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Linear Free Energy Correlations for Reversible Dioxygen Binding of a Cobalt–Porphyrin Complex: A Solvent Effect Study

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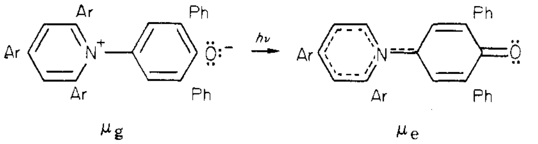
The dioxygen uptake ability of Co(T(p-CH_3O)PP)B, where T(p-CH_3O)PP is the dianion of 5,10,15,20-tetrakis(p-methoxphenyl)porphyrin and B is pyridine, piperidine, and N-methylimidazole, was studied in several solvents. Log K_{O_2} (standard state of 1 torr of O_2) and ΔH_{O_2} were found to depend on both specific and nonspecific solute–solvent interactions. Linear correlations of log K_{O_2} and ΔH_{O_2} were found with electrophilic solvating ET(30) factors, the Taft π^* function, and the polarity function $(\epsilon - 1)/(\epsilon + 2)$, where ϵ is the solvent dielectric constant. The correlation coefficients of the trends were ~0.99 for the solvents methylene chloride, chloroform, and toluene. Comparison of log K_{O_2} correlations with ET(30) and π^* values indicated that the ET(30) correlations were more precise when excluding methanol from the trend whereas the π^* correlation gave a better overall fit. Reactions in N,N'-dimethylformamide were included in log K_{O_2} trends, those in chlorobenzene fit the log K_{O_2} vs. ET(30) and ΔH_{O_2} vs. $(\epsilon - 1)/(\epsilon + 2)$ plots. Deviations from the observed trends were explained in terms of π bonding between solute and solvent in chlorobenzene and o-nitrotoluene, solvent coordination to the sixth coordination site of the precursor complex requiring it to dissociate prior to reaction with dioxygen in N,N'-dimethylformamide and methanol, and hydrogen-bonding effects of the solvent for reactions in methanol. The general trends are attributed to stabilization of the charge separated product, $Co^{\delta+}$–$O^{\delta-}$–O and this interpretation was further substantiated by dioxygen uptake studies in salt solutions.

Introduction

It is general knowledge that polar solvents facilitate dioxygen uptake by cobalt– and iron–porphyrin complexes. It was first reported that Co(PP(IX)DME)N-MeIm, where N-MeIm is N-methylimidazole and PP(IX)DME is protoporphyrin(IX) dimethyl ester, was a 33 times better dioxygen carrier in dimethylformamide (DMF) than in toluene solution at −23 °C[1] and the pyridriate adduct was 25 times more effective at carrying dioxygen in methylene chloride than in toluene solution at the same temperature.[2] Similar results were also obtained for the iron "strapped" porphyrin systems reported by Traylor et al.[3] and led to the conclusion that the Fe–O–O bond was highly dipolar as has theoretically been discussed for cobalt dioxygen systems.[4-6] The obvious conclusions about both cobalt and iron complexes is that the polarity of the solvents must enhance formation of the dioxygen adduct via stabilization of the charge-separated, dipolar product.

According to Koppel and Palm,[7] the influence of solvent on chemical reactivity can be understood on the basis of four separate contributions. Two of these result from nonspecific solute–solvent factors; the other two from specific interactions. Polarity and polarizability fall into the former category and can be respectively expressed theoretically or at least "quasi-theoretically" as functions of the dielectric constant ϵ[8,9] or the index of refraction, η.[9] The specific solvent interactions are separated into electrophilic (electron-accepting) and nucleophilic (electron-donating) components. The magnitude of these effects has been arrived at empirically through a number of experimental methods related to specific systems. The application of these empirical correlations requires a careful match between the conditions and limitations of the specific system used to define the effect compared to the one under study.

The specific systems that most closely resemble those of cobalt dioxygen carriers are Z and Et(30) values.[10] Et(30) values are based on the transition energies for the intramolecular change transfer band of pyridinium phenol betaine.[11]



(1)

Ar = Ph or p-MeC_6H_4; $\mu_g \gg \mu_e$

The transition energy reflects the degree of solvation prior to excitation. The greater the degree of solvation, the higher in energy is the optical transition, and consequently the greater the ET(30) values. The fact that a scale based on only one system could contain data resulting from specific solvent effects or spectral anomalies prompted Taft and co-workers[12] to develop the π^* scale. This scale is based on the average $\pi \rightarrow \pi^*$ transition shifts of seven compounds. Both ET(30) and π^* values then should lead to a free energy correlation for solutions where charge

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separation is stabilized by "electron-accepting" solvents.

Gutmann[13] has set up a solvent electron-donating (nucleophilicity) scale based on reaction 2 in methylene

$$\text{solvent} + \text{SbCl}_5 \rightleftharpoons \text{solvent:SbCl}_5 \qquad (2)$$

chloride. Donor numbers were assigned based on the enthalpy change for the reaction. Other reactions following eq 2 and having near constant entropy changes should correlate with donor numbers according to the donor number concept. Free energy correlations for reactions requiring the dissociation of solvent would be expected to vary inversely with donor numbers.

The preceding concepts form the basis of this manuscript and are considered in the analysis of our data. The goal was to arrive at a basic understanding of the role played by the solvent in reversible dioxygenations of metal porphyrin and Schiff-base complexes. The reaction of $Co(T(p\text{-}CH_3O)PP)B$, where $T(p\text{-}CH_3O)PP$ is the dianion of 5,10,15,20-tetrakis(*p*-methoxyphenyl)porphyrin and B represents pyridine (py), piperidine (pip), or *N*-methylimidazole (*N*-MeIm), with dioxygen was studied in various solvents.

Experimental Section

Preparation of the complex and purification and drying of the solvents has been previously discussed.[14] Absorption spectral changes used for determining equilibrium constants were recorded on a Cary 14 recording spectrophotometer. A low-temperature pyrex cell designed so that a slush bath could completely surround the solution in the light path (5.2 cm) without interfering with the light beam was used in the measurements.[15] Liquids were used for slushes as described by Shriver[16] and include carbon tetrachloride (−23.4 °C), anisole (−36.8 °C), 3-pentanone (−41.4 °C), chlorobenzene (−45.0 °C), ethyl malonate (−49.0 °C), benzaldehyde (−54.0 °C), mesityl oxide (59.0 °C), chloroform (−63.5 °C), and ethyl acetate (−83.0 °C). Solution temperatures were determined with a Honeywell potentiometer and an iron–constantan thermocouple referenced against 0 °C.

Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared by standard techniques,[17] recrystallized three times from hot ethanol–water mixtures, and dried for 10 h in vacuo at 70 °C.

Conductivity. Dilution conductivity studies of TBAH in methylene chloride were carried out with a Beckman Model RC-18A conductivity bridge and a CEL-3B conductivity cell having a cell constant of 0.498 24. The cell constant was determined with a 0.0200 M KCl solution having a specific conductance of 0.002 768 ohm^{-1} at 25 °C.[18] Temperatures were maintained at 25 °C with a Haake FK-2 temperature bath. The measured equivalent conductances were 15.9, 13.9, and 13.0 ohm^{-1} and the equivalent concentrations were 0.0800, 0.110, 0.158, and 0.224 $M^{1/2}$, respectively. Clearly TBAH is a weak electrolyte in methylene chloride.

Equilibrium Constant Measurements. A solution of $Co(T(p\text{-}CH_3O)PP)$ was prepared under nitrogen and the concentration was adjusted by dilution techniques until it had an absorbance from 0.75 to 0.85 in the titration cell. The concentration was approximately 1×10^{-5} M under the conditions. A 25-mL aliquot of solution was then added by pipet to the low-temperature cell which had previously been flushed with nitrogen. The cell was evacuated and the solution was degassed by boiling off a small amount (<2%) of the solvent to assure that no dioxygen had inadvertently been dissolved in the solution or had entered the titration vessel. The amount of base needed to form 99.9% of the base adduct at the desired temperature was then added. The concentration needed for this was first calculated from the thermodynamic parameters obtained from the base addition reactions.[14]

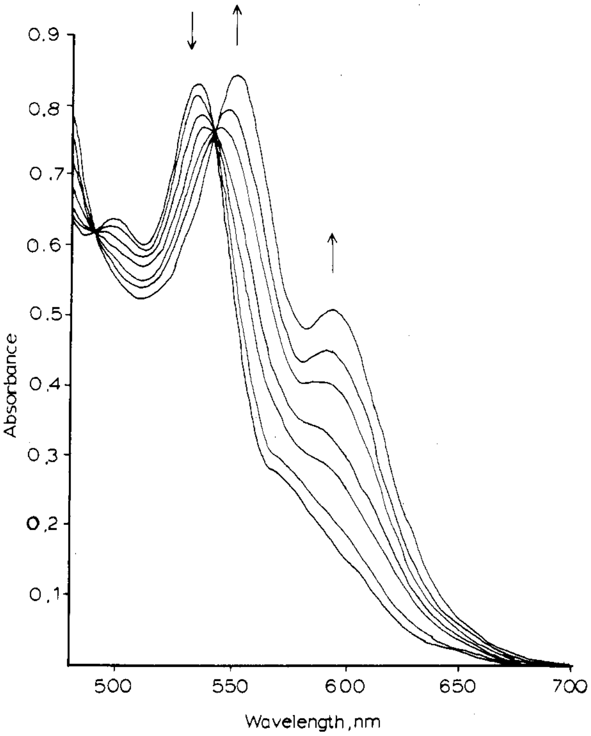

Figure 1. Spectral changes of $Co(T(p\text{-}CH_3O)PP)(pip)$ in chlorobenzene at −40.2 °C as the oxygen pressure was increased over the solution.

After the titration solution was completely prepared, the cell was then evacuated, and the cryostatic bath of the required temperature was added. The solution was allowed to stand about 20 min to come to thermal equilibrium, and the cell was then mounted in the cell compartment of the Cary 14. A spectrum was then recorded between 700 and 450 nm. Next the cell was connected to a vacuum manifold, which had both a closed end manometer and a source of dioxygen attached. The vapor pressure of the solution was first measured, and the titration with dioxygen was started.

The titration was carried out by increasing the pressure of dioxygen in the cell and the manifold stepwise from 0 to about 830 torr. The observed vapor pressure of the solution was subtracted from each pressure reading. After each dioxygen addition, the cell was shaken vigorously to stir the solution and to ensure that the maximum amount of dioxygen had been dissolved. The required mixing time for each system was determined by adding a small amount of dioxygen and repetitively shaking the cell and recording the spectrum until two successive spectra reproduced each other.

The reversibility of the oxygenation reaction in a given solvent and base combination was verified by evacuating the cell at the end of the titration and recording a spectrum after several seconds of shaking. If the spectrum so obtained reproduced the original spectrum, the reaction was considered to be reversible in that solvent.

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TABLE I: Equilibrium Constants for the Reaction of Co(T(p-CH$_3$O)PP)B with Dioxygen in Various Nonaqueous Solvents

	Co(T(p-CH$_3$O)PP)py		Co(T(p-CH$_3$O)PP)pip		Co(T(p-CH$_3$O)PP)N-MeIm	
solvent	T,[a] °C	log K_{O_2}[b]	T,[a] °C	log K_{O_2}[b]	T,[a] °C	log K_{O_2}[b]
chlorobenzene	−30.8	−3.23	−23.2	−3.16	−21.0	−2.41
	−34.6	−3.06	−30.4	−2.76	−24.6	−2.30
	−36.8	−2.95	−30.6	−2.79	−30.8	−2.02
	−40.8	−2.78	−32.4	−2.67	−32.2	−1.92
	−41.4	−2.75	−32.8	−2.60	−36.6	−1.69
			−32.6	−2.57	−36.6	−1.67
			−36.3	−2.57		
			−36.2	−2.48		
			−37.0	−2.61		
			−39.4	−2.34		
			−40.2	−2.40		
chloroform	−30.6	−2.79	−30.8	−2.37	−30.8	−1.50
	−36.8	−2.52	−36.8	−2.37	−36.6	−1.24
	−45.0	−2.15	−41.0	−1.85	−36.6	−1.23
	−55.0	−1.66	−46.0	−1.63	−39.2	−1.11
	−59.4	−1.42	−49.0	−1.55	−41.6	−1.03
					−44.4	−0.79
					−48.5	−0.64
25% ONTOL[c]	−36.8	−3.18				
	−41.0	−3.05				
	−45.0	−2.88				
	−50.6	−2.63				
methanol	−42.5	−2.63				
	−49.0	−2.08				
	−59.5	−1.74				
	−61.2	−1.60				
N,N'-dimethylformamide	−31.1	−2.49				
	−36.8	−2.23				
	−41.8	−2.04				
	−44.8	−1.86				
	−51.0	−1.56				

[a] ±0.1 °C. [b] mm^{-1}, ±0.09. [c] ONTOL = o-nitrotoluene. 25% ONTOL = 25% ONTOL (by volume) in toluene.

Results

Dioxygen Uptake. Figure 1 illustrates the spectral changes observed as the pressure of dioxygen was increased over a solution of Co(T(p-CH$_3$O)PP)B, where B is pyridine, or piperidine, or N-methylimidazole. As the dioxygen pressure increased, the band at 532 nm decreased in absorbance and was replaced by two bands at approximately 550 and 590 nm which were characteristic of the dioxygen adduct. Two isosbestic points were observed at 513 and 553 nm. The actual positions of these peaks and isosbestic points varied slightly from solvent to solvent, and from base adduct to base adduct. The equilibrium constants of formation of the dioxygen adduct (eq 3) were determined from the increase in absorbance of the bands at 550 and 590 nm and were collected in the temperature range of −20 to −60 °C.

$$\mathrm{Co(T(}p\text{-}\mathrm{CH_3O)PP)B} + \mathrm{O_2} \overset{K_{O_2}}{\rightleftharpoons} \mathrm{Co(T(}p\text{-}\mathrm{CH_3O)PP)B\cdot O_2} \tag{3}$$

The equilibrium constants were obtained from the Hill equation[19]

$$\log\,[Y/(1-Y)] = n \log P_{O_2} + \log K_{O_2} \tag{4}$$

where Y equals the total fraction of metal porphyrin binding dioxygen. Least-squares analyses determined on the data from systems in which oxygenation was nearly complete showed that the slopes in plots of log $Y/(1-Y)$ vs. log P_{O_2} were very close to one. Normally, oxygenation was not complete. In order to calculate formation constants for the latter systems, we used a modified least-squares analysis program which adjusted the slope of the line to one by successive approximations. Log K_{O_2} values were thus obtained from the intercepts. Figure 2 shows some typical examples of straight lines of slopes constrained to one for plots of log $[Y/(1-Y)]$ vs. log P_{O_2}. The very small deviations of the data points from the least-squares lines justified the assumption that the reaction between the base adduct and oxygen always occurred in a 1:1 ratio. Equilibrium constants and the temperature at which they were determined for reactions in some solvents are given in Table I. Data for reactions in toluene and methylene chloride has been published previously.[20]

Equation 5, as given by Drago,[21] was also used to

$$K^{-1} = P_{O_2}\left[\frac{[\mathrm{BCoP}]_\mathrm{A} b(\epsilon_\mathrm{A} - \epsilon_\mathrm{C})}{A_0 - A} - 1\right] \tag{5}$$

spot-check calculations of the equilibrium constants determined above. The variables in the equation are as follows: b is the optical cell path length, ϵ_A is the absorption coefficient of Co(T(p-CH$_3$O)PP)B, ϵ_C is the absorption coefficient of Co(T(p-CH$_3$O)PP)B·O$_2$, $[\mathrm{BCoP}]_\mathrm{A}$ is the initial concentration, A_0 is the initial absorbance of Co(T(p-CH$_3$O)PP)B, and A is the absorbance of the solution at the pressure of oxygen, P_{O_2}. Equation 5 was modified to eq 6 and fitted to a least-squares analysis. The

$$\left[\frac{[\mathrm{BCoP}]_\mathrm{A} b(\epsilon_\mathrm{A} - \epsilon_\mathrm{C})}{A_0 - A} - 1\right]^{-1} = P_{O_2}K \tag{6}$$

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TABLE II: Thermodynamic Parameters for the Reaction of Co(T(p-CH_3O)PP)B with Dioxygen in Various Solvents

	Co(T(p-CH_3O)PP)(py)			Co(T(p-CH_3O)PP)(pip)			Co(T(p-CH_3O)PP)(N-MeIm)		
	log K_{O_2},[a] mm^{-1}	ΔH_{O_2},[b] kcal/mol	ΔS_{O_2},[b] eu	log K_{O_2},[a] mm^{-1}	ΔH_{O_2},[b] kcal/mol	ΔS_{O_2},[b] eu	log K_{O_2},[a] mm^{-1}	ΔH_{O_2},[b] kcal/mol	ΔS_{O_2},[b] eu
methylene chloride	−1.68	−11.9 (0.3)	−61 (1)	−0.86	−13.4 (0.7)	−64 (3)	−0.15	−13.0 (0.5)	−59 (2)
chlorobenzene	−2.31	−11.7 (0.3)	−63 (1)	−2.23	−12.0 (1.3)	−64 (5)	−1.03	−13.0 (0.5)	−63 (2)
chloroform	−1.83	−11.3 (0.1)	−59 (1)	−1.48	−12.1 (0.9)	−61 (4)	−0.55	−12.6 (0.6)	−59 (2)
toluene	−2.84	−9.6 (0.4)	−56 (2)	−2.88	−10.0 (0.3)	−58 (2)	−1.83	−10.4 (0.5)	−55 (2)
methanol	−2.12	−11.0 (2.0)	−59 (8)						
N,N'-dimethylformamide	−1.72	−11.4 (0.1)	−59 (1)						
25% ONTOL[c]	−2.74	−9.7 (0.5)	−56 (2)						

[a] Calculated from ΔH_{O_2} and ΔS_{O_2} values at −50 °C. Standard state of 1 torr. [b] Error is in parentheses; at 90% confidence level. [c] 25% ONTOL = a toluene solution containing 25% o-nitrotoluene by volume.

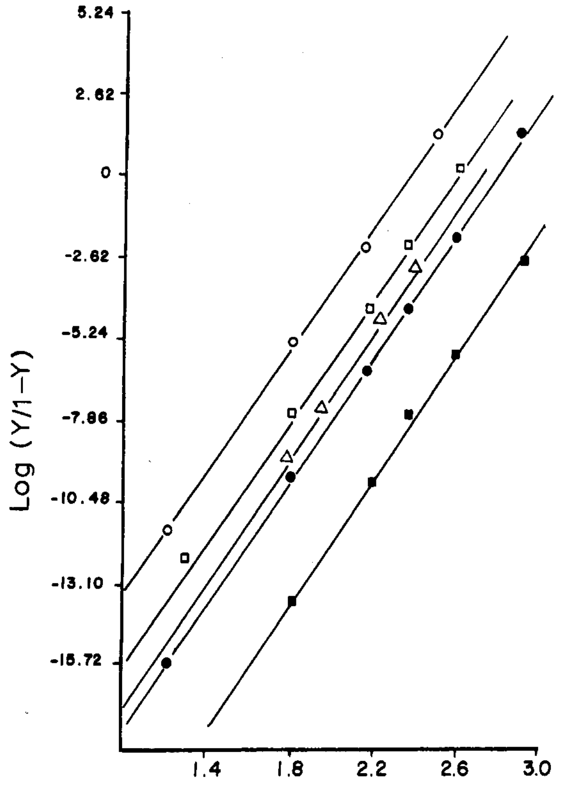

Figure 2. Plot of log [$Y/(1 - Y)$] vs. log P_{O_2} for Co(T(p-CH_3O)PP)(pip) in chlorobenzene at several temperatures: ○, −39.4; □, −32.6; △, −32.4; ●, −30.4; ■, −23.2 °C.

equilibrium constants K obtained from eq 6 were similar to the ones calculated from the Hill equation verifying the fact as pointed out by others[22] that the above calculations reduce to the Hill equation under the conditions where the concentration of ligand is much greater than the complex. In this case, $[O_2] \sim 10^{-2}$ M $\gg$ [BCoP] $\sim 10^{-5}$ M.

In most cases the amount of base needed to form 99.9% of the base adduct precursor complex at the desired temperature was added to the solution prior to the dioxygen titration. However, a modified procedure was needed to prepare methanol solutions of Co(T(p-CH_3O)PP)(py) due to the insolubility of Co(T(p-CH_3O)PP) in methanol. This problem was circumvented by first dissolving the cobalt complex in neat pyridine and then adding the appropriate amount of this solution to methanol. At −50 °C, log K_{O_2} values were −2.08, −2.03, and −2.08 mm^{-1} for methanol solutions that were 0.478, 0.0495, and 0.0149 M in pyridine, respectively. This suggested that, after the optimum concentration of base was added to the solvent to form the precursor complex, log K_{O_2} remained nearly constant. In order to determine the validity of these results, we titrated Co(T(p-CH_3O)PP)(pip) at −49 °C with O_2 in methylene chloride solutions which were 3.85×10^{-5}, 7.81×10^{-5}, 1.12×10^{-4} (optimum concentration), 1.04×10^{-3}, and 0.100 M with respect to piperidine. The respective log K_{O_2} values were −1.14, −0.85, −0.78, −0.79, and −0.79 mm^{-1}. The data indicate that log K_{O_2} increased to a maximum at the optimum base concentration and then remained constant for solutions of higher base concentration, up to 0.100 M in piperidine. These results verified the fact that reaction 7 could be ignored under the reaction conditions.[23]

$$\text{Co(T(}p\text{-CH}_3\text{O)PP)B} + \text{B} \rightleftarrows \text{Co(T(}p\text{-CH}_3\text{O)PP)B}_2 \qquad (7)$$

The enthalpy and entropy parameters for the dioxygen titration results were derived from van't Hoff plots of log K_{O_2} vs. $1/T$ as illustrated in Figure 3. The data, including errors as derived from the linear least-squares regression analysis, are given in Table II. In general, errors of less than 1 kcal/mol were found for ΔH_{O_2} and 2 eu or less for ΔS_{O_2}.

Electrolyte. Values of log K_{O_2} for the reaction of Co(T(p-CH_3O)PP)(py) with dioxygen in methylene chloride at −36.6 °C were determined in neat solvent and in solutions that were 1.00×10^{-4}, 1.00×10^{-3} 2.00×10^{-2}, and 0.100 M with respect to the electrolyte TBAH. The log of the dioxygen uptake constants were respectively −2.24, −2.15, −2.13, −2.06, and −2.04 mm^{-1}. The results indicate that log K_{O_2} increased by a small amount and then remains nearly constant as the concentration of electrolyte continues to rise in solution.

Discussion

Nonspecific Solvation Factors, Dielectric Constant, and log K_{O_2}. Early in our research work, we designed a set of experiments to study dioxygen uptake of Co(T(p-CH_3O)PP)B in mixtures of toluene and o-nitrotoluene where the dielectric constant of the medium could be varied from 2.84 to 25.7. Enhanced dioxygen uptake was expected at high dielectric constant based on the Born[8a] expression

$$\Delta G = \frac{Z^2e^2}{r}\left(1 - \frac{1}{\epsilon}\right) \qquad (8)$$

where Ze is the charge of a gaseous ion of radius r in a solvent of dielectric constant ϵ. However, at −5 °C there was little evidence of dioxygen uptake by Co(T(p-CH_3O)PP)(py) in o-nitrotoluene and certainly not enough

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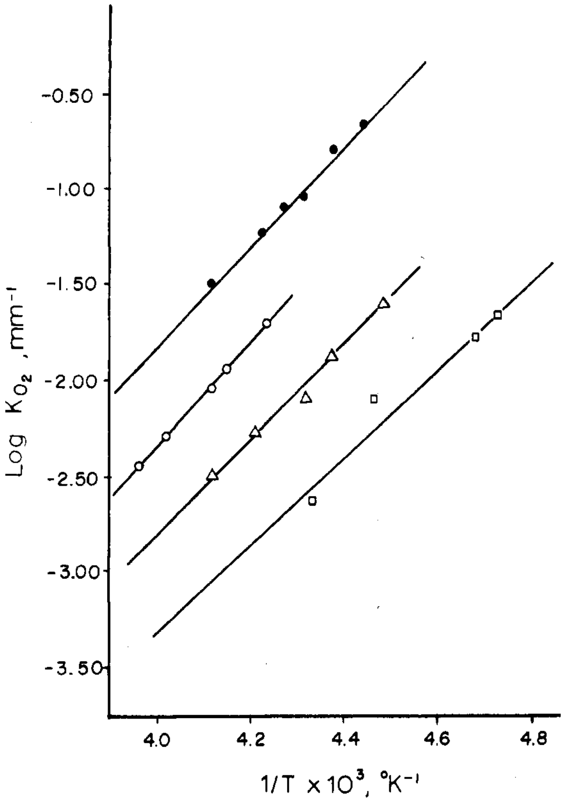

Figure 3. Van't Hoff plots for enthalpy and entropy change determinations for the formation of oxygen adducts in several solvent base combinations: ●, chloroform/*N*-MeIm; ○, chlorobenzene/*N*-MeIm; △, *N*,*N*′-dimethylformamide/pyridine; □, methanol/pyridine.

to obtain data, except at high oxygen pressures. From these results it appeared that the dielectric constant of the medium had only a small effect on the magnitude of dioxygen uptake.

For solvents *N*,*N*′-dimethylformamide, methylene chloride, chloroform, and toluene examined later there was a definite correlation between log K_{O_2} and $1/\epsilon$ as was theoretically expected. Other functions of ϵ were considered,[8,9] and it was found that better correlation coefficients were obtained by using $(\epsilon - 1)/(\epsilon + 2)$ as the polarity descriptor. Plots of log K_{O_2} vs. $(\epsilon - 1)/(\epsilon + 2)$ as shown in Figure 4 gave correlation coefficients of 0.99, 0.99, and 0.99, slopes of 3.87, 4.58, and 2.75, and intercepts, of −3.17, −4.49, and −3.77 for the *N*-methylimidazolate, piperidinate, and pyridinate adducts of Co(T(p-CH$_3$O)PP, respectively. The results can be expressed mathematically as

$$\log K_{O_2} = p\left(\frac{\epsilon - 1}{\epsilon + 2}\right) + C \qquad (9)$$

where p is the slope of the appropriate base adduct and C is the intercept.

The experimental log K_{O_2} values for reactions in chlorobenzene deviate negatively from the correlation by an average of 0.86 log units, the one for the reaction of Co(T(p-CH$_3$O)PP)(py) with O_2 in methanol is low by 0.92 log units. This lower sensitivity in methanol compared to *N*,*N*′-dimethylformamide has also been reported for reactions of vitamin B$_{12r}$ with dioxygen in the same solvents.[24]

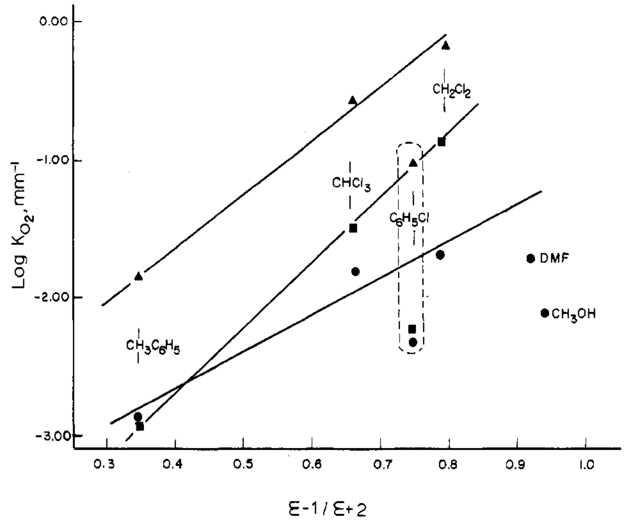

Figure 4. Free energy dependence of log K_{O_2} on the dielectric constant for Co(T(p-CH$_3$O)PP)B reactions with dioxygen at −50 °C: ●, Co(T(p-CH$_3$O)PP)(py); □, Co(T(p-CH$_3$O)PP)(pip); ▲, Co(T(p-CH$_3$O)PP)(*N*-MeIm). Dielectric Constants were estimated at −50 °C. Methylene chloride (12.6) determined from an equation in "The Handbook of Chemistry and Physics", 42nd ed; Chemical Rubber Publishing Co.: Cleveland, 1960; p 2515; chlorobenzene (7.2), value from the above reference, p 2519; chloroform (6.7) and toluene (2.1), both values were extrapolated from data in "International Critical Tables"; Maple, Press: York, PA, 1929; Vol VI p 820; methanol (48.4), value from "Internation Critical Tables"; Maple Press: York, PA 1929; Vol VI, p 83; *N*,*N*′-dimethylformamide (36.7), value from ref 11, room temperature value.

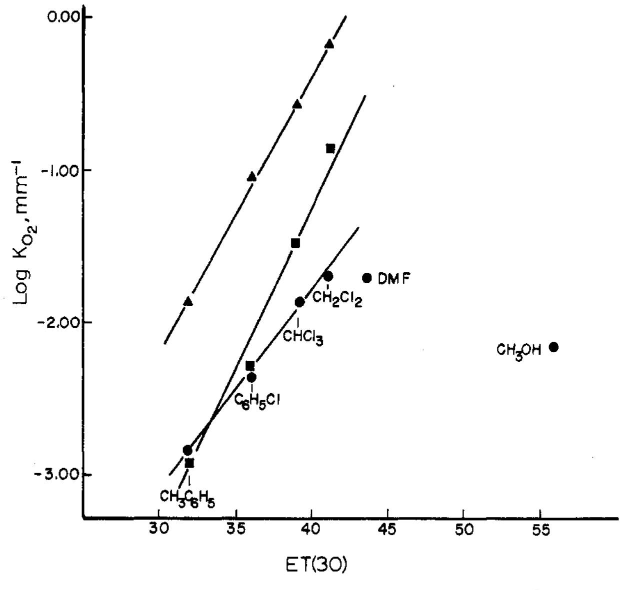

Figure 5. Free energy dependence of log K_{O_2} (at −50 °C) for the reaction of Co(T(p-CH$_3$O)PP)B with dioxygen on solvation ET(30) values: ●, Co(T(p-CH$_3$O)PP)(py); ■, Co(T(p-CH$_3$O)PP)(pip); ▲, Co(T(p-CH$_3$O)PP)(*N*-MeIm). Et(30) values were taken from ref 10 and 11, units are kcal/mol.

Specific Solvation Factors, ET(30) Values, and log K_{O_2}. Figure 5 is a plot of ET(30) values as a function of log K_{O_2}. Reactions in chlorobenzene were included in the correlation. The correlation coefficients were 0.99, 0.98, and 0.98, the slopes were 0.24, 0.28, and 0.17, and the intercepts were −9.86, −12.6, and −8.58 for the *N*-methylimidazolate, piperidinate, and pyridinate adducts of Co(T(p-CH$_3$O)PP), respectively. Adjustment of the linear relationship to the ET(30) value expected in the gas phase (ET(30)g = 27.9 kcal/mol)[25] results in eq 10 where e is the slope of the

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[24] Carter, M. J.; Engelhardt, L. M.; Rillema, D. P.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1973**, 810.

[25] ET(30)g was determined from the intercept of a plot of $(\epsilon - 1)/(\epsilon + 2)$ vs. ET(30) (vertical axis) values for *N*,*N*-dimethylformamide, methylene chloride, chloroform, and toluene. This plot is linear with a correlation coefficient of 0.999, an intercept of 27.9, and a slope of 17.1. Chlorobenzene is anomalous and falls below the line.

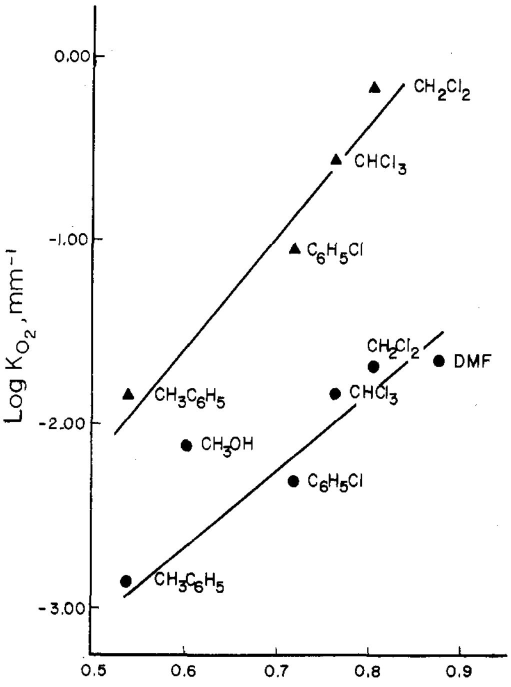

Figure 6. Free energy dependence of log K_{O_2} (at −50 °C) for the reaction of Co(T(p-CH_3O)PP)B with dioxygen on the Taft π^* empirical solvent scale: ●, Co(T(p-CH_3O)PP)(py); ▲, Co(T(p-CH_3O)PP)(N-MeIm).

appropriate base adduct and the constants C' are −3.27, −4.56, and −3.85, respectively.

$$\log K_{O_2} = e(\mathrm{ET}(30) - 27.9) + C' \qquad (10)$$

Comparison to the polarity results gives rise to the following conclusions. First of all, constants C and C' are approximately the same for each base adduct. This suggests that ET(30) values and polarity measure basically the same thing. However, ET(30) values incorporate some feature of solvation by chlorobenzene not included in the polarity description. The opposite is true for dioxygen uptake in methanol. Now the experimental log K_{O_2} value deviates by 2.45 log units compared to 0.92 log units found before in the polarity description.

Specific Solvation Factors, π^* Values vs. log K_{O_2}. Figure 6 is a plot of π^* values as a function of log K_{O_2}. Shown are data for the N-methylimidazolate and pyridinate adducts of Co(T(p-CH_3O)PP). The former gives a correlation coefficient of 0.98, a slope of 6.05, and an intercept of −5.13 while the latter gives a correlation coefficient of 0.95, a slope of 3.69, and an intercept of −4.79. The π^* function does a much better job of predicting the correct trend for all the solvents. The correlation, however, is less precise than that found by using ET(30) values. The probable reason for this may be the close similarity between the ET(30) model system and the charge-separated cobalt–dioxygen adduct.

Nonspecific Solvation Factors, Dielectric Constant, and ΔH_{O_2}. The Born[8a] expression for the enthalpy change dependence on the dielectric constant of the medium is given by eq 11. If the temperature dependence of ϵ is

$$\Delta H = \frac{Z^2e^2}{2r}\left[1 - \frac{1}{\epsilon} - \left(\frac{T}{\epsilon^2}\frac{\partial\epsilon}{\partial T}\right)\right] \qquad (11)$$

neglected, plots of ΔH vs. $1/\epsilon$ should be linear. For consistency the $\epsilon - 1/(\epsilon + 2)$ function was used although both $1/\epsilon$ or $\epsilon - 1/(\epsilon + 2)$ vs. ΔH_{O_2} plots were linear and gave similar correlation coefficients. The correlation coefficients for the linear relationships in Figure 7 are 0.99 for N-methylimidazole and pyridine adducts and 0.94 for the piperidinate complex. Interepts are −8.3, −8.3, and −7.6 kcal/mol, respectively. There is a positive deviation of 1.19 kcal/mol for the reaction of Co(T(p-CH_3O)PP)py with dioxygen in N,N'-dimethylformamide and a positive 1.31 kcal/mol deviation for the same reaction in methanol. It should also be noted that ΔH_{O_2} values in chlorobenzene correlate with the polarity results found in other solvents. In the log K_{O_2} vs. $(\epsilon - 1)/(\epsilon + 2)$ plot (Figure 4), log K_{O_2} values in chlorobenzene were anomalous.

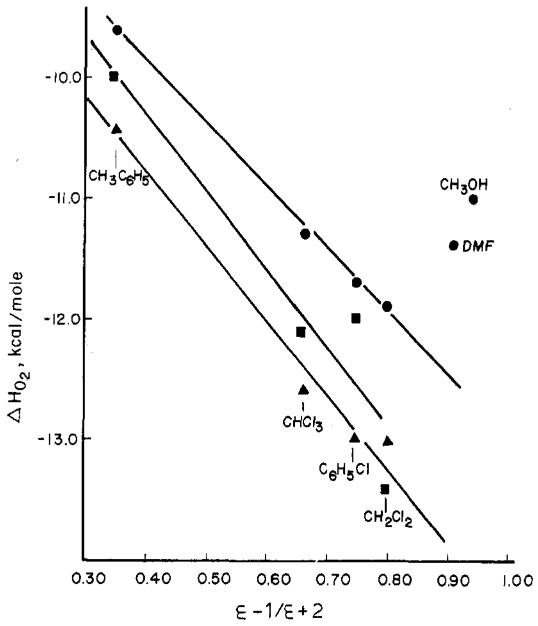

Figure 7. Enthalpy change dependence for the reaction of Co(T(p-CH_3O)PP)B with dioxygen on the dielectric constant at −50 °C: ●, Co(T(p-CH_3O)PP)(py); ■, Co(T(p-CH_3O)PP)(pip); ▲, Co(T(p-CH_3O)PP)(N-MeIm). Dielectric constants were estimated at −50 °C. For details see legend to Figure 4.

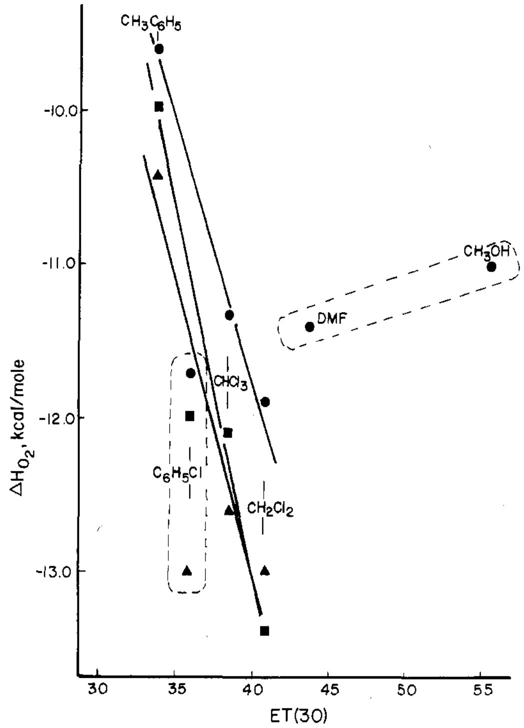

Figure 8. Dependence of ΔH_{O_2} for the reaction of Co(T(p-CH_3O)PP)B with dioxygen on solvation ET(30) values: ●, Co(T(p-CH_3O)PP)(py); ■, Co(T(p-CH_3O)PP)(pip); ▲, Co(T(p-CH_3O)PP)(N-MeIm). ET(30) values were taken from ref 10 and 11, units are kcal/mol.

Specific Solvation Factors, ET(30) Values, and ΔH_{O_2}. Plots of ΔH_{O_2} vs. ET(30) values are given in Figure 8. The solvents chosen for the correlation were methylene chloride, chloroform, and toluene. The correlation coefficients are 0.99, 0.99, and 0.99, the slopes are −0.41, −0.46, and −0.32, and the intercepts are 3.42, 5.60, and 1.27 for dioxygen uptake by *N*-methylimidazole, piperidine, and pyridine adducts of Co(T(*p*-CH_3O)PP), respectively. The respective ΔH_{O_2} "gas-phase values" (−7.9, −7.2, and −7.6 kcal/mol) were calculated from the linear relationships and the ET(30)g value.[25]

Figure 8 indicates that ΔH_{O_2} is $\simeq$1 kcal/mol more negative for reactions in chlorobenzene than expected. This should lead to larger log K_{O_2} values than predicted. However, the data in Figures 4 and 5 indicate that this is not so. Rather an unfavorable entropy term must compensate for the more favorable enthalpy factor. The entropy values in Table II for the reactions in chlorobenzene indeed are more negative than others. It is suggested that the mechanism responsible for this effect is π interaction between the solvent and solute molecules as previously has been reported.[26,27] The π cloud of the solvent apparently interacts with the π cloud of the porphyrin ring diminishing the stabilizing effect of dipole–dipole interactions and hence accounts for the negative deviation found for log K_{O_2} in chlorobenzene as shown in Figure 4. The π mechanism apparently causes a concomitant ordering of the system resulting in a more negative entropy change. The same mechanism would account for the lack of enhanced dioxygen uptake in *o*-nitrotoluene where the effect is much larger than in chlorobenzene due to delocalization of π electrons over the nitro group and benzene ring.[27d,e]

It has been suggested that the lower enthalpy changes found for acid–base reactions in CH_2Cl_2 compared to CCl_4 was due to hydrogen bonding[28] between the base and the solvent. Another possible explanation for the deviation of reactions in chlorobenzene then is a less favorable enthalpy change in CH_2Cl_2 and $CDCl_3$ due to hydrogen-bonding effects.

As shown in Figure 8, the enthalpy change for dioxygen uptake by Co(T(*p*-CH_3O)PP)py in *N,N′*-dimethylformamide is less negative than expected even though free energy plots based on log K_{O_2} values show only a small deviation. The lower enthalpy values most likely result from the coordination of the solvent to the vacant coordination site of the precursor complex requiring displacement of the bound solvent prior to reaction with dioxygen. The extra bond breakage step then accounts for the smaller enthalpy change and the positive deviation of ΔH_{O_2} in Figures 7 and 8. Mechanistically, ΔS will be the sum of two reactions, the one involving displacement of the solvent from the sixth coordination site and the second addition of dioxygen in that position. Thus, ΔS will be more positive for the sum of the two reactions than the case where only the dioxygenation reaction occurs. The net result gives rise to offsetting terms (both ΔH and ΔS more positive) causing ΔG (log K_{O_2}) to follow anticipated trends.

The reaction of Co(T(*p*-CH_3O)PP)py in methanol fails to follow any of the correlations in Figures 4, 5, 7, and 8 and only somewhat in Figure 6. The dielectric constant of methanol (ϵ_{20} = 32) is similar to that of *N,N′*-dimethylformamide (ϵ_{20} = 36). Thus, it is expected that methanol will coordinate with Co(T(*p*-CH_3O)PP)py and give rise to low ΔH_{O_2} values. The greater deviations in methanol compared to *N,N′*-dimethylformamide can be explained by the fact that methanol is a hydrogen-bonding solvent and this suggests that such solvent structural effects play a dominant role in decreasing the sensitivity of the complex to reversible dioxygenation.

In this respect it is interesting to note the rapid dioxygen uptake rates reported by James and co-workers[29] for the reaction of Co(PP(IX)DME)B, B is imidazole and benzimidazole, with dioxygen and the larger dioxygen uptake constants reported by Drago and co-workers[30] for the reaction of CoSMDPT (bis(salicylideniminato-3-propyl)-methylaminocobalt(II)) with dioxygen in the presence of small amounts of 2,2,2-trifluoroethanol. Both anomalies were attributed to hydrogen-bonding effects. Apparently dioxygen uptake in a hydrogen-bonding solvent is counterproductive due to solvent structure effects and further emphasizes the need of the protein environment for protection of the heme group in order to carry out reversible oxygenation reactions in biological systems.

Nonspecific Solvent Effects—Polarization. The polarizing effect of solvents on solute–solvent interactions can be deduced noting the dependence of ΔH_{O_2} or log K_{O_2} on $\eta^2 - 1/(\eta^2 + 2)$, where η is the index of refraction of the solvents. This function is nearly a constant for the solvents studied in this work. According to Koppel and Palm,[7] the actual magnitude of this effect is at most 10–14% of the polarity function. Thus, it is not a major contributor to the overall analysis.

Specific Solvent Effects—Nucleophilicity. The nucleophilicity of solvents where ET(30) factors were employed was assumed to be small and set equal to zero.[7] The center of positive charge in the model molecule, pyridinium phenol betaine, is embedded in the molecule and unavailable for electron donation of the solvent molecules for steric reasons. Similar reasoning applies to the cobalt dioxygen carrier system.

The mechanism of electron donation by solvent to a vacant coordination site, however, is important for the experimental system, not the standard used to determine ET(30) values. The only solvent systems where this effect appeared important were reactions in *N,N′*-dimethylformamide and methanol. These effects have more recently been accounted for by the donor number concept.[13] According to the donor number concept, log K_{O_2} should vary inversely with the donor number of the solvent for reactions requiring the dissociation of a ligand prior to reaction with another. For reactions of Co(T(*p*-CH_3O)PP)(py) with dioxygen in dimethylformamide and methanol, there is indeed a decrease in log K_{O_2} as the donor number of the solvents increases. The donor numbers in dimethylformamide and methanol are 26.6 and 33.8, respectively, and the corresponding log K_{O_2} values at −50 °C are −1.72 and −2.74 atm^{-1}.

Salt Effects. Closely associated with ET(30) values are *Z* values. Both very linearly. Kosower[31] reported that *Z* values increased as the concentration of pyridinium iodide increased in chloroform. This suggested that dioxygen uptake would be enhanced as an electrolyte was added to

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[26] Walker, F. A. *J. Am. Chem. Soc.* **1970**, *92*, 4235.

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a solvent containing Co(T(p-CH_3O)PP)B. To test this hypothesis, methylene chloride solutions of tetrabutylammonium hexafluorophosphate (TBAH) were prepared and dioxygen uptake of Co(T(p-CH_3O)PP)(py) in each solution was determined at −34.6 °C. The dioxygen sensitivity of the complex increased from $\log K_{O_2} = -2.24$ mm^{-1} with no electrolyte present in the solution and reached a maximum at 0.02 M TBAH where $\log K_{O_2} = -2.06$ mm^{-1}. From 0.02 M to higher electrolyte concentrations, the dioxygen uptake ability of the complex remained nearly constant. The results of a dilution conductivity study based on the Onsager equation[32] and methods published by Boggess and Zatko indicate that TBAH is a weak electrolyte in methylene chloride and it is interesting to note that the point at which the equivalent conductivity of the solution ceases to change is near the point of which dioxygen uptake levels off. The small change in the dioxygen uptake ability of the complex in salt solutions is consistent with a small change in Z values. Unfortunately, the Z values of the TBAH solutions are unknown.

Conclusion

The dependence of reversible dioxygen uptake of Co(T(p-CH_3O)PP)B complexes on solvents is determined by a number of complex variables related to an intricate interplay of properties of solvent and solute molecules. The gross effects are accounted for by analyzing the dependence of $\log K_{O_2}$ and ΔH_{O_2} on the dielectric constant of the medium and the electrophilic solvating power of the solvents using π^* and ET(30) values as a guide. The intercepts of polarity plots and "gas-phase values" calculated from ET(30) plots are similar and suggest both functions measure similar solute–solvent properties. The constants obtained from the intercepts of polarity plots and "gas-phase" values deduced from ET(30) plots may contain a small contribution ($\log K_{O_2}$, ≤ 0.3 mm^{-1}; $\Delta H_{O_2} \leq 0.3$ kcal/mol) from the polarizability function. Deviations from the general trend can be explained on the basis of the physical and chemical properties of the solute and/or solvent and the thermodynamics of the system. It was found that enthalpy and entropy changes were off-setting terms in the ΔH_{O_2} and $\log K_{O_2}$ trends for reactions in chlorobenzene and N,N'-dimethylformamide. Thus, an analysis of the intricate details of dioxygen uptake indicated that entropies do change somewhat, rather than remaining constant as has previously been suggested.

Acknowledgment. We thank the Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Foundation of the University of North Carolina at Charlotte for support.

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Activity Coefficients of Mixed Electrolytes from Liquid–Liquid Partitioning Measurements

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Distribution of an uncharged metal chelate between aqueous and nonaqueous solutions is shown to depend upon, inter alia, the activity coefficient of the metal ion when the distribution ratio is small. From this dependence, mean ionic activity coefficients may be determined of metal salts in the presence of nonreactive electrolytes. Experimental results are given for copper(II) salts in the presence of three different strong electrolytes and the resulting activity coefficients are compared with ion selective electrode measurements and with calculated activity coefficients based on three different theories of mixed electrolytes. Further variations on the method and application to biological and environmental studies are discussed.

Introduction

Methods for the determination of activities of dissolved electrolytes at low and trace levels in the presence of relatively large concentrations of other solutes are of interest in environmental chemistry, biology, and the theory of electrolyte solution. An approach is described here which is of rather general applicability and results are presented for copper(II) salts in the presence of several common electrolytes. This method relies on the partitioning of an uncharged chelate of the metal ion of interest between an aqueous solution and an immiscible solvent. Thus, it is amenable to those metal ions which form stable complexes and the major electrolytes present must be inert to the same reaction. It is also clear that proton activity in the solution is important since suitable chelate ligands are universally weak acids. In other respects, liquid–liquid partitioning is quite analogous to other methods which have been used for the determination of activities of solutes; the commonality is that some intensive property of a phase in contact with the solution under study is measured as a function of solute concentration or ionic strength.

Liquid–liquid partition equilibrium (LLPE) has been recognized[1] to have promise for the measurement of chemical potentials, but thus far applications have been made to only two systems involving ion-pair formation. In the first,[2] ionic activity coefficients of uranyl nitrate in the presence of various concentrations of sodium nitrate were obtained by equilibration with a solution of uranyl nitrate in ether. The idea was based upon the concept of "isoactive" solutions. In practice, a series of solutions was prepared containing uranyl nitrate and sodium nitrate, and one reference solution of uranyl nitrate alone. In ether the uranium salt dissolves as an uncharged molecule. Thus,

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[2] E. Glueckauf, H. A. C. McKay, and A. R. Mathieson, *J. Chem. Soc.*, S299 (1949).

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