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# Adsorption of Tetrachloro-*p*-benzoquinone from Various Solvents on Metal Oxides

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Adsorption of tetrachloro-*p*-benzoquinone(chloranil) from basic and acidic solvents on metal oxides, such as alumina and titania was carried out to understand the acid-base interaction at the interface. The amount of chloranil adsorbed decreases with an increase of acid-base interaction between the basic solvent and chloranil and also decreases with an increase of acid-base interaction between the acidic solvent and electron donor sites of the metal oxides for both metal oxides. Furthermore, the change in concentration of chloranil radicals formed on their metal oxides by the adsorption is correlated with the acid-base interaction at the interfaces.

Recently, the acid-base theory has been applied to colloidal systems. Fowkes et al.[1,2] have studied the interactions between inorganic solids and basic adsorbates by using the Drago correlation of the heats of acid-base interaction and have determined the Drago parameters for several solids, such as silica, rutile, and magnetite. Esumi et al.[3,4] have examined the adsorption of a strong electron acceptor such as tetracyanoquinodimethane from various solvents on metal oxides and they have demonstrated that the acid-base interaction is an important factor for the adsorption.

In this work, further to confirm the importance of acid-base interaction at solid-liquid interface, the adsorption of chloranil similar to TCNQ on metal oxides was performed.

## Experimental

**Materials.** Alumina and titania were used as metal oxides. These metal oxides were prepared as follows: excess aqueous methanol (water:methanol=4:1 in weight) was vigorously added to a 1-butanol solution of each alkoxide. Stirring was continued for 5 h at about 90°C. The precipitate obtained was separated by centrifuging, washed with methanol, finely ground, and then evacuated at 100°C. Finally, the dried products were calcined for 2 h at 500°C, and used as samples.

Chloranil was obtained from Tokyo Kasei Ltd., and purified by repeated recrystallization from toluene. The solvents used in this study were dried by the use of molecular sieves.

**Procedure.** The metal oxide was placed in an L-type test tube and a solution of chloranil in an organic solvent was then poured in. After the tube had subsequently been shaken for 2 h at 25°C, the metal oxide was collected by centrifuging and dried at room temperature in vacuo. The dried sample was then used for an 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 amount of chloranil adsorbed was determined from the difference in concentrations before and after the adsorption. The absorbance of chloranil was measured by means of an UV spectrophotometer (Hitachi 220A). The maximum absorption wavelengths of the absorption band of chloranil in three basic solvents were 367 nm in acetonitrile, 365 nm in ethyl acetate, and 286 nm in 1,4-dioxane while the maxima of the two acidic solvents were 372 nm in dichloromethane and 375 nm in chloroform.

The specific surface areas of the samples were determined with a Sorptograph, Model ADS-1B(Shimadzu Seisakusho Co., Ltd.): alumina, 227.4 $m^2 g^{-1}$ and titania, 54.7 $m^2 g^{-1}$.

## Results and Discussion

The amount of chloranil in solutions adsorbed on the surfaces of alumina and titania was determined from three basic and two acidic solvents. The adsorption isotherms of chloranil are shown in Fig. 1; it is seen that their isotherms are of the Langmuir type for both metal oxides. Table 1 gives the saturated amounts of chloranil adsorbing on the metal oxides estimated from the Langmuir plots. In order to interpret this adsorption result in terms of the acid-base theory, the Drago equation[5] is 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). It has been demonstrated[5] for the above equation that $\Delta H^{ab}$ values can be predicted within 3%. Furthermore, a useful approach for relating the interfacial inter-

Table 1. Data of Chloranil Adsorption

| Sample | Saturated amount($\times 10^4$ mmol $m^{-2}$) | | |
|---|---|---|---|
| | Acetonitrile | Ethyl acetate | 1,4-Dioxane |
| Alumina | 3.82 | 1.49 | 1.05 |
| Titania | 5.33 | 0.32 | 0 |
| | Dichloromethane | | Chloroform |
| Alumina | 3.59 | | 2.85 |
| Titania | 1.97 | | 1.80 |

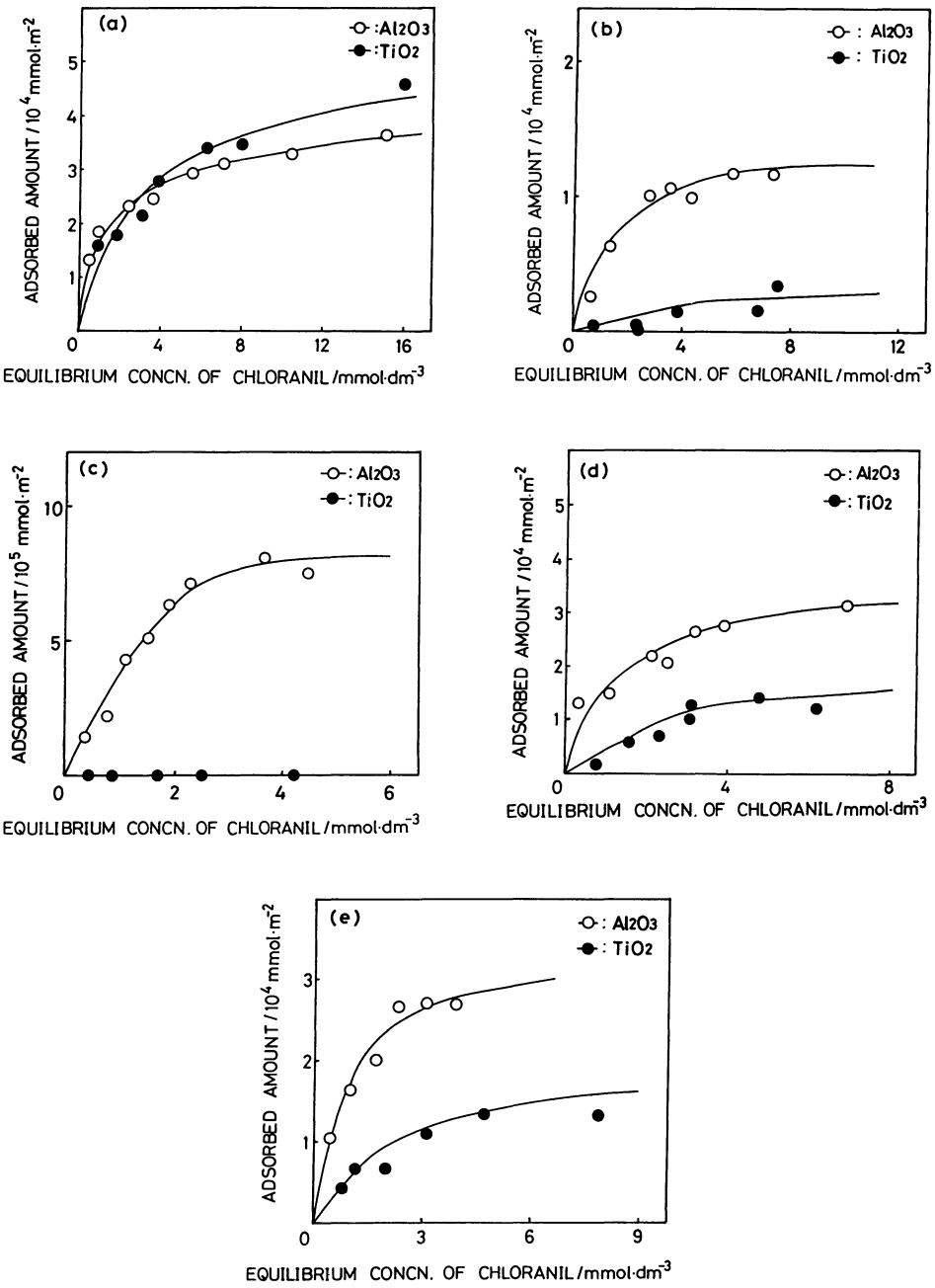


Fig. 1. Adsorption isotherms for Chloranil adsorbing on metal oxides from three basic and two acidic solvents. (a): Acetonitrile, (b): Ethyl acetate, (c): 1,4-Dioxane, (d): Dichloromethane, (e): Chloroform.

actions quantitatively has been the Drago equation of enthalpy changes in acid-base complexation. To apply the Drago equation to this work, the $E$ and $C$ values for the solvents and chloranil should be known, the former is available, but the latter is not reported in the literature.[5] However, from the enthalpy values[6,7] of chloranil and some electron donor solvents, the $E$ and $C$ values of chloranil can be calculated using the Drago equation. The Drago constants and their enthalpy values are listed in Table 2. Figure 2 shows that the saturated amounts of chloranil adsorbed on both metal oxides decrease with an increase of acid-base enthalpy between chloranil and their basic solvents. The behavior of the saturated amounts of chloranil adsorbed in the system of the acidic solvents is similar to that for the basic solvent systems; the saturated amounts of chloranil adsorbed decrease also with an increase of acid-base enthalpy between the acidic solvents and the electron donor sites of metal oxides. In addition, the adsorption results show that the saturated amount of chloranil on alumina is considerably larger than that on titania for both basic

Table 2. Acid-Base Parameters

| Solvent | $C_B$ | $E_B$ | $C_A$ | $E_A$ | $\Delta H^{ab}$ with *Chloranil or Acetone (Kjoule/mol) |
|---|---|---|---|---|---|
| Acetonitrile | 2.74 | 1.812 | — | — | 11.19 |
| Ethyl acetate | 3.56 | 1.994 | — | — | 13.61 |
| 1,4-Dioxane | 4.87 | 2.23 | — | — | 17.35 |
| Dichloromethane | — | — | 0.02 | 3.40 | 6.96 |
| Chloroform | — | — | 0.307 | 6.77 | 15.13 |

*Chloranil($C_A$=2.39, $E_A$=2.56), Acetone($C_B$=4.77, $E_B$=2.019).

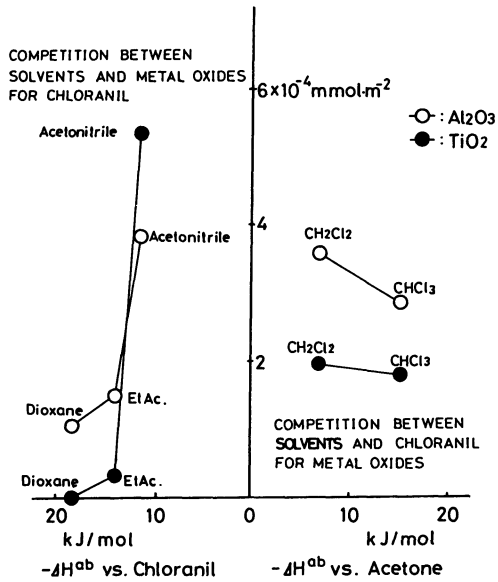


Fig. 2. The Change in the saturated amount of Chloranil on metal oxides as a function of the basicity or acidity of the solvent.

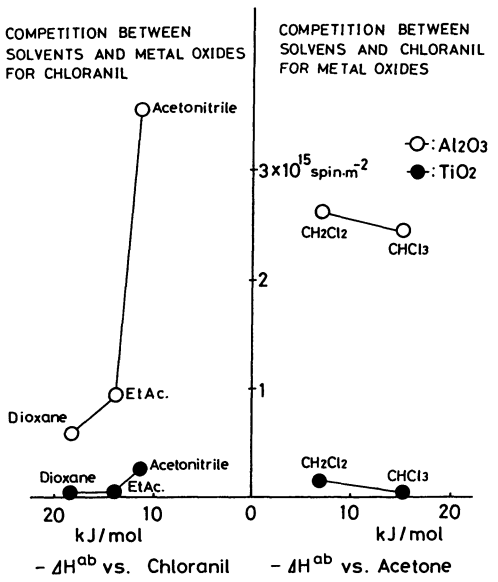


Fig. 3. The Change in the Chloranil radical concentration on metal oxides as a function of the basicity or acidity of the solvent.

and acidic solvent systems.

When chloranil is adsorbed on the metal oxides from the basic and acidic solvents, the surfaces develop characteristic colors; the colors for both alumina and titania were violet, whereas the color strength was dependent on the kind of solvent. It has been reported[8–10] that the colored oxide samples obtained by adsorption of electron acceptors exhibit ESR signals indicating the presence of the free anion radicals of their acceptors. In the present study, the colored samples obtained by the adsorption of chloranil gave an unresolved ESR spectra having a $g$-value of 2.011.[11] To compare the concentration of the chloranil anion radicals formed on the surfaces as a function of acid-base enthalpy, their concentrations obtained at corresponding to the half-value of the saturated amounts, are given in Fig. 3. It is apparent that the concentrations of chloranil anion radicals decrease with an increase of the acid-base interaction between basic solvents and chloranil or between acidic solvents and electron donor sites on their oxides. Furthermore, it is noteworthy that the concentrations of these radicals formed on alumina are higher than those on titania in all the solvent systems, implying that the electron donor sites on alumina provide a higher electron donicity than those on titania, for which the result is in good agreement with previous data.[3]

Thus, the results obtained from the adsorption of chloranil show a similar trend to those from the adsorption of TCNQ for the acid-base interaction.

For the electron donor sites for both metal oxides, surface hydroxide ions are responsible, because they exist at a relatively low activation temperature. Further, Flockhart et al.[12,13] have confirmed that such hydroxide ions are formed below 500°C which are correlated with electron donicity. Also, Che et al.[14] have reported that electron donor sites for titania at relatively low temperature (<500 °C) are assigned to surface hydroxide ions.

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