Enhancement of the Pfeiffer Effect Arising from the Cation-Cation Interaction*

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The influence of added sodium and potassium chloride, bromide, and sulfate was examined on the Pfeiffer effect of the $[Co(phen)_3]^{2+}$– and $[Ni(phen)_3]^{2+}$–*d*-cinchoH$^+$ systems in water (phen=1,10-phenanthroline, and *d*-cinchoH$^+$=*dextro*-cinchoninium ion). It was found that the added anions enhance the circular dichroism (CD) induced in the d-d transition region of $[Co(phen)_3]^{2+}$ and $[Ni(phen)_3]^{2+}$ ions, and that the CD-enhancing order is $Br^- > Cl^- > SO_4^{2-}/2$. These findings were well interpreted in terms of reduced electrostatic repulsion between $[Co(phen)_3]^{2+}$ or $[Ni(phen)_3]^{2+}$ and *d*-cinchoH$^+$ by the added anions, and of the resulting enhanced enantiomerization of these cationic complexes in favor of Δ-isomers in the presence of *d*-cinchoH$^+$. Logarithm of the magnitude of the induced CD was found to be a linear function of logarithm of the total anion concentration in all the systems examined. This fact gives a strong support to the above interpretation, and suggests a close resemblance of these Pfeiffer-active systems to aqueous cationic surfactant solutions.

When a racemic mixture of a labile metal complex is added to a solution containing a certain chiral molecule called an environment compound, additional optical activity is sometimes developed. This phenomenon is known as the Pfeiffer effect,[1] and several possible mechanisms have been proposed, *e.g.*, configurational activity,[2] differential association,[1c,3] equilibrium shift (enantiomerization),[4] hydrogen bonding,[5] and hydrophobic bonding.[1c,6] The fact that partial resolution of some metal complexes is performed by exploiting this phenomenon,[4a,4b,7] provides decisive evidence for the equilibrium shift mechanism by which metal complexes enantiomerize in favor of either *d*- or *l*-isomer, depending on the spacial demand of the chiral environment compound present. As a result, the Pfeiffer effect is successfully applied to assign the absolute configuration of metal complexes,[5,7–9] in particular for those which are so labile that conventional resolution techniques fail to isolate them as antipodes.[10,11]

It seems convenient to classify the Pfeiffer-active systems into three groups according to their charge type as far as tris-phen or tris-bpy complexes are concerned; i) systems of the same charge, *e.g.*, $[M(phen)_3]^{2+}$–*l*-stryH$^+$ and –*d*-cinchoH$^+$ in water, ii) systems of opposite charge, *e.g.*, $[M(phen)_3]^{2+}$–*d*-BCS$^-$ in water, and iii) systems containing nonelectrolytes, *e.g.*, $[M(phen)_3]^{2+}$–*l*-malic acid and –*d*-tartaric acid in water, and $[Ni(phen)_3]^{2+}$ in *l*-2,3-butanediol[4b] (M(II)=Co(II) or Ni(II), phen=1,10-phenanthroline, bpy=2,2′-bipyridine, *l*-stryH$^+$=*levo*-strychninium ion, *d*-cinchoH$^+$=*dextro*-cinchoninium ion, and *d*-BCS$^-$=*dextro*-3-bromocamphor-9-sulfonate ion). Among these groups, the first group is seemingly unusual in the sense that the Pfeiffer effect is well observed despite the inevitable electrostatic repulsion between cationic complexes and cationic environment compounds even at a low concentration in water. Thus, some mechanisms must operate which force these cations to attract each other against their mutual repulsion. In this paper, we present some experimental results suggesting a close resemblance of these Pfeiffer systems to aqueous ionic surfactant solutions in which hydrophobic ions of the same charge associate to form aggregates called micelles.

Experimental

Sample solutions containing both $[Co(phen)_3]Cl_2$ and *d*-cinchoHCl were prepared by diluting respective stock solutions with water in volumetric flasks. To prevent the decomposition of the complex, a small amount of free phen was added.[4b] To these solutions were added varying amounts of NaCl or KCl. Completely the same operation was employed to prepare the corresponding bromide and sulfate solutions, and NaBr or KBr, and Na_2SO_4 or K_2SO_4 were added respectively in place of NaCl or KCl. Tetraalkylammonium bromides R_4NBr (R=methyl to butyl) were also added to the bromide solution in place of NaBr or KBr. A similar procedure was applied to the $[Ni(phen)_3]^{2+}$–*d*-cinchoH$^+$ system, but the sample solutions thus prepared were allowed to stand for two weeks at room temperature to attain an enantiomerization equilibrium.[4a] Absorption (AB) and circular dichroism (CD) spectra were recorded on a Shimadzu UV-200 and a Jasco J-40CS spectrometer at ambient temperature, and optical rotations were measured with a Union-Giken PM-71 polarimeter in a 5 cm cell. All chemicals used were of reagent grade.

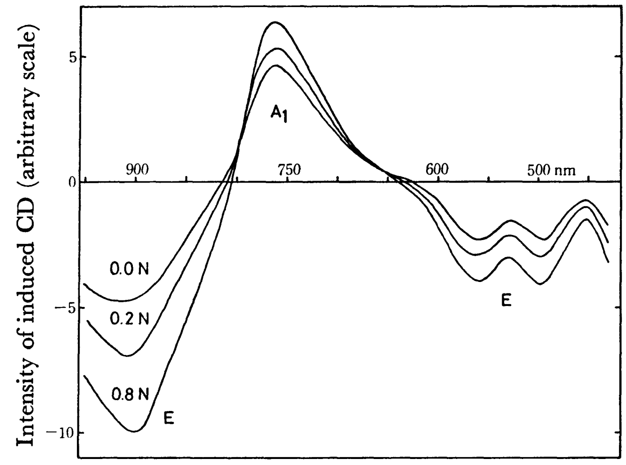

Fig. 1. CD spectra induced in the $[Ni(phen)_3]SO_4$ (0.03 M)–*d*-cinchoH1/2SO$_4$(0.03 M) systems containing various amounts of Na_2SO_4.

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* Preliminary results of this work were reported in, H. Yoneda, K. Miyoshi, and S. Suzuki, *Chem. Lett.*, **1974**, 349; K. Miyoshi, K. Sakata, and H. Yoneda, *ibid.*, **1974**, 1087.

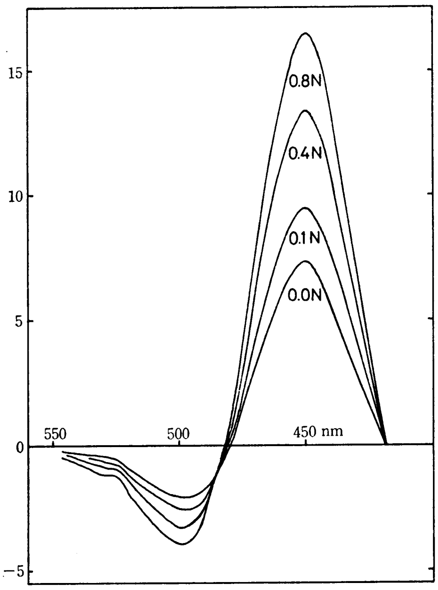

Fig. 2. CD spectra induced in the $[Co(phen)_3]Cl_2$(0.015 M)-*d*-cinchoHCl (0.03 M) systems containing various amounts of NaCl.

Results and Discussion

Figures 1 and 2 show the CD induced in the d-d transition region for the $[Ni(phen)_3]SO_4$-*d*-cinchoH1/2SO_4 and the $[Co(phen)_3]Cl_2$-*d*-cinchoHCl systems in water, where varying amounts of Na_2SO_4 and NaCl are added respectively. It is seen that the CD spectrum for the former system is almost the same in shape as that of *levo*-$[Ni(phen)_3]^{2+}$ ion,[4b,12] and that its intensity is enhanced uniformly throughout the spectrum upon the addition of Na_2SO_4. These facts mean that an enantiomerization of $[Ni(phen)_3]^{2+}$ ion actually takes place in favor of its *levo*- or Δ-isomer[13] in the presence of *d*-cinchoH$^+$ and is enhanced by added Na_2SO_4, and that the same will be true for the $[Co(phen)_3]Cl_2$-*d*-cinchoHCl system. Similar results obtained in other systems are summarized in Table 1, which clearly indicates that the intensities of the induced CD are dependent on the kind of the added anions, but not of cations when they are compared at a fixed concentration of added salts. Therefore, it is concluded that the added anions are responsible for the enhancement of the Pfeiffer effect shown in Figs. 1 and 2 and Table 1.

The influence of added inert counter-ions on the optical activity of metal complexes has been extensively studied[14] and has been usually attributed to outer-sphere association of the complexes with added counter-ions. However, the anion effect shown in Figs. 1 and 2 and Table 1 is not ascribed to usual ion association, because each component of the induced CD in $[Ni(phen)_3]^{2+}$ and $[Co(phen)_3]^{2+}$ ions is affected uniformly but not differently by the added anions.[12c,14] Instead, it is attributed to reduced electrostatic repulsion between these cationic complexes and *d*-cinchoH$^+$ by the added anions and to the resulting enhanced enantiomerization of $[Ni(phen)_3]^{2+}$ or $[Co(phen)_3]^{2+}$ ion in the presence of *d*-cinchoH$^+$.

In order to confirm the above interpretation, an

Table 1. Intensities of the induced CD

$[Ni(phen)_3]SO_4$(0.03M)-*d*-cinchoH1/2SO_4(0.03M)

Na_2SO_4	$\Delta\varepsilon_{497}$	$\Delta\varepsilon_{560}$
0.05N	9.1×10^{-4}	8.6×10^{-4}
0.1 N	9.9×10^{-4}	9.3×10^{-4}
0.2 N	10.6×10^{-4}	10.1×10^{-4}
0.4 N	12.3×10^{-4}	11.5×10^{-4}
0.8 N	14.1×10^{-4}	13.1×10^{-4}
slope	0.23	0.23

K_2SO_4	$\Delta\varepsilon_{497}$	$\Delta\varepsilon_{560}$
0.05N	9.4×10^{-4}	8.6×10^{-4}
0.1 N	10.1×10^{-4}	9.1×10^{-4}
0.2 N	10.8×10^{-4}	9.9×10^{-4}
0.4 N	12.5×10^{-4}	11.6×10^{-4}
0.8 N	14.1×10^{-4}	13.3×10^{-4}
slope	0.23	0.24

$[Co(phen)_3]SO_4$(0.015M)-*d*-cinchoH1/2SO_4 (0.03M)

Na_2SO_4	$\Delta\varepsilon_{450}$	K_2SO_4	$\Delta\varepsilon_{450}$
0.05N	1.66×10^{-2}	0.05N	1.68×10^{-2}
0.1 N	1.82×10^{-2}	0.1 N	1.82×10^{-2}
0.2 N	2.04×10^{-2}	0.2 N	2.06×10^{-2}
0.4 N	2.34×10^{-2}	0.4 N	2.34×10^{-2}
0.6 N	2.59×10^{-2}	0.6 N	2.57×10^{-2}
0.8 N	—	0.8 N	2.79×10^{-2}
slope	0.24	slope	0.25

$[Co(phen)_3]Cl_2$(0.015M)-*d*-cinchoHCl(0.03M)

NaCl	$\Delta\varepsilon_{450}$	KCl	$\Delta\varepsilon_{450}$
0.05N	1.74×10^{-2}	0.05N	1.76×10^{-2}
0.1 N	1.96×10^{-2}	0.1 N	1.98×10^{-2}
0.2 N	2.22×10^{-2}	0.2 N	2.26×10^{-2}
0.4 N	2.77×10^{-2}	0.4 N	2.71×10^{-2}
0.8 N	3.42×10^{-2}	0.8 N	3.38×10^{-2}
slope	0.32	slope	0.31

$[Co(phen)_3]Br_2$(0.015M)-*d*-cinchoHBr(0.03M)

NaBr	$\Delta\varepsilon_{450}$	KBr	$\Delta\varepsilon_{450}$
0.05N	1.86×10^{-2}	0.05N	1.80×10^{-2}
0.1 N	2.04×10^{-2}	0.1 N	1.98×10^{-2}
0.2 N	2.34×10^{-2}	0.2 N	2.32×10^{-2}

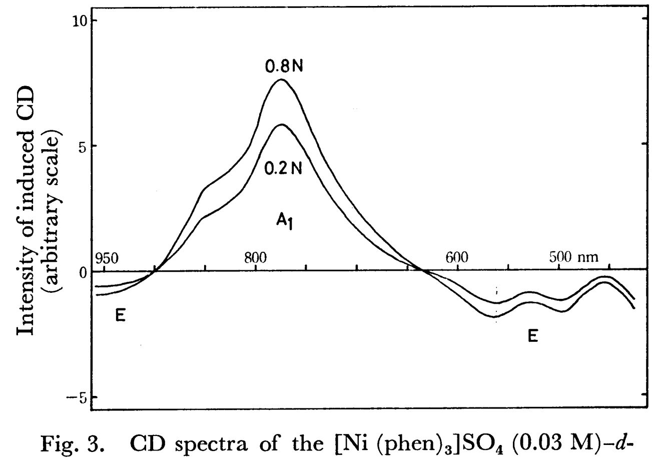

Fig. 3. CD spectra of the [Ni $(phen)_3]SO_4$ (0.03 M)-*d*-cinchoH1/2SO_4 (0.03 M) systems containing various amounts of Na_2SO_4, measured after they are re-dissolved in acetone–water mixtures (1:1 volume ratio).

Table 2. Degree of optical resolution

$[Ni(phen)_3]SO_4(0.03M)$-*d*-cinchoHl/2$SO_4(0.03M)$[a]			
0.2N	Na_2SO_4	2.2%(497 nm)	2.0%(562 nm)
0.8N	Na_2SO_4	3.0%(497 nm)	2.9%(562 nm)
$[Co(phen)_3]Cl_2(0.015M)$-*d*-cinchoHCl(0.03M)[b]			
0.2N	NaCl	1.1%(492 nm)	
0.4N	NaCl	1.4%(492 nm)	

a) $\Delta\varepsilon_{497}=-4.57\times10^{-2}$ and $\Delta\varepsilon_{562}=-5.12\times10^{-2}$ for optically-pure Δ-$[Ni(phen)_3]^{2+}$ in an acetone–water mixture. Racemization of $[Ni(phen)_3]^{2+}$ in this mixed solvent is not taken into account. See, N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, **50**, 1325 (1954).
b) $\Delta\varepsilon_{492}=-1.29$ for optically-pure Δ-$[Co(phen)_3]^{3+}$ in water. See, Ref. 18. Oxidation of $[Co(phen)_3]^{2+}$ with H_2O_2 to $[Co(phen)_3]^{3+}$ is not necessarily quantitative.

excess amount of $NaClO_4$ was added to the $[Ni(phen)_3]SO_4$-*d*-cinchoHl/2SO_4 system and resulting precipitates containing both $[Ni(phen)_3](ClO_4)_2$ and *d*-cinchoHClO_4 were re-dissolved in acetone–water mixtures (1 : 1 volume ratio). In Fig. 3 are shown their CD spectra, which are completely the same in shape as that of Δ-$[Ni(phen)_3]^{2+}$ ion in an acetone–water mixture.[12c] Since the Pfeiffer effect is not exhibited in this mixed solvent, our interpretation is verified, and the degree of optical resolution estimated is given in Table 2. However, a detailed examination of Fig. 1 reveals that the CD induced in the $[Ni(phen)_3]SO_4$-*d*-cinchoHl/2SO_4 system is somewhat different in shape from that of Δ-$[Ni(phen)_3]^{2+}$ ion resolved by a usual method,[12c] in particular at a long wavelength region, *e.g.*, the $^3A_{2g}\rightarrow{}^3T_{2g}$ transition in an Oh approximation. That is, the $E(^3T_{2g})$ component is greater in magnitude than the $A_1(^3T_{2g})$ component in the Pfeiffer system,[15] while the corresponding E component of resolved $[Ni(phen)_3]^{2+}$ ion is not detected in water unless acetone or some polyoxyanions are added.[12c] This difference is attributed to marked association of $[Ni(phen)_3]^{2+}$ ion with *d*-cinchoH$^+$, because the Pfeiffer effect is not exhibited unless the complex comes into direct contact with chiral environment compounds.[16]

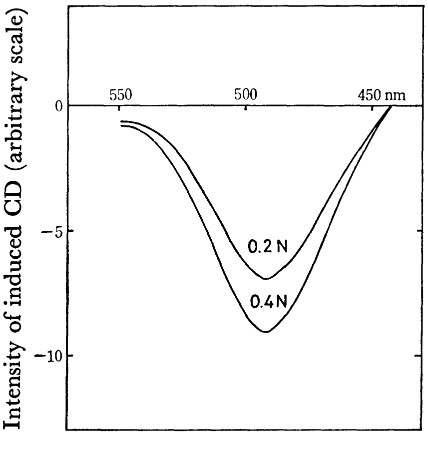

Fig. 4. CD spectra of the $[Co(phen)_3]Cl_2$ (0.015 M)-*d*-cinchoHCl (0.03 M) systems containing various amounts of NaCl after oxidation with H_2O_2.

Figure 4 shows the CD spectra of the $[Co(phen)_3]Cl_2$-*d*-cinchoHCl systems containing varying amounts of NaCl after they are oxidized with H_2O_2 in the presence of MnO_2. It is seen that their CD spectra are the same in shape as that of resolved *levo*- or Δ-$[Co(phen)_3]^{3+}$ ion,[12b,17,18] and that their intensity is increased as the amount of NaCl added to these systems is increased. Since $[Co(phen)_3]^{3+}$ ion does not exhibit the Pfeiffer effect with *d*-cinchoH$^+$, it is confirmed that $[Co(phen)_3]^{2+}$ ion also enantiomerizes[7] in favor of its Δ-isomer in the presence of *d*-cinchoH$^+$ like $[Ni(phen)_3]^{2+}$ ion does. By comparing the CD intensities, the degree of optical resolution is estimated as before for the $[Co(phen)_3]Cl_2$-*d*-cinchoHCl systems and is included in Table 2.

It is now well known that ionic surfactants associate to form aggregates called micelles at relatively low concentrations against their mutual electrostatic repulsion in water. In the process of micellization, two opposing factors[19] are usually taken into account, *i.e.*, electrostatic repulsion between surfactant ions of the same charge, and the hydrophobic interaction[20] which is regarded as a main driving force for the aggregation of surfactants in water. If anions (or cations) are added to cationic (or anionic) surfactant solutions, the resulting reduced electrostatic repulsion leads to increased micelle

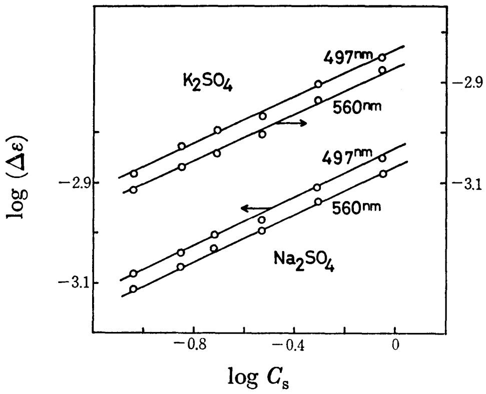

Fig. 5. Plots of log (Δε) at 497 and 560 nm *vs.* log C_s for the $[Ni(phen)_3]SO_4$(0.03 M)-*d*-cinchoHl/2SO_4(0.03 M) system.

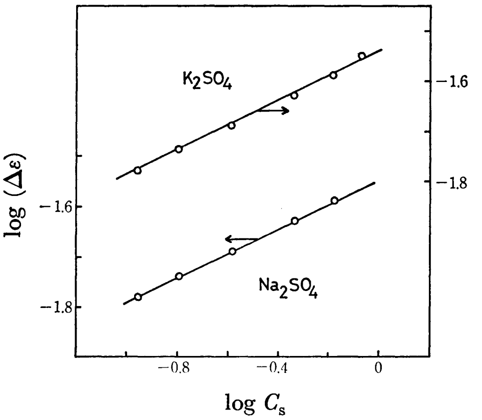

Fig. 6. Plots of log (Δε) at 450 nm *vs.* log C_s for the $[Co(phen)_3]SO_4$ (0.015 M)-*d*-cinchoHl/2SO_4 (0.03 M) system.

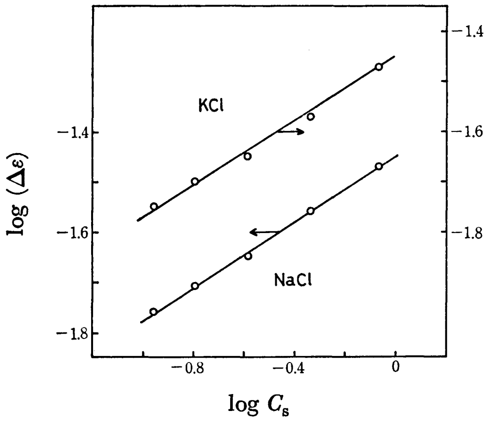

Fig. 7. Plots of log(Δε) at 450 nm *vs.* log C_s for the $[Co(phen)_3]Cl_2$(0.015 M)-*d*-cinchoHCl(0.03 M) system.

stability.[21] That is, the CMC (critical micelle concentration) is greatly lowered by added ions possessing charges opposite in sign to those of surfactant ions. According to the theory of micellization for ionic surfactants,[21] the CMC is expressed as a function of the total equivalent counter-ion concentration C_s by

$$\log(\mathrm{CMC}) = -K_g \log C_s + \text{constant},$$

where K_g is a measure of the degree of charge neutralization on the micelle surface. Since *d*-cinchoH$^+$ is a bulky organic ion with its positive charge localized on its nitrogen atom like usual cationic surfactant molecules, and since tris-phen complexes are surrounded by bulky organic ligands, they are all regarded as hydrophobic. In fact, the hydrophobic nature of $[Fe(phen)_3]^{2+}$ ion[22,23] and some compounds[24] like *d*-cinchoH$^+$ or *l*-stryH$^+$ has been recently examined by some workers. Consequently, it is fairly plausible for these hydrophobic cations to attract each other through the hydrophobic interaction to form aggregates in water like cationic surfactants. Though the structure and the aggregation number of the aggregates are not known, highly aggregated species are improbable, judging from the molecular structures of $[M(phen)_3]^{2+}$ and *d*-cinchoH$^+$. Then, by analogy with aqueous ionic surfactant solutions, log (Δε) is plotted against log C_s for both the $[Co(phen)_3]^{2+}$– and $[Ni(phen)_3]^{2+}$–*d*-cinchoH$^+$ systems in Figs. 5—7. Good linear relationships are observed in these plots, derived slopes of which are listed in Table 1. It should be noted here that these plots have an almost constant slope for a given system irrespective of the kind of added cations and of the wavelength chosen for the CD measurement, and that the slope is constant for sulfate systems whether the central metal ion is Co(II) or Ni(II). These findings are completely consistent with the above interpretation for the anion effect shown in Figs. 1 and 2 and Table 1. Furthermore, the increasing order of the degree of charge neutralization, *i.e.*, the increasing order of the induced CD is $Br^- > Cl^- > SO_4^{2-}/2$,[25] which is in agreement with the decreasing order of the CMC of usual cationic surfactants in water (Hofmeister or lyotropic series).[26] This order is also consistent with the influence of the added anions on the chemical potential of cationic tris-phen complexes in aqueous solutions.[27] That is, hydrophobic cations like these complexes are more stable when their counter-ions are structure-breaking anions like Br^- than when they are structure-making anions like SO_4^{2-}.[28]

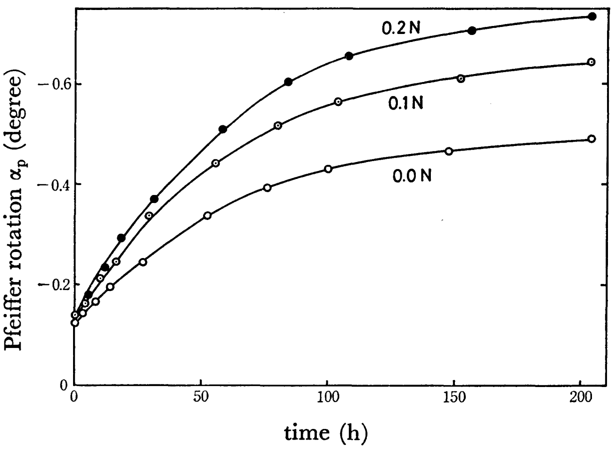

Fig. 8. Plots of the Pfeiffer rotation α_p *vs.* time (h) for the $[Ni(phen)_3]Cl_2$ (0.016 M)-*d*-cinchoHCl (0.016 M) systems containing various amounts of NaCl, measured at 436 nm in a 5 cm cell. 0.0 N NaCl; $\alpha_p(0) = -0.122°$, $\alpha_p(\infty) = -0.505°$, 0.1 N NaCl; $\alpha_p(0) = -0.138°$, $\alpha_p(\infty) = -0.661°$, 0.2 N NaCl; $\alpha_p(0) = -0.135°$, $\alpha_p(\infty) = -0.759°$.

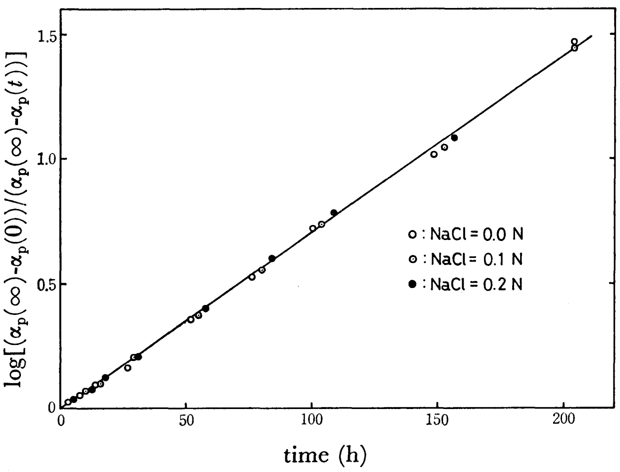

Fig. 9. Plots of $\log[(\alpha_p(\infty)-\alpha_p(0))/(\alpha_p(\infty)-\alpha_p(t))]$ *vs.* time (h) for the $[Ni(phen)_3]Cl_2$(0.016M)-*d*-cinchoHCl (0.016M) systems containing various amounts of NaCl.

In order to elucidate the anion effect more clearly, we examined the influence of the added NaCl on the time-dependence[4a,11] of the Pfeiffer rotation α_p.[1] Figure 8 shows the plots of α_p *vs.* time after mixing $[Ni(phen)_3]Cl_2$ with *d*-cinchoHCl in water, where varying amounts of NaCl are added. It is seen that α_p increases exponentially with time,[1,4a] and is enhanced by the added NaCl. In Fig. 9 is plotted $\log[(\alpha_p(\infty)-\alpha_p(0))/(\alpha_p(\infty)-\alpha_p(t))]$ against time t, $\alpha_p(0)$ and $\alpha_p(t)$ being the Pfeiffer rotation immediately after mixing and at a time t after mixing, respectively, and $\alpha_p(\infty)$ the Pfeiffer rotation at enantiomerization equilibrium. It is seen that the value of $\log[(\alpha_p(\infty)-\alpha_p(0))/(\alpha_p(\infty)-\alpha_p(t))]$ is almost constant at a given time after mixing whether NaCl is added or not. This suggests that added NaCl has no effect at all on the rate constant of the enantiomerization of $[Ni(phen)_3]^{2+}$ in the presence of *d*-cinchoH$^+$, but increases the number of $[Ni(phen)_3]^{2+}$ ion interacting with *d*-cinchoH$^+$, thereby enhancing the Pfeiffer effect. The same will be true for the sulfate system as well as for the $[Co(phen)_3]^{2+}$–*d*-cinchoH$^+$ systems, though the enantiomerization is too rapid[7] to be measured for the latter systems under our experimental conditions.

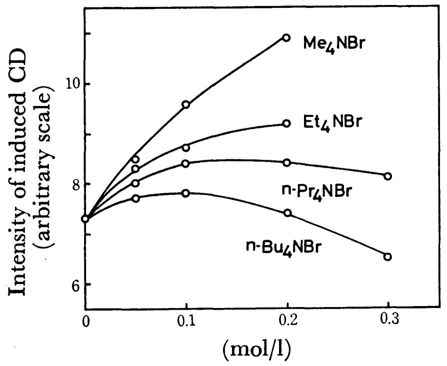

Fig. 10. Plots of the intensity of induced CD at 450 nm *vs.* molar concentration of added R_4NBr (R=methyl to butyl) for the $[Co(phen)_3]Br_2$(0.0075M)–*d*-cinchoHBr (0.03M) system.

In Fig. 10 is plotted the intensity of the induced CD at 450 nm as a function of molar concentration of added tetraalkylammonium bromides R_4NBr (R=methyl to butyl) for the $[Co(phen)_3]Br_2$–*d*-cinchoHBr system. It is seen that the intensity of the induced CD ceases to increase and finally decreases as the alkyl group of added R_4N^+ ion becomes bulky, in other words, as the R_4N^+ ion bears hydrophobic character.[29] This may be interpreted to mean that, when the added R_4N^+ ion is hydrophobic, the hydrophobic bond is formed between R_4N^+[23,30] and $[Co(phen)_3]^{2+}$ or *d*-cinchoH$^+$, and that as a result, the hydrophobic bonding between the complex and *d*-cinchoH$^+$ giving rise to the Pfeiffer effect, is thereby prohibited. Interestingly enough, Steigman *et al.*[31] have found the addition of hydrophobic R_4NBr to raise the CMC of a cationic surfactant, hexadecyltrimethylammonium bromide in aqueous solutions despite the accompanying increase in the counter-ion (Br^-) concentration. They attributed this anomalous cation effect to highly organized water-structure brought about by the added R_4N^+ ion. However, it is still difficult at this stage to decide which explanation is more probable.[26d,32]

Finally, Kirschner and Ahmad,[1b] and Kan and Brewer[33] have reported that Λ-isomer[13,34,35] is enriched in both the $[Co(ox)_3]^{3-}$– and $[Cr(ox)_3]^{3-}$–*d*-cinchoH$^+$ systems in water (ox=oxalate anion). On the other hand, Δ-isomer is enriched in the present $[Co(phen)_3]^{2+}$– and $[Ni(phen)_3]^{2+}$–*d*-cinchoH$^+$ systems, though the same environment compound as above is used. Consequently, the Pfeiffer effect does not work as an absolute tool for the determination of the absolute configuration of labile metal complexes.[9]

In conclusion, $[Co(phen)_3]^{2+}$ or $[Ni(phen)_3]^{2+}$ ion comes into contact with *d*-cinchoH$^+$ to enantiomerize in favor of its Δ-isomer, and added anions reduce the electrostatic repulsion between the cationic complexes and *d*-cinchoH$^+$, thereby enhancing the enantiomerization of these complexes. This situation is similar to that encountered in aqueous cationic surfactant solutions in which ions of the same charge associate to form aggregates against their mutual electrostatic repulsion and added anions facilitate their aggregation greatly. Therefore, so-called long-range interaction is not important to the chiral discrimination even in the Pfeiffer-active systems of the same charge, contrary to the speculation of Schipper.[1d]

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