

Dielectric Properties of Binary Mixtures.¹ 5. Dilute Alcohol/Nonpolar Solvent Systems

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A simple model is used for dilute polar/nonpolar systems, based on the additivity of electric susceptibilities of a solute/solvent interaction species and a nonpolar solvent. A spherical cavity is considered. Permittivity values, calculated as a function of concentration, are in good agreement with experimental results when the model is applied to systems containing water or lower alcohols in nine nonpolar solvents.

Introduction

In very dilute solutions of polar solutes in nonpolar solvents, the permittivity is found experimentally to be a linear function of solute concentration. This is an important region because permittivity (ϵ), specific volume (\bar{V}), and refractive index (η) are measured therein to calculate the dipole moment (μ) of the solute. However, there is so far no satisfactory model to describe completely the details of this behavior at very low solute concentrations.

The sizable amount of work reported on water and the lower alcohols (R-OH, wherein R = H, Me, Et, *n*-Pr, *n*-Bu) as polar solutes in a number of nonpolar solvents (benzene, *n*-hexane, dioxane, carbon tetrachloride, cyclohexane, carbon disulfide, and toluene) makes these systems good candidates with which to reexamine the problem.

Six known equations based on spherical cavity models were used to evaluate the existing data, but they do not predict satisfactorily the linear behavior of permittivity as a function of concentration. An equation based on a simple model was developed, which proved to be adequate in the case of the chosen systems.

Examination of Data

In very dilute solutions the gradient of the linear concentration response observed experimentally for the permittivity could have any one of several origins: (i) the dielectric properties of the pure components may remain unchanged in mixtures regardless of their proportions, (ii) there may exist some form of ideal behavior, or (iii) there could be solute/solvent interactions of some kind. Known data can be examined considering each of them.

Values calculated through direct use of the pure-component permittivities and a simple additive law of the form

$$\epsilon_{12} = \epsilon_1 w_1 + \epsilon_2 w_2 \quad (I)$$

(subscripts: 1 = solvent, 2 = solute, and 12 = solution; w represents the weight fraction concentration) rule out the first possibility (i) because of the large differences between experimental and calculated values (see third column, Table II). Consequently eq I can be discarded.

The second possibility (ii) requires that no interactions exist at all. On this basis, in the particular case of water, Oehme² calculated a very low permittivity ($\epsilon = 28.3$ at 298 K) using Onsager's equation³ with the dipole moment

(1) See part 3: *An. Asoc. Quim. Argent.*, **67**, 203-6 (1979).

(2) F. Oehme, "Dielektrische Messmethoden", Verlag Chemie, Weinheim, West Germany, 1962, p 110.

TABLE I: Permittivities at 298 K

compd	exptl	calcd
H ₂ O	78.45	28.3
MeOH	32.70	11.3
EtOH	24.55	8.6
<i>n</i> -PrOH	20.33	6.5
<i>n</i> -BuOH	17.10	6.02

measured in the vapor phase. Doing the same for the lower alcohols also gave values that are much lower than those measured on the pure compounds (Table I).

Oehme suggested that the low calculated ϵ values represented "idealized water". On the other hand, low numbers as these are not uncommon. Steru⁴ claimed $\epsilon = 20$ (at 298 K) measured on water adsorbed on the surface of solids and in fine capillaries. Also Foster and Resing⁵ estimated values of $\epsilon = 14$ and $\epsilon = 20$ for interstitial water in hydrated zeolites.

But since these values are a consequence of the interaction of water molecules with the silicate surface, it is not logical to consider them a result of idealized water. What is actually being studied is a system formed by water adsorbed on the surface of a solid silicate.

Therefore both solute/solute interactions (i) and ideal behavior (ii) must be discarded. This leaves the third possibility (iii) to be considered, in other words, interactions of solute molecules with the surrounding medium. These are the solute/solvent interactions or solvation suggested by Muller⁶ while discussing the influence of solvent effects on dipole moments.

Discussion

Studies on the state of aggregation of water and the lower alcohols in nonpolar solvents have already been made.^{1,8-13} In all cases the plots of $\epsilon = f(w_2)$ (wherein w_2

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(4) M. Steru, *Ind. Chim. Belge*, **32**, 147-51 (1967).

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(9) Hugo, M. Giansanti, Seminario de Licenciatura en Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Buenos Aires, Argentina, 1980.

(10) S. D. Christian, A. A. Taha, and B. W. Gash, *Q. Rev. Chem. Soc.*, **24**, 20 (1970), and references therein cited.

is the solute weight fraction concentration) appear as a succession of straight lines suggesting different forms of interactions as the solute concentration increases. This can be seen in Figure 1 for methanol in benzene, *n*-hexane, and CCl₄.⁹ The first region in these and the other systems mentioned corresponds to the high dilution conditions used for dipole moment calculations. This stems from the generally made assumption that it contains the solute not only in a monomeric state but also free of interactions, either solute/solute (due to the distance between the solute molecules) or solute/solvent (as claimed in the above-mentioned references). Consequently these have to be discarded after the preceding discussion.

An alternative possibility would imply evaluating known equations. But their number is very large, starting with the original one by Mossotti and Clausius. So, it was decided to begin with only those models based on a spherical cavity introducing no correction factors. This narrowed the choice to just six equations: Mossotti-Clausius (MC), Mossotti-Clausius-Debye (MCD), Debye (D), Onsager (O), Onsager-Grosse-Grefe (OGG), and Grosse-Grefe (GG), the difference between the first two and the last four being the introduction of molecular parameters in the latter. The initials in parentheses correspond to the respective headings in Table II. All of them were discussed in detail and expressed in coherent form recently by Grosse and Grefe.¹⁴

Suitable computer programs were prepared for each equation, and previously reported data were evaluated.^{9-12,15-17} In each case the slope (*S*) and the extrapolated solution permittivity (ϵ_{120}) were calculated (ϵ_{120} corresponds to the permittivity of the solution in the limit of zero solute concentration). Under the corresponding initials the results are listed in Table II and they show the following: (a) The basic model for the MC and MCD treatments seems to provide values for the change in permittivity (slope) of the binary systems considered, which are within the order of magnitude of the experimental results. (b) Equations due to D, O, and OGG show no coincidence in the slopes. The equations by GG show very good coincidence for the solution in benzene, but none with the other solvents. (c) Although a cavity model appears promising, the introduction of molecular parameters does not lead to any improvement.

A different approach was attempted on the basis of electrical susceptibilities and the auxiliary use of a cavity as will be discussed in the next section.

Proposed Equation

As already mentioned, there is enough experimental evidence indicating that water and the lower alcohols interact with nonpolar solvents.^{1,7-12} But all of the models and equations mentioned do not describe this situation in a satisfactory manner because the calculated values for *S* and ϵ_{120} do not agree with the experimental results. To overcome this problem, we propose a different approach.

If solute/solvent interactions are to be considered in order to describe the linear behavior of the permittivities of all of these solutions (ϵ_{12}) with solute concentration, at the lowest concentration, it is convenient to describe properties of the solution through the number of molecular species present per unit volume. To do so, one can consider the existence of N_1 molecules of solvent and N_2 molecules of solute, related to each other in some form of molecular species. This latter would then be formed by one solute molecule and the solvent molecules that surround it. Therefore, because of the observed linear behavior in these solutions, it is necessary to accept that the external and the dipolar fields become superimposed.

This allows one to consider the electric susceptibility of the solution as being

$$\chi_{12} = \chi_1 + \chi_3$$

where χ_{12} is the electric susceptibility of the solution, χ_1 is the electric susceptibility of the solvent, and χ_3 is the electric susceptibility of the species formed by solute and solvent.

In the case of the linear behavior of mixture permittivities, the following fundamental equations are valid,¹⁹ since they are applicable to all material systems:

$$E(\epsilon - 1)/4 = P = \chi E$$

or

$$\epsilon = 1 + 4\pi\chi \quad \chi = N\alpha$$

where χ is the total susceptibility and α is the total molecular polarizability. Therefore, if α_1 is the total solvent polarizability

$$\chi_1 = N_1\alpha_1$$

$$\chi_3 = N_2\alpha_3$$

$$\chi_{12} = \alpha_1 N_1 + N_2\alpha_3$$

$$\epsilon_{12} = 1 + 4\pi\chi_{12}$$

so that substitution gives

$$\epsilon_{12} = 1 + 4\pi[\alpha_1 N_1 + \alpha_3 N_2]$$

However, since the solute concentrations are very small, it can be accepted that

$$\epsilon_1 = 1 + 4\pi\alpha_1 N_1$$

so

$$\epsilon_{12} = 1 + 4\pi[\alpha_1 N_1 + \alpha_3 N_2]$$

leaving

$$\epsilon_{12} = \epsilon_1 + 4\pi\alpha_3 N_2 \quad (\text{II})$$

The α_3 term in eq II, representing the polarizability of the solute/solvent interaction product, contains the contributions of both solute and solvent. As a consequence, the dipole moment of the species will have to be different from that of the pure solute.

However, in highly dilute systems, these are weak changes, and a model with additive polarizabilities is still valid, so that now α_3 contains the contributions of the solute molecule plus the unchanged atom and electron polarizabilities, in its particular state of interaction with the solvent. Therefore, the total polarizability of the interaction species can be written as

$$\alpha_3 = \alpha_{30} + \alpha_{2e} + \alpha_{2a}$$

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(17) A. L. McClellan, "Tables of Experimental Dipole Moments", Vol. 2, Rahara Enterprises, El Cerrito, CA, 1974.

(18) J. D. Jackson, "Classical Electrodynamics", Wiley, New York, 1962, pp 109, 119.

TABLE II: Permittivities as a Function of Concentration

systems		ϵ_{12}		MC	MCD	D	O	OGG	GG	M	
		exptl	ref								calcd ^a
H ₂ O/benzene	S	16.555		76.267	18.348	23.417	12.982	7.711	-2.610	19.369	15.924
	ϵ_{120}	2.2726	1	2.2727	2.3049	2.3049	2.2727	2.2727	2.2727	2.2727	2.2727
H ₂ O/dioxane	S	26.776		76.326	21.625	27.595	15.076	9.358	-2.505	13.638	18.575
	ϵ_{120}	2.2137	8	2.2138	2.3049	2.3049	2.2138	2.2138	2.2138	2.2138	2.2138
MeOH/benzene	S	9.404		30.426	7.987	10.098	4.260	9.456	4.860	8.072	8.019
	ϵ_{120}	2.2740	9	2.2740	2.3072	2.3072	2.2752	2.2767	2.2754	2.2763	2.2740
MeOH/benzene	S	8.790		30.428	9.138	11.545	4.886	10.862	5.592	9.127	8.008
	ϵ_{120}	2.2724	12	2.2724	2.3051	2.3051	2.2721	2.2721	2.2721	2.2721	2.2721
MeOH/CCl ₄	S	20.248		30.473	16.045	20.211	8.913	20.200	10.814	11.241	18.601
	ϵ_{120}	2.2261	9	2.2268	2.2249	2.2248	2.2268	2.2268	2.2268	2.2268	2.2268
MeOH/CCl ₄	S	14.522		30.473	16.024	21.181	8.909	20.191	10.809	11.236	15.843
	ϵ_{120}	2.2268	12	2.2268	2.2268	2.2268	2.2268	2.2268	2.2268	2.2268	2.2268
MeOH/n-C ₆ H ₁₄	S	6.146		30.797	5.431	6.798	3.317	9.599	7.481	0.741	5.368
	ϵ_{120}	1.9033	9	1.9033	1.9187	1.9192	1.9045	1.9068	1.9033	1.9033	1.9033
MeOH/C ₆ H ₁₂	S	5.873		30.686	7.333	9.193	1.059	2.792	1.769	0.02	6.391
	ϵ_{120}	2.0146	12	2.0144	2.0347	2.0347	2.0164	2.0196	2.0177	2.0144	2.0144
MeOH/dioxane	S	12.436		30.491	10.634	13.510	5.479	12.837	6.975	5.964	11.042
	ϵ_{120}	2.2095	12	2.2092	2.3099	2.3101	2.2102	2.2115	2.2105	2.2103	2.2112
EtOH/C ₆ H ₆	S	6.373		22.278	6.395	8.021	2.778	5.334	3.609	2.822	5.971
	ϵ_{120}	2.2725	13	2.2724	2.3051	2.3102	2.2724	2.2729	2.2725	2.2724	2.2724
EtOH/CCl ₄	S	10.289		22.326	11.288	14.283	5.136	22.466	15.585	7.815	11.603
	ϵ_{120}	2.2269	12	2.2269	2.2249	2.2249	2.2268	2.2268	2.2268	2.2268	2.2268
EtOH/CCl ₄	S	11.868		22.322	11.296	14.283	5.406	22.618	15.682	8.151	11.032
	ϵ_{120}	2.2280	13	2.2280	2.3051	2.3051	2.2280	2.2280	2.2280	2.2280	2.2280
EtOH/C ₆ H ₁₂	S	4.444		22.536	5.236	4.617	13.133	10.033	1.817	0.098	3.581
	ϵ_{120}	2.0143	12	2.0142	2.0346	2.0376	2.0144	2.0144	2.0156	2.0144	2.0167
EtOH/C ₆ H ₁₂	S	4.678		22.533	5.233	6.533	2.573	9.997	13.102	0.0183	5.072
	ϵ_{120}	2.0167	13	2.0165	2.0346	2.0346	2.0165	2.0165	2.0165	2.0165	2.0164
EtOH/dioxane	S	8.428		22.342	7.407	9.376	3.116	14.322	9.986	4.151	7.078
	ϵ_{120}	2.2078	12	2.2078	2.3096	2.3098	2.2098	2.2118	2.2110	2.2090	2.2105
EtOH/n-C ₆ H ₁₄	S	3.473		22.671	4.401	5.473	2.266	12.384	10.901	0.802	4.299
	ϵ_{120}	1.8795	13	1.8786	1.9167	1.9167	1.8786	1.8812	1.8786	1.8786	1.8787
EtOH/CS ₂	S	9.621		21.917	10.448	13.391	3.655	14.098	7.947	58.139	9.016
	ϵ_{120}	2.6330	13	2.6330	2.7522	2.7522	2.6330	2.6330	2.6330	2.6330	2.6330
EtOH/p-xylene	S	6.225		22.291	6.303	7.958	2.275	11.912	8.112	4.695	4.908
	ϵ_{120}	2.2585	13	2.2587	2.3116	2.3116	2.2594	2.2587	2.2587	2.2601	2.2602
PrOH/C ₆ H ₆	S	4.658		18.058	4.673	5.910	1.572	13.891	10.785	4.883	4.731
	ϵ_{120}	2.2729	12	2.2714	2.3051	2.3051	2.2724	2.2724	2.2724	2.2724	2.2724
PrOH/CCl ₄	S	8.362		18.103	8.273	10.414	2.968	25.875	20.338	5.786	8.502
	ϵ_{120}	2.2269	12	2.2270	2.2249	2.2249	2.2268	2.2268	2.2268	2.2268	2.2268
PrOH/C ₆ H ₁₂	S	3.601		18.316	2.774	3.461	1.117	11.630	8.851	0.007	2.849
	ϵ_{120}	2.0143	12	2.0144	2.0364	2.0368	2.0151	2.0216	2.0205	2.0144	2.0162
PrOH/dioxane	S	6.393		18.122	5.604	7.108	1.834	17.262	13.651	3.202	5.739
	ϵ_{120}	2.2081	12	2.2083	2.3082	2.3081	2.2092	2.2088	2.2089	2.2091	2.2091
n-BuOH/C ₆ H ₆	S	3.516		18.058	3.010	3.796	0.666	11.888	9.983	2.995	3.216
	ϵ_{120}	2.2727	12	2.2724	2.3062	2.3065	2.2727	2.2780	2.2771	2.2735	2.2736
n-BuOH/CCl ₄	S	7.065		18.103	6.625	8.322	1.663	31.150	26.494	4.577	7.147
	ϵ_{120}	2.2265	12	2.2266	2.2249	2.2249	2.2268	2.2268	2.2268	2.2268	2.2268
n-BuOH/C ₆ H ₁₂	S	3.100		18.316	2.269	2.819	0.690	15.911	14.391	0.006	2.446
	ϵ_{120}	2.0144	12	2.0144	2.0360	2.0364	2.0148	2.0240	2.0231	2.0144	2.0159

TABLE II (Continued)

systems		ϵ_{12}			MC	MCD	D	O	OGG	GG	M
		exptl	ref	calcd ^a							
n-BuOH/dioxane	S	5.071		18.123	4.451	5.635	0.981	20.899	17.934	2.533	4.775
	ϵ_{120}	2.2077	12	2.2073	2.3058	2.2082	2.2092	2.2087	2.2087	2.2091	2.2091
	ϵ_1	2.2073									

^a These values were calculated by using the permittivities of the pure components and a simple additive law.

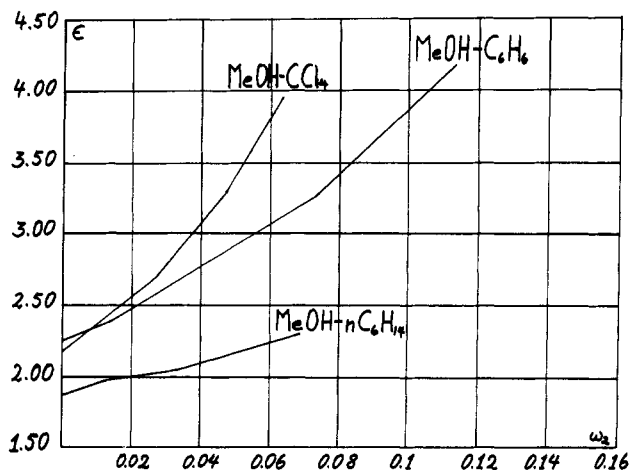


Figure 1. $\epsilon = f(w)$ for MeOH in CCl_4 , C_6H_6 , and $n\text{-C}_6\text{H}_{14}$.

Since the behavior of an isolated molecule immersed in a sea of solvent is considered, it is possible to apply Onsager's cavity model³ whereby

$$\alpha_{30} = \mu\mu^*/(3kT)$$

where μ is the dipole moment within the cavity and μ^* is the external moment of the immersed dipole. Both of these moments can be calculated as proposed by Onsager:³

$$\mu = \frac{(\eta_2^2 + 2)(2\epsilon_1 + 1)}{3(2\epsilon_1 + \eta_2^2)} \mu_0$$

$$\mu^* = \frac{\epsilon_1(\eta_2^2 + 2)}{(2\epsilon_1 + \eta_2^2)} \mu_0$$

where η_2 is the refractive index of the solute and μ_0 is the dipole moment of the solute under vacuum.

But this is a very dilute system, so it is possible to assign to each molecule its own cavity as if it were immersed in solvent. The approximation or model is then applicable, wherein η_2 represents the refractive index of the cavity filled with the corresponding solute molecule. Consequently the following Onsager³ relations can be used:

$$\alpha = [(\eta^2 - 1)/(\eta^2 + 2)]a^3$$

$$\alpha_{2e} = [(\eta_2^2 - 1)/(\eta_2^2 + 2)]a_2^3$$

a_2 being calculated with the approximation that $4\pi N\alpha^3/4 = 1$ where $N = N_A/(M_2\bar{V}_2)$ (N_A = Avogadro's number; M_2 : solute molecular weight; \bar{V}_2 = solute specific volume) leaving

$$a_2 = [3\bar{V}_2 M_2 / (4\pi N_A)]^{1/3}$$

Regarding α_{2a} , it could be either disregarded or estimated as a certain percentage of α_{2e} . The latter seems far more reasonable because there is sufficient evidence that

justifies considering α_{2a} as being between 5% and 15% of α_{2e} . Therefore, to cover all possibilities, it is best to take the upper value so that

$$\alpha_{2a} = 0.15\alpha_{2e}$$

Consequently eq II then becomes

$$\epsilon_{12} = \epsilon_1 + 4\pi(\alpha_{30} + \alpha_{2e} + \alpha_{2a})N_2$$

$$\epsilon_{12} = \epsilon_1 + 4\pi \left\{ \frac{(\eta_2^2 + 2)(2\epsilon_1 + 1)}{3(2\epsilon_1 + \eta_2^2)} \frac{\epsilon_1(\eta_2^2 + 2)}{(2\epsilon_1 + \eta_2^2)} \frac{\mu_0^2}{3kT} + \frac{(\eta_2^2 - 1)}{(\eta_2^2 + 2)} a_2^3 + \left[0.15 \frac{(\eta_2^2 - 1)}{(\eta_2^2 + 2)} a_2^3 \right] \right\} N_2 \quad (\text{III})$$

wherein μ_0 is the dipole moment of the solute under vacuum (gas-phase measurements) as previously indicated.

The same experimental data were evaluated with eq III, and the results are listed in Table II under M. All calculated values are in good agreement with experiment.

In the above discussion, although a cavity is considered and solute and solvent properties are included, the solution is viewed as a system formed by a solute/solvent species in a sea of solvent. This is substantially simpler than many previous treatments, because eq III only contains the permittivity of the pure solvent and the refractive index of the solute, the vapor-phase dipole moment of the solute, and the molecular radius of the solute (calculated from bulk properties).

Conclusions

(1) Spherical cavity models with no correction factors do not describe the behavior of the permittivity as a function of concentration of simple hydroxyl compounds (R-OH; R = H, Me, Et, *n*-Pr, and *n*-Bu) in very dilute solutions of nonpolar solvents.

(2) The original Mossotti-Clausius model is an exception regarding only the slope, while the Grosse-Grefe model is useful only to describe those systems having benzene as solvent.

(3) The permittivity of the candidate systems, as a function of concentration, can best be described considering a solute/solvent interaction product or species located in a spherical cavity immersed in a sea of solvent. Under these conditions the electric susceptibilities of both components are additive and their values can be calculated by using the permittivity and the refractive index of the pure solute, the dipole moment of the solute in the vapor state, and the molecular radius of the pure solute calculated from experimental weights and volumes.

(4) In the water/dioxane system there is no agreement between the experimental and calculated values, using the proposed equation. Such behavior can be attributed to a solute/solvent interaction, typical of these two components, which differs significantly from what occurs when one of the hydrogen atoms in the water molecule is replaced by a small alkyl group ($\text{C}_1\text{-C}_4$). This singular situation is by no means unexpected since Jaffer²⁰ already

found evidence for particular solute/solvent associations in the water/dioxane system.

(5) With the proposed equation, calculated values of ϵ for very dilute solutions as a function of concentration, with one exception, are in good agreement with experiment.

(20) S. Jaffer, Ph.D. Thesis, The American University, Washington, DC, 1974.

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Strong Interaction of Metallotetraphenylporphyrins with Supporting Metal Oxides Observed in the Catalytic Decomposition of Hydrogen Peroxide

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The catalytic activities of metallotetraphenylporphyrins (M-TPP's) and their supported forms on some oxides for the decomposition of hydrogen peroxide were studied in buffers of pH ranging between 6.5 and 10.2. Unsupported M-TPP's including H₂-TPP showed a small but definite constant activity at pH 10.2 regardless of their central metal ions and the first oxidation potentials. Supporting M-TPP on the oxides distinguished Co-TPP from other complexes and TPP ligand. The activity of the former complex was much enhanced by being supported on alumina and nickel oxide, whereas the others lost their activity, suggesting a strong and selective interaction of the catalyst material with the supports. The large conjugate ring of the ligand which has much the same oxidation potential regardless of the central metal ions may provide the active site for the catalysis common to the unsupported catalysts. In contrast, the active site of supported Co-TPP may be assumed to be the central metal ion, which can be modified to be active by the electronic transfer to the support through its axial coordination bond. Increased effective surface area and the hydrophilic nature of the supported catalyst may also contribute to the increase of the activity.

Introduction

The catalytic decomposition of hydrogen peroxide has been extensively studied by using various metal ions and their complexes as a model for the catalysis promoted by catalase.¹ The reaction has often been explained in terms of the Haber-Weiss mechanism,² including the redox of the central ion. We have reported that the activities of transition-metal ions exchanged onto zeolites vary in a bell-shaped pattern against their redox potentials.³ Such a dependency on their redox potentials suggests that the proper modification of the redox potential of an ion by any means may enhance its catalytic activity. Suitable coordination has been known to increase the catalytic activity.⁴ Some chelating ligands brought remarkable enhancement⁵ to give an activity comparable to that of catalase.

A series of metallotetraphenylporphyrins (M-TPP's) are known to show a sequence of redox potentials, and their catalytic activities have been examined in several systems.⁶ Some of the oxide carriers are reported to be able to modify the properties of the metals and some complexes supported on them through their electronic interactions.⁷ We found that Co-TPP showed a very high catalytic activity for the

reduction of nitric oxide after being supported on titanium dioxide. The enhancement can be assumed to be due to an electron transfer from the support to the complex.⁸ Such a strong interaction of the catalytic material with the support may be a key factor for the development of a novel catalyst.⁹

In the present study, catalytic activities of some M-TPP's for the decomposition of hydrogen peroxide were investigated to describe the roles of their metal ions and ligands in this catalysis and to reveal the effects of metal oxide supports on their activities since a sequence of the redox potentials and their strong interaction with the support may attract interest. The interaction can be evaluated not only in the catalytic reaction but also in the chemistry of the complex which may play a role as a probe to reflect the interaction. The supports were selected from fairly large varieties to define what properties were essential for the interaction. Although Okura et al.¹⁰ already reported the activities of Cu-TPP and Co-TPP supported on silica gel for the same reaction, their activities were rather limited to decomposing only 4 mol of the peroxide per mole of the catalyst even at 70 °C. Sigel et al.¹¹ ex-

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