Solvent Effect on Adsorption of TCNQ onto Metal Oxides

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7,7,8,8-Tetracyanoquinodimethan(TCNQ) was adsorbed on the surfaces of alumina and titania from three basic solvents. The amount of TCNQ adsorbed decreased with an increase in the acid-base interaction between TCNQ and the basic solvent for both metal oxides. The TCNQ anion radicals were formed as a result of electron transfer from the metal oxide surfaces to adsorbed TCNQ. Further, the concentration of TCNQ anion radicals formed on the oxides after the TCNQ adsorption decreased also with an increase in the acid-base interaction between TCNQ and the basic solvent.

It is well known[1,2] that, when strong electron acceptors or donors are adsorbed on metal oxides, the corresponding radicals are formed as a result of electron transfer. By measuring the concentrations of the radicals formed, the electron-donor-acceptor properties of metal oxides have been evaluated.[3–5] Furthermore, Esumi *et al.*[6,7] attempted to determine the distribution of Lewis sites with different strengths of metal oxides; they found that the distribution of Lewis sites with different strengths on alumina was much wider than that on titania.

Recently, the acid-base theory has been applied to colloidal systems. Fowkes *et al.*[8] studied the interactions between polymers and inorganic solids by using the Drago correlation[9] of the heats of acid-base interaction and reported that strong polymer adsorption is observed only from solvents more neutral than the adsorbate polymer or the adsorbent surface sites. Thus, the acid-base interaction is a very important factor at interfaces.

In this work, electron-donor-acceptor interactions on metal oxides were examined by means of 7,7,8,8-tetracyanoquinodimethan(TCNQ) adsorption from various solvents.

Experimental

Materials. Two kinds of metal oxides, alumina and titania, were used. These metal oxides were prepared as follows: excess aqueous methanol (water: methanol,4:1 in weight) was vigorously added into a butanolic solution of each alkoxide. Stirring was continued for 5 h at about 90 °C. The precipitate was then separated by centrifuging, washed with methanol, finely ground, and then evacuated at 100 °C. The dried products were calcined for 2 h at 500 °C.

The TCNQ was obtained from Wako Chemicals and purified by repeated recrystallization. The solvents used in this study were dried by the use of molecular sieves.

Procedure. The metal oxide was placed in a L-type test tube, and a solution of TCNQ in an organic solvent was then poured in. After the tube had subsequently been shaken for 2 h at 25 °C, the dispersion thus obtained was used for the zeta potential measurement. The metal oxide was collected by centrifuging and dried at room temperature *in vacuo*. The dried sample was then used for the ESR measurement.

The ESR spectra were measured by means of a Japan Electrons Optics Laboratory ESR spectrometer (JES-FE3X) operating with an X-band microwave 100 kHz field modulation. The radical concentrations were estimated by comparing the area under the absorption curves for the sample and for standard solutions of 2,2-diphenyl-1-picrylhydrazyl in benzene.

The zeta potential of metal oxide after the adsorption was measured by means of an electrophoresis apparatus (Laser Zee 500, Pen Kem).

The amount of TCNQ adsorbed was determined from the difference in concentrations before and after the adsorption. The absorbance of TCNQ was measured by means of an UV spectrophotometer (Hitachi 220A). The maximum absorption wavelengths of the absorption band of TCNQ in the three basic solvents were 393 nm in acetonitrile, 395 nm in ethyl acetate, and 403 nm in 1,4-dioxane.

The specific surface areas of the samples were determined with a Sorptograph, Model ADS-1B (Shimadzu Seisakusho Co., Ltd.).

Results and Discussion

The amount of TCNQ in solutions adsorbed on the surfaces of alumina and titania was determined using three basic solvents: acetonitrile, a very weak base; ethyl acetate, a weak base, and 1,4-dioxane, a moderately weak base. The adsorption isotherms of TCNQ from these basic solvents are given in Fig. 1; it is apparent that their isotherms may be classified as the Langmuir type for both metal oxides. From the Langmuir plots of these isotherms, the saturated amounts of TCNQ were obtained; their values are listed in Table 1. It may be seen that the amount of TCNQ adsorbed decreases very appreciably with an increase in the basicity of the solvent for both metal oxides. To interpret this result in terms of the acid-base theory, the Drago equation[9] was employed:

$$-\Delta H^{ab} = C_A C_B + E_A E_B$$

where E and C are the Drago constants for the acidic compound(A) and the basic compound(B). Drago determined many E and C values for organic solvents from measurements of the heat of acid-base interaction made by his group and by others using calorimetric and spectroscopic methods.[9,10] These studies demonstrated that the Drago equation usually predicted ΔH^{ab} values within 3%. A very useful approach for relating the

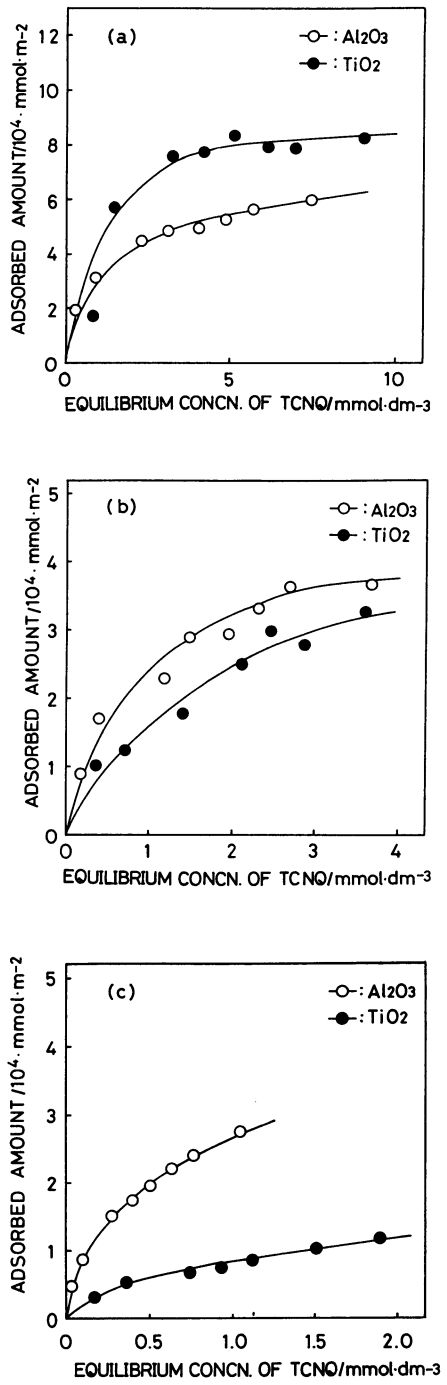

Fig. 1. Adsorption isotherms for TCNQ adsorbing from basic solvents onto metal oxides: (a) Acetonitrile, (b) Ethyl acetate, (c) 1,4-Dioxane.

Table 1. Data of TCNQ adsorption

Sample	Color of oxide surfaces		
	Acetonitrile	Ethyl acetate	1,4-Dioxane
Alumina	Blue green	Yellowish green	Yellowish white
Titania	Violet	Pale violet	—
	Amount adsorbed ($\times 10^4$ mmol/m^2)		
Alumina	6.2	4.4	2.9
Titania	7.7	5.7	1.7

Table 2. Acid-base parameters

Solvent	C_B	E_B	$-\Delta H^{ab}$ with TCNE[a] (kcal/mol)
Acetonitrile	1.34	0.889	3.51
Ethyl acetate	1.74	0.975	4.27
1,4-Dioxane	2.38	1.09	5.23

a) TCNE (C_A=1.51, E_A=1.68). (1 cal$_b$=4.184 J).

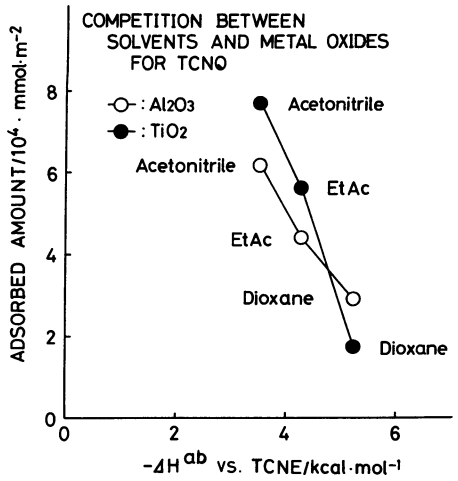

Fig. 2. Saturated amount of TCNQ adsorbing onto metal oxides *vs.* acid-base interaction enthalpy.

interfacial interactions quantitatively has been the Drago equation of enthalpy changes in acid-base complexation. When the Drago equation is applied to this work, the basic compounds correspond to the solvents, such as acetonitrile, ethyl acetate, and 1,4-dioxane, and the acidic compound, to TCNQ. The E and C values for three basic solvents are available,[9] but not for TCNQ. Therefore, in this study, the E and C values[9] of tetracyanoethylene(TCNE), which is similar to TCNQ, are employed insteads of these of TCNQ. These acid-base parameters are listed in Table 2.

Figure 2 shows the amount of TCNQ saturated on alumina and titania as a function of ΔH^{ab}; the amount of TCNQ saturated decreases with an increase in the acid-base interaction (ΔH^{ab}) between the basic solvent and TCNQ.

When TCNQ was adsorbed from the solutions on alumina and titania, the surfaces of the metal oxides developed a remarkable coloration. The color was dependent on the kind of solvent; the results are shown in Table 1. It has previously been reported[4,5] that the adsorption of electron acceptors on metal oxides produces a surface coloration and gives unresolved ESR spectra. The samples colored by the TCNQ adsorption gave unresolved ESR spectra with a g-value of 2.003. These spectra have been identified[4,5] as being those of TCNQ anion radicals.

The above results support the idea that the TCNQ anion radicals are formed as a result of electron transfer from the metal oxide surface to the TCNQ adsorbed.

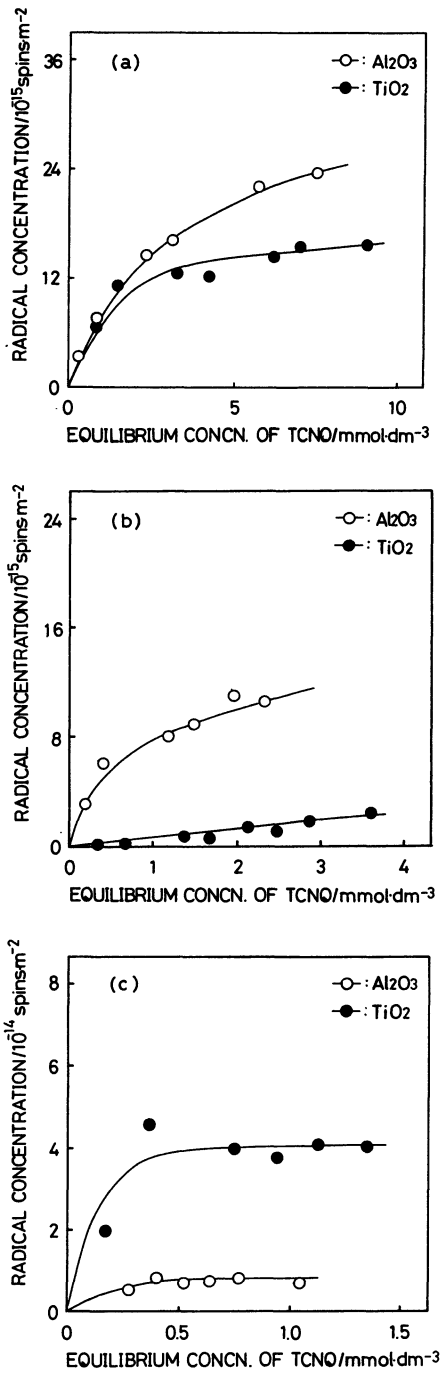

Fig. 3. TCNQ radical concentration onto metal oxides *vs.* equilibrium concentration of TCNQ into basic solvent:
(a) Acetonitrile, (b) Ethyl acetate; (c) 1,4-Dioxane.

The TCNQ-radical concentrations formed on the surface of metal oxides are plotted against the equilibrium concentration of TCNQ in Fig. 3. The TCNQ-radical concentration decreased with an increase in the basicity of the basic solvents. Furthermore, in order to compare the TCNQ-radical concentration on the surface of metal oxide as a function of ΔH^{ab}, the TCNQ-radical concentration corresponding to the half-value of the saturated amount of TCNQ was obtained; the results are illustrated in Fig. 4. The TCNQ-radical concentrations of alumina decreased gradually in the weak acid-base interaction and steeply in the moderate acid-base interaction. On the other hand, in the case of titania, they decreased steeply in the weak acid-base interaction and gradually in the moderate acid-base interaction. The TCNQ-radical concentrations on alumina were larger than those on titania for two of the three basic solvents, but not 1,4-dioxane, indicating that the concentration of electron-donor sites having relatively weak strengths on alumina is larger than that on titania. Furthermore, in the case of 1,4-dioxane, the TCNQ-radical concentration on titania was larger than that on alumina. This result suggests that the concentration of electron-donor sites having relatively strong strengths on titania is larger than that on alumina. These results agreed fairly well with similar measurements previously reported by us.[6]

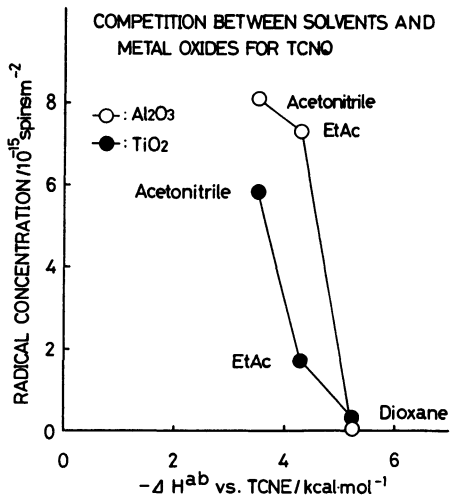

Fig. 4. TCNQ radical concentration corresponding to half-value of saturated amount of TCNQ onto metal oxides *vs.* acid-base interaction enthalpy.

The zeta potentials of metal oxides before and after TCNQ adsorption were also measured. The zeta potential of alumina and titania in the basic solvent alone decreased with an increase in the basicity of the solvents. In this case, the acid sites of alumina and titania interacted with the basic solvent. After the TCNQ adsorption, the zeta potentials of alumina and titania decreased with an increase in the concentration of TCNQ for the three basic solvents. Further, the magnitude of the decrease in the zeta potential of both metal oxides was dependent on the acid-base interaction between TCNQ and the basic solvent; the order of magnitude of the decrease was acetonitrile>ethyl acetate>1,4-dioxane. Labib *et al.*[11] measured the zeta-potential for several solids in a series of organic liquids chosen to cover a wide range of electron-donor properties; they reported that, for most of the solids, the zeta potential changes its sign for

some value of the liquid donicity because of the acid-base interaction between solids and organic liquids.

The electron-donor sites of metal oxides for the electron transfer are considered as follows: two possible electron-donor sources exist on the alumina surface. One of these has electrons trapped at intrinsic defects, while the other has hydroxide ions. Free electrons derived from the intrinsic defects on the surface of the alumina would normally be expected to participate in the electron-transfer adsorption. However, since it has been reported[1] that the electron-donor defect site on the surface of alumina was created at an activation temperature above 500 °C, it may be suggested that the electron-donor defect site does not play an important role in this study. The other site is the surface hydroxide ions which have been confirmed to exist on the surface of alumina. The ionization potentials of the hydroxide ions are comparatively small[12] (≈2.6 eV in the gas phase). It seems likely that the surface hydroxide ions on alumina as an electron-donor site can be attributed to the electron-transfer adsorption. Indeed, Fomin *et al.*[13] have reported that electron transfer from the hydroxide ion can occur in certain solvent systems, provided a suitable acceptor molecule is present. The electron-donor sites of titania have been associated with surface hydroxide ions and Ti^{3+} ions.[14] The latter site has been reported[14] to be formed at high temperatures *in vacuo*. In the present study, the hydroxide ions on the titania surface have been found to operate mainly as an electron-donor site.

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