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Adsorption of Aliphatic Acids from Aqueous Solutions onto Activated Carbon

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The radioisotope technique was applied to study the removal of aliphatic acid contaminants found in byproduct waters of fossil fuel conversion processes at three different temperatures. Five pure component systems (acetic acid, propionic acid, *n*-butyric acid, *n*-hexanoic acid, and *n*-heptanoic acid) were investigated at three different temperatures, 278, 298, and 313 K, by using activated carbon as the adsorbent. The results were modeled by a three-parameter adsorption isotherm equation.

Introduction

In recent years, the adsorption of organic contaminants from aqueous solution was studied primarily by chromatographic techniques and the uptake was calculated from the invariant adsorption equation (*3*, *8*). Several different systems have been reported for different adsorbents at different temperatures (*1*–*4*, *6*, *7*, *9*–*13*). However, only a few systems have been studied over wide concentration ranges. Among those works mentioned above, Hansen et al. (*3*), Hansen and Craig (*2*), Linner and Gortner (*4*), and Parkash (*6*) presented experimental data for the adsorption of aliphatic acids on various types of activated charcoal over moderate concentration ranges. This study presents the adsorption data of five carboxylic acids at three different temperatures obtained over a wide concentration range by using radioactive tracer techniques. Analytical sensitivity can be improved by the use of radioactive tracer techniques with an expected 10^3–10^6 increase in sensitivity over conventional spectroscopic or chromatographic quantitation methods (*5*). The amount of uptake can be determined by counting the radioactivity of the solution after the equilibrium is reached. Neither the assumption of very dilute solution in using the invariant adsorption equation (*7*, *14*) nor the surface excess calculation (*12*) is needed when using this method. The data obtained are important for developing theoretical adsorption models applicable to wide concentration ranges.

Experimental Section

The major experimental apparatus used in this study was a Beckman Instrument Co. liquid scintillation counter, Model LS-9000. All of the organic acids were obtained from Pfaltz Bauer, Inc. The purities were 99+% as determined by a chromatographic analysis. Radioactive acetic acid, propionic acid, and *n*-butyric acid were obtained from the Radiochemical Center, Amersham, England, whereas *n*-hexanoic acid and *n*-heptanoic acid were obtained from ICN Pharmaceutical, Inc. The lignite-based activated carbon was obtained from Darco Co., Denver, Col. A 20 × 40 mesh material with a total surface area of 667 m^2/g was used.

According to the report from the manufacturer, the 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 was further cleaned for this study by washing with double distilled water until no flocculation was seen. Then the washed activated carbon was heated at 428 K for 9 h. The same procedures were repeated twice before taking adsorption data. The concentrations of acetic, propionic, and *n*-butyric acids varied from 1 to 5000 ppm. The concentration of *n*-hexanoic acid varied from 100 to 2500 ppm, and the concentration of *n*-heptanoic acid varied from 100 to 2000 ppm.

The radioanalytical approach used in these adsorption experiments involved the addition of a small mass (less than 1 μg) of high specific activity radioactive solute to each of the stock solutions of solute made up at varying concentrations. This imparted a uniform and high solute specific activity to each of the stock solutions with negligible change to the final solute concentration. This method provides an equally sensitive and accurate radioanalysis for determining solute concentrations at both high and low levels. The net result is that the overall statistical variance and accuracy of the results obtained are the same over the entire concentration range.

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 (out of 5 mL) of each sample with 12 mL of Dimilume-30, Packard Instrument Co. Ninety-five milliliters of each sample solution was shaken with 0.5 g of activated carbon in a shaker bath set at either 278, 298, or 313 K, for 48 h to reach equilibrium. Samples were placed in the liquid scintillation counter and dark adapted for at least 30 min prior to counting. Counting was performed in a wide open ^{14}C window and continued until a 2σ count rate error of 0.1% or less was achieved. Random coincidence monitoring was used to ensure that the contribution of counting events not due to radioactivity disintegrations, e.g., chemiluminescence, was less than 0.2%. The counting efficiency was determined for each sample and was used to compute the absolute activity as disintegrations per minute (DPM). Efficiency corrections were made by instrumental measurement of the Compton edge inflection point (a Beckman modification

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Table I. Adsorption Isotherm Data of Acetic Acid

278 K		298 K		313 K	
q, mmol/g	C_f, mol/L	q, mmol/g	C_f, mol/L	q, mmol/g	C_f, mol/L
1.60	7.46×10^{-2}	1.23	7.69×10^{-2}	1.06	7.78×10^{-2}
1.14	3.61×10^{-2}	8.83×10^{-1}	3.70×10^{-2}	8.04×10^{-1}	3.74×10^{-2}
6.83×10^{-1}	1.33×10^{-2}	5.47×10^{-1}	1.41×10^{-2}	4.58×10^{-1}	1.43×10^{-2}
4.38×10^{-1}	5.98×10^{-3}	3.65×10^{-1}	6.52×10^{-3}	2.84×10^{-1}	6.84×10^{-3}
2.71×10^{-1}	2.74×10^{-3}	2.29×10^{-1}	2.96×10^{-3}	1.75×10^{-1}	3.25×10^{-3}
1.35×10^{-1}	9.56×10^{-4}	1.16×10^{-1}	1.06×10^{-3}	8.10×10^{-2}	1.24×10^{-3}
7.50×10^{-2}	4.40×10^{-4}	6.98×10^{-2}	5.04×10^{-4}	4.25×10^{-2}	5.10×10^{-4}
1.73×10^{-2}	7.58×10^{-5}	1.50×10^{-2}	7.77×10^{-5}	1.16×10^{-2}	1.06×10^{-4}
1.62×10^{-3}	6.01×10^{-6}	2.68×10^{-3}	9.00×10^{-6}	1.58×10^{-3}	8.34×10^{-6}

Table II. Adsorption Isotherm Data of Propionic Acid

278 K		298 K		313 K	
q, mmol/g	C_f, mol/L	q, mmol/g	C_f, mol/L	q, mmol/g	C_f, mol/L
1.88	5.77×10^{-2}	1.30	2.71×10^{-2}	1.60	5.63×10^{-2}
1.55	2.71×10^{-2}	8.80×10^{-1}	8.79×10^{-3}	1.28	2.63×10^{-2}
1.00	8.98×10^{-3}	5.72×10^{-1}	3.80×10^{-3}	8.03×10^{-1}	9.30×10^{-3}
6.40×10^{-1}	3.39×10^{-3}	3.55×10^{-1}	1.51×10^{-3}	4.95×10^{-1}	4.15×10^{-3}
3.94×10^{-1}	1.41×10^{-3}	1.70×10^{-1}	5.00×10^{-4}	3.10×10^{-1}	1.75×10^{-3}
1.80×10^{-1}	3.81×10^{-4}	8.95×10^{-2}	2.10×10^{-4}	1.56×10^{-1}	5.61×10^{-4}
9.46×10^{-2}	1.78×10^{-4}	2.02×10^{-2}	2.80×10^{-5}	8.50×10^{-2}	2.28×10^{-4}
2.07×10^{-2}	2.62×10^{-5}			2.00×10^{-2}	3.60×10^{-5}
2.57×10^{-3}	2.06×10^{-6}			2.40×10^{-3}	8.22×10^{-7}

Table III. Adsorption Isotherm Data of Butyric Acid

278 K		298 K		313 K	
q, mmol/g	C_f, mol/L	q, mmol/g	C_f, mol/L	q, mmol/g	C_f, mol/L
2.72	9.70×10^{-2}	2.43	1.00×10^{-1}	1.93	1.04×10^{-1}
2.05	4.66×10^{-2}	1.87	4.75×10^{-2}	1.65	4.80×10^{-2}
1.62	2.04×10^{-2}	1.42	2.12×10^{-2}	1.39	2.11×10^{-2}
1.11	6.30×10^{-3}	9.24×10^{-1}	6.50×10^{-3}	8.45×10^{-1}	6.92×10^{-3}
7.04×10^{-1}	1.98×10^{-3}	6.57×10^{-1}	2.22×10^{-3}	5.96×10^{-1}	2.54×10^{-3}
4.30×10^{-1}	5.70×10^{-4}	4.08×10^{-1}	6.38×10^{-4}	3.77×10^{-1}	8.55×10^{-4}
1.95×10^{-1}	1.11×10^{-4}	1.98×10^{-1}	1.48×10^{-4}	1.84×10^{-1}	1.66×10^{-4}
1.03×10^{-1}	2.87×10^{-5}	1.00×10^{-1}	4.10×10^{-5}	9.72×10^{-2}	5.66×10^{-5}
		3.11×10^{-2}	5.44×10^{-6}	2.09×10^{-2}	3.62×10^{-6}

Table IV. Adsorption Isotherm Data of Hexanoic Acid

278 K		298 K		313 K	
q, mmol/g	C_f, mol/L	q, mmol/g	C_f, mol/L	q, mmol/g	C_f, mol/L
1.72	1.25×10^{-2}	1.66	1.28×10^{-2}	1.56	1.33×10^{-2}
1.30	2.32×10^{-3}	1.20	2.30×10^{-3}	1.08	2.90×10^{-3}
7.66×10^{-1}	2.80×10^{-4}	7.19×10^{-1}	3.72×10^{-4}	7.04×10^{-1}	6.05×10^{-4}
3.90×10^{-1}	3.87×10^{-5}	4.00×10^{-1}	6.45×10^{-5}	3.92×10^{-1}	8.87×10^{-5}
		1.62×10^{-1}	7.16×10^{-6}	1.62×10^{-1}	1.02×10^{-5}

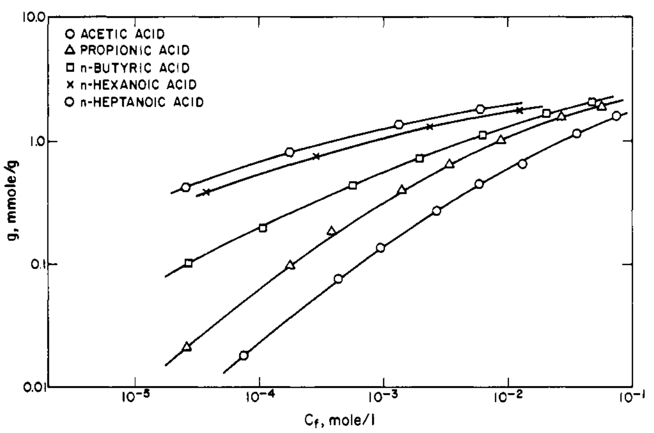

Figure 1. Adsorption isotherms at 278 K.

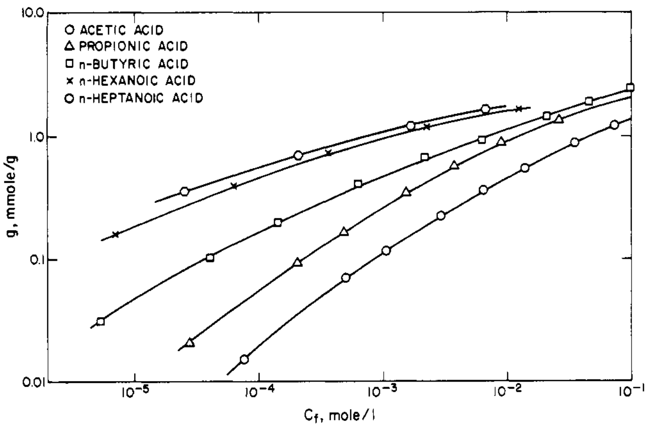

Figure 2. Adsorption isotherms at 298 K.

of the external standardization method) and determination of the counting efficiency was made from a calibration curve previously obtained from a series of water quenched ^{14}C standards prepared in Dimilume. Final DPM values were corrected by sub-

Table V. Adsorption Isotherm Data of Heptanoic Acid

278 K		298 K		313 K	
q, mmol/g	C_f, mol/L	q, mmol/g	C_f, mol/L	q, mmol/g	C_f, mol/L
1.76	6.13×10^{-3}	1.60	6.96×10^{-3}	1.47	7.10×10^{-3}
1.31	1.31×10^{-3}	1.19	1.73×10^{-3}	1.09	1.97×10^{-3}
6.97×10^{-1}	1.76×10^{-4}	6.90×10^{-1}	2.13×10^{-4}	6.30×10^{-1}	2.49×10^{-4}
4.10×10^{-1}	2.65×10^{-5}	3.60×10^{-1}	2.55×10^{-5}	3.40×10^{-1}	4.03×10^{-5}
				1.41×10^{-1}	6.22×10^{-6}

Table VI. Parameters of Equation I

aliphatic acid	temp, K	a	b	β
acetic	278	0.2811	0.2743	0.4288
	298	0.2357	0.2181	0.4155
	313	0.1324	0.1706	0.4602
propionic	278	0.8827	0.5202	0.3404
	298	0.8594	0.4024	0.3895
	313	0.7138	0.3377	0.4144
n-butyric	278	9.0113	0.5620	0.3462
	298	6.7248	0.5010	0.3457
	313	3.0223	0.4921	0.3133
n-hexanoic	278	72.0000	1.0265	0.2260
	298	52.4989	0.9349	0.2444
	313	43.4166	0.8185	0.2547
n-heptanoic	278	111.3755	1.1626	0.2487
	298	70.0420	1.0411	0.2286
	313	46.7134	0.9278	0.2446

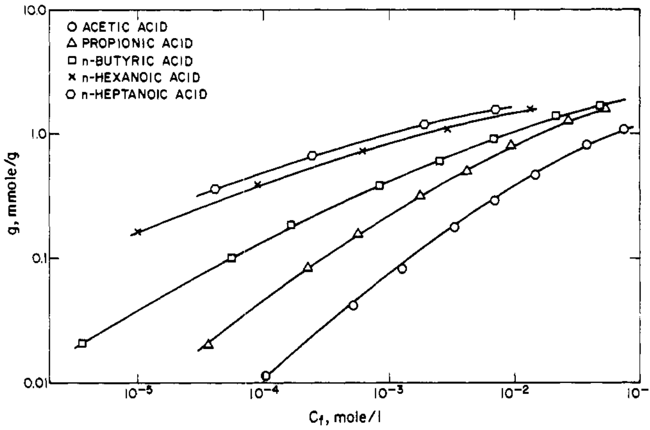

Figure 3. Adsorption isotherms at 313 K.

traction of background count rate.

Results and Discussion

The experimental adsorption data are presented in Tables I–V. A direct comparison of this work was made with the study of Parkash (*6*) at 278 K. For an equilibrium concentration of 0.1 M, the uptake of the various acids in this study is about 37% greater than the uptake found by Parkash for the same adsorbent. The greater uptake found in this work can be attributed to the more extensive pretreatment of the carbon prior to beginning the study. An examination of the adsorption data shows that the adsorption of lower aliphatic acids from aqueous solutions increases with increasing chain length. This result agrees with Traube's rule; i.e., the addition of the CH_2 group to the aliphatic acid molecule reduces its solubility in water.

The experimental data were fitted with a three-parameter empirical equation proposed by Radke and Prausnitz (*7*)

$$\frac{1}{q} = \frac{1}{aC_f} + \frac{1}{bC_f^{\beta}} \qquad (1)$$

where q is the uptake of the solute by the solid, mmol/g, C_f is the final concentration of the solute in the solution, mmol/L, and β is constrained to be less than 1. The data were fitted to within 1% by using the parameters given in Table VI. The broad range of the experimental data is shown in Figures 1, 2, and 3 with the curve fit given by eq 1.

In the dilute solution limit, eq 1 will give a straight line and the parameter "a" becomes the Henry constant. As shown in Table VI, the parameter "a" decreases with increasing temperature and increases with increasing molecule size as expected.

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