic of the most preferentially hydrated monovalent cation.

Previously, the present authors have discussed semiquantitatively the solvation enthalpies for halide ions in the W-rich and intermediate regions based on a modified hydration model, and noted that the exothermic shift of the ΔH°_t values in the intermediate region may be attributed to the reduction in the cavity formation energy.[7)] Therefore, the exothermic shift of ΔH°_t values for cations in the range of x_{AN} may also be attributed to the change in the solvent structure of the mixtures, although it is difficult to discuss the solvation enthalpies for cations quantitatively. However, the difference in ΔH°_t values at an x_{AN} value between Ni^{2+} and Mg^{2+} ions may not be influenced by the solvent structure, since these ions have similar ionic radii.

As shown in Fig. 2, when a small amount of water is added to a pure AN solution, the ΔH°_t values for the Ni^{2+} and Mg^{2+} ions decrease markedly. And the ΔH°_t values for both ions are almost twice as negative as those for the Li$^+$ ion in the range of $x_{AN}<$ca. 0.9. Therefore, the x_{AN} dependence of the ΔH°_t values suggests that both Ni^{2+} and Mg^{2+} ions are totally preferentially hydrated in water–acetonitrile mixtures. The same conclusion can be drawn from the electronic spectral measurements of a nickel perchlorate solution to be described below. However, the more negative ΔH°_t values for the Ni^{2+} ion than for the Mg^{2+} ion indicate that the Ni^{2+} ion has a stronger affinity for AN than the Mg^{2+} ion over the whole x_{AN} region. The nickel and Mg^{2+} ions have quite different electronic configurations in spite of the similar ionic sizes. The magnesium ion is a hard divalent cation, while the Ni^{2+} ion is situated on the borderline between hard and soft divalent cations.[18)] The σ value, which is used as a parameter of the softness for metal ions, is largest for the Ni^{2+} ion among the borderline cations.[19)] Furthermore, as has been pointed out by Munatake, Kitagawa, and Myajima, the covalent bonding in the metal ion–CH$_3$CN bonds is enhanced in this order;

$Mg^{2+}<Ni^{2+}<Ag^{+}$. Therefore, the stronger solvation of the Ni^{2+} ion in AN can be ascribed to its acid property being less hard than the Mg^{2+} ion. In view of the HSAB principle it is very reasonable, that the much more rapid increase in ΔH_t° values is observed for the Mg^{2+} ion in the extremely AN-rich region.

Electronic Absorption Spectra of Nickel Perchlorate Solutions in Water-Acetonitrile Mixtures. The electronic absorption spectra have been measured in order to obtain more information concerning the average number of water molecules in the solvation cosphere of the Ni^{2+} ion in these solvent mixtures. Figure 3 shows the variation in the electronic absorption maxima, λ_{max}, as a function of the $Ni(ClO_4)_2$ concentration at $x_{AN}=0.2$, 0.6, and 0.9; Fig. 3-a corresponds to those with shorter wavelength λ_{max} values, and Fig. 3-b, to those with longer wavelength λ_{max} values. In aqueous solutions, the absorption maxima λ_{max} are 395 and 656 nm, while in AN solutions they are 365 and 580 nm. It has been confirmed that there is a linear relationship between the number of water molecules coordinated in the $[Ni(NH_3)_{6-N}(H_2O)_N]^{2+}$ ion and the wavenumber ν.[11] Since a similar relationship is expected to hold in the case of the $[Ni(CH_3CN)_{6-N}(H_2O)_N]^{2+}$ ion, the number of water molecules coordinated in the aquaacetonitrile nickel complex ion can be estimated from the absorption spectral data. The values estimated at the electrolyte concentrations of 0.005, 0.05, and 0.32 M (1 M=1 mol dm^{-3}) are 5.0, 5.1, and 5.5 ($x_{AN}=0.2$); 4.9, 5.3, and 4.4 ($x_{AN}=0.6$), and 3.2, 3.2, and 2.0 ($x_{AN}=0.9$), respectively. The number of water molecules in the actual solvation sphere is always greater than that calculated on the basis of the bulk solvent composition, therefore, water is clearly enriched preferentially in the cosphere of the nickel ion. The λ_{max} value in the W-rich region ($x_{AN}=0.2$) approaches that observed as in an aqueous solution as the electrolyte concentration increases. In contrast with this, in the AN-rich region ($x_{AN}=0.9$), the λ_{max} value approaches that observed as in the AN solution. In the intermediate region ($x_{AN}=0.6$), the increase in electrolyte concentration causes the shift of λ_{max} to the longer wavelength side, as in the W-rich region when electrolyte concentration is small. On the contrary, a further increase in the electrolyte concentration beyond a certain limit causes a shift of the λ_{max} value to the shorter wavelength side, as in the AN-rich region. Such dependence of the λ_{max} value on the electrolyte concentration in the mixtures may be attributed to the ion-pair formation of nickel species, since it is difficult to explain the such behavior in terms only of the variation in the equilibrium concentration of the $[Ni(CH_3CN)_{6-N}(H_2O)_N]^{2+}$ species.

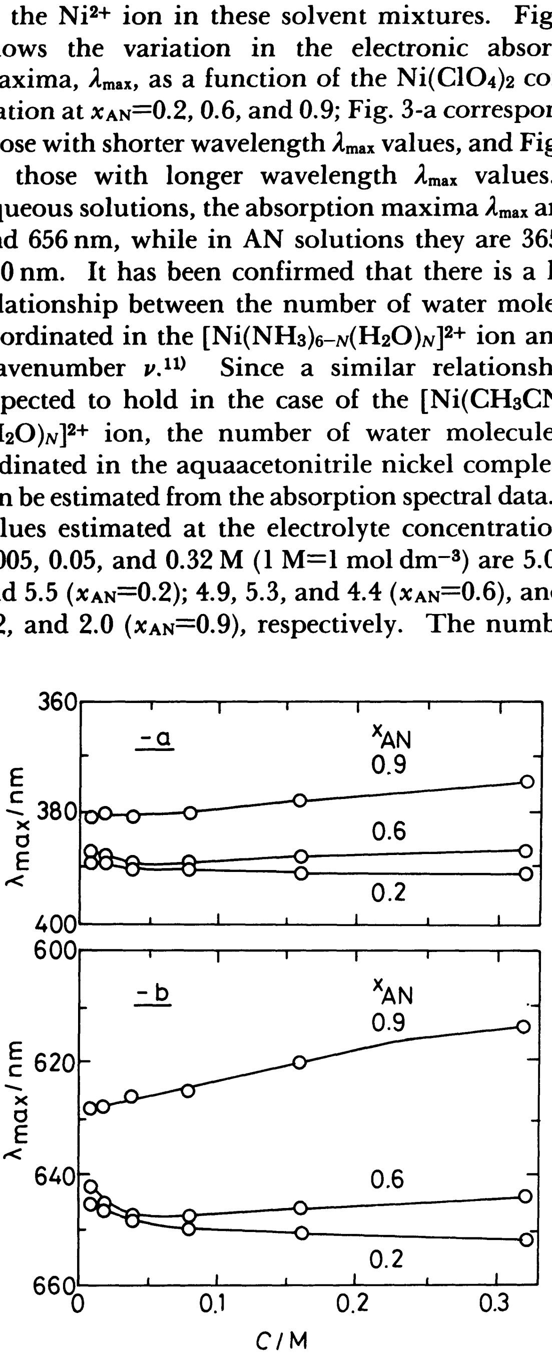

Fig. 3. Dependences of the electronic absorption maxima (λ_{max}) for Ni^{2+} ion on the electrolyte concentration in the mixtures; -a: maximum at shorter wavelength, -b: maximum at longer wavelength.

Relationship between Enthalpies of Transfer and Conductance for Nickel and Magnesium Perchlorates. Finally, the difference in the conductance behavior of nickel and magnesium perchlorates in the mixtures will be discussed in connection with the ΔH_t° values described above. It has been reported that the Ni^{2+} and Mg^{2+} ions were differentiated only in the x_{AN} range from 0 to 0.4, that is, the limiting ionic conductances (λ_0^+) for the Ni^{2+} ion were smaller than those for the Mg^{2+} ion in this range.[5] In this range, the ΔH_t° values for the Ni^{2+} ion are found to be more negative than those for the Mg^{2+} ion. This indicates that the Ni^{2+} ion has a stronger affinity for acetonitrile than does the Mg^{2+} ion. The smaller limiting ionic conductance for the Ni^{2+} ion may be related to the larger ionic species resulting from the displacement of the water molecule by a larger acetonitrile molecule in its solvation cosphere. Spectral measurements show that the Ni^{2+} ion becomes increasingly hydrated with an increase in the concentration in this range. Consequently, the hydration state of the Ni^{2+} ion can be expected to be similar to that of the Mg^{2+} ion at a certain concentration. In fact, nearly equal molar conductances are observed for 10 mmol dm^{-3} solutions of $Ni(ClO_4)_2$ and $Mg(ClO_4)_2$.[5]

The enthalpies of transfer from pure acetonitrile to mixtures ($x_{AN}=0.9$) clearly indicate that the Mg^{2+} ion is more strongly hydrated than the Ni^{2+} ion. In the extremely AN-rich region ($x_{AN}\geqq 0.95$), the limiting ionic conductances are found to be nearly equal for the Ni^{2+} and Mg^{2+} ions. However, the molar conductance for $Mg(ClO_4)_2$ is much smaller than that for $Ni(ClO_4)_2$ at 10 mmol dm^{-3}. From spectral measurements at $x_{AN}=0.9$, acetonitrile appears to be increasingly enriched in the cosphere of the Ni^{2+} ion with an increase in the electrolyte concentration. A similar concentration dependence may not necessarily be expected for the Mg^{2+} ion in view of its stronger affinity for water. The notable decrease in molar conductance for $Mg(ClO_4)_2$ in the extremely AN-rich region may be due to the easier formation of the solvent (water)-separated ion-pair, as is suggested by the ^{35}Cl NMR measurements for the 1.0 mol dm^{-3} AN solution containing a small amount of water.[21]

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