Effect of hydrophobic and hydrophilic interactions on the stability of diastereoisomers of Δ- and Λ-[Ru(*S*-am)(bpy)$_2$]$^+$ complexes (am = Ala, Phg, Leu, Phe or Tyr ligand) in aqueous solutions

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Abstract

The equilibrium constant (K) of photochemical inversion between Δ- and Λ-[Ru(*S*-am)(bpy)$_2$]$^+$ (bpy = 2,2′-bipyridine (bpy); *S*-am = (*S*)-alaninato (*S*-Ala), (*S*)-phenylglycinato (*S*-Phg), (*S*)-leucinato (*S*-Leu), (*S*)-phenylalaninato (*S*-Phe) or (*S*)-tyrosinato (*S*-Tyr) ligand) was obtained in H_2O, D_2O, CH_3OH and CH_3CN–H_2O (1:1 in molar ratio) solutions at temperatures of 0 to 100 °C, and $\Delta H°$ and $\Delta S°$ were estimated. The hydrophilic solvation favored the Δ isomer in water, appearing on the enthalpy difference, and the hydrophobic solvation preferred the Λ isomer, controlling the entropy difference. These opposite effects dominated the stability of the two isomers of the complex containing the *S*-Leu, *S*-Phe or *S*-Tyr ligand in water. The results suggested the importance of intramolecular hydrophobic bonding. The photochemical inversion hardly occurred in pure acetonitrile.

Introduction

No inversion of the diastereoisomers of [Ru(*S*-am)(diimine)$_2$]$^{n+}$ (diimine = 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen); am = aminoacidato ligand; $n = 0$ and 1) takes place in the dark. However, the photochemical inversion has been reported by Vagg and Williams [1]. They have obtained the equilibrium constants for the reactions

$$\Delta\text{-[Ru}(S\text{-am})(\text{diimine})_2]^{n+} \rightleftharpoons \Lambda\text{-[Ru}(S\text{-am})(\text{diimine})_2]^{n+} \quad (1)$$

by the use of various kinds of aminoacidato ligands and discussed them in relation to stability of the diastereoisomers in aqueous solutions [2–8].

It is known that this kind of complex usually prefers the Λ configuration at the metal centers due to the steric repulsion between a hydrogen atom of the bpy or phen ligand and the β-methylene group of the (*S*)-aminoacidato ligand. (Figs. 1 and 2) [9, 10]. It has also been reported that little change was seen in the magnitudes of the equilibrium constant at 298 K for bulkier β-substituents of aminoacidato ligands because of no considerable change in the steric requirement. However, there have been some other observations that cannot be explained solely by the intramolecular steric requirements. Solvation effects such as hydrophobic and hydrogen bonding (hydrophilic) effects have also been

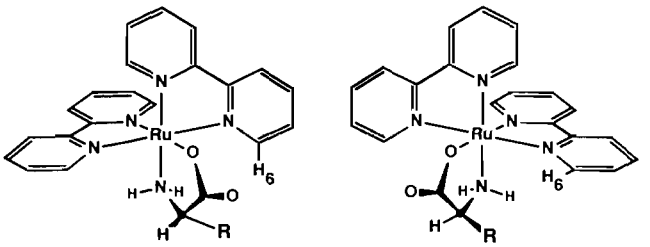

Fig. 1. Structures of Δ- and Λ-[Ru(*S*-am)(bpy)$_2$]$^+$.

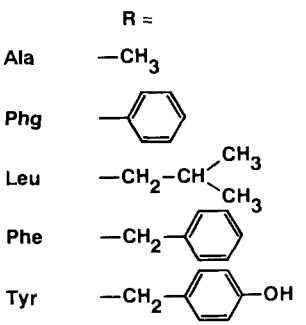

Fig. 2. Side chains of the aminoacidato ligand.

nominated as the discrimination factors of the stability of the diastereoisomers in aqueous solutions [4, 5].

Recently, I have reported that Δ-[Ru(*S*-am)(bpy)$_2$]$^+$ (Δ-*S*) isomer is more hydrophilic than Λ-[Ru(*S*-

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am)(bpy)$_2$]$^+$ (Λ-*S*) isomer from a study on normal-phase adsorption high-performance liquid chromatography (HPLC) [11]. The mechanism for separation of Δ-*S* and Λ-*S* isomers was explained by a difference of hydrogen bonding interaction with a stationary phase through the amine hydrogen atoms in the aminoacidato ligand; silica gel adsorbed the Δ-*S* isomer more strongly than the Λ-*S*. Higher resolution was achieved in the [Ru(*S*-phe)(bpy)$_2$]$^+$ complex than in [Ru(*S*-ala)-(bpy)$_2$]$^+$, which indicated that the large hydrophobic side chain enlarged the discrimination energies. Furthermore, it is known that intramolecular ligand–ligand hydrophobic interaction plays an important role on the stability of this kind of ternary complex [12].

The present complexes have hydrophilic and hydrophobic moieties in a molecule. It is an interesting problem to examine how the amphiphilic properties contribute to the stability in an aqueous solution. I report here temperature dependence and solvent effect on the equilibrium constants for the photochemical inversion of Δ- and Λ-[Ru(*S*-am)(bpy)$_2$]$^+$ complexes (am = Ala, Phg, Leu, Phe or Tyr ligand), and discuss how the solvation energy contributes to the determination of the equilibrium positions in water in addition to the intramolecular steric requirements.

Experimental

Materials

Methanol used in the equilibrium measurements was freshly distilled and dried over 4 Å molecular sieves. Deuterium oxide (D at.% = 99.9) was supplied by Aldrich. All other materials were of reagent or HPLC grade and used as received. Δ- and Λ-[Ru(*S*-am)-(bpy)$_2$]$ClO_4 \cdot nH_2O$ (n = 0–2) were prepared according to ref. 13.

Instruments

The HPLC system consists of an Hitachi model 638-30 system equipped with a Rheodyne model 7125 injector and a Hitachi L-4200 variable-wavelength spectrophotometric detector with a 17.7 μl flow cell. The ^{1}H NMR spectra were measured using a JEOL GSX-400 Fourier transform NMR spectrometer under the conditions reported in the previous paper [11].

Equilibrium measurements

Crystals of Δ,Λ-[Ru(*S*-am)(bpy)$_2$]$ClO_4 \cdot nH_2O$ (n = 0–2) were dissolved in doubly distilled water, deuterium oxide, methanol and acetonitrile–water mixture (1:1 in molar ratio) in the dark, and used as starting solutions. The complex solution (10^{-4}–10^{-5} mol dm^{-3}) was placed in a Pyrex glass vessel equipped with thermostat jacket to keep the temperature constant (0–98 ± 0.1 °C), and continuously purged with nitrogen gas. The solution was irradiated with light from a 300 W short-arc Xe-lamp through an optical glass filter (Kenko L-42) cutting light with wavelengths less than 420 nm. Thus, the MLCT band [bpy(π^*) → Ru(dπ)] at about 490 nm [14, 15] was irradiated, so isomerization between the diastereoisomers (Δ-*S* and Λ-*S*) (inversion at Ru center) occurred in the solution. The ratio of the two diastereoisomers in the solution was analyzed by normal-phase HPLC with tartaric acid-immobilizing silica gel column (stainless-steel column, 250 × 4 mm i.d.) using $CH_3OH/CH_2Cl_2/H_2O = 6/2/2 + 0.005$ mol dm^{-3} LiCl solution as a mobile phase [11]. All of the analytical procedures were performed in the dark to prevent unexpected photochemical reactions of the isomers. Less than 20 μl of sample solutions was injected on the column. The solvents used in the photochemical reaction did not affect the elution because of their small quantity. The Λ-*S* isomer was eluted faster than the Δ-*S* isomer. Inversion at the Ru center and racemization of the aminoacidato ligand did not occur on the column. The areas of chromatogram peaks were detected by absorption at 294 nm. When two peaks overlapped, the areas were calculated by the least-squares method. The ratio of the peak areas of the two isomers changed with the irradiation, but converged with time. The value of the convergent ratio was taken as an equilibrium constant (K). For all of the complexes, the same K value was obtained from at least two kinds of mixtures having different concentration ratios of the two isomers at the same temperature. For the *S*-Phe and *S*-Tyr complexes, it was confirmed that the same K value was obtained in light irradiation to either of the solutions of pure Δ-*S* isomer and pure Λ-*S* isomer at the same temperature. During the irradiation small amounts of decomposition products appeared as separated peaks in HPLC, but they did not affect the value of the equilibrium constant. Molar extinction coefficients of the Δ-*S* and Λ-*S* isomers at 294 nm in a mobile phase agreed with each other within experimental error. The rate of the inversion increased with increasing both temperature and light intensity, and the reaction did not occur in the dark under the present experimental conditions. The equilibrium constant for the [Ru(*S*-ala)(bpy)$_2$]$^+$ complex was obtained by CD spectrophotometric method because of difficulty of the resolution.

The photochemical inversion hardly occurred in pure acetonitrile in either case when using Δ-*S* or Λ-*S* as the starting material.

Equilibrium constants

I have reported the thermal racemization of phenylalaninato ligand in [Ru(*S*-phe)(bpy)$_2$]$^+$ complex [13] (eqn. (2)). Considering the equilibrium, this thermal

and reversible reaction has the same energy balance as the inversion reaction at the Ru center, since the Δ-*S* isomer is energetically equivalent to the Λ-*R* isomer and the Δ-*R* to the Λ-*S*.

$$\Delta\text{-}S \text{ (or } \Lambda\text{-}R) \overset{OH^-}{\rightleftharpoons} \Delta\text{-}R \text{ (or } \Lambda\text{-}S) \text{ (in the dark)} \quad (2)$$

The equilibrium constant of eqn. (2) obtained by HPLC analysis was 1.67 ± 0.06 in 10^{-3} mol dm^{-3} NaOH solution at 100 °C in the dark, consistent with 1.68 ± 0.04 of the corresponding *K* of the photochemical inversion in the present experiment. This indicates that the equilibrium constant of the photochemical inversion represents the thermodynamical energy difference between the Δ-*S* and Λ-*S* isomers in a solution. From this observation, the following consideration can be made.

The energy relations between triplet excited states [16] and the ground state in the Δ-*S* isomer are almost equivalent to that in the Λ-*S* isomer, because the two isomers in a solution exhibit the same electronic spectra within experimental error. Then, formation efficiency and life time of the excited states in the Δ-*S* isomer would be the same as those in the Λ-*S* isomers. Hence, the ratio of the concentrations of the ground and excited states of the Δ-*S* isomer can be considered to be the same as that of the Λ-*S* isomer during the irradiation. Therefore, the equilibrium constant of the reaction

$$\Delta\text{-}S \rightleftharpoons \Lambda\text{-}S \quad (3)$$

can be represented by the concentration ratio of the isomers in the steady state brought about by the irradiation of light. Thus, the equilibrium constant *K* in this study is defined as

$$K = [\Lambda\text{-}S]_e / [\Delta\text{-}S]_e \quad (4)$$

where the subscript e refers to the concentration in the steady state. This equilibrium constant is the same as that defined by Vagg and Williams [1].

Results and discussion

The logarithms of the equilibrium constants are plotted against the reciprocal of temperature as shown in Figs. 3 and 4, and the thermodynamical data are listed in Table 1. In aqueous solutions (Fig. 3), linear or almost linear relationships were shown for the (*S*)-leucinato (*S*-Leu), (*S*)-alaninato (*S*-Ala) and (*S*)-phenylglycinato (*S*-Phg) complexes. However, the (*S*)-phenylalaninato (*S*-Phe) and (*S*)-tyrosinato (*S*-Tyr) complexes showed non-linear relationships, namely, abnormality. As a whole, the enthalpy differences were zero or positive, indicating that the inversion from Δ-*S* to Λ-*S* was endothermic. The entropy differences

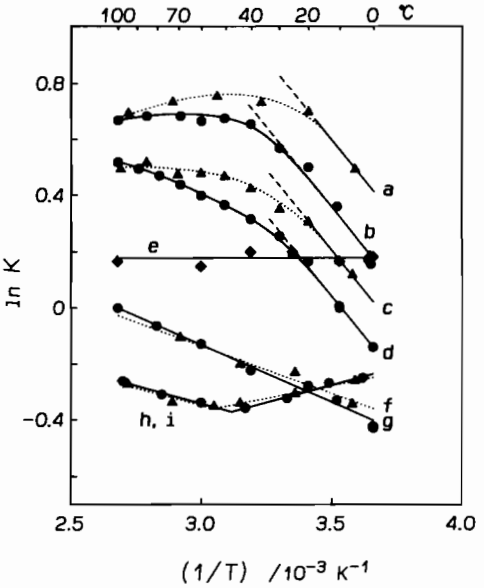

Fig. 3. Temperature dependence of ln *K* of the inversion of $[Ru(S\text{-am})(bpy)_2]^+$ in water (——) and deuterium oxide (· · · · ·): a and b, *S*-Tyr; c and d, *S*-Phe; e, *S*-Ala; f and g, *S*-Leu; h and i, *S*-Phg complexes. The *S*-Tyr and *S*-Phe complexes show linear relationships at lower temperature region.

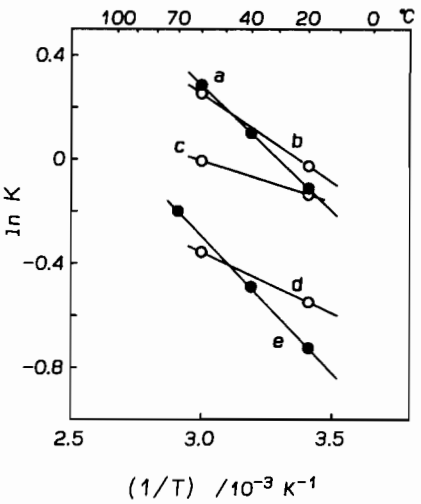

Fig. 4. Temperature dependence of ln *K* of the inversion of $[Ru(S\text{-am})(bpy)_2]^+$ in methanol; a, *S*-Phe; b, *S*-Tyr; c, *S*-Leu; d, *S*-Phg complexes and in acetonitrile–water mixture (1:1 in molar ratio); e, *S*-Phe complex.

were positive, favoring the the Λ-*S* isomer, except for the Phg complex at lower temperatures. Figure 4 indicates that organic solvents stabilize the sterically unfavorable Δ-*S* isomers for most of the complexes as compared with aqueous solutions, which suggests the considerable effect of solvation on the stability of diastereoisomers. Hence, I divided the enthalpy difference into three contributions as follows

$$\Delta H^\circ = \Delta H^\circ(\text{Rep}) + \Delta H^\circ(\text{NHO}) + \Delta H^\circ(\text{Hphobic})$$

TABLE 1. Thermodynamic parameters

Complex	Solvent	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J K^{-1} mol^{-1})
[Ru(*S*-phe)(bpy)$_2$]$^+$	H_2O[a]	9.5	34
	D_2O[a]	9.5	35
	CH_3CN-H_2O[b]	8.7±0.1	24±0
	CH_3OH	8.0±0.0	26±0
[Ru(*S*-tyr)(bpy)$_2$]$^+$	H_2O[a]	9.5	36
	D_2O[a]	9.5	38
	CH_3OH	5.6±0.3	19±1
[Ru(*S*-leu)(bpy)$_2$]$^+$	H_2O	3.4±0.1	9.1±0.5
	D_2O	2.8±0.4	7.4±1.3
	CH_3OH	2.6±0.7	7.9±2.2
[Ru(*S*-phg)(bpy)$_2$]$^+$	H_2O[c]	−2.1±0.2	−9.6±0.7
	H_2O[d]	2.1±0.3	3.6±0.9
	D_2O[c]	−1.5±0.1	−7.7±0.3
	D_2O[d]	2.0±0.7	3.2±2.1
	CH_3OH	3.9±0.3	8.7±1.1
[Ru(*S*-ala)(bpy)$_2$]$^+$	H_2O[e]	0	1.5±0.1

[a]Less than *c.* 30 °C. [b]1:1 in molar ratio. [c]Less than *c.* 50 °C. [d]More than *c.* 50 °C. [e]Little deuterium effect has been reported [4].

where $\Delta H°$(Rep) is the contribution from intramolecular steric repulsion expected as a negative value (favors Λ-*S*), $\Delta H°$(NHO) is that from hydrophilic solvation through the amine hydrogen atoms of the aminoacidato ligand, and $\Delta H°$(Hphobic) that from hydrophobic solvation. The Δ-*S* isomer is more hydrophilic than the Λ-*S* isomer as mentioned above. Thus, $\Delta H°$(NHO) would become a positive value (favors Δ-*S*).

$\Delta H°$(Hphobic) should be considered when an intramolecular ligand–ligand hydrophobic bond forms in one of the isomers. Hydrophobic bonding between intramolecular ligands can be regarded as essentially the partial or complete reversal of the solution process of these non-polar groups in water [17]. Shinoda has shown [18, 19] that the enthalpy of solution of hydrocarbons in water has a small or negative value at room temperature as a result of a large positive enthalpy of mixing ($\Delta H°$(mix)) and a large negative enthalpy of iceberg formation ($n\Delta H°$(ice), where *n* moles of solvent form icebergs). Thus, at room temperature $\Delta H°$(Hphobic) is expected as

$$\Delta H°(\text{Hphobic}) = \Delta H°(\text{mix}) + n\Delta H°(\text{ice}) \sim 0 \text{ or small} \quad (5)$$

although hydrophobic bonding is partially constructed or destroyed during the inversion process.

The structural model shows that a non-polar β-substituent of the aminoacidato ligand faces to one of the pyridine rings of the bpy ligands in the Λ-*S* isomer (Fig. 5). It can be thought that inter-ligand forces such as charge transfer and dispersion interactions contribute to $\Delta H°$(Hphobic). But it is inferred that this kind of

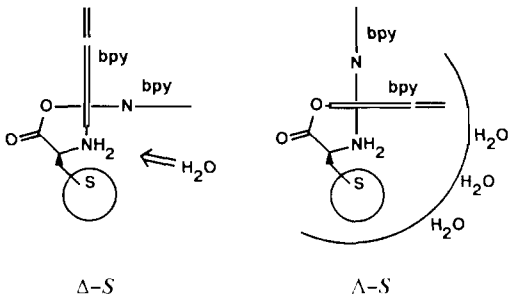

Fig. 5. Schematic representation of a difference of hydration. S is the β-substituent group, which forms a hydrophobic bond with the bpy ligand in the Λ-*S* isomer.

force might be very weak, since the two groups are too distant to interact strongly with each other. Additionally, the ^{1}H NMR for the *S*-Tyr complex indicates that the aromatic ring of the aminoacidato ligand rotates in the Λ-*S* as well as in the Δ-*S*, indicating the absence of strong interactions. I subsequently discuss the hydrophobic bonding between non-polar groups caused by hydrophobic solvation but do not consider these forces for the above reasons.

Vagg and co-workers have reported [6] the crystal structure of Δ,Λ-[Ru(*S*-ala)(bpy)$_2$]$ClO_4 \cdot 0.5H_2O$ and pointed out the significance of the steric repulsion between the methyl group of the *S*-Ala ligand and H-6 of one of the bipyridine hydrogens in the Δ-*S* isomer. The fact that $\Delta H°$ for the *S*-Ala complex is almost zero (Table 1) leads us to the idea that the negative $\Delta H°$(Rep) and the positive $\Delta H°$(NHO) are almost the same magnitude. However, the *S*-Leu, *S*-Phe and *S*-Tyr complexes gave positive $\Delta H°$ values at least in the

lower temperature region. This can be explained as a result of enlargement of $\Delta H°$(NHO).

Deuterium isotope effect

The deuterium isotope effect was observed in the *S*-Phe and *S*-Tyr complexes as shown in Fig. 3; $K_{D_2O}/K_{H_2O} = 1.22$ for the *S*-Tyr and 1.14 for the *S*-Phe complexes at 20 °C. This effect cannot be accounted for by an acid–base equilibrium, since the equilibrium constant is independent of pH of the solution (Fig. 6). Figure 3 shows that in the lower temperature region the entropy largely contributes to the isotope effect. Miyoshi *et al.* [20] have reported that the formation of hydrophobic bonding was accompanied by an entropy gain in D_2O as compared with in H_2O in Pfeiffer systems composed of hydrophobic solutes, because of the higher 'structuredness' of D_2O. Considering the interaction between intramolecular ligands instead of the association with environment compounds, phenomena in the Pfeiffer system resemble those in the present system. Hence, it is reasonable to suggest that the difference in equilibria observed in H_2O and D_2O arises from the formation of hydrophobic bonds in the Λ-*S* isomer in the present system (Fig. 5).

Solvent effect

The equilibrium constants were also measured in methanol and acetonitrile–water (1:1 in molar ratio) solutions for the *S*-Phe complex, exhibiting linearity as shown in Fig. 4 (lines a and e). These solvents would have an ability of hydrogen bonding but lower structuredness property. The positive $\Delta H°$ values in the two solvents are also explainable by the difference of hydrophilic solvation of the isomers.

The thermodynamical data in Table 1 show that the entropy dominates this solvent effect. For the *S*-Phe complex, the change of solvent from methanol to water leads to unstabilization of the Λ-*S* isomer as to enthalpy effect ($\Delta(\Delta H°) = \Delta H°_{water} - \Delta H°_{methanol} = 1.5$ kJ mol^{-1}) but to stabilization of the isomer as to entropy effect ($\Delta(\Delta S°) = \Delta S°_{water} - \Delta S°_{methanol} = 8$ J K^{-1} mol^{-1}; 2.4 kJ mol^{-1} at 298 K), stabilizing the Λ-*S* isomer in water as the net result. A similar relation was also observed in the *S*-Tyr complex ($\Delta(\Delta H°) = 3.9$ kJ mol^{-1} and $\Delta(\Delta S°) = 17$ J K^{-1} mol^{-1}; 5.1 kJ mol^{-1} at 298 K). This large entropy effect can be attributed to stabilization of the Λ-*S* isomer by hydrophobic bonding in water [$\Delta S°$(Hphobic)]. Hence, for the *S*-Leu complex, small entropy effect is explained as a result of little hydrophobic bonding effect in water ($\Delta(\Delta H°) = 0.8$ kJ mol^{-1} and $\Delta(\Delta S°) = 1.2$ J K^{-1} mol^{-1}; 0.4 kJ mol^{-1} at 298 K).

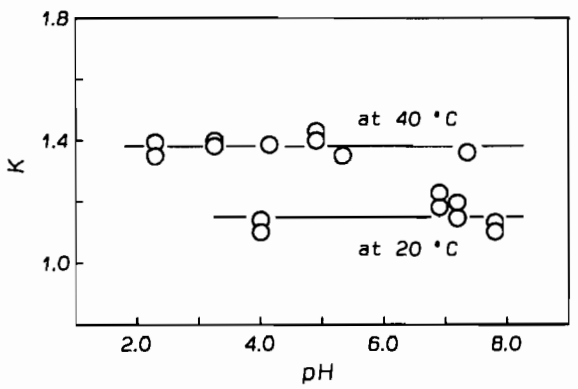

Fig. 6. The pH dependence of the equilibrium constant on the inversion of Δ, Λ-[Ru(*S*-phe)(bpy)$_2$]$^+$ in an aqueous solution.

Abnormality for the S-Phe and S-Tyr complexes

As shown in Fig. 3, the curves for the *S*-Phe and *S*-Tyr complexes deviate downward with increasing temperature from straight lines observed in the lower temperature region, in contrast with linearity for other complexes. This abnormality appears at temperatures higher than about 20 °C. While at the same time, the deuterium isotope effect gradually diminishes, which implies loss of the stabilization of the Λ-*S* isomer through hydrophobic bonding. The ^{1}H NMR spectra of each isomer of the *S*-Phe and *S*-Tyr complexes indicated that the structural relationship of the two isomers was unchanged in elevated temperatures up to 90 °C [11], even though the stability of the hydrophobic bonding was lowered in the Λ-*S* isomer. As the reaction proceeds from Δ-*S* to Λ-*S*, part of the water forming icebergs around the Δ-*S* isomer are released (positive $n\Delta H°$(ice)) and re-form the hydrogen bonds with adjacent water (negative $\Delta H°$(mix)) because of the formation of a hydrophobic bond in the Λ-*S* isomer. Higher temperature diminishes the iceberg formation, which decreases n of $n\Delta H°$(ice) (eqn. (5)), and leads to the appearance of the effect of negative $\Delta H°$(mix). Therefore, the negative $\Delta H°$(mix) effect for *S*-Phe and *S*-Tyr complexes results in the gradual downward deviation as temperature rises (Fig. 3). Other complexes, in which little deuterium effects were observed due to a weak hydrophobic bonding effect, did not exhibit this negative enthalpy effect. In methanol and acetonitrile–water solvent, because the icebergs hardly exist, linearity was observed for the *S*-Phe complex (Fig. 4).

Conclusions

The Δ- and Λ-[Ru(*S*-am)(bpy)$_2$]$^+$ complexes studied consist of two kinds of moieties having opposite properties. One is a hydrophilic moiety, which has polar groups in the aminoacidato ligand, and hydrates through

hydrogen bonds with water. The other is a hydrophobic moiety, which is bpy and the non-polar side chain of the aminoacidato ligand. The different solvation of amine hydrogen atoms in the hydrophilic moiety appeared as an enthalpy effect, stabilizing the Δ-*S* isomer. On the other hand, the presence of hydrophobic bonding derived from hydrophobic solvation contributed to an entropy effect, stabilizing the Λ-*S* isomer. As regards the entropy effect, the contribution from hydrophilic solvation [$\Delta S°$(NHO)] must also be considered in the present system. $\Delta S°$(NHO) is expected to be a positive value (favors the Λ-*S* isomer), and the magnitude is closely related to that of $\Delta H°$(NHO). In the case of aminoacidato ligands containing non-polar bulkier β-substituents, the energy of the enthalpy and entropy effects became larger than that of the steric repulsion, and these effects primarily determined the equilibrium positions. Since the magnitudes of the contrary effects are very close to each other, the position was easily altered in response to circumstances such as temperature and solvents. The small influence of the steric repulsion would be attributed to the flexibility of the bpy ligand [7].

Unexplainable results were found in the Phg complex. I cannot explain the data of this complex, although the large steric repulsion is expected due to a phenyl group attached to the α-carbon of the Phg ligand.

I also found that the photochemical inversion hardly occurred in pure acetonitrile. Photolysis of $[Ru(bpy)_2L]^{2+}$ (L=pyridyltriazole) in acetonitrile solutions has been reported [21] and was discussed with regard to the mechanism of substitution of L with the solvent. This implies that the photochemical inertness observed for $[Ru(S\text{-am})(bpy)_2]^{+}$ complexes in this solvent originates from the aminoacidato ligands. The mechanism of the photochemical inversion has not been elucidated so far, although photosubstitution and a photoracemization mechanism of the $[Ru(bpy)_3]^{2+}$ complex has been proposed [22]. This phenomenon would be a clue to probing into the mechanism of the inversion.

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