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OPTICAL ROTATORY DISPERSION AND THE PFEIFFER EFFECT IN COORDINATION COMPOUNDS

S. KIRSHNER, NASIR AHMAD AND K. MAGNELL

Department of Chemistry, Wayne State University, Detroit, Michigan 48202 (U.S.A.)

In 1931 Pfeiffer and Quehl[1] observed that the optical rotation of a solution of an optically active compound (hereinafter called the "environment" compound) such as *dextro*-α-bromocamphor-π-sulfonate, is changed upon the addition of racemic mixtures of certain optically active coordination compounds, such as D,L-$[Zn(o\text{-phen})_3]_2$, where *o*-phen = *ortho*-phenanthroline. This effect is referred to as the "Pfeiffer Effect" in honor of its discoverer[2], who did considerably more work in the field[3,4]. Fig. 1 shows the effect on the optical rotatory dispersion of ammonium α-bromocamphor-π-sulfonate caused by the addition of racemic $[Ni(o\text{-phen})_3]SO_4$.

Not all combinations of environments, metal ion-ligand complexes, and solvents were found to exhibit the effect, however. Tables 1 and 2 list a few systems which exhibit this effect and some which do not. One purpose of this work is to determine whether systems containing complexes, environments, and solvents, other than those already studied, can be found which also exhibit the Pfeiffer Effect. Further, an attempt is made during this study to express the Pfeiffer Effect in quantitative terms, by means of equations analogous to those used for the expression of optical rotation. Still further, optical rotatory dispersion techniques are employed in an effort to understand the nature and source of the effect, and to try to propose a rational explanation for it which is in agreement with the observed experimental data.

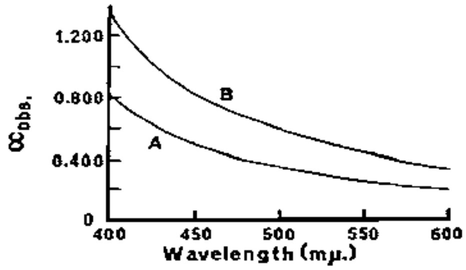

Fig. 1. The Pfeiffer Effect: A: Optical rotatory dispersion of 0.016 *M* ammonium *d*-α-bromocamphor-π-sulfonate in water (2 cm cell, 25° C). B: Optical rotatory dispersion of 0.016 *M* ammonium-α-c-bromocamphor-π-sulfonate + 0.008 *M* D,L-$[Ni(o\text{-phen})_3]SO_4$ in water (2 cm cell, 25° C).

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TABLE 1

SOME SYSTEMS EXHIBITING THE PFEIFFER EFFECT

*Complex**	*Optically active compound or ion*	*Solvent*
$[Zn(o\text{-}phen)_3]^{2+}$	*d*-bromocamphorsulfonate	Water
$[Zn(o\text{-}phen)_3]^{2+}$	*l*-strychnine sulfate	Water
$[Zn(dipy)_3]^{2+}$	*d*-camphorsulfonate	Water
$[Zn(dipy)_3]^{2+}$	*d*-bromocamphorsulfonate	Water
$[Ni(o\text{-}phen)_3]SO_4$	*d*-bromocamphorsulfonate	Water

TABLE 2

SOME SYSTEMS FOUND NOT TO EXHIBIT THE PFEIFFER EFFECT

*Complex**	*Optically active environment*	*Solvent*
$[Zn(bzac)_2]$	*d*-camphor	Ethanol
$[Ni(en)_3]Cl_2$	*d*-α-bromocamphor-π-sulfonate	Water
$[Ni(dipy)_3]Cl_2$	3-*d*-bromocamphor	Ethanol
$[Fe(o\text{-}phen_3](ClO_4)_2$	*d*-SbOtart	Water
$[Ni(o\text{-}phen)_3]Cl_2$	*d*-Na_2tart	Water

Several investigators have proposed explanations of the Pfeiffer Effect[5–8], but, as yet, there is by no means complete agreement as to the correct or best explanation. Dwyer[6] has proposed that the activity of one enantiomer of a racemic mixture of an optically labile complex is different from the activity of the opposite enantiomer in the presence of an optically active "environment" (*e.g.*, an optically active solvent or an inactive solvent in which is dissolved an optically active solute that does not react chemically with the complex). In such cases, an equilibrium is postulated to exist between the two enantiomers in solution, but the equilibrium constant is not equal to one. However, these ideas do not lead to the prediction of that combinations of solvents, complexes, and environment compounds will produce (or fail to produce) the Pfeiffer Effect (*e.g.*, not all optically labile complexes exhibit the effect).

Environment compounds.—It was decided to study environment compounds to determine whether others than those already studied could be found. Three compounds of this type have been found, sodium(-)-dibenzoyl-*d*-tartrate, *dextro* and *levo*-malic acid, and *d*-tartaric acid. Table 3 includes these in the systems where they exhibit the Pfeiffer Effect.

SOLVENTS.—1. *Alcohols.* Landis[8–10] has reported that the effect does not occur in methanol with the tris(*ortho*-phenanthroline)zinc(II) complex and α-bromocamphor-π-sulfonate as the optically active environment. During this work, the authors were unable to detect the effect in absolute ethanol. The fact that the environment compounds utilized in these experiments are essentially non-ionic may have been a factor in the absence of the effect in these cases. Of course, it is

TABLE 3

NEW PFEIFFER EFFECT SYSTEMS

*Complex**	*Optically active environment*	*Solvent*	*Molar Pfeiffer Rotation* $[P_M]^{25°}_{589 m\mu}$
$[\mathrm{Ni}(o\text{-phen})_3]^{+2}$	*l*-malic acid	Water	269.6°
$[\mathrm{Ni(dipy)}_3]^{+2}$	*l*-malic acid	Water	48.4°
$[\mathrm{Co}(o\text{-phen})_3]^{+2}$	*l*-malic acid	Water	257.5°
$[\mathrm{Mn}(o\text{-phen})_3]^{+2}$	*l*-malic acid	Water	185.0°
$[\mathrm{Mn(dipy)}_3]^{+2}$	*l*-malic acid	Water	52.5°
$[\mathrm{Ni}(o\text{-phen})_3]^{+2}$	*d*-Tartaric acid	Water	237.6°
$[\mathrm{Ni(dipy)}_3]^{2+}$	*d*-Tartaric acid	Water	35.2°
$[\mathrm{Mn}(o\text{-phen})_3]^{+2}$	*d*-Tartaric acid	Water	1045.0°
$[\mathrm{Mn}(o\text{-phen})_3]^{+2}$	*l*-Tartaric acid	Water	995.0°
$[\mathrm{Mn}(o\text{-phen})_3]^{+2}$	$\mathrm{Na_2}$-*d*-Tartrate	Water	1495.0°
$[\mathrm{Ni}(o\text{-phen})_3]$	DBT	DMF/H_2O (1 : 1)	340.0°
$[\mathrm{Al(acac)}_3]$	Brucine	DMF	500.0°
$[\mathrm{Al(dbm))}_3]$	*d*-α-BCS	DMF	150.0°
$[\mathrm{Al(hfa)}_3]$	*d*-α-BCS	DMF	−160.0°
$[\mathrm{Zn}(o\text{-phen})_3]^{+2}$	*d*-α-BCS	DMF	20.0°
$[\mathrm{Zn}(o\text{-phen})_3]^{+2}$	*d*-α-BCS	Acetic acid	−140.0°
$[\mathrm{Zn(dipy)}_3]^{+2}$	*d*-α-BCS	Acetic acid	−25.0°
$[\mathrm{Zn(pybim)}_3]^{+2}$	*d*-α-BCS	Acetic acid	−65.0°
$[\mathrm{Zn}(o\text{-phen})_3]^{+2}$	*d*-Cinconine	Acetic acid	320.0°

*ABBREVEVIATIONS

o-phen = 1,10-phenanthroline
dipy = 2,2 -dipyridyl
pybim = 2,(2-pyridyl)-benzimidazoline
acac = acetylacetonate anion
hfa = hexafluoroacetylacetonate anion
dbm = dibenzoylmethane

d-α-BCS = *d*-α-bromocamphor-π-sulfonate
DBT = (-)-dibenzoyl-*d*-tartaric acid
DMF = N,N -dimethylformamide
bzac = benzoylacetonate anion
en = ethylenediamine.

possible that the effect does occur, but that the magnitude is too small to be observed with present-day instrumentation.

2. *Amides and acids*. It has also been found during the course of this work that both N,N-dimethylformamide and glacial acetic acid are solvents in which the Pfeiffer Effect occurs (see Table 3). It should be noted that the magnitude of the effect is smaller in water than in the non-aqueous solvents, and that in glacial acetic acid the Pfeiffer Effect is of opposite sign to that in water. The explanation of this latter observation is as yet not clear.

LIGANDS.—Further, two new complexes have been synthesized which exhibit the Pfeiffer Effect. The zinc complexes of 2-(2-pyridyl)-imidazoline and 2-(2-pyridyl)-benzimidazoline exhibit the Pfeiffer Effect both in water and glacial acetic acid. Some aluminum complexes have also been included**.

** The aluminum complexes were supplied through the courtesy of Dr. J. Fortman, Wright State University, Dayton, Ohio, U.S.A.

METAL IONS.—Although the Pfeiffer Effect has been reported to occur for complexes of zinc and cadmium (Table 1), there has been no mention in the literature of the occurrence of an effect with a mercury(II) complex. Such an effect has been found for mercury by Kirschner and Magnell[11]. It might be expected that the observed Pfeiffer Effect would be greatest for the most labile complex of the series Zn, Cd, Hg ions containing identical ligands in the same system, if an equilibrium such as postulated by Dwyer[6] exists. This has been found to be the case in this system, as is shown by the following table giving the Pfeiffer rotations and stability constants for solutions of the tris(*ortho*-phenanthroline) complexes of zinc, cadmium, and mercury(II) in water containing ammonium bromocamphor-π-sulfonate.

Complex	*Log* K_3	*Observed Pfeiffer Rotation* $\lambda = 435$ $m\mu$; $t = 25°$ *C*
$[\text{Zn}(o\text{-phen})_3]$	5.20	0.100°
$[\text{Cd}(o\text{-pehn})_3]$	4.10	0.160°
$[\text{Hg}(o\text{-phen})_3]$	3.70	0.175°

OPTICAL ROTATORY DISPERSION AND THE SOURCE OF THE PFEIFFER EFFECT.—A comparison of the optical rotatory dispersion curve of the resolved L-$[\text{Ni}(o\text{-phen})_3]^{++}$ ion and the Pfeiffer rotatory dispersion curve of the same cation (Fig. 2) shows that the curves are quite similar in shape, indicating that an excess of one enantiomer is formed as a result of the occurrence of the Pfeiffer Effect. Further, the appearance of a Cotton Effect in a Pfeiffer Effect system observed for a different complex in an earlier paper[7] also supports the idea that the nature of the labile complex itself is a primary factor in whether or not a Pfeiffer Effect will occur in a given system.

It should also be pointed out that the Pfeiffer Effect has been most often observed to occur in systems containing labile complexes in which the ligand has a

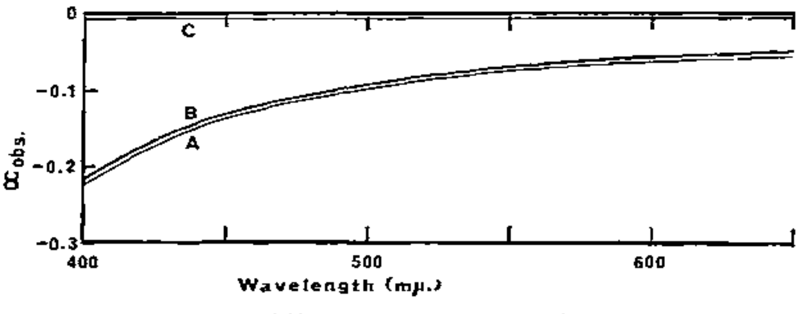

Fig. 2. The Optical and Pfeiffer rotatory dispersion of the L-$[\text{Ni}(o\text{-phen})_3]^{++}$ ion. A: The ORD of 5.4×10^{-4} *M*. L-$[\text{Ni}(o\text{-phen})_3]^{++}$ in water (1 cm cell, 25° C). B: The ORD of 0.05 *M* D,L-$[\text{Ni}(o\text{-phen})_3]^{++}$ + 0.05 *M levo*-malic acid in water (1 cm cell, 25° C). C: The ORD of 0.05 *M levo*-malic acid in water (1 cm cell, 25° C).

high degree of unsaturation—usually involving benzenoid ring systems or similar conjugated rings.

QUANTITATIVE MEASUREMENTS OF THE PFEIFFER EFFECT.—Kuhajek[8] has developed an equation for the calculation of the Pfeiffer Effect which the authors find cumbersome. The following definitions are proposed for Pfeiffer Effect measurements;

$$P_{\text{obs.}} = \pm(\alpha_{e+c} - \alpha_e) \tag{1}$$

$$[P_M]^t_\lambda = \frac{P_{\text{obs.}}}{[e]\cdot[c]\cdot d_m} \tag{2}$$

where $P_{\text{obs.}}$ is the observed Pfeiffer rotation, α_{e+c} is the observed rotation in degrees of the solution containing both the environment compound (e) and the complex (c), α_e is the observed rotation of the solution containing only the optically active environment compound, $\pm$ represents *either* (+) or (−), whichever is the sign of the solution containing only the environment compound, $[P_M]^t_\lambda$ is the molar Pfeiffer rotation at a particular temperature and wavelength, [e] is the molar concentration of the environment compound, [c] is the molar concentration of the complex ion, and d_m is the solution path length in meters. Equation (2) is analogous to that used for the molar rotation of optically active compounds under usual conditions:

$$[M]^t_\lambda = \frac{\alpha_{\text{obs.}}}{[C]\cdot d_m} = \frac{[\alpha]\cdot MW}{100} \tag{3}$$

where $[M]^t_\lambda$ is the molar rotation of an optically active compound, $\alpha_{\text{obs.}}$ is its observed optical rotation, [C] is its molar concentration, d_m is the path length in meters, [α] is the specific rotation, and MW is the molecular weight.

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