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ADSORPTION OF ACETIC AND PROPIONIC ACIDS FROM CARBON TETRACHLORIDE SOLUTIONS BY SOLID METAL COMPLEXES

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ABSTRACT

The adsorption of acetic and propionic acids from carbon tetrachloride solutions by solid metal complexes has been studied. For all the complexes studied, adsorption of acetic acid occurs to a greater extent than does that of propionic acid, the ratio being from 1.7 to 16 depending on the metal complex. In general, the greater the total number of ions in the complex, the higher the ratio of acetic to propionic acid adsorbed. The amount of butanoic acid adsorbed was found to be negligible in all cases. Adsorption of acetic acid by $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ was found to obey the Langmuir isotherm.

INTRODUCTION

Classical adsorption studies have long been a part of physical chemistry. The theory of adsorption has been treated extensively (Young and Crowell, 1962; Adamson, 1960, and Somorjai, 1971), and will not be reviewed here. Adsorption of gases by solids, including metals, is important in heterogeneous catalytic processes (Bond, 1962; Thomas and Thomas, 1967). Also adsorption processes are of importance in chromatographic techniques (Karger, Snyder, and Horvath, 1973).

In view of the considerable practical application of adsorption processes, it is not surprising that a large body of literature exists on the subject. Adsorbents like metals, alumina, quartz, magnesia, titanium dioxide, silica gel, charcoal, cellulose, and graphite have been extensively studied, as have been many simple inorganic salts. It is somewhat surprising that there appears to have been no utilization of solid transition metal complexes as adsorbents for organic compounds from solutions. Here we describe the results of a study of that type.

EXPERIMENTAL

Solutions were prepared using reagent grade acetic, propanoic, and butanoic acids in carbon tetrachloride. Potassium hexacyanoferrate(II), potassium hexacyanoferrate(III), hexaaquocobalt(II) chloride, and sodium trisoxalatoferrate(III) were reagent grade commercial materials. Other solid complexes used were prepared by standard procedures. Prior to use, each solid was screened through a standard sieve to insure that the particle size was uniformly below 106 microns (0.0041 in.).

The 1.00 gram samples of the solid complexes were allowed to stand in contact with 100 ml of the carboxylic acid solutions for 24 hrs. Solutions were maintained at 25 ^{0}C and were agitated to assure equilibrium. After standing for the desired time, the solid complex was removed by filtration and the concentration of the acid remaining in the solution was determined by heterogeneous phase titration of three 25 ml aliquots of each solution using standard base. Mixing time and speed were uniform for all titrated samples. The amount of acid adsorbed by each solid complex was thus determined.

RESULTS

Early in this work it became apparent that the amount of acetic acid adsorbed per gram of complex was dependent on the concentration of the acetic acid solution. To study this behavior, adsorption by four of the complexes. $K_4[Fe(CN)_6]\cdot H_2O$, $K_3[Fe(CN)_6]$, $Na_3[Fe(C_2O_4)_3]\cdot 2H_2O$, and $[Co(NH_3)_6](NO_3)_3$, was studied as a function of the concentration of the acid solution. Acid solutions from 0.01 M to 0.1 M were used. The results of these studies are shown in Table 1. This table also shows the adsorption data for some other complexes which were studied at only one initial acid concentration. Two of the compounds, $Na_3[Co(NO_2)_6]$ and $[Co(NH_3)_3(NO_2)_3]$, were dried at 110^0 for one hour and then used directly. The amount of acetic acid adsorbed was found to be within experimental error of that adsorbed by the original complex.

Table 2 shows the adsorption data for propionic

Table 1. Adsorption of acetic acid from CCl_4 at 25 °C.

Adsorbent	Molar Acid Concentration Initial	Molar Acid Concentration Equilibrium	10^5 x Moles Adsorbed per Gram of Complex
$K_4[Fe(CN)_6]\cdot 3H_2O$	0.0101	0.00920	9.0
	0.0496	0.0483	13.0
	0.0985	0.0975	9.9
$K_3[Fe(CN)_6]$	0.0101	0.00943	6.7
	0.0496	0.0488	7.9
	0.0985	0.0980	5.5
$Na_3[Fe(C_2O_4)_3]\cdot 2H_2O$	0.00941	0.00935	0.60
	0.0487	0.0469	18.0
	0.0975	0.0973	2.4
$[Co(NH_3)_6](NO_3)_3$	0.0114	0.0112	2.0
	0.0445	0.0439	5.2
	0.0895	0.0893	2.1
$[Co(H_2O)_6]Cl_2$	0.0489	0.0483	6.1
$K_4[Ni(NO_2)_6]\cdot H_2O$	0.0489	0.0479	11.0
$Na_3[Co(NO_2)_6]$	0.0445	0.0427	18.0
	0.0489	0.0475	14.0
$[Co(NH_3)_3(NO_2)_3]$	0.0455	0.0438	7.2
	0.0489	0.0481	7.9

Table 2. Adsorption of propionic acid from CCl_4 at 25 °C.

Adsorbent	Equilibrium Concentration of Acid, M	10^5 x Moles of Acid per Gram of Complex	Adsorbed Acid Ratio Acetic Propionic
$K_3[Fe(CN)_6]$	0.04642	3.8	2.1
$K_4[Fe(CN)_6]\cdot 3H_2O$	0.04672	0.80	16.7
$Na_3[Co(NO_2)_6]$	0.04656	2.4	6.7
$[Co(NH_3)_3(NO_2)_3]$	0.04637	4.3	1.7
$Na_3[Fe(C_2O_4)_3]\cdot 2H_2O$	0.04647	3.3	5.5

*Initial concentration 0.04681 M in all cases.

acid solutions with the solid metal complexes. Although attempts to study the adsorption of butanoic acid were made, the adsorption occured to such a slight extent that reproducible data could not be obtained.

In all the cases where the effect of acid concentration was studied, within the range of acetic acid concentration from 0.01 to 0.1 M, the amount of acid adsorbed was greatest at the concentration of 0.05 M. These results may be explained by the fact that the dimerization of acetic acid,

$$2\ CH_3COOH_{(solv)} \rightleftharpoons [CH_3COOH]_{2(solv)}$$

is concentration dependent and that it is the monomer which is adsorbed on the solid complexes. It is plausible to expect the monomer to be the major species adsorbed owing to the polarity of the free carboxyl group. At a concentration of 0.01 M, there is simply too little acid present and at 0.1 M, dimerization ties up most of the acid so that the effective monomer concentration is not increased. Of course, the effects of solvation on the monomer-dimer equilibrium are sizeable as well (Joesten and Schaad, 1974; Fletcher, 1971). For example, alcohols undergo much greater self association in n-decane than they do in CCl_4 because of the greater tendency of CCl_4 to solvate polar OH groups and prevent association (Fletcher and Heller, 1967). For the same reason, benzoic acid has a smaller heat of dimerization in benzene than it does in cyclohexane.

A second observation is that in every case where a comparison of the adsorption of acetic and propionic acids by the same solid complex can be made, a considerably greater amount of acetic acid is adsorbed per gram of complex. In all cases where adsorption of butanoic acid was attempted, the amount adsorbed was so small that for all practical purposes it appeared that none was adsorbed. The complexes used were $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]$, $Na_3[Co(NO_2)_6]$, and $[Co(NH_3)_3(NO_2)_3]$. From these obervations, it is apparent that with regard to the adsorption on solid metal complexes the behavior of carboxylic acids is acetic $>$ propionic $>$ butanoic ≈ 0. However, all these acids have about the same tendency to dimerize in the gas phase so that different extent of dimerization does not seem to be a factor (Joesten and Schaad, 1974).

In the case of $K_4[Fe(CN)_6]$ as the adsorbent, about 16 times as much acetic acid is adsorbed per gram of complex as is propionic acid. In the case of $[Co(NH_3)_3(NO_2)_3]$, only about 1.7 times as much acetic acid is adsorbed. Part of this difference may be due to the fact that the two acids were used at slightly different initial concentrations. However, if the data for $K_3[Fe(CN)_6]$ are ignored for the moment, it is apparent that the ratio of the amount of acetic acid adsorbed to that of propionic acid per gram of complex increases approximately as the square of the number of ionic charges present. Thus, the nonionic $[Co(NH_3)_3(NO_2)_3]$ does not discriminate acetic and propionic acids to nearly as great an extent as does the compound $K_4[Fe(CN)_6]$ which contains a total of eight ionic charges. This pattern would lead one to expect that the compounds $Na_3[Fe(C_2O_4)_3]$, $Na_3[Co(NO_2)_6]$, and $K_3[Fe(CN)_6]$ should yield an acetic/propionic ratio which is intermediate between the values obtained for $K_4[Fe(CN)_6]$ and $[Co(NH_3)_3(NO_2)_3]$. This is, in fact, observed for these three complexes. However, the acetic/propionic adsorption ratio for $K_3[Fe(CN)_6]$ is considerably lower than that for $Na_3[Co(NO_2)_6]$ and $Na_3[Fe(C_2O_4)_3]$. We have no explanation for this observation; however, it does not alter the conclusion that solid complexes having larger numbers of ions exhibit a greater preference for adsorbing acetic acid than propionic acid. The effect of the water of hydration in some of these complexes appears slight. Comparison of the adsorption data for $K_4[Fe(CN)_6]\cdot 3H_2O$ and $Na_3[Fe(C_2O_4)_3]\cdot 2H_2O$ shows a great difference in adsorption even though both are hydrates. There are six molecules of water in $[Co(H_2O)_6]Cl_2$, but the complex by no means adsorbs the most acetic acid.

The Langmuir isotherm can be written as (Langmuir, 1916, 1918)

$$\frac{N}{N_M} = \frac{kc}{1 + kc}$$

Where N is the number of moles adsorbed per gram of solid at an equilibrium solute concentration, c; N_M is the number of moles required to form a monolayer; and k is a constant. Rearranging the equation, one obtains

$$\frac{c}{N} = \frac{c}{N_M} + \frac{1}{kN_M}$$

This equation indicates that the rate of desorption and adsorption are equal at equilibrium, and it applies to cases where chemisorption of a monolayer is the dominant process. If the Langmuir isotherm adequately describes the adsorption process in a certain system, a plot of c/N versus c should give a straight line.

Figure 1 shows a Langmuir isotherm plot for the adsorption of acetic acid by $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$. The fit of the data to these linear plots is reasonable, the correlation coefficients being 0.986 and 0.985, respectively. Data for $Na_3[Fe(C_2O_4)_3]$ and $[Co(NH_3)_6](NO_3)_3$ do not provide as nearly linear relationships. Although the fit is not perfect, it appears that $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ adsorbing acetic acid are adequately described by the Langmuir isotherm. Using slopes of the lines determined by means of a least squares routine, the values of N_M obtained for $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ are 9.9×10^{-5} and 5.3×10^{-5} mole/gram, respectively. Thus, at equilibrium the molar ratios of complex to amount of acetic acid adsorbed are 28 and 59 for $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$, respectively. These values indicate that $K_4[Fe(CN)_6]$ is a better adsorbent than $K_3[Fe(CN)_6]$ for acetic acid.

We are currently investigating the adsorption of other organic solutes on solid metal complexes. In these studies, the relationship between number and type of ions present and the degree of adsorption is being investigated. We are also attempting to determine heats of adsorption for some of these systems.

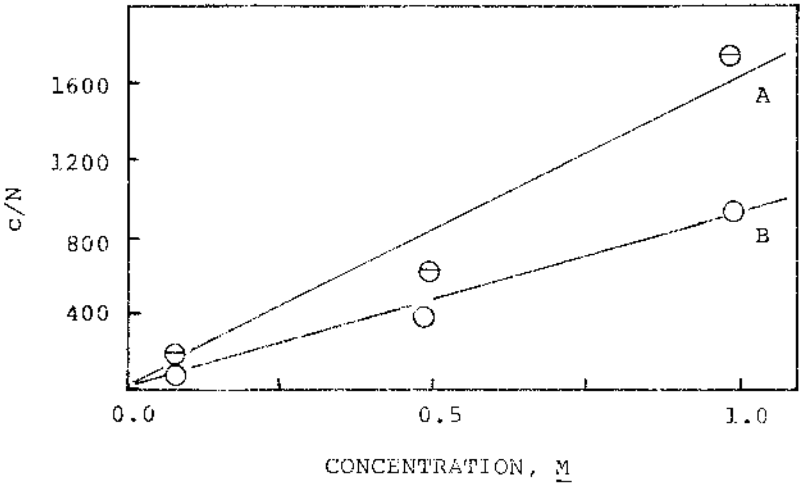

Figure 1. Langmuir plot for adsorption of acetic acid by $K_3[Fe(CN)_6]$ (A) and $K_4[Fe(CN)_6]$ (B).

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