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Basicity of Water in Hydrogen-Bonded Networks of Methanol-1,2-Dichloroethane Mixtures Using the [(1*R*,4*S*,8*R*,11*S*)-1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane]nickel(II) Cation as a Probe of Electron-Pair Acceptance

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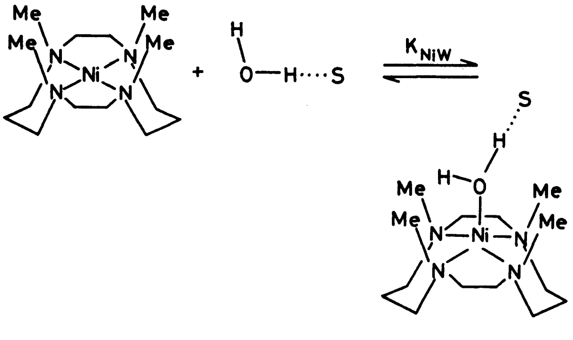
The basicity of water in methanol (MeOH) and MeOH-1,2-dichloroethane (DCE) mixtures was examined by using spectral data of the title square planar chelate cation ($[Ni(tmc)]^{2+}$). Although MeOH molecules are hardly coordinated to the chelate, the water molecules hydrogen-bonded with MeOH are easily coordinated to the cation, depending on the degree of hydrogen-bonded networks of MeOH. A fitting method showed that in the MeOH-rich mixtures the dimerization of water occured and only the terminal monomeric water molecule in the MeOH oligomer could be coordinated. The equilibrium constant $K_{NiW1}=[Ni(tmc)(H_2O)^{2+}]/[Ni(tmc)^{2+}][H_2O]$ was 3.2 in the 0.1 MeOH mole fraction mixture, 3.0 in 0.3, 3.2 in 0.5, 6.2 in 0.7, 9.5 in 0.9, 10.0 in 1.0. Linear relationships of ^1H chemical shift of the OH group for MeOH in various solvents with the K_{NiW1} values and Gutmann's donor number (DN) were found and DN values were estimated for the DCE-MeOH mixtures. The enhancement of basicity of the water molecules was discussed from the viewpoints of the charge transfer effect through hydrogen bonding and the development of hydrogen-bonded networks.

In our previous papers,[1,2] effects of intermolecular interactions between water and dipolar aprotic solvent molecules on the basicity of water have been studied by using spectral data of [(1*R*,4*S*,8*R*,11*S*)-1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane]nickel(II) ($[Ni(tmc)]^{2+}$) with an 1*R*,4*S*,8*R*,11*S*- set of nitrogen configurations as a probe of electron pair acceptance. Although it is known that the red, square planar chelate cation forms a green, five-coordinate square pyramidal complex by axial ligation with a donor solvent or ion,[3-5] we found that oxygen donor coordinating molecules such as H_2O, MeOH, acetone (AC), and 1,2-propanedyl carbonate (PDC) of which DNs are less than 20, were not coordinated to the nickel cation in nitrobenzene (NB) as a diluent.[1,6] However, the water molecules in pure water and in hydrogen bonding acceptor solvents such as AC, PDC, and *N*,*N*-dimethylacetamide (DMA) can be coordinated and furthermore the dimerization of water in nitromethane (NM), PDC, and AC leads to coordination of water, of which the equilibrium constant increases with increasing the basicity of the bulk solvent molecules, i.e. in the order NM<PDC<AC. The basicity of water was related with the formation constant (K_{NiW}) of the aqua chelate cation in Reaction 1



(1)

where S is hydrogen-bonding acceptors or basic solvents.

The above phenomena are explained by the increase in the charge density on the oxygen atom of water due to hydrogen bonding with such basic molecules. Thus, the donor number 18 of water proposed by Gutmann[7,8] is ascribed to the isolated water molecules of the lowest basicity, for example, dissolved in much lower basic DCE and NB. Mayer and Gutmann[9] also introduced the term "bulk donicity" to characterize the basic properties of water. The basicity of water greatly depends on the strength of hydrogen bonding and little is known concerning the nature of water basicity, especially, in protic solvents. The water molecule in aqueous mixtures is the solute or the solvent that takes our major interest.

The purpose of this work is to study the effect of network structure of MeOH on the basicity of water in DCE-MeOH mixtures. The two- or three-dimensional cross-linked polymer for the amphiprotic solvent, unlike aprotic solvents, make it more difficult to understand the water-solvent interactions. However, mixtures of MeOH with inert DCE give information concerning the network structure which is relatively easily obtained using IR and NMR data. Hydrogen-bonded networks of MeOH are promoted with increasing the MeOH fraction and the K_{NiW} value for the water molecules present in the DCE-MeOH mixtures is expected to increase with growing hydrogen bonds among MeOH molecules.

Experimental

The metal chelate electrolyte (*R*,*S*,*R*,*S*)-$[Ni(tmc)](ClO_4)_2$ was prepared as described previously.[1-3] DCE, MeOH, pyridine (Py), hexamethylphosphoric triamide (HMPA), *N*,*N*-dimethylformamide (DMF), DMA, dimethyl sulfoxide (DMSO), AC, and PDC (Reagent grade, Wako Pure Chemical Industries Ltd.) were purified by fractional distillation through a 1.2-m column without washing. NB (Reagent grade, Wako Pure Chemical Industries Ltd.) was purified by fractional distillation under reduced pressure after washing with 1.5 mol dm^{-3} H_2SO_4 and 1 mol dm^{-3} $NaHCO_3$. Tetrahydrofuran (THF) (Wako Pure Chemical Industries Ltd.) and benzonitrile (BN) (Aldrich Chemical Company) were used without further purifications. All solvents were used after standing over molecular sieves (Type 4A) for one week.

The apparatus and the procedures used for measurements of the water content, the high-resolution proton chemical shift, and infrared spectra have been described earlier.[1,2]

Results and Discussion

Typical visible spectra of the chelate cation in a mixture of the 0.7 MeOH mole fraction with DCE containing water are shown in Fig. 1. The absorption peak at 520 nm is referred to the four-coordinate planar complex, and the peaks at 396 nm and ca. 660 nm are referred to the five-coordinate square pyramidal complex. When the water content is 8.30$\times$10^{-3} mol dm^{-3}, the chelate is almost four-coordinate. The absorbance at 520 nm decreases with increasing the water concentration. This shows that the bulk solvent molecules can not be coordinated to the chelate, but the water molecules in this solution can be coordinated. The dependence of the absorbance on the water concentration in various DCE-MeOH mixtures is shown in Fig. 2 together with the results for Py. Although highly basic Py (DN=33.1[7]) molecules can not be coordinated due to steric hindrance,[6] it is seen that the water in Py can become much easily coordinated.

Ionic association of the nickel complex with the perchlorate ion may occur in mixtures containing DCE with a low dielectric constant. In our previous study,[6] ionic association effects on coordination were hardly observed even in AC solution with a first association constant of 12200. Since the basicity of the perchlorate ion is very weak, it is reasonably assumed that there is no ionic association effect on the water coordination.

IR and NMR of Water and MeOH in DCE-MeOH Mixtures. As the coordination ability of water mole-

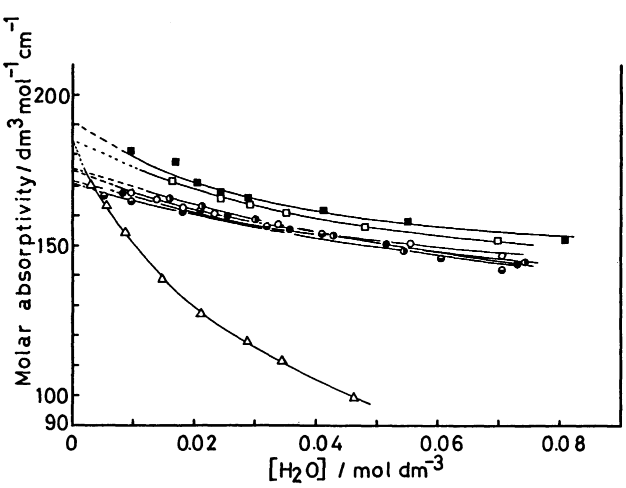


Fig. 2. Variation of molar absorptivity at 520 nm with the water concentration in various solvents at 25 °C. Δ, Py; DCE-MeOH mixtures (MeOH mole fraction): □, 1.0; ■, 0.9; ○, 0.7; ●, 0.5; ◒, 0.3; ◑, 0.1.

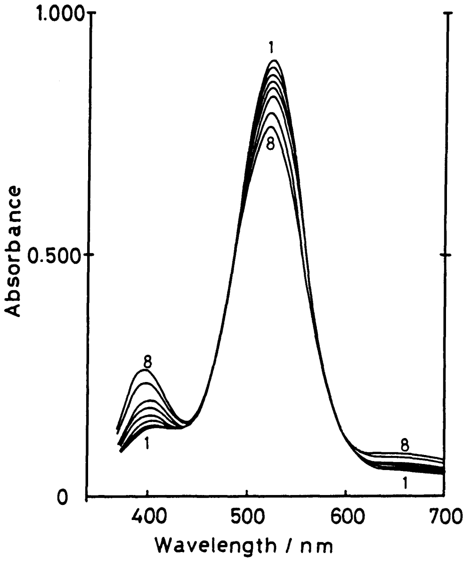


Fig. 1. Visible spectrum variation with the concentration of water of a 1.12$\times$10^{-3} mol dm^{-3} solution of $[Ni(tmc)](ClO_4)_2$ at the 0.7 MeOH mole fraction and 25 °C. Water concentration (mol dm^{-3}): 1, 0.00830; 2, 0.0125; 3, 0.0153; 4, 0.0206; 5, 0.0278; 6, 0.0348; 7, 0.0561; 8, 0.0739.

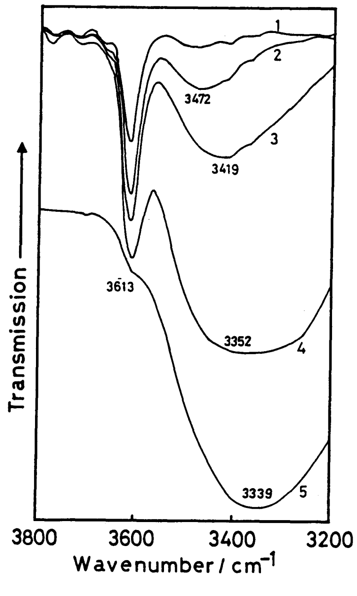


Fig. 3. IR spectra of MeOH in DCE-MeOH mixtures. MeOH mole fraction: 1, 0.03; 2, 0.07; 3, 0.10; 4, 0.30; 5, 0.70. CaF_2 cell (0.25 mm) for 1, 2, 3, and 4, and CaF_2 demountable cell for 5.

cules to the cation depends on the degree of complex formation of water with solvent molecules or self-association,[1,2] it is necessary to consider the structure of water complexes and MeOH net works.

Figure 3 shows IR spectra for MeOH in DCE-MeOH mixtures. A sharp band at 3613 cm^{-1} and a broad band at 3472 cm^{-1} exist below the 0.1 MeOH mole fraction (spectra 1, 2, and 3). The sharp high-frequency band and the broad low frequency band are assigned to the free O-H oscillator of MeOH molecules and to the bonded O-H oscillator in MeOH dimers, respectively, comparing with IR spectra of MeOH in dichloromethane (DCM) by Symons and Thomas.[10] Dependence of the IR spectrum on the MeOH fraction below the 0.1 mole fraction is predominantly elucidated by dimerization equilibrium for MeOH. As the MeOH fraction increases, the broad band is shifted to lower frequency region (toward 3300 cm^{-1} of polymer) and the band of the freee O-H group relatively decreases, and moreover, the free O-H group almost disappeared at the 0.7 MeOH mole fraction.

Chemical shifts of the O-H proton resonance of MeOH are shown as a function of the MeOH mole fraction in Fig. 4. There is a linear relationship between them below the 0.2 MeOH mole fraction. This can be explained by dimerization of MeOH, as supported by the IR results in Fig. 3. The dimer model yields a simple expression for the chemical shift ν which is referenced to TMS as inner standard at low MeOH concentrations

$$\nu=(1-2x)\nu_{\mathrm{m}}+2x\nu_{\mathrm{d}} \tag{1}$$

$$x=(4+1/K_{\mathrm{M2}}C)-[(4+1/K_{\mathrm{M2}}C)^2-16]^{1/2}/8 \tag{2}$$

where ν_{m} is the chemical shift of the monomer protons, ν_{d} is the hypothetical mean chemical shift of the dimer protons, K_{M2} is the dimer formation constant in molar unit and C is a molar concentration of MeOH. A ν_{m} value of 75.2 Hz at the 0.03 MeOH mole fraction where the MeOH monomers are predominant was used for evaluating the K_{M2} value. A K_{M2} value of 0.29 and a ν_{d} value of 175 Hz were obtained. At the 0.1 MeOH mole fraction (1.4 mol dm^{-3}), for example, the K_{M2} value indicates that 34% of MeOH is dimerized.

However, the IR and NMR results could not give information as to whether the electron pairs of the oxygen atom of water remains free or not, and whether the water molecules dimerizes or not.

Estimation of K_{NiW} Values. The K_{NiW} value was estimated at each concentration of water for the data given in Fig. 2 using the equation

$$K_{\mathrm{NiW}}=(\varepsilon_0-\varepsilon)/(\varepsilon-\varepsilon_{\mathrm{s}})[\mathrm{W}] \tag{3}$$

where ε is the apparent molar absorptivity at 520 nm, ε_0 is the molar absorptivity at the zero water concentration, ε_{s} is the molar absorptivity of the water coordinate-chelate cation and [W] is the analytical concentration of water. A constant value of $\varepsilon_{\mathrm{s}}=10$ $dm^3\,mol^{-1}\,cm^{-1}$ obtained in the oxygen-atom donor solvent, *N,N*-diethylformamide[6] was used. The K_{NiW} values are plotted as a function of the water concentration in Fig. 5.

The K_{NiW} values in the 0.1 and 0.3 MeOH mole fraction mixtures do not depend on the water concentration, but those in mixtures above the 0.5 MeOH mole fraction decrease with increasing the water concentration, showing a decrease in activity of water molecules. Since the isolated monomeric water which is not hydrogen-bonded to bulk solvents is hardly coordinated to the nickel,[1,2] the results in Fig. 5 show that the water molecules in the mixed solvents are hydrogen bonded to MeOH and suggest that the heterodimer with MeOH is dominant in the MeOH poor region and additional species of water leading to a decrease in activity of water appear in the MeOH rich region.

As shown in Fig. 3, in the MeOH rich region the free OH group for MeOH was hardly found, the oligomerization being enhanced. This may make it

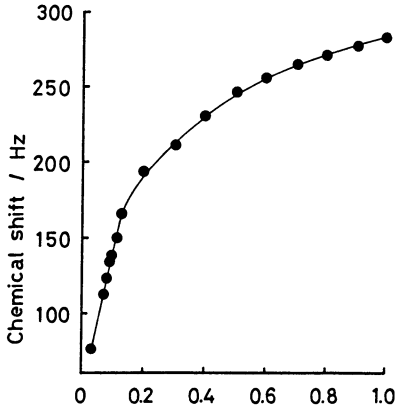


Fig. 4. Dependence of ^{1}H NMR chemical shift for hydroxyl group of MeOH referenced to TMS on the mole fraction of MeOH in DCE-MeOH mixtures.

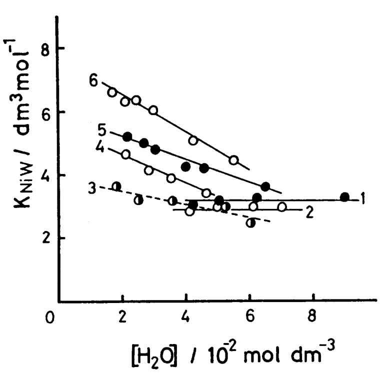


Fig. 5. Dependence of K_{NiW} on the water concentration in DCE-MeOH mixtures at 25 °C. Mole fraction of MeOH: 1, 0.1; 2, 0.3; 3, 0.5; 4, 0.7; 5, 0.9; 6, 1.0. K_{NiW} values were estimated by Eq. 3 at each concentration of water.

difficult for MeOH to act as a proton donor to water, and so it is assumed that the possibility of dimerization of water is present.

When the dimerization of water occurs, the apparent coordination constant of water $K_{\mathrm{NiW(app)}}$ can be written by

$$K_{\mathrm{NiW(app)}}=(K_{\mathrm{NiW1}}+K_{\mathrm{NiW2}}K_{\mathrm{W2}}[\mathrm{H_2O}])/(1+K_{\mathrm{W2}}[\mathrm{H_2O}]) \quad (4)$$

where K_{NiW1} and K_{NiW2} are the coordination constants for the monomeric water (heterodimer) and dimeric water, respectively, K_{W2} is the dimerization constant of water, and $[\mathrm{H_2O}]$ is the concentration of the monomeric water. Therefore, the apparent molar absorptivity ε is expressed by

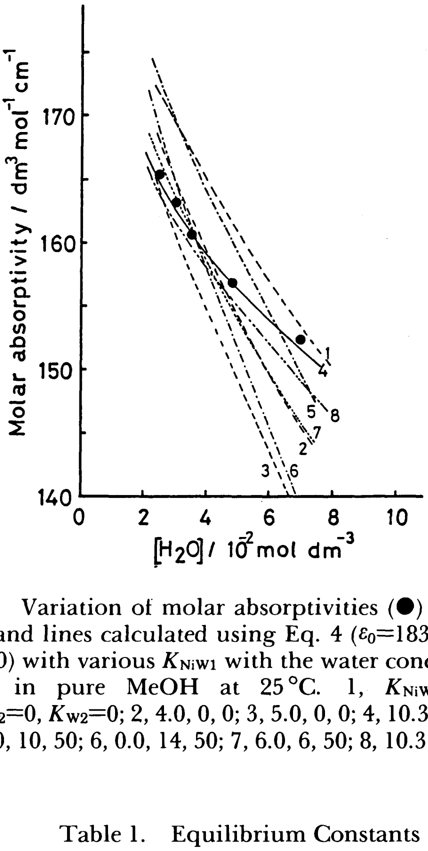


Fig. 6. Variation of molar absorptivities (●) at 520 nm and lines calculated using Eq. 4 (ε_0=183.7 and ε_s=10) with various K_{NiW1} with the water concentration in pure MeOH at 25 °C. 1, K_{NiW1}=3.0, K_{NiW2}=0, K_{W2}=0; 2, 4.0, 0, 0; 3, 5.0, 0, 0; 4, 10.3, 0, 50; 5, 0.0, 10, 50; 6, 0.0, 14, 50; 7, 6.0, 6, 50; 8, 10.3, 0, 40.

$$\varepsilon=(\varepsilon_0+\varepsilon_s K_{\mathrm{NiW(app)}}[\mathrm{H_2O'}])/(1+K_{\mathrm{NiW(app)}}[\mathrm{H_2O'}]) \quad (5)$$

where $[\mathrm{H_2O'}]$ is the sum of concentrations of the monomeric and dimeric water.

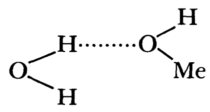
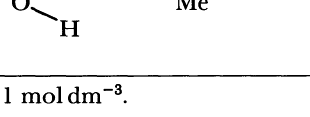
It is assumed that all the water species are hydrogen-bonded to the MeOH oligomers, and that these are terminal water molecules with the free electron pairs except water molecules which are the proton acceptor in the dimer. Typical results for the fitness in the pure MeOH are shown in Fig. 6. It should be noted that the best fitness was obtained when only the monomeric water was regarded as a coordinated species with a K_{W2} value of 50 dm^3 mol^{-1} and a K_{NiW1} value of 10.3 dm^3 mol^{-1} and the dimeric water is hardly coordinated. In this connection protic MeOH in the hydrogen-bonded networks is remarkably contrastive with aprotic solvents such as AC and PDC in which the dimeric water is coordinated. Since the dimeric water is more basic and more acidic than the monomeric water,[1,2,11–16] it seems that the strengthened basicity and acidity of the dimer allow itself to be a member of the oligomers of MeOH which mask the electron pair effective for coordination. This is compatible with the suggestion from Symons[17] that the linear dimer of MeOH in DCM-MeOH mixtures should be more basic and more acidic than the monomer, and this would lead to a less of dimers and a gain of oligomers.

In the same way, the best fitting values for K_{W2} and K_{NiW1} were obtained in the 0.5—0.9 MeOH fractions and the results are given in Table 1. Both the values of K_{NiW1} and K_{W2} increase with increasing the MeOH fraction, that is, the hydrogen-bond energy of networks for MeOH.

In Py,[18] water forms the 1 : 1 and 1 : 2 water-Py species below 0.1 mol dm^{-3} of water. The K_{NiW1} values were estimated at each concentration of water using Eq. 3, and the average value 21±2 was obtained.

Figure 7 shows a correlation of logarithm of K_{NiW} with ^{1}H chemical shift (ν_{OH}) of the hydroxyl group for

Table 1. Equilibrium Constants (K_{NiW1}) for Monomeric Water Coordination to [Ni(tmc)]$^{2+}$, Dimerization Constant (K_{W2}) of Water, and Donor Number (DN) of Mixtures in DCE-MeOH Mixtures at 25 °C

X_{MeOH}	K_{NiW1} / dm^3 mol^{-1}		$K_{\mathrm{W2}}$$^{a)}$ / dm^3 mol^{-1}	Water$^{b)}$ Monomer (%)	Water$^{b)}$ Dimer (%)	Donor species	DN
0.1	3.4±0.2	3.2±0.1	0	100	0		—
0.3	3.0±0.1		0	100	0		23
0.5	3.2±0.1	3.1±0.1	1±1	83	17		29
0.7	6.6±0.1	5.7±0.1	16±1	42	58		33
0.9	9.1±0.2	9.9±0.3	19±1	40	60		35
1.0	9.7±0.1	10.3±0.2	50±1	27	73		36

a) Average of two determinations. b) Water concentration is 0.1 mol dm^{-3}.

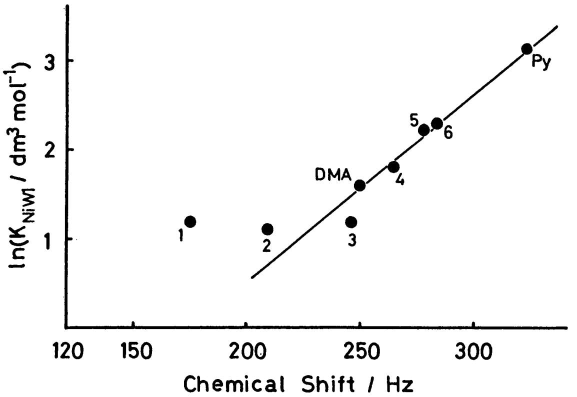


Fig. 7. Relationship of the K_{NiW1} value with ^{1}H NMR chemical shift (Hz) of hydroxyl group of MeOH in DMA, Py, and the DCE-MeOH mixtures. Dimeric MeOH: 1, 0.1 MeOH mole fraction; oligomers: 2, 0.3; 3, 0.5; 4, 0.7; 5, 0.9; 6, 1.0.

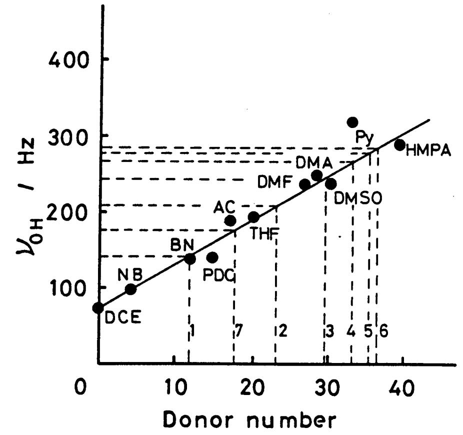


Fig. 8. Relationship between the ^{1}H NMR chemical shift (Hz) in MeOH complexes and donor number of the donor component. The apparent chemical shift of MeOH in various mixtures with DCE: 1, 0.1 mole fraction of MeOH; 2, 0.3; 3, 0.5; 4, 0.7; 5, 0.9; 6, 1.0. The hypothetical mean chemical shift of the MeOH dimer protons: 7.

MeOH in DCE-MeOH mixtures, DMA, and Py. The ν_{OH} for DCE-MeOH mixtures are mean values for protons under various circumstances in MeOH oligomers, but there is a good linear relationship between ln K_{NiW1} and ν_{OH} , indicating that the ν_{OH} mean values reflect the basicity of the oxygen atom for terminal water molecules attached to MeOH oligomers. Thus, it can be said that the basicity of the terminal waters increases with increasing the hydrogen bond energy for the oligomer. This property of basicity of protic solvents is agreement with that expected by the theoretical calculations.[11–16)]

^{1}H NMR chemical shifts of the O-H group for MeOH in various organic solvents were plotted as a function of their donor number (DN) (Fig. 8). The ν_{OH} values for DCE, NB, BN, and PDC were obtained by extrapolating observed ν_{OH} values at the zero concentration of MeOH. There was found a good linear relationship expressed with Eq. 5

$$\mathrm{DN} = 0.167\,\nu_{OH} - 11.7 \qquad (5)$$

where ν_{OH} is the ^{1}H NMR chemical shift in Hz of the O-H group of MeOH.

Since the ν_{OH} value for the 0.1 MeOH mole fraction mixture is a mean value for the monomer and dimer of MeOH, the corresponding DN value only indicates a mean DN value for DCE and the monomeric MeOH. In spite of the equal number of the hydrogen-bonding proton and the free proton for dimeric MeOH, its hypothetical mean ν_{OH} value 175 gives a DN value of 18 which is very close to 19[7)] for MeOH. Therefore, it is reasonably assumed that ν_{OH} values in the higher MeOH mole fraction mixtures in which the number of the free proton is much less, give meaningful DN values.

The chemical shift and K_{NiW1} in the 0.5 MeOH mole fraction mixture are nearly the same as those in DMA (DN=27.8[7)]). This means that the charge transfer among MeOH molecules in the mixture is the same as that from the DMA molecule to the MeOH molecule, and moreover, the charge-transfer effect of MeOH on the water basicity is closely similar to that from DMA to the water molecules. Therefore, a DN value of 29 is reasonable for the 0.5 MeOH mole fraction mixture. In the same way, DN values 23, 33, 35, and 36 were evaluated for the MeOH mole fractions 0.3, 0.7, 0.9, and 1.0, respectively. The K_{NiW1} value for the heterodimer of water and MeOH which is between those for the water dimer (DN=26[2)]) in PDC and that (DN=27[2)]) in AC, gives a DN value of 26.5 for the heterodimer. The DN value for the pure MeOH is higher than DNs estimated by using other methods (DN=24—33.5).[19–22)] In view of the linear relationships of ln K_{NiW}-ν_{OH} and ν_{OH}-DN plots (Figs. 7 and 8), DN of Py should be 42 in place of 33.1 with respect to charge transfer for hydrogen bonding.

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