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Adsorption of Oxalic, Malonic, and Succinic Acids on Activated Carbon

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Adsorption studies of a homogeneous series of dicarboxylic acids were performed at 5 and 40 °C, with oxalic, malonic, and succinic acids being adsorbed from dilute aqueous solutions onto activated carbon. Experimental data were compared with the calculated equilibrium uptakes as predicted by three different models: Freundlich isotherm, Langmuir isotherm, and the potential theory. A single generalized characteristic curve for these dicarboxylic acids was obtained in accordance with the potential theory. The average errors between the values calculated by the potential theory and the experimental data ranged from 1.80% to 5.44%. In this study the potential theory provided a better fit to the experimental data than did either the Freundlich or Langmuir isotherm equations.

Introduction

Organic acids are frequently found in industrial waste waters, particularly byproduct wastes produced from synthetic fuel processes. Although the adsorption of these compounds has received considerable attention, the adsorption data of dicarboxylic acids from dilute aqueous solutions (less than 1% by weight) are not available in the literature.

Kipling (*1*) gives an excellent review of adsorption at the liquid–solid interface for research up to 1965, including references on studies of dicarboxylic acids. Linner and Gortner (*2*) studied the adsorption of 31 organic acids onto decolorizing carbon at room temperature. The equilibrium concentrations generally ranged between 0.01 and 0.25 M and were determined by titrimetric methods. They found that at below 0.25 M equilibrium concentration the adsorption of dicarboxylic acids increased with increasing number of carbon atoms. Ermolenko and Papkovich (*3*) studied the characteristics of adsorption of dibasic organic acids on silica gel. They found that the adsorption isotherms of dibasic organic acids on silica gel exhibited a periodicity. It is hypothesized that this periodicity is associated with characteristics of association of the acid molecules and is independent of changes in the structure of silica gel or changes in the nature of the polar medium. Skorokhod and Sembur (*4*) studied the adsorption of dibasic aliphatic acids on a strongly basic polystyrene anion exchange resin. They found that both molecular adsorption and ion exchange are involved in the adsorption process with molecular adsorption being the determining mechanism.

Granular and powdered activated carbon have been widely used to remove organic contaminants from water. Singh and Shukla (*5*) studied the adsorption of dicarboxylic acids on 100- and 200-mesh charcoal. Wang, Chow, and Ku (*6*) studied the adsorption of single and mixed dicarboxylic acids (C_2–C_6) by sugar charcoal, which was activated at either 400 or 800 °C. They found that the adsorption of the dicarboxylic acids on 400 °C charcoal agreed with Traube's rule; that is, adsorption increases with increasing molecular weight of the adsorbate. The adsorption priority on the 800 °C charcoal depended on the concentration. When the concentration was greater than 0.02 M, the adsorption order was opposite to Traube's rule. The quantity adsorbed from solutions of mixed acids was always lower than that from solutions of single acids. This study addresses the adsorption of oxalic, malonic, and succinic acids at 278 and 313 K at low concentrations on activated carbon.

Experimental Section

Granular DARCO activated carbon was selected as the adsorbent for this study. It had a total surface area of 595 m^2/g (as found by standard nitrogen adsorption), a total pore volume of 1.00 mL/g, and a mean pore radius of 29 × 10^{-8} cm. Prior to use, the activated carbon was screened to 200 × 325 U.S. mesh, washed with distilled water, and dried in an oven at a temperature of 175 °C for 9 h. It was then placed in a closed container until it was to be weighed for the adsorption study. Oxalic, malonic, and succinic acids were chosen as the adsorbates. All the acids were obtained from Rasher & Betzold, Inc., Chicago, and had purities greater than 99.8%.

Adsorption isotherm data were determined by adding 100 mL of each acid solution with initial concentrations ranging from 200 to 10 000 mg/L to 0.5 g of activated carbon (weighed to 0.0001 g) in separate 250-mL Erlenmeyer flasks. The solution was then placed in a shaker bath for 1 h to reach equilibrium. Although the equilibrium time was found to be approximately 15 min from a batch kinetic study, an equilibration time of 1 h was used for all adsorption runs. After equilibration, the mixture was filtered twice with Whatman No. 40 and No. 42 filter paper, to ensure that all activated carbon particles were removed from the liquid. Filtrate samples ranging from 20 to 2000 μL were collected and their concentrations were measured by using a Beckman Instrument Co. liquid scintillation counter (LSC), Model LS-9000, and an Oceanography International Corp. total organic carbon analyzer (TOC). After several trial runs, it was found that when the LSC was used to measure equilibrium concentrations in the low concentration ranges, the radioactivity in the solution was not high enough to give the LSC countings within the desired precision. Therefore, the TOC analyzer was also used to measure solute concentrations.

In the radioanalytical approach a small mass (less than 1 μL) of high specific activity radioisotope of each solute, labeled by ^{14}C, was added to each of the stock solutions. This imparted a uniform and high solute specific activity to each of the solutions with negligible change to the final solute concentration. This provides an accurate method for determining solute concentrations at both high and low levels. After preparing the radioactive solutions, samples of 5 mL were taken before and after equilibration with the activated carbon. The radioactivity was counted after mixing 1 mL of each sample with 12 mL of Dimulume-30 (Packard Instrument Co.). Samples were placed in the liquid scintillation counter and dark adapted for at least 30 min prior to counting. The counting efficiency was determined for each sample and was used to compute the absolute activity as disintegrations per minute (DPM). Final DPM values were obtained by subtracting the background count rate.

A total carbon analyzer was used to determine the total organic carbon (TOC) content of the solution by employing the ampule technique. The ampules were filled in the following order: 0.2 g of potassium persulfate ($K_2S_2O_8$), 20–2000 μL of

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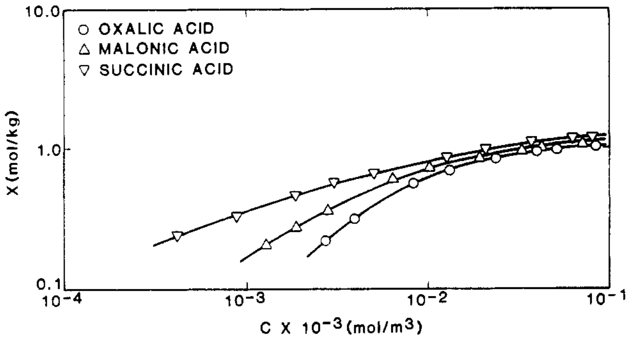

Figure 1. Adsorption isotherms of oxalic, malonic, and succinic acids at 5 °C.

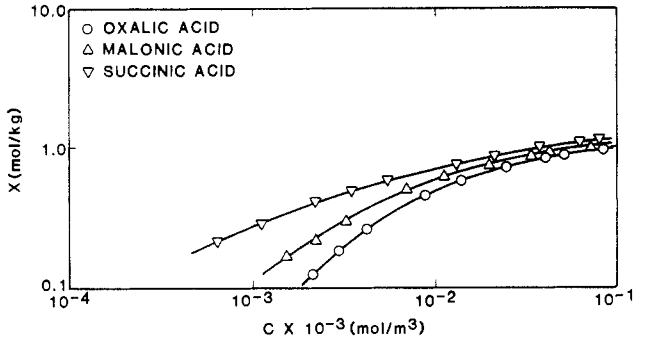

Figure 2. Adsorption isotherms of oxalic, malonic, and succinic acids at 40 °C.

acid solution sample, double distilled water to make the solution in the ampule to be 10 mL, and 0.25 mL of 6% phosphoric acid solution (H_3PO_4). Each ampule was purged with oxygen to remove carbonate ions and then sealed. All organics were then oxidized in the sample ampules to carbon dioxide by heating the ampules in a heated pressure vessel at 175 ± 5 °C for 8 h. After oxidizing the sample, each sealed ampule was placed in the ampule analyzing unit where it was opened; the amount of carbon was then measured with an infrared analyzer. The TOC present in the sample solution was found by comparing the measured results with a calibration curve that was prepared from a standard solution.

To assure the precision of the experimental methods, two identical runs were made and the final concentrations were measured with both the total carbon analyzer and the liquid scintillation counter. The resulting differences calculated from the data by the two methods were quite small.

Results and Discussion

The equilibrium data for the adsorption of oxalic, malonic, and succinic acids onto 200 × 325 mesh activated carbon at both 5 and 40 °C are presented in Table I. As shown in Figures 1 and 2, the adsorption of the lower dicarboxylic acids increases with increasing chain length. This agrees with the findings of Linner and Gortner (*2*) who noted that at low concentrations (lower than 0.025 M) the adsorption of dicarboxylic acids obeys Traube's rule.

A direct comparison of this work was made with the study of Belotserkovskii et al. (*7*), who studied the adsorption of several dicarboxylic acids onto activated carbon at moderately high concentrations. Belotserkovskii's data, obtained for adsorption by KAD activated carbon at 20 °C, was compared to the data obtained in this study, and the results are given in Figure 3. As shown by the figure, the data of Belotserkovskii et al. falls between the equilibrium data at 5 and 40 °C for this study.

The equilibrium data were compared to the Freundlich, Langmuir, and Polanyi potential models. The Freundlich (*8*) expression is empirical but has found considerable use in industrial practice, particularly for adsorption from liquids. The Freundlich equation has the general form

Table I. Adsorption Isotherm Data for Oxalic, Malonic, and Succinic Acids

	5 °C		40 °C	
acid	*C*, mol/m³	*q*, mol/kg	*C*, mol/m³	*q*, mol/kg
oxalic	2.709	0.224	2.109	0.127
	3.886	0.316	2.909	0.186
	8.105	0.570	4.163	0.264
	12.88	0.717	8.716	0.454
	23.18	0.870	13.66	0.570
	39.30	0.970	23.87	0.738
	50.24	1.002	40.00	0.844
	83.25	1.059	50.79	0.897
			83.70	0.973
malonic	1.288	0.212	1.518	0.168
	1.884	0.281	2.191	0.223
	2.835	0.374	3.219	0.301
	6.342	0.621	6.919	0.511
	10.38	0.767	11.05	0.639
	19.22	0.913	19.89	0.785
	33.15	1.004	33.63	0.913
	42.52	1.050	43.00	0.959
	70.93	1.130	71.40	1.041
succinic	0.419	0.242	0.635	0.212
	0.889	0.330	1.101	0.288
	1.872	0.473	2.176	0.412
	3.015	0.583	3.455	0.495
	5.039	0.686	5.505	0.593
	12.53	0.881	13.04	0.779
	20.33	1.016	21.00	0.881
	36.63	1.143	37.26	1.016
	61.74	1.206	62.25	1.101
	78.55	1.228	79.85	1.118

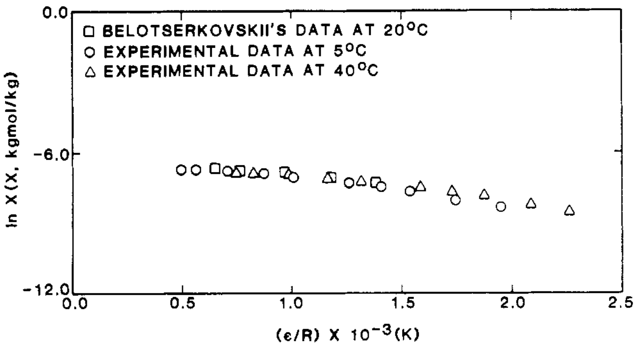

Figure 3. Comparison of the experimental adsorption data with literature data available for succinic acid.

$$q = X/m = KC^{1/n} \quad (1)$$

where q is the amount of adsorbate per unit weight of adsorbent at equilibrium and C is the equilibrium solution concentration. The constants K and $1/n$ were obtained by using a nonlinear least-squares fitting subroutine MARQ (*9*). Roughly speaking, the value K gives a measure of the adsorbent capacity and $1/n$ is a measure of the intensity of adsorption. The shape of the isotherm is such that n has values greater than unity. The parameters obtained for the Freundlich model using the nonlinear curve fit to the data are presented in Table II.

The Langmuir (*10–12*) equation, which can be derived by using statistical thermodynamics or kinetic considerations, has the form

$$q = \frac{K_1 K_2 C}{1 + K_1 C} \quad (2)$$

where q and C were defined previously. The term K_1 is a characteristic constant often defined as the "capillarity" of the substance. The term K_2 is a characteristic constant defined

Table II. Parameters of the Freundlich Equation[a]
$q = KC^{1/n}$

				av abs deviation, %	
acid	T, °C	K	$1/n$	nonlinear fit	linear fit
oxalic	5	0.174	0.452	14.22	15.20
	40	0.106	0.549	14.91	15.07
malonic	5	0.226	0.419	12.48	12.50
	40	0.162	0.479	12.19	12.38
succinic	5	0.363	0.310	9.67	20.56
	40	0.290	0.339	9.61	9.40

[a] C is the equilibrium solution concentration (mol/m^3) and q is the amount of adsorbate per unit weight of adsorbent at equilibrium (mol/kg). The parameters K and $1/n$ were obtained from a nonlinear curve fit to the data.

Table III. Parameters of the Langmuir Equation[a]
$q = K_1K_2C/(1 + K_1C)$

				av abs deviation, %	
acid	T, °C	K	$1/n$	nonlinear fit	linear fit
oxalic	5	0.087	1.26	4.33	5.74
	40	0.063	1.20	3.93	7.49
malonic	5	0.162	1.21	1.15	1.32
	40	0.110	1.16	0.88	1.31
succinic	5	0.470	1.11	10.06	13.84
	40	0.328	1.04	8.59	10.00

[a] C is the equilibrium solution concentration (mol/m^3) and q is the amount of adsorbate per unit weight of adsorbent at equilibrium (mol/kg). The values for K_1 and K_2 were obtained from a nonlinear curve fit to the data.

as the amount of adsorption which would saturate the unit surface with a monolayer. If $1/q$ is plotted vs. $1/C$, a straight line should be obtained over the region in which the Langmuir equation holds. This line will have a slope of $1/(K_1K_2)$ and an intercept of $1/K_2$. In this study, however, a nonlinear least-squares curve fit was used to obtain the best values for K_1 and K_2. The coefficients of the Langmuir equation are presented in Table III.

An approach to multilayer adsorption was first formalized by Polanyi (*13*) in 1914. The basic formulation is based on the concept of a force field surrounding a solid, which influences the adsorbate molecules. The forces are long range and decrease as the distance from the surface increases. Polanyi defined the adsorption potential, ϵ, of any molecule within the attractive force field of the solid surface (which is the sum of the attractive forces of all the contributing atoms of the solid) as the work required to remove the molecule to infinity from its location in the adsorption space. For a given adsorbent, the magnitude of ϵ depends on the nature of the adsorbate and its proximity to the adsorbent. The potential theory proposed by Polanyi (*14*–*16*) has been applied successfully for both monolayer and multilayer adsorption of gases on porous as well as nonporous adsorbents. The adsorption potential is given as

$$\epsilon = RT \ln (P_s/P) \tag{3}$$

Polanyi originally proposed that adsorption of solid solutes from solution would be analogous to the adsorption of gases with precipitation of solids taking the place of liquefaction of gases. For this case the adsorption potential is given as

$$\epsilon = RT \ln (C_s/C) \tag{4}$$

where C_s is the saturation concentration at the equilibrium temperature and C is the equilibrium concentration. A plot of the cumulative volume vs. ϵ is called a "characteristic curve". For a given adsorbate–solid system, the theory postulates the existence of a single characteristic curve for all temperatures.

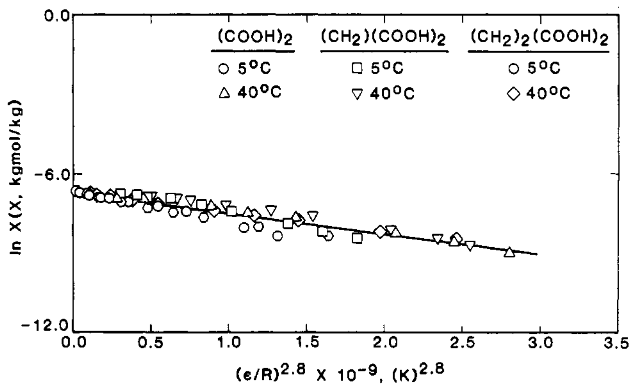

Figure 4. Generalized adsorption correlation for oxalic, malonic, and succinic acids.

Table IV. Generalized Correlation Curve Parameters

acid	W_0, mol/kg	$\beta = E/E_0$[a]
oxalic	1.6278	0.8625
malonic	2.4585	1.1063
succinic	1.3848	1.0000

[a] β is the affinity coefficient. Succinic acid was chosen as the standard substance, $E_{\text{succinic}} = E_0$.

In this study the experimental data for each acid at all temperatures lie close to a single curve as predicted by the Polanyi theory.

The theory of pore filling proposed by Dubinin and co-workers (*17*, *18*) is particularly suited for describing adsorption onto microporous solids. As shown by Bering, Dubinin, and Serpingsky (*19*), the volume adsorbed in the pores can be described by the Dubinin–Astakhov equation

$$W = W_0 \exp\left[-\left(\frac{\epsilon}{\beta E_0}\right)^n\right] \tag{5}$$

where W is the filled volume, defined as $W = X/\rho$, W_0 is the total pore volume, E_0 is a characteristic energy of a standard adsorbate, n is a constant, and β is an affinity coefficient and is equal to E/E_0. The value of β has been shown to be nearly equal to the ratio of the liquid molar volumes of the adsorbates. Substitution of eq 4 for ϵ gives

$$\ln (X) = \ln (W_0\rho) - \left(\frac{RT}{\beta E_0}\right)^n \left[\ln \left(\frac{C_s}{C}\right)\right]^n \tag{6}$$

A plot of $\ln (X)$ vs. $[\ln (C_s/C)]^n$ should yield a straight line with a slope of $-[RT/(\beta E_0)]^n$ and an intercept of $\ln (W_0\rho)$. Values of n equal to 3.7, 3.3, and 2.7 give the best fit to the experimental data for the oxalic, malonic, and succinic acids, respectively.

A generalized characteristic curve for the adsorption of all three dicarboxylic acids on 200 × 325 Darco activated carbon is shown in Figure 4. The solid line was determined by a linear regression analysis. An n value of 2.8 was chosen for all components to yield the best correlation coefficients. Table IV gives the parameters of the characteristic equation and the affinity coefficients. From the generalized curve it is obvious that the potential theory may be applied to the adsorption data obtained in this study. From the results presented, the Freundlich and Langmuir models do not appear to provide a good fit to the experimental data. Figure 5 shows a comparison of the predicted and experimental data. The average absolute deviations between predicted and experimental loading capacities range from 9.61 to 14.91% for the Freundlich isotherm, from 0.88 to 10.06% for the Langmuir isotherm, and from 1.80 to 5.44% for the potential theory. The potential theory provides the best overall correlation of the adsorption data.

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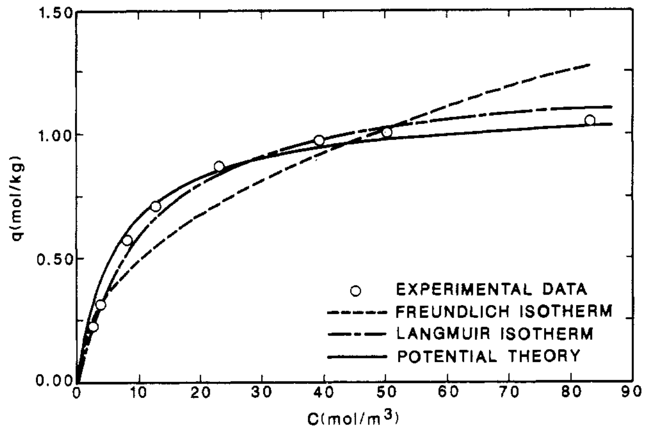

Figure 5. A comparison of experimental and predicted isotherms for oxalic acid at 5 °C.

Glossary

C	equilibrium solution concentration
C_s	solubility in water
E	characteristic energy
E_0	characteristic energy of a standard component
K	a parameter of the Freundlich isotherm
K_1, K_2	parameters of the Langmuir isotherm
n	parameter of the Dubinin–Astakhov or Freundlich equation
P	equilibrium pressure
P_s	vapor pressure of the adsorbate liquid at the equilibrium temperature
q	equilibrium uptake
R	gas constant
T	temperature
W_0	parameter of the Dubinin–Astakhov equation (total pore volume)
X	weight of substance adsorbed
β	affinity coefficient
ϵ	adsorption potential
ρ	liquid density

Registry No. $(COOH)_2$, 144-62-7; $(CH_2)(COOH)_2$, 141-82-2; $(CH_2)_2(COOH)_2$, 110-15-6; C, 7440-44-0.

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Extraction of Several Metals from Chloride Salt Solutions with Heptafluorodimethyloctanedione

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Distribution coefficients for 17 metals between aqueous chloride salt solutions and 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione–trioctylphosphine oxide solutions in dodecane were determined in the pH range 2–12. Loading isotherms, distribution coefficient dependence on extractant concentration, and synergistic effects of extractant mixtures vs. the individual components are shown for several metals, representative of their periodic class.

Introduction

The solvent extraction of metals from near-neutral to basic salt solutions with β-diketones has been reported by many investigators (*1–7*). In general, the extraction mechanism involves the formation of an organic-phase-soluble chelate of the metal with the β-diketone. Studies of the extraction of lithium from aqueous solutions of alkali metal salts (*8*, *9*) with β-diketones have shown lithium distribution coefficients adequately high for efficient extraction and significant separation from the other alkali metals; however, pH values of 10–12 are necessary for enolization of the diketone, exchange of the proton, and formation of the lithium chelate. It is known that substitution of fluorine for hydrogen in the alkyl radicals adjacent to the keto group lowers the pH at which β-diketones enolize and ionize the hydrogen (*10*), thus making such extractants more useful in the pH range 5–9 (*11*, *12*). The addition of a neutral coordinator such as trioctylphosphine oxide (TOPO) appears to further decrease the pH at which compound formation occurs, as evidenced by increased metal extraction (*8*, *9*, *11*, *12*). Additionally, the β-diketone–TOPO mixture is found to be synergistic in the extraction of most metals; that is, the distribution coefficient shown by the mixture is greater than the sum of the coefficients obtained when the two extractants are used separately. Considerable interest has been shown in these compounds because of their ability to form volatile metal complexes (*13–18*). This would add the interesting potential for separation of the metal diketonates by gas chromatography. This paper describes the extraction of the alkali metals, alkaline earths,

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