CHEMISTRY LETTERS, pp. 1087-1088, 1974. Published by the Chemical Society of Japan

EVIDENCE FOR THE HYDROPHOBIC INTERACTION IN PFEIFFER EFFECT OF TRIS(1,10-PHENANTHROLINE)ZINC(II)-ℓ-STRYCHNINE SYSTEM

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The addition of tetraalkylammonium bromides R_4NBr ($R = C_2H_5$, n-C_3H_7 and n-C_4H_9) did not enhance Pfeiffer effect of $[Zn(phen)_3]^{2+}$-ℓ-strychnine system in water, while $(CH_3)_4NBr$ enhanced it like simple salts. This could be best interpreted by assuming that hydrophobic R_4N^+ ions interfere with hydrophobic interaction between $[Zn(phen)_3]^{2+}$ and strychnine cation (stryH$^+$), by forming hydrophobic bonding with $[Zn(phen)_3]^{2+}$ and/or stryH$^+$.

Pfeiffer effect[1)] is one of the most interesting but less clarified phenomena in coordination chemistry. In a preceding paper,[2)] it was reported that Pfeiffer effect in tris(1,10-phenanthroline)zinc(II)-ℓ-strychnine cation system (abbreviated to $[Zn(phen)_3]^{2+}$-stryH$^+$), is enhanced on the addition of simple salts such as NaCl and Na_2SO_4 and that the enhancement is attributed to weakened electrostatic repulsion between the positive charges on $[Zn(phen)_3]^{2+}$ and stryH$^+$, and the importance of the hydrophobic interaction between the two cations was suggested. A similar suggestion has been made firstly by Brasted et al.[1a)] and recently by Ogino and Kumagai.[3)] However, little experimental evidence is available for the hydrophobic interaction in the Pfeiffer-active system. We obtained here strong evidence for it by examining the influence of hydrophobic ions on the Pfeiffer effect of the above system.

EXPERIMENTAL

Optical rotations were measured at 405 nm in a 5 cm cell with a Union-Giken polarimeter PM-71 maintained at 25°C. All chemicals used were of reagent grade. A stock solution containing $[Zn(phen)_3]SO_4$ in 0.1 mol/l, was prepared by directly dissolving $ZnSO_4\cdot 7H_2O$ and phen$\cdot H_2O$ in an appropriate ratio in water. Sample solutions contained $[Zn(phen)_3]SO_4$ and ℓ-strychnine$\cdot 0.5H_2SO_4$ both in 0.01 mol/l. Care had to be taken in weighing tetraalkylammonium bromides because of their hygroscopic nature.

RESULTS AND DISCUSSION

Table I shows some of the observed optical rotations of $[Zn(phen)_3]^{2+}$-stryH$^+$ system in water, where α_e is the optical rotation of stryH$^+$ and α_p a so-called Pfeiffer rotation.[1,2)] It is seen that α_p is greatly influenced by added salts, while α_e remains unaffected except for n-Pr_4NBr and n-Bu_4NBr.

In Fig. 1 is plotted α_p vs. the concentration of simple salts added. A close inspection of Fig. 1 indicates that all salts examined increase α_p and that bromides seem to enhance it to a greater extent than chlorides for a given cation. This behavior is quite similar to that observed in cationic surfactant solutions, viz.,

TABLE I

Observed optical rotations at 25°C (405 nm)

α_e	α_{obs}	α_p	(salts added)
-0.160°	-0.391°	0.231°	
-0.160°	-0.485°	0.325°	(NaAc)[a]
-0.160°	-0.451°	0.291°	(Na_2SO_4)[a]
-0.160°	-0.434°	0.274°	(Me_4NBr)[b]
-0.159°	-0.412°	0.253°	(Et_4NBr)[a]
-0.158°	-0.405°	0.247°	(n-Pr_4NBr)[b]
-0.156°	-0.386°	0.230°	(n-Bu_4NBr)[b]
-0.150°	-0.353°	0.203°	(n-Bu_4NBr)[a]

a) added in 0.2 mol/l; b) added in 0.1 mol/l

the CMC is much lowered by bromides than by chlorides.[4] Thus, it follows that Br^- ion is more effective as a charge-neutralizer[2] than Cl^- ion. This may be connected with the difference in the affinity for water between Cl^- and Br^- ions.

Fig. 2 shows the effect of tetraalkylammonium bromides R_4NBr on α_p in $[Zn(phen)_3]^{2+}$-$stryH^+$ system. Quite different features are observed; when R in R_4NBr is CH_3 group, α_p is enhanced in almost the same manner as done by NH_4Br, however, as R becomes bulky, viz., hydrophobic,[5] R_4NBr ceases to enhance and finally diminishes α_p. These apparently anomalous features can be reasonably interpreted by assuming that hydrophobic R_4NBr functions as a partner of the hydrophobic bonding with $[Zn(phen)_3]^{2+}$ and/or $stryH^+$ rather than as a charge-neutralizer, thereby interfering with hydrophobic interaction between $[Zn(phen)_3]^{2+}$ and $stryH^+$. This assumption seems to be supported by the fact that Me_4NBr of no hydrophobic nature[5] has no appreciable effect on α_e like simple salts, while the most hydrophobic n-Bu_4NBr diminishes it, probably by forming hydrophobic bonding with $stryH^+$. (See Table I)

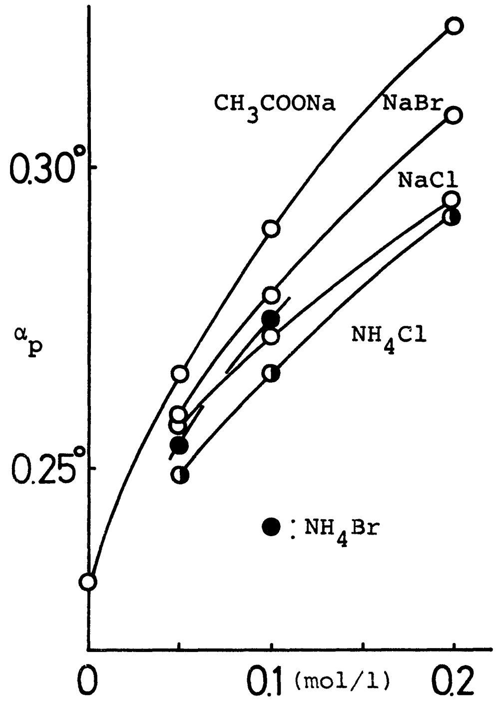

Fig. 1. Effect of simple salts on Pfeiffer rotations

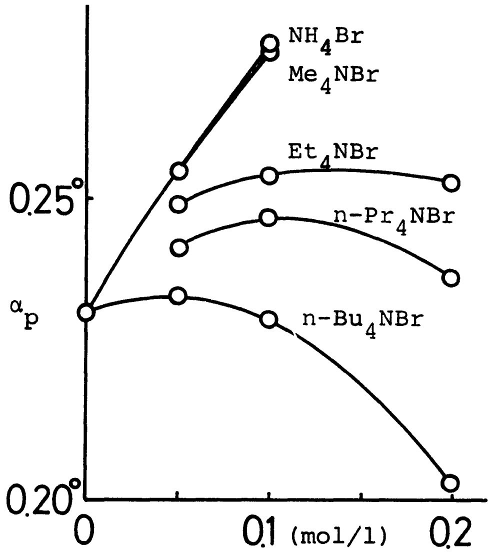

Fig. 2. Effect of R_4NBr on Pfeiffer rotations

REFERENCES

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2) H. Yoneda, et al., Chem. Lett., 1974, 349.
3) K. Ogino and T. Kumagai, Bull. Chem. Soc. Jap., 47, 855 (1974).
4) See Ref. 8 in Ref. 2.
5) Many interesting studies have been reported on the anomalous behavior of tetraalkylammonium ions originated from their hydrophobic nature. See, for example, T. S. Sarma and J. C. Ahluwalia, Chem. Soc. Rev., 2, 203 (1973) and references cited therein.

(Received July 27, 1974)