Characterization and Equilibrium of Beryllium(II) Solvates $[\text{BeS}_n(\text{H}_2\text{O})_{4-n}]^{2+}$ ($n=0-4$, $\text{S}=\text{N}, \text{N}$ -Dimethylformamide and 1,1,3,3-Tetramethylurea) Studied by ^9Be NMR Spectroscopy

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Beryllium(II) solvates $[\text{BeS}_n(\text{H}_2\text{O})_{4-n}]^{2+}$ ($n=0-4$, $\text{S}=\text{N}, \text{N}$ -dimethylformamide (dmf) and 1,1,3,3-tetramethylurea (tmu)) in acetonitrile have been characterized by ^9Be NMR spectroscopy. The difference in steric effects of the bound dmf and tmu molecules on the structures of the solvates has been clarified by ^9Be NMR chemical shifts. The stepwise formation constants, $K_n = \frac{[\text{BeS}_n(\text{H}_2\text{O})_{4-n}]^{2+}[\text{H}_2\text{O}]}{[\text{BeS}_{n-1}(\text{H}_2\text{O})_{5-n}]^{2+}[\text{S}]}$ ($n=1-4$), obtained from the ^9Be NMR signal intensities for the tmu system drastically decrease between K_1 and K_2 and between K_3 and K_4 , while those for the dmf system decrease statistically with an increase in n . Such a difference in the stability of the two systems is discussed in connection with the steric effects.

Keywords Characterization of beryllium(II) solvate, ^9Be NMR spectroscopy, steric effect of solvent

Information on the solvation state of metal ions in solution is essential in the field of analytical and coordination chemistry, because such information gives us a good understanding of the thermodynamic and kinetic behaviors of the metal ions.¹ However, structural information for the solvated alkali and alkaline earth metal ions in solution is rather less accessible compared with that for the transition metal ions due to difficulties of applying spectrophotometric methods. Under the circumstances, NMR spectroscopy is a helpful tool which provides us plenty of information for investigation on the solvated alkali and alkaline earth metal ions. Though there are some studies on the donating ability of nonaqueous solvents using the NMR chemical shift of alkali metal ions²⁻⁵, few approaches from the structural aspects of the solvated alkali and alkaline earth metal ions have been made so far.

The hydration structure of the beryllium(II) ion in an aqueous solution and a solid state has been determined to be four-coordinate tetrahedron by NMR spectroscopy⁶ and X-ray and neutron diffraction studies.^{7,8} Considering that the beryllium(II) ion has the smallest ion radius among the alkali and alkaline earth metal ions⁹, the solvation of the beryllium(II) ion is rather strong but can be sterically restrained concurrently, especially in bulky solvents. In the present work, to clarify the implication of the electronic and steric factors in the solvation of the beryllium(II) ion, we have selected two coordinating solvents, *N,N*-dimethylformamide (DMF) and 1,1,3,3-

tetramethylurea (TMU), which have analogously a carbonyl donor oxygen but differences in the steric bulk. The competitive solvation with water for the dmf- and tmu-solvated beryllium(II) ions in acetonitrile, which does not act as a coordinating solvent for the beryllium(II) ion, has been investigated by means of the accessible ^9Be NMR parameters. The solvation structures will be discussed by taking advantage of the electronically sensitive NMR chemical shift.

Experimental

Solvents

DMF (Wako, Sp. Gr.) and TMU (Wako, Sp. Gr.) were dried over calcium hydride (Wako) and activated 4A molecular sieves, respectively, and then distilled under reduced pressure. Acetonitrile (Wako, Sp. Gr.) was distilled after refluxing for 3 h in the presence of P_2O_5 (Wako, Sp. Gr.) and distilled again after refluxing in the presence of calcium hydride.

Preparation of $[\text{Be}(\text{dmf})_4](\text{ClO}_4)_2$ and $[\text{Be}(\text{tmu})_4](\text{ClO}_4)_2$

Beryllium flakes (Wako, 99.5%) were dissolved in an aqueous solution of perchloric acid (Wako, S. S. Gr.). The residue was removed by filtration and the filtrate was concentrated. The resultant crystals were recrystallized from distilled water. The hydrate obtained was dissolved in DMF containing a large amount of 2,2-

dimethoxypropane (Wako) as a dehydrating reagent. The following procedures were carried out appropriately under nitrogen: The dehydrated solution was concentrated under reduced pressure to obtain crystals which were twice recrystallized from a DMF/dichloromethane (Wako, Sp. Gr.) (1:9 v/v) solution by adding diethyl-ether (Wako, Sp. Gr.). The tmu solvate was similarly prepared using TMU instead of DMF. *Anal.* Calcd for $[\text{Be}(\text{dmf})_4](\text{ClO}_4)_2$: C, 25.20; H, 4.95; N, 9.81%. Found: C, 25.04; H, 5.18; N, 9.91%. Calcd for $[\text{Be}(\text{tmu})_4](\text{ClO}_4)_2$: C, 35.70; H, 7.10; N, 16.60%. Found: C, 35.69; H, 7.30; N, 16.46%.

Sample preparation and measurements

Sample solutions for NMR measurements were prepared in a glovebox by dissolving a known amount of $[\text{Be}(\text{dmf})_4](\text{ClO}_4)_2$ or $[\text{Be}(\text{tmu})_4](\text{ClO}_4)_2$ in freshly distilled acetonitrile and adding a known amount of water. The ^9Be NMR measurements at various temperatures were performed on a JEOL JNM-GX270 FT-NMR spectrometer operating at 38.0 MHz. The temperature was measured by a substitution technique using a thermistor (A810, Takara Thermistor Co.). About 15 min were required for the temperature equilibration of the sample solution and the temperature of the solutions was controlled within ± 0.2 K.

Results and Discussion

Chemical shift

As shown by spectra a and b in Fig. 1, the solution of $[\text{Be}(\text{dmf})_4](\text{ClO}_4)_2$ in acetonitrile exhibits one main ^9Be NMR signal (1), and the other four signals (2–5) appear in the higher field with increasing the concentration of water. Further increase in the water concentration gives no new signal and results in the signals in the higher field being increased and those in the lower field being decreased. The solution of $[\text{Be}(\text{tmu})_4](\text{ClO}_4)_2$ in acetonitrile exhibits a similar trend of variation in the ^9Be NMR spectra by increase in the water concentration, although the parent signal (1') is observed in the highest field and the additional signals (2'–5') come out in a lower field than the parent one (see spectra c, d, and e in Fig. 1). The chemical shift of signal 5' in the lowest field for the tmu system is completely the same as that of signal 5 for the dmf system. Taking account of the weak donicity of acetonitrile and the high affinity of the beryllium(II) ion with an oxygen donor atom, the above ^9Be NMR spectral behaviors are interpreted as the stepwise replacement of the bound dmf or tmu by the added water. Consequently, the five signals 1–5 and 1'–5' are assigned to $[\text{Be}(\text{S})_4]^{2+}$, $[\text{BeS}_3(\text{H}_2\text{O})]^{2+}$, $[\text{BeS}_2(\text{H}_2\text{O})_2]^{2+}$, $[\text{BeS}(\text{H}_2\text{O})_3]^{2+}$, and $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ (S=dmf and tmu), respectively.¹⁰ Such results indicate that the four-coordinate structure of the beryllium(II) ion is maintained in these solvent systems as in an aqueous solution. Furthermore, because the addition of perchloric acid to the sample solutions has not affected the

Fig. 1 Changes in 38.0 MHz ^9Be NMR spectra of the dmf and tmu solvates of the beryllium(II) ion in acetonitrile by adding water: (a) $C_{\text{Be}(\text{dmf})_4}=0.33 \text{ mol kg}^{-1}$ (245.1 K); (b) $C_{\text{Be}(\text{dmf})_4}=0.36 \text{ mol kg}^{-1}$ and $C_{\text{H}_2\text{O}}=6.2 \text{ mol kg}^{-1}$ (245.7 K); (c) $C_{\text{Be}(\text{tmu})_4}=0.15 \text{ mol kg}^{-1}$ and $C_{\text{H}_2\text{O}}=2.1 \text{ mol kg}^{-1}$ (258.3 K); (d) $C_{\text{Be}(\text{tmu})_4}=0.15 \text{ mol kg}^{-1}$ and $C_{\text{H}_2\text{O}}=0.61 \text{ mol kg}^{-1}$ (258.3 K); (e) $C_{\text{Be}(\text{tmu})_4}=0.15 \text{ mol kg}^{-1}$ room temperature), where $C_{\text{Be}(\text{dmf})_4}$, $C_{\text{Be}(\text{tmu})_4}$, and $C_{\text{H}_2\text{O}}$ denote the initial concentrations of $[\text{Be}(\text{dmf})_4](\text{ClO}_4)_2$, $[\text{Be}(\text{tmu})_4](\text{ClO}_4)_2$, and water, respectively. The chemical shifts are given versus the signal 5 for $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$: 1, 1.79; 2, 1.34; 3, 0.89; 4, 0.45; 1', -1.47; 2', -1.21; 3', -0.84; 4', -0.47 ppm.

chemical shifts at all, it is reasonable to conclude that the chemical shift is not influenced by the ion-pair formation of the solvated beryllium(II) ion and/or the ion-pair is quantitatively formed under the present conditions. It is also obvious that there is no hydroxo complex formation as expected from the low-proton-accepting ability of acetonitrile.

According to the overlap model², the paramagnetic shielding expressed in terms of the sum of the overlap integrals between the outer p orbitals of alkali or alkaline earth ions and the outer orbitals of the bound donor atoms should determine the chemical shifts. In fact, Popov and co-workers have made some attempts to correlate the chemical shifts of alkali metal ions with the Gutmann solvent donor numbers^{2,4,5,11} which are the enthalpy change for the adduct formation between SbCl_5 and the solvent molecule in 1,2-dichloroethane. They found a fair correlation for the ^{23}Na NMR chemical shifts, where the only discrepancy appears to be water.¹² However, such a correlation is not essential for all alkali or alkaline earth metal ions, considering the difference in the energy levels of the ion's outer p orbitals and the steric factors varied with the metal ions. In the present case, the difference in shielding for the ^9Be nucleus of $[\text{Be}(\text{dmf})_4]^{2+}$, $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$, and $[\text{Be}(\text{tmu})_4]^{2+}$ indicates that the electron donation from the oxygen atom toward the beryllium(II) ion increases in the order, $\text{dmf} < \text{H}_2\text{O} < \text{tmu}$.¹³

We should mention the change in the chemical shift with the stepwise formation, *i.e.*, the five signals for the dmf system, 1–5, are observed at regular intervals of 17 Hz, while the signal intervals for the tmu system are 18, 14, 14, and 10 Hz, decreasing with an increase in the number of bound tmu molecules. These observations indicate that the shielding effects by the individual bound dmf and H₂O molecules are both constant in the five solvates, [Be(dmu)_n(H₂O)_{4-n}]²⁺ (*n*=0–4), while the shielding by the bound tmu molecules is not equivalent among the tmu solvates, [Be(tmu)_n(H₂O)_{4-n}]²⁺ (*n*=1–4). If we refer to the expression of the overlap model, the irregularity in the chemical shifts of the tmu system can be attributed to the decrease in the overlap of the *p* orbitals between the beryllium(II) ion and the donor oxygen in each tmu molecule with an increase in *n*, which is caused by the elongation of the Be–O bonds (radial distortion around the beryllium(II) ion) and/or the deviation of the bond angles around the bound oxygens from the proper direction of the donor orbital (angular distortion around the oxygen atom). It is certain that such distortions are due to the steric repulsion between the bound bulky tmu molecules.

Considering that the beryllium(II) ion is not so retentive of the regular tetrahedral geometry, we conclude that the steric repulsion between the neighboring tmu molecules in [Be(tmu)₂(H₂O)₂]²⁺ and [Be(tmu)₃(H₂O)]²⁺ is relaxed by distortion from the tetrahedral geometry without radial distortion around the beryllium(II) ion. Therefore, the decrease in the shielding by each bound tmu oxygen compared with [Be(tmu)(H₂O)₃]²⁺ is attributed to the angular distortion around the oxygen atom which may be caused by the neighboring tmu repulsion. It is possible then that the radial distortion around the beryllium(II) ion is responsible for the further decrease in the shielding for [Be(tmu)₄]²⁺ in which the four bound tmu molecules should be equivalent and the relaxation of the steric repulsion by the distortion from the regular tetrahedral geometry is not probable.

Equilibrium

In order to compare the stability of the present solvates of the beryllium(II) ion, the stepwise formation constants *K_n* defined by Eq. (1) were evaluated by the initial concentrations of the beryllium(II) ion and water and the relative integration intensity of the ⁹Be NMR signals.

$$K_n = \frac{[\text{BeS}_n(\text{H}_2\text{O})_{4-n}^{2+}][\text{H}_2\text{O}]}{[\text{BeS}_{n-1}(\text{H}_2\text{O})_{5-n}^{2+}][\text{S}]} \quad (\text{S} = \text{dmf and tmu, } n = 1-4) \quad (1)$$

The stepwise formation constants were obtained at sufficiently low temperatures, *i.e.*, at 235.0 K and 258.3 K for the dmf and tmu systems, respectively, where all the ⁹Be NMR signals are well resolved (Table 1). Because the values of *K_n* for the dmf system decrease statistically with an increase in *n*¹⁴, it is expected that the respective Be–O bonds for dmf and water are energetically equiv-

Table 1 Stepwise formation constants *K_n* for [BeS_n(H₂O)_{4-n}]²⁺ (*n*=1–4)

S	T/K	<i>K</i> ₁	<i>K</i> ₂	<i>K</i> ₃	<i>K</i> ₄
dmf	235.0	14 ± 10	6.3 ± 1.3	3.2 ± 0.4	1.2 ± 0.2
tmu	258.3	3.3 ± 0.1	0.59 ± 0.04	0.83 ± 0.07	0.02 ± 0.015

alent in all the species, [BeS_n(H₂O)_{4-n}]²⁺ (*n*=0–4). However, the stepwise formation constants for the tmu system drastically decrease between *K*₁ and *K*₂ and between *K*₃ and *K*₄. These findings indicate the destabilization of [Be(tmu)₂(H₂O)₂]²⁺ and the further destabilization of [Be(tmu)₄]²⁺ due to the steric repulsion between the bound bulky tmu molecules which is discussed above in connection with the chemical shifts.

To compare the relative stability of the corresponding dmf and tmu solvates, we should consider the following factors: (i) the intrinsic Be–O bond strength, (ii) the repulsion between the bound solvents, and (iii) the degree of freedom of the bound solvents. The first factor is favorable to the relative stabilization of the tmu solvates compared with the dmf ones as observed in the direction of the ⁹Be NMR chemical shifts, whereas the reverse is true for the second and third factors as observed in the chemical shift intervals. At this point, we refer to available reaction mechanisms for solvent exchange on the beryllium(II) ion¹⁵ and complexation of aqua beryllium(II) ion.¹⁶ The large positive value of the activation volume (10.5 cm³ mol⁻¹) for the tmu exchange allows us to expect a much more dissociative mechanism compared with the dmf exchange of which the activation volume is rather negative (–3.1 cm³ mol⁻¹).¹⁵ Such a difference in the reaction mechanism arises from the difference in the steric crowding around the beryllium(II) center. In addition, it has been demonstrated that the large negative values of entropy and volume of activation (Δ*S*[‡]=–83.5 J mol⁻¹ K⁻¹, Δ*V*[‡]=–7.1 cm³ mol⁻¹) for complexation of the beryllium(II) ion with 4-isopropyltropolone in an acidic aqueous solution strongly indicate a mechanism with an associative mode of activation for the complexation.¹⁶ With the present results, we can expect that the complexation reaction of the beryllium(II) ion in TMU will become less associative than those in DMF and water.

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 13. The shielding for the ^{23}Na nucleus in the corresponding solvents increases in the order, $\text{dmf} < \text{tmu} < \text{H}_2\text{O}$.
 14. If the probability of the replacement of water by dmf and that of dmf by water depends on the numbers of the applicable substitution sites in each species, the ratios of the stepwise formation constants $K_1 : K_2 : K_3 : K_4$ become 48 : 18 : 8 : 3 statistically.
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