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Adsorption of Glutaric, Adipic, and Pimelic Acids on Activated Carbon

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Experimental data are reported for the adsorption of three dicarboxylic acids onto activated carbon from dilute aqueous solutions. Glutaric, adipic, and pimelic acids were studied at 278 and 313 K over a concentration range of 10^{-1} to 10^{-4} (kg mol)/m^3. A single generalized characteristic curve for the dicarboxylic acids was obtained by using the potential theory.

Introduction

Green River Formation oil shale and the shale process waters contain a certain amount of solvent extractable acids and metal salts of α,ω-dicarboxylic acids (*1*). Yet, as discussed by Lee et al. (*2*), adsorption data of these compounds from dilute aqueous solutions are not available in the literature. Although it is recognized that various adsorbents can be used to adsorb organic materials, activated carbon has evolved as the most effective and dependable adsorbent for the removal of the dissolved organic impurities found in waters and waste waters.

This work presents the study of adsorption of the organic dibasic acids: glutaric, adipic, and pimelic acids, at two different temperatures, 5 and 40 °C, on activated carbon. This work in conjunction with the previous work by Lee et al. (*2*) provides a relatively comprehensive study of the application of activated carbon as a means for adsorbing organic dibasic acids (C_2–C_7) at low concentrations from dilute aqueous solutions.

Experiment

Glutaric, adipic, and pimelic acids were used as the adsorbates in this study. All of the acids were obtained from Rasher & Betzold, Inc., Chicago, IL, and had purities greater than 99.8%. Granular DARCO activated carbon, which was used in the work of Lee et al. (*2*), was selected as the adsorbent for this study. According to the report from the manufacturer, the Darco activated carbon was washed by a strong acid to leach out undesirable inorganics such as calcium, magnesium, iron, and aluminum. This was followed by water washing until the water extract reached a pH of 6. The activated carbon had a total surface area of 595 m^2/g (as found by a BET analysis), 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.

A batch kinetic study was used to determine the equilibrium time for the dicarboxylic acid–activated carbon systems. The kinetic data were obtained by mixing 100 mL of 2000 ppm adipic acid solution with 0.5 g of either 20 × 40 mesh or 200 × 325 mesh activated carbon in an Erlenmeyer flask. The flask was then sealed and placed in a shaker bath. Periodically, small samples were withdrawn and analyzed to determine their carbon content. When no change in the carbon content was observed, adsorption equilibrium was assumed to have been reached; this required a time of only 15 min. The quantity of sample withdrawn for analysis was insignificant compared to the total amount of solution used in the adsorption study.

Table I. Adsorption Isotherm Data for Glutaric, Adipic, and Pimelic Acids

	5 °C		40 °C	
acid	C, mol/m^3	X, mol/kg	C, mol/m^3	X, mol/kg
glutaric	0.250	0.253	0.318	0.239
	0.530	0.348	0.689	0.316
	1.370	0.483	1.643	0.428
	2.301	0.600	4.504	0.613
	4.012	0.712	11.05	0.818
	10.45	0.939	18.09	0.924
	17.49	1.045	32.55	1.060
	31.93	1.188	54.69	1.173
	54.12	1.287	69.64	1.211
	69.07	1.325		
adipic	0.168	0.240	0.171	0.240
	0.356	0.339	0.431	0.324
	0.883	0.508	1.081	0.468
	3.079	0.753	1.902	0.578
	8.827	0.972	3.524	0.664
	15.05	1.095	9.306	0.876
	27.98	1.249	15.60	0.985
	47.90	1.369	28.57	1.129
	61.31	1.423	48.52	1.245
			61.93	1.300
pimelic	0.128	0.224	0.134	0.223
	0.269	0.321	0.306	0.313
	0.718	0.481	0.724	0.480
	2.529	0.743	1.455	0.583
	7.554	0.987	2.716	0.706
	13.11	1.124	7.867	0.924
	24.82	1.280	13.49	1.049
	42.77	1.436	25.29	1.186
	54.79	1.530	43.39	1.311
			55.72	1.342

The batch adsorption isotherm study was based on determining the acid solution concentrations before and after contact with the activated carbon. Sample solutions were prepared for each acid over the concentration range of 200–10 000 ppm. All of the solutions used in this experiment were prepared with double distilled water as the solvent. One hundred milliliters of each sample solution was mixed with 0.5 g (weighed to 0.0001 g) of 200 × 325 mesh activated carbon. The solution was then placed in a shaker bath for 1 h to reach equilibrium. After equilibration, the mixture was filtered twice with Whatman No. 40 and No. 42 filter paper, respectively, to ensure that all activated carbon particles were removed. The filtrate samples were then analyzed on an Oceanography International Corp. Total Carbon Analyzer for TOC content. A detailed description of the experimental procedure is given by Lee et al. (*2*).

Results and Discussion

The equilibrium data for the adsorption of glutaric, adipic, and pimelic acids on 200 × 325 mesh activated carbon at both 5 and 40 °C are presented in Table I and in Figures 1 and 2. An examination of the adsorption data presented in the figures shows that the adsorption of these dicarboxylic acids increases with increased chain length. This agrees with the findings of Linner and Gortner (*4*), who noted that at concentrations lower than 0.025 M the adsorption extent of dicarboxylic acids obeys Traube's rule, and with the findings of Lee et al. (*2*). The experimental data were compared to the available literature data (*3*) and the resulting differences were quite small.

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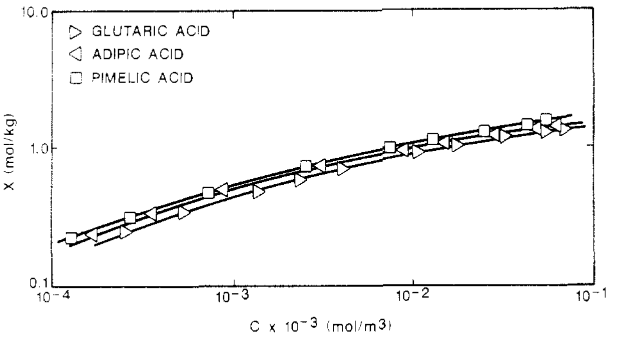

Figure 1. Adsorption isotherms of glutaric, adipic, and pimelic acids at 5 °C.

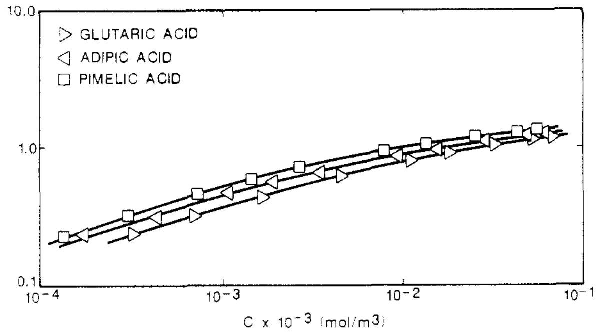

Figure 2. Adsorption isotherms of glutaric, adipic, and pimelic acids at 40 °C.

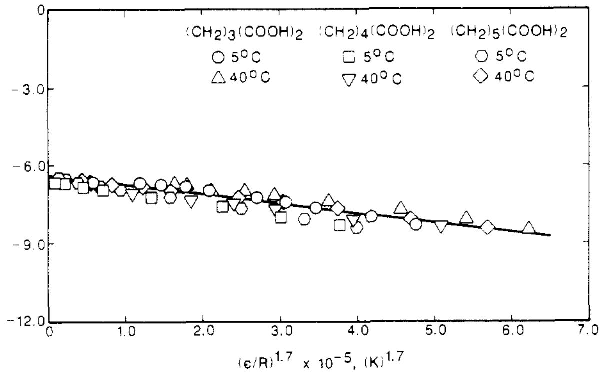

Figure 3. Generalized adsorption correlation for glutaric, adipic, and pimelic acids.

The equilibrium data were expressed in terms of the adsorption potential by using the potential theory proposed by Polanyi (*5–8*) and an expression developed by Dubinin and co-workers (*9–13*), which describes the volume of adsorbate adsorbed in the pores of a microporous solid. The adsorption potential is given as

$$\epsilon = RT \ln (C_s/C) \qquad (1)$$

where C_s is the saturation concentration at the equilibrium temperature and C is the equilibrium concentration. A plot of the volume adsorbed vs. ϵ provides a characteristic curve for a given adsorbate–solid system; the theory postulates the existence of a single characteristic curve for all temperatures. The equation of Dubinin and Astakhov (*12*) was used to express the amount adsorbed. It may be written as

$$\ln (X) = \ln (W_0\rho) - [RT/(\beta E_0)]^n[\ln (C_s/C)]^n \qquad (2)$$

where X is the weight of substance adsorbed, W_0 is the total pore volume, E_0 is a characteristic energy of a standard absorbate, n is a constant, and β is an affinity coefficient and is equal to E/E_0. Introducing the definition for β into eq 2 gives

$$\ln (X) = \ln (W_0\rho) - [RT/E]^n[\ln (C_s/C)]^n \qquad (3)$$

In the above expression, E is defined as the characteristic energy of the adsorbate and is numerically equal to the adsorption potential, ϵ, at a point for which the degree of filling of the adsorption space, W/W_0, is equal to exp(−1), i.e.

$$E = \epsilon \quad \text{at } W/W_0 = \exp(-1) \qquad (4)$$

where W is defined as the filled volume and is expressed in terms of the uptake as $W = X/\rho$. A plot of ln (X) vs. [ln $(C_s/C)]^n$ should yield a straight line with a slope of $-(RT/E)^n$ and an intercept of ln $(W_0\rho)$. Values of n equal to 2.3, 1.8, and 1.5 were found to give the best fit to the experimental data for the glutaric, adipic, and pimelic acids, respectively.

A generalized characteristic curve for all three acids is given in Figure 3. An n value of 1.7 provides the best fit to the data. A generalized curve for the dicarboxylic acids studied in this work and the acids studied by Lee et al. (*2*) is shown in Figure 4. An n value of 2.1 provided the best correlation of all six acids. The parameters of the characteristic equation and the affinity coefficients for all of the acids, C_2–C_7, are given in Table II.

The Freundlich and Langmuir isotherm equations were also used to fit the equilibrium data. Since neither provided as good

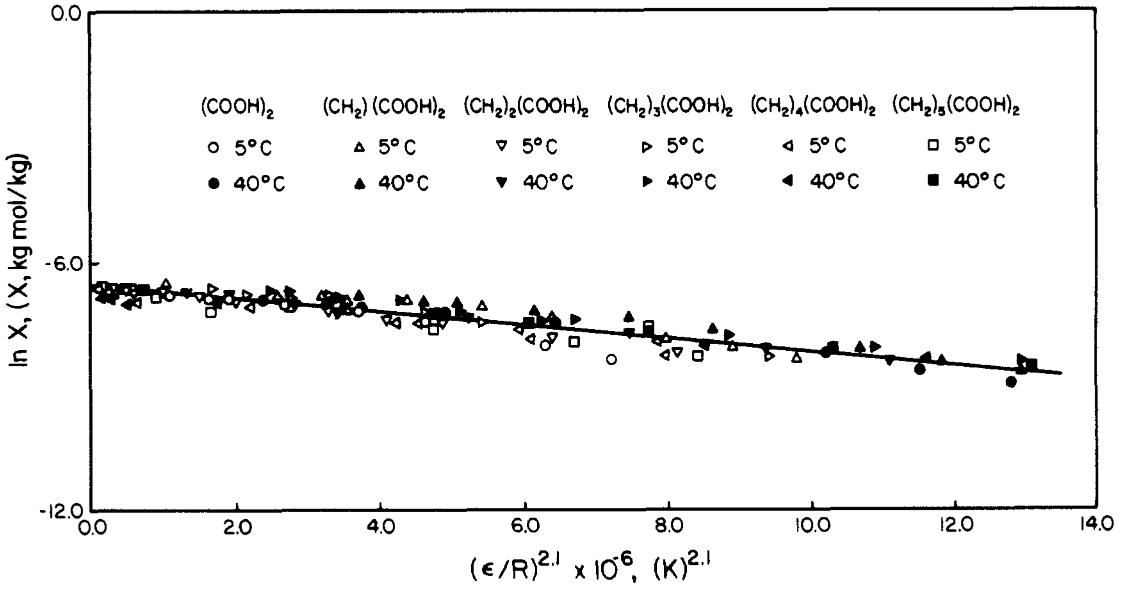

Figure 4. Generalized adsorption correlation for the dicarboxylic acids, C_2–C_7.

Table II. Generalized Correlation Curve Parameters

acid	W_0, mol/kg	$(RT/E)^{2.1}$	affinity coeff[a]
oxalic	1.6278	0.04488	0.8625
malonic	2.4585	0.02711	1.1063
succinic	1.3848	0.02927	1.0000
glutaric	1.8347	0.01692	1.2750
adipic	1.2093	0.03349	0.9125
pimelic	1.4156	0.02735	0.9938

[a] $\beta = E/E_0$. Succinic acid was chosen as the standard substance, $E_{\text{succinic}} = E_0$.

a fit to the data as did the potential theory, they are not shown in this paper. The application of these equations to the adsorption of dicarboxylic acids was shown by Lee et al. (*2*) to be inferior to the potential theory.

Glossary

C	equilibrium solution concentration
C_s	solubility in water
E	characteristic energy
E_0	characteristic energy of a standard component
n	parameter of the Dubinin-Astakhov equation
R	gas constant
T	temperature
W	filled volume, $W = X/\rho$
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. Carbon, 7440-44-0; glutaric acid, 110-94-1; adipic acid, 124-04-9; pimelic acid, 111-16-0.

Literature Cited

(1) Haug, P.; Schnoes, H. K.; Burlingame, A. L. *Chem. Geol.* **1971**, *7*, 213.
(2) Lee, C.; Pedram, E. O.; Hines, A. L. *J. Chem. Eng. Data* **1986**, *31*, 133.
(3) Belotserkovskii, G. M.; Dashkovskii, I. D.; Emel'yanova, N. A.; Proskuryakov, V. A. *Zh. Prikl. Khim.* (*Leningrad*) **1973**, *46*(8), 1770.
(4) Linner, E. R.; Gortner, R. A. *J. Phys. Chem.* **1935**, *39*, 35.
(5) Polanyi, M. *Verh. Dsch. Phys. Ges.* **1914**, *16*, 1012.
(6) Polanyi, M. *Verh. Dsch. Phys. Ges.* **1916**, *18*, 55.
(7) Polanyi, M. *Z. Elektrochem.* **1920**, *26*, 370.
(8) Polanyi, M. *Z. Phys.* **1920**, *2*, 111.
(9) Dubinin, M. M.; Radushkevich, L. V. *Dokl. Akad. Nauk SSSR* **1947**, *1*, 5.
(10) Dubinin, M. M. *Q. Rev.* **1955**, *9*(*2*), 101.
(11) Dubinin, M. M. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1965**, *39*(6), 697.
(12) Dubinin, M. M.; Astakhov, V. A. *Izv. Akad Nauk SSSR, Ser. Khim.* **1971**, *1*, 5.
(13) Bering, B. P.; Dubinin, M. M.; Serpingsky, V. V. *J. Colloid Interface Sci.* **1972**, *38*(1), 185.

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Bubble Pressures and Saturated Liquid Molar Volumes of Trifluorotrichloroethane–Fluorochlorohydrocarbon Mixtures. Experimental Data and Modelization

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An apparatus described elsewhere has been used to get bubble pressure and saturated liquid molar volume data at four temperatures for binary systems composed of trifluorotrichloroethane (Refrigerant R113) with trifluoromethane (Refrigerant R23) and difluoroethane (Refrigerant R152A), and a ternary system composed of trifluorotrichloroethane–difluoroethane–difluorodichloromethane (Refrigerant R12). Experimental bubble pressures of the two binary systems are represented within 2% by a one adjustable parameter cubic equation of state. Without use of an interaction parameter, the cubic equations of state are not able to reproduce accurately the experimental data (standard deviations as high as 20 and 25%). A volume translation, used in combination with the Peng–Robinson equation of state, makes it possible to simultaneously represent vapor–liquid equilibria and saturated liquid molar volumes within 2%.

Introduction

This work is a part of a project to extend the thermodynamic data base on refrigerant mixtures. A bibliographic study was cited in a paper by Meskel-Lesavre (*1*) along with new experimental results. Other new data on refrigerant systems are available in ref *2* and *3* along with details about the apparatuses used.

The static method with a variable volume cell which is very convenient for liquid-phase studies was used here. The corresponding apparatus is the same as that in ref *3*.

Experimental Section

Details about the experimental equipment are given in papers *3* and *4*. The accuracy of pressure, temperature, and composition measurements are given in the tables of results.

Chemicals. Difluoroethane was supplied by Matheson with a certified GPC minimum purity of 98%, trifluorotrichloroethane by Labosi with a certified GPC minimum purity of 99.9%, and trifluoromethane and difluorodichloromethane by Dehon with respective certified GPC minimum purities of 99 and 99.9%.

Results

Experimental results appear in Tables I–III. Experimental errors on mole fractions and saturated molar volumes reported in the tables come from expressions cited in paper 3.

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