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ENHANCEMENT OF THE PFEIFFER EFFECT IN TRIS(1,10-PHENANTHROLINE)-ZINC(II)-ℓ-STRYCHNINE SYSTEM

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The Pfeiffer effect in $[Zn(phen)_3]^{2+}$-ℓ-strychnine sulfate system was found to be enhanced by the addition of electrolytes. This phenomenon was interpreted in terms of the weakened electrostatic repulsion between the complex and ℓ-strychnine cations. Hydrophobic bonding between the two cations was suggested from the observation that the Pfeiffer rotation of this system is diminished by the addition of non-electrolytes.

The Pfeiffer effect is well known as an anomalous change in optical rotation of a solution containing an optically active compound (often referred to as an environment compound$^{1)}$) such as d-α-bromocamphor-π-sulfonate and ℓ-strychninium$^{*)}$ (abbreviated to BCS^- and $StryH^+$, respectively), on the addition of racemic mixtures of labile dissymmetric coordination compounds such as d,ℓ-$[Zn(phen)_3]^{2+}$ and d,ℓ-$[Ni(phen)_3]^{2+}$ (phen = 1,10-phenanthroline). Some excellent reviews on the nature and the mechanism of the Pfeiffer effect have already appeared.$^{1-5)}$ Its source probably lies in any differential interactions$^{6)}$ of the enantiomers with the environment compound. However, only a little has been known yet on the nature of the interactions. We report here some experimental evidences suggesting the hydrophobic interaction between them.

We can summarize many characteristics found so far in the Pfeiffer-active systems as follows:$^{1-5)}$ i) In general, the Pfeiffer effect is best exhibited in aqueous solutions and diminishes rapidly with increase in temperature. ii) Both environment compound and labile coordination compound are hydrophobic and may carry either positive or negative charges. These characteristics lead us to assume that the labile coordination compound interacts with the environment compound through so-called hydrophobic bonding5) between them, to show optical activity. This assumption should hold at least when the charges of both compounds are of the same sign, because the electrostatic repulsion would otherwise interfere with their mutual approach. This is the reason why we focused our attention on $[Zn(phen)_3]^{2+}$-$StryH^+$ system. In fact, the evidence for cation-cation contact has been found for the hydrophobic ion $(C_2H_5)_4N^+$ in aqueous solution by Hertz et al.7)

Experimental

All chemicals used were of reagent grade. $[Zn(phen)_3]SO_4$ solution was prepared by directly dissolving $ZnSO_4 7H_2O$ and 1,10-phenanthrolineH_2O in the mole ratio of 1:3 in water. Sample solutions whose optical rotations were to be measured, were made up so that they contained both $[Zn(phen)_3]SO_4$ and ℓ-strychnine1/$2H_2SO_4$ in 2×10^{-2} mol/l. Electrolytes and non-electrolytes added included KCl, NaCl, $MgCl_2$, $AlCl_3$, Na_2SO_4, ethanol(EtOH), iso-propanol(i-PrOH), n-butanol(n-BuOH), dioxan, dimethylsulfoxide(DMSO), N-methylformamide(NMF), and N-methylacetamide(NMA). Optical rotations at 405 nm were measured in a 1 cm quartz cell at 20°, 24° and 30°C with a Union-Giken PM-71 polarimeter. ORD and AB spectra were recorded on JASCO ORD/UV-5 and Shimazu UV-200 spectrometers, respectively at 24°C.

Results and Discussion

TABLE 1. Observed optical rotations.

T°C	α_e	$\alpha_{obs.}$	α_p
20°	-0.068°	-0.265°	0.197°
24°	-0.072°	-0.261°	0.189°
30°	-0.074°	-0.237°	0.163°

cell length = 1 cm, λ = 405 nm

$[Zn(phen)_3^{2+}] = [StryH^+] = 2 \times 10^{-2}$ mol/l

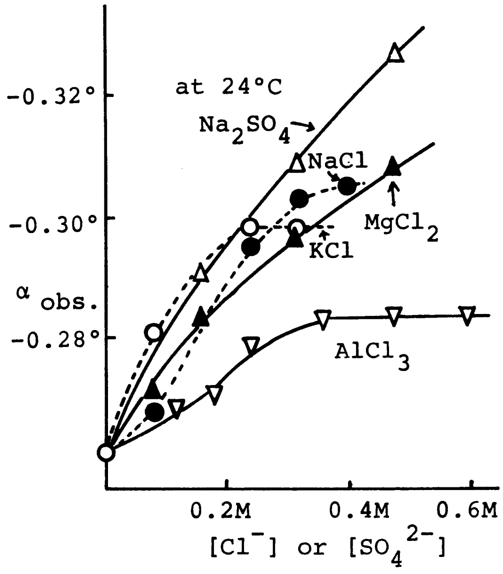

Fig. 1 Effect of electrolytes on observed optical rotations.

The observed optical rotations at 405 nm are given in Table 1, where α_e is the optical rotation of $StryH^+$ and α_e the Pfeiffer rotation ($= \pm(\alpha_{obs.} - \alpha_e)$). The molar Pfeiffer rotation at 405 nm is estimated to be ca. 47300° at 24°C according to its definition.2) Fig. 1 shows the effect of added electrolytes on the observed optical rotations at 24°C, where the abscissa refers to the concentration of anions added in mol/l. It is seen from the figure that all electrolytes except $AlCl_3$ increase the Pfeiffer rotation roughly in a similar manner (the optical rotation of $StryH^+$ itself is not changed by the addition of them). Thus anions are thought to be responsible for the enhancement of the Pfeiffer rotation. This is reasonably interpreted by assuming that added anions weaken the electrostatic repulsion between the two cations, by neutralizing the positive charges accumulated by their mutual approach. Quite similar situation is encountered in the micelle formation of cationic surfactants which are thought to aggregate through the hydrophobic bonding in aqueous solution, that is, the CMC is lowered by the addition of electrolytes.[8)]

In order to ascertain whether the Pfeiffer effect is really enhanced by the addition of electrolytes, ORD curves of the Pfeiffer rotations in the systems with and without added Na_2SO_4 were analyzed by the Drude equation[5)] with a single term. Results depicted in Fig. 2 clearly indicate that the two straight lines acquire the same λ_0-value of 305 nm, at which, nevertheless this system has not any absorption band. This strange fact has already been pointed out by Brasted et al.[5)] However, it seems reasonable to suppose that the enhancement of the Pfeiffer rotation by Na_2SO_4 is not due to the development of a new absorption band with optical activity (e.g., charge-transfer from SO_4^{2-} to d- or ℓ-enantiomer), for the Drude plot of the system with Na_2SO_4 would otherwise have a curvature and/or not acquire 305 nm as the value of λ_0. Of course, aqueous phen solution does not exhibit any extra optical activity when $StryH^+$ is added to it (so-called Kuhn effect is not observed).

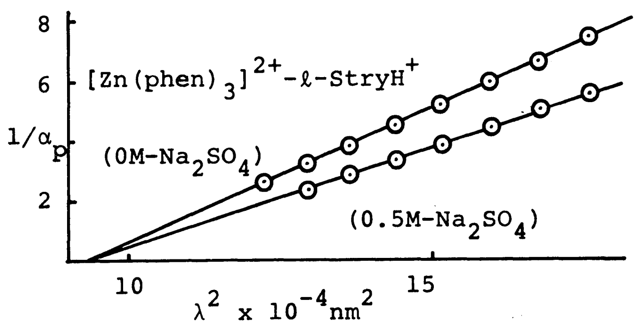

Fig. 2 Plots of the Drude equation.

Smaller increment by $AlCl_3$ than by other electrolytes examined may be attributable to lower concentration of chloride ions available as a charge-neutralizer owing to ion-pairing of $AlCl_3$. Other anions than sulfate and chloride ions could not be examined on account of the appearance of turbidity in solution and of the precipitation of the complex and/or $StryH^+$. At other temperatures, similar trend was observed with general result that the higher the temperature, the smaller the Pfeiffer rotation.

As described above, if the Pfeiffer effect in $[Zn(phen)_3]^{2+}$-$StryH^+$ system stems from the differential interactions of the enantiomers with $StryH^+$ through the hydrophobic bonding, it is expected that a considerable change in the Pfeiffer rotation of this system will be brought about by the addition of some substances that affect the structure of water. In Fig. 3 are plotted the observed optical rotations (at 405 nm) at 20° and 30°C vs. the concentration of non-electrolytes added in mol/l. It is seen that all non-electrolytes examined decrease the Pfeiffer rotation, since the optical rotation of $StryH^+$ is not changed by them in the concentration range investigated. Though any definite relation can not easily be found out between the change in the Pfeiffer rotations and the extent of the influence on the structure of water,$^{9)}$ we feel the effect of the addition of them to be similar to that of temperature rise.

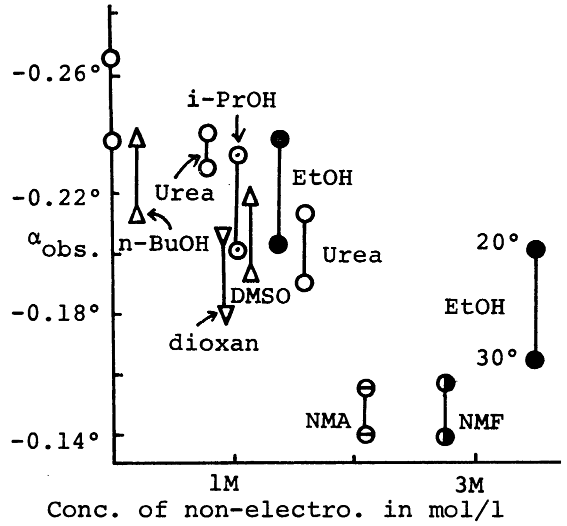

Fig. 3 Effect of non-electrolytes on optical rotations.

There also exists one possibility that the decrease in dielectric constant by the addition of non-electrolytes, may introduce the decrease in the Pfeiffer rotation, by strengthening the electrostatic repulsion between the complex and $StryH^+$ cations. This possibility is reinforced especially when non-electrolytes added are relatively non-polar. In this respect, it seems interesting to examine the Pfeiffer-active systems with opposite charges, e.g., $[Zn(phen)_3]^{2+}$- BCS^-. Such systematic studies are under way in our laboratory.

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