March, 1976] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(3), 679—682 (1976) 679

Influence of Added Alcohols on the Pfeiffer Effect of Tris-(1,10-phenanthroline)zinc(II)-*l*-Malic Acid and -*d*-Tartaric Acid Systems in Water

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(Received August 15, 1975)

Influence of lower alcohols (methanol to butanol) was examined on the Pfeiffer effect of the $[Zn(phen)_3]^{2+}$-*l*-malic acid and -*d*-tartaric acid systems in water at 25 °C (phen=1,10-phenanthroline). It was found that the Pfeiffer rotation α_p decreases linearly with molar concentration C_A of added alcohols for both systems, and that the logarithm of the rate of the decrease in α_p with C_A is a linear function of the number of methylene groups in added alcohol molecules. This is well interpreted on the assumption that added alcohol molecules adhere to $[Zn(phen)_3]^{2+}$ ion, thereby preventing the complex and chiral acid from coming into contact with each other. The enthalpy change per methylene group on passing from the alcohol environment to the complex environment was estimated to be *ca.* 0.7 *RT*.

When a racemic mixture of a certain labile complex is added to a solution containing a chiral compound which is not subject to usual racemization, additional optical activity is developed. This phenomenon is called the Pfeiffer effect[1)] and is usually ascribed to spontaneous enantiomerization of the complex in favor of either the *dextro-* or *levo*-form, depending on the spacial demand of the chiral compound present.[2)] Partial resolution of some complexes was successfully performed by utilizing this phenomenon,[3)] which provides so far the strongest evidence for the occurrence of the enantiomerization in the Pfeiffer-active systems.[4)] However, little is known yet as regards the nature of the interaction of the complex with the chiral environment compound.[1)]

The Pfeiffer systems are classified into three groups according to their charge types: (1) systems of the same charge, *e.g.*, $[Zn(phen)_3]^{2+}$-*l*-stryH$^+$ and -cinchoH$^+$ systems in water (phen=1,10-phenanthroline, *l*-stryH$^+$ =*l*-strychninium, and cinchoH$^+$=cinchoninium), (2) systems of the opposite charge, *e.g.*, $[Zn(phen)_3]^{2+}$-*d*-BCS$^-$ system in water (*d*-BCS$^-$=*d*-α'-bromocamphor-9-sulfonate), and (3) systems containing nonelectrolytes, *e.g.*, $[Zn(phen)_3]^{2+}$-*l*-malic acid and -*d*-tartaric acid systems in water.[5)] The influence of some additives was examined on the systems of the first group and the hydrophobic bonding was proposed as one of the essential driving forces by which $[Zn(phen)_3]^{2+}$ cation could associate with cationic environment compounds such as *l*-stryH$^+$ and cinchoH$^+$ against mutual electrostatic repulsion.[6)] In this paper, we report the results of an investigation of the influence of some lower alcohols, dioxane, and urea on the systems of group (3). Zinc-complex systems were chosen since they exhibit an instantaneous Pfeiffer rotation.

Experimental

A stock solution of $[Zn(phen)_3]SO_4$ was prepared by dissolving $ZnSO_4 \cdot 7H_2O$ and phen$\cdot H_2O$ in water in a mole ratio of 1:3. Sample solutions containing $[Zn(phen)_3]SO_4$ and *l*-malic acid or *d*-tartaric acid were prepared by diluting respective stock solutions appropriately in volmetric flasks (25 ml). To these solutions were added methanol, ethanol, 1- and 2-propanol, 1- and 2-butanol, *iso-* and *tert*-butyl alcohol, dioxane, and urea, all of which were of reagent grade. Optical rotations were measured in a 5-cm cell at 405 nm with a Union-Giken PM-71 polarimeter kept at 25±0.1 °C.

Results and Discussion

In Table 1 are listed the observed optical rotations of the $[Zn(phen)_3]^{2+}$-*l*-malic acid and -*d*-tartaric acid systems without additives, where code numbers are attached to identify the systems. In Figs. 1—4 is plotted the Pfeiffer rotation α_p, defined as the observed rotation of the Pfeiffer system minus that of the chiral environment compound α_e, as a function of molar concentration

Table 1. Observed rotations in degrees at 405 nm of the Pfeiffer systems[a)]

System	Racemic complex	Chiral compd	Rotation of chiral compd, α_e	Obsd Rotation, α_{obsd}	Pfeiffer Rotation, α_p
	$[Zn(phen)_3]SO_4$				
		l-malic acid			
1a	0.02M	0.02M	−0.002	−0.219	−0.217
1b	0.02M	0.03M	−0.003	−0.335	−0.332
	$[Zn(phen)_3]SO_4$				
		d-tartaric acid			
2a	0.02M	0.02M	+0.034	+0.453	+0.419
2b	0.01M	0.03M	+0.049	+0.379	+0.330

a) In a 5 cm cell at 25 °C.

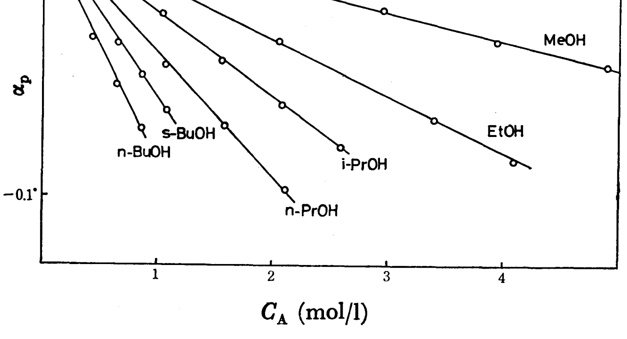

Fig. 1. Plots of α_p as a function of molar alcohol concentration C_A for the $[Zn(phen)_3]^{2+}$ (0.02 M)-*l*-malic acid (0.02 M) system (system 1a).

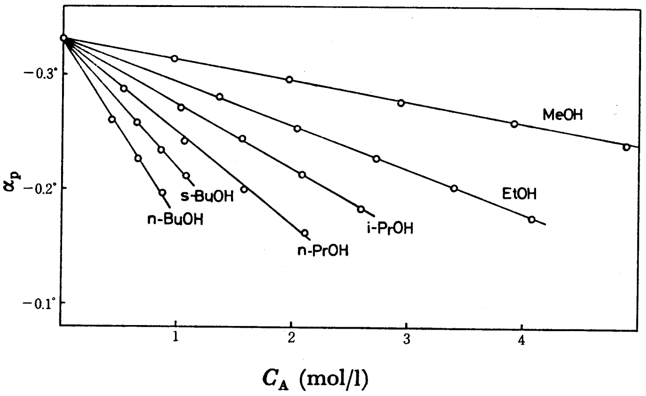

Fig. 2. Plots of α_p as a function of molar alcohol concentration C_A for the $[Zn(phen)_3]^{2+}$ (0.02 M)-*l*-malic acid (0.03 M) system (system 1b).

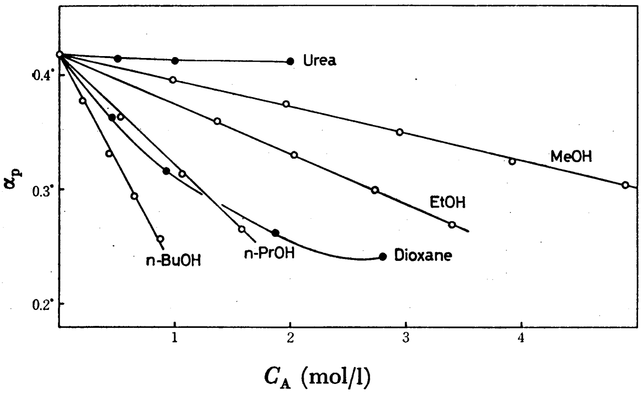

Fig. 3. Plots of α_p as a function of molar concentration of additives C_A for the $[Zn(phen)_3]^{2+}$ (0.02 M)-*d*-tartaric acid (0.02 M) system (system 2a).

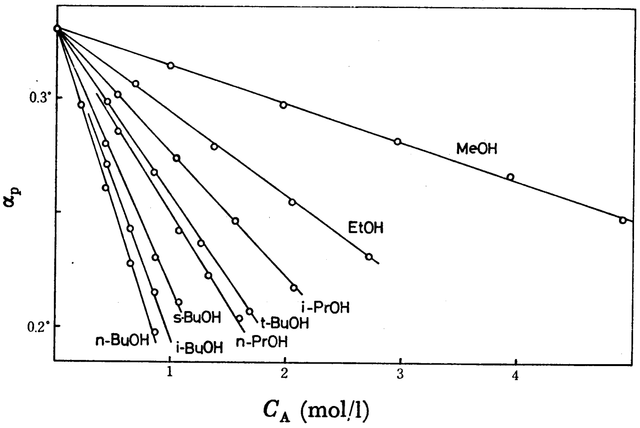

Fig. 4. Plots of α_p as a function of molar alcohol concentration C_A for the $[Zn(phen)_3]^{2+}$ (0.01 M)-*d*-tartaric acid (0.03 M) system (system 2b).

of additives. Since α_e was somewhat affected by the additives, all the α_p's plotted are corrected values as regards small changes in α_e. It is seen that α_p decreases linearly with molar alcohol concentration C_A for both systems, and that the longer the carbon chain of the alcohol molecules, and the greater the Pfeiffer rotation, the steeper the slopes. We are thus led to suppose that added alcohol molecules intervene between the complex and chiral acid, thereby preventing them from coming into contact with each other. In other words, it is assumed that added alcohol molecules are distributed between aqueous phase and the aggregate composed of the complex and chiral acid, the latter being called the Pfeiffer aggregate.[7)]

According to the regular solution theory,[8)] the chemical potential of the alcohol transferred to water, μ_w, is given by

$$\mu_w = \mu^\circ + RT \ln x_w + m\omega_w^{CH_2} + \omega_w^{OH} \tag{1}$$

where x_w is mole fraction of the alcohol in water, $\omega_w^{CH_2}$ and ω_w^{OH} represent the enthalpy change of CH_2- and OH-groups, respectively on passing from the alcohol environment to water, and m is the number of CH_2-groups in the alcohol molecule.[9)] The corresponding chemical potential in the Pfeiffer aggregate, μ_p, is given in a similar manner by

$$\mu_p = \mu^\circ + RT \ln x_p + m\omega_p^{CH_2} + \omega_p^{OH} \tag{2}$$

where x_p is mole fraction of the alcohol in the Pfeiffer aggregate, and $\omega_p^{CH_2}$ and ω_p^{OH} represent the corresponding enthalpy changes from the alcohol environment to the Pfeiffer aggregate. In distribution equilibrium, μ_w must be equal to μ_p. Then, from Eqs. (1) and (2),

$$\ln (x_p/x_w) = m(\omega_p^{CH_2} - \omega_p^{CH_2})/RT + (\omega_w^{OH} - \omega_p^{OH})/RT \tag{3}$$

It seems reasonable to assume that α_p is proportional to the concentration of the Pfeiffer aggregate, and its decrease upon the addition of alcohols is in turn proportional to that of the alcohols in the Pfeiffer aggregate. Then, x_p is expressed as

$$x_p = K_i d\alpha_p/\alpha_p \tag{4}$$

where K_i is a proportionality constant and $d\alpha_p$ is the decrease in α_p when added alcohol concentration is dC_A. On the other hand, x_w is approximated to $C_A/55.5$, since C_A is sufficiently low and the amount of the alcohol transferred to the Pfeiffer aggregate is at most equal to or less than that of the complex or chiral acid present. Substituting the above relations, Eq. (3) is rearranged into

$$\ln (d\alpha_p/\alpha_p dC_A) = m(\omega_w^{CH_2} - \omega_p^{CH_2})/RT + (\omega_w^{OH} - \omega_p^{OH})/RT + C_i \tag{5}$$

where C_i is a constant for a given Pfeiffer system. Equation (5) indicates that a linear relationship holds between ln $(d\alpha_p/\alpha_p dC_A)$ and *m*.

TABLE 2. DERIVED VALUES OF $(d\alpha_p/\alpha_p dC_A)$ AND $(\omega_w^{CH_2} - \omega_p^{CH_2})$

Added alcohol	1a	1b	2a	2b
MeOH	5.87×10^{-2}	5.70×10^{-2}	5.83×10^{-2}	5.16×10^{-2}[a)]
EtOH	1.13×10^{-1}	1.16×10^{-1}	1.06×10^{-1}	1.09×10^{-1}
n-PrOH	2.44×10^{-1}	2.45×10^{-1}	2.40×10^{-1}	2.41×10^{-1}
i-PrOH	1.70×10^{-1}	1.72×10^{-1}		1.65×10^{-1}
n-BuOH	4.89×10^{-1}	4.83×10^{-1}	4.65×10^{-1}	4.67×10^{-1}
s-BuOH	3.44×10^{-1}	3.44×10^{-1}		3.43×10^{-1}
i-BuOH				4.16×10^{-1}
t-BuOH				2.23×10^{-1}
$(\omega_w^{CH_2} - \omega_p^{CH_2})$[b)]	0.714 *RT*	0.716 *RT*	0.705 *RT*	0.728 *RT*

a) Omitted in the calculation because of somewhat large deviation. b) Calculated using the values for normal alcohols only.

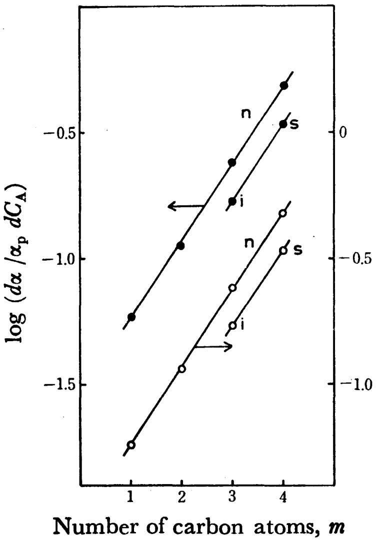

Fig. 5. Plots of $\log(d\alpha_p/\alpha_p dC_A)$ *vs.* m for the $[Zn(phen)_3]^{2+}$-*l*-malic acid system. Filled circles (system 1a) and open circles (system 1b) correspond to left- and right-hand scales, respectively.

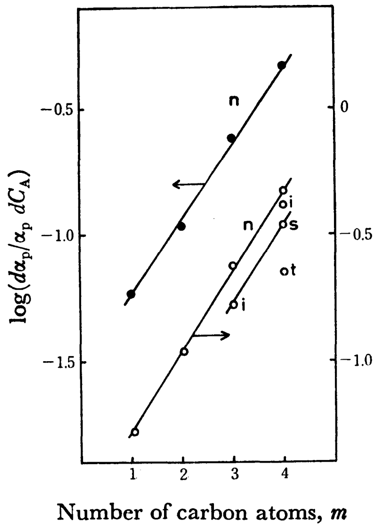

Fig. 6. Plots of $\log(d\alpha_p/\alpha_p dC_A)$ *vs.* m for the $[Zn(phen)_3]^{2+}$-*d*-tartaric acid system. Filled circles (system 2a) and open circles (system 2b) correspond to left- and right-hand scales, respectively.

In Table 2 are listed the values of $(d\alpha_p/\alpha_p dC_A)$, where code numbers correspond to those in Table 1. It is seen that for a given alcohol, these values are almost constant for a given system irrespective of the magnitude of its Pfeiffer rotation. This supports the validity of Eq. (5). In Figs. 5 and 6 is plotted log $(d\alpha_p/\alpha_p dC_A)$ *vs.* m for the $[Zn(phen)_3]^{2+}$-*l*-malic acid and -*d*-tartaric acid systems, respectively. We see that a good linearity holds, as expected from Eq. (5), and that the slope for *n*-alcohols is nearly equal to that for 2-propanol and 2-butanol. The α_p-decreasing order of butanol isomers is found to follow the order of their solubility in water. From these figures, the value of $(\omega_w^{CH_2}-\omega_p^{CH_2})$ corresponding to the enthalpy change per CH_2-group of the alcohol molecule on passing from the Pfeiffer aggregate to water, was estimated by the least squares method and is included in Table 2.

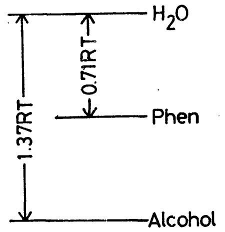

Fig. 7. Energy diagram for the CH_2-group in different environments.

The value of $\omega_w^{CH_2}$ was estimated by Kinoshita *et al.*[10] to be 1.37 RT from the solubility measurement of higher alcohols in water. The energy diagram for the CH_2-group in different environments is established as shown in Fig. 7. The value of $(\omega_w^{CH_2}-\omega_p^{CH_2})$ for the $[Zn(phen)_3]^{2+}$-*l*-malic acid and -*d*-tartaric acid systems is nearly equal to the value (0.67 RT) found for the $[Zn(phen)_3]^{2+}$-*l*-stryH$^+$ and -cinchoH$^+$ systems, but somewhat different from that (0.57 RT) for the $[Zn(bipy)_3]^{2+}$-cinchoH$^+$ systems (bipy=2,2′-bipyridine).[6,11] The value depends on the kind of racemic complexes but not the chiral environment compound. This suggests that added alcohol molecules adhere to the complex, rather than being distributed between the Pfeiffer aggregate and aqueous phase, thereby diminishing the Pfeiffer effect. It seems necessary for the complex and chiral acid to come into direct contact with each other in order to exhibit additional optical activity.

The influence of dioxane and urea on the $[Zn(phen)_3]^{2+}$-*d*-tartaric acid system is shown in Fig. 3. The striking feature is that the system is considerably affected by dioxane but not appreciably by urea, though both additives diminish the Pfeiffer effect of the first group greatly.[6] This implies that the driving force in developing the Pfeiffer effect in the third group differs from that in the first group[6] for which we have proposed the hydrophobic bonding.[1b,13] For the system of the third group Kirschner[2,12] proposed the hydrogen bonding between the hydrogen in the -COOH and -OH groups of the environment substance and the complex's pi electrons of the aromatic rings. The present result in which addition of urea has little influence on the Pfeiffer effect clealy contradicts the hydrophobic bonding mechanism. We are inclined to assume the hydrogen bonding as the probable cause of the Pfeiffer effect in the system of the third group.

The authors wish to thank the Ministry of Education for the financial support granted for this research.

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9) Strictly speaking, the interaction of the CH_3-group with water, alcohol, and the Pfeiffer aggregate differs from that of the CH_2-group. However, the difference was not detected under our experimental conditions. Therefore, m is put equal to the number of all carbon atoms in the alcohol molecule. For the group additivity of enthalpy changes, see, C. V. Krishnan and H. L. Friedman, *J. Phys. Chem.*, **73**, 1572 (1969); *ibid.*, **75**, 3598 (1971).

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11) Though the values of $(\omega_W^{CH_2}—\omega_P^{CH_2})$ for the $[Zn(phen)_3]^{2+}$-*l*-stryH$^+$ and -*d*-cinchoH$^+$ systems are not given in Ref. 6, they are derived from the data listed in Table 2 of Ref. 6. The value for the $[Zn(bipy)_3]^{2+}$-cinchoH$^+$ system is from our unpublished data.

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