Equilibrium Adsorption of Carbon Dioxide by Aqueous Slurries of Solid Particles

Gerd Quicker, Zuohu Li, and Wolf D. Deckwer

Institut fuer Technische Chemie, Universitaet Oldenburg, Oldenburg, Federal Republic of Germany

Erdogan Alper*

Chemical Engineering Department, Kuwait University, P.O. Box 5969, 13060 Safat, Kuwait

The adsorption capacities of the aqueous slurries of activated carbon, kieselguhr (containing 10% gypsum), and alumina for carbon dioxide have been measured in equipment working at isocratic conditions at 298 ± 0.1 K. It was found that the addition of kieselguhr did not increase the capacity of the slurry to any measurable extent. For alumina, the increase in the adsorption capacity was considerable, to the extent that the amount of carbon dioxide which was adsorbed on 1 g of alumina was about 3 times that which dissolved in 1 g of water. This was even more significant for activated carbon with an adsorption capacity which was approximately 3–4 times that of the alumina. The presence of salts, such as $NaNO_3$, in the solution did not alter the trend in the adsorption capacities. These results are important in interpreting the rate of absorption of a gas into a slurry which is then followed by adsorption on solid particles.

Absorption of a gas into a slurry which is then followed by adsorption on solid particles is of considerable importance because of its applications in separation processes and in chemical reaction engineering. In the latter case, finely powdered porous particles are often used either as an actual catalyst itself or as a support for the active species (*1*). One of these solids is activated carbon, and it has been observed experimentally that the finely powdered activated carbon affects the gas absorption rates of O_2 and CO_2 (*2–5*). These results have been explained by a mechanistic feature that postulates the circulation of fine solid particles; when near the gas–liquid interface the particles adsorb dissolved gas in the dissolved gas-rich layer and then desorb the gas as they move into the bulk (*2*, *5*). Adsorption of gases in slurries may also be important in separation processes if the adsorptive capacity of solid adsorbent is of the same magnitude in the wet and dry states. An appropriate liquid may be used as a "filter" to selectively absorb the gas from a mixture, which is then adsorbed on the solid. The theory of slurry sorption separations has been discussed by Myers and Moses (*6*); Kars et al. (*7*) considered the sorption of propane in aqueous slurries of activated carbon.

Experimental equilibrium adsorption data of gases by suspensions of solid adsorbents in liquids are scarce. However, Li and Deckwer (*8*) have reported some data concerning aqueous slurries of activated carbon. Here, the adsorption capacities of the slurries of activated carbon, kieselguhr (containing 10% gypsum), and alumina for carbon dioxide will be reported.

Experimental Section

The experiments were carried out in equipment working at isocratic conditions (that is, at a constant temperature and volume) that was used previously to measure the gas solubilities (Schumpe et al. (*10*)). This equipment had a marking so that excess liquid could be evaporated under vacuum to bring down the volume of degassed liquid to the exactly known level so that it could be contacted with the gas. The drop in the pressure was then recorded. In the case of slurries, the aqueous slurry was stirred and kept under vacuum for about 4 h in order to remove all of the adsorbed gases while also removing the excess water to bring down the slurry volume to the desired level. From the measured pressure drop and the known gas and slurry volumes, the solubility of gas either in the clear solution or in the slurry could be calculated. In addition to water, some experiments were also conducted with suspensions of particles in a 1.5 M $NaNO_3$ solution. For all the experiments, temperature was kept at 298 ± 0.1 K.

Table I. Densities and Surface Areas of the Investigated Solids

solid	density, g/cm^3	surface area, m^2/g
activated carbon	1.80	1078.6
kieselguhr	2.36	2.0
alumina	3.18	129.2

Table II. Particle-Size Distribution (%) of Alumina, Kieselguhr, and Activated Carbon

	32–63 μm	20–31 μm	10–20 μm	6–10 μm	4–6 μm	2–4 μm	0–2 μm
alumina	0.2	2.0	24.2	30.2	24.2	19.2	
kieselguhr		1.1	15.6	24.7	26.4	32.2	
activated carbon	0.4	1.6	9.1	15.4	26.0	32.9	14.6

The powdered solids (activated carbon), alumina, and kieselguhr (containing 10% gypsum)) were purchased from Riedel de Haen, FRG. The density of solids were measured pycnometrically. The surface areas were measured by use of an area meter (Strohlein) which employs a low-temperature nitrogen adsorption technique according to BET method as described by Haul and Dumbgen (*9*, *10*). An omnicon Alpha Image Analyzer was employed to measure the particle-size distributions. Finally, all the particles were also examined under microscope; in all cases their shapes were irregular and deviated from those of perfect spheres.

Results and Discussion

Table I shows the densities and the surface areas of the particles. Table II shows the particle-size distributions for alumina, kieselguhr, and activated carbon. Table I shows clearly that both activated carbon and alumina have porous structure whereas the porosity of kieselguhr is much less than the others. For all the solids, a considerable portion of the particles is smaller than 6 μm; however, only the activated carbon has particles that are smaller than 2 μm in size. None of the solids contains a significant fraction of particles whose sizes exceed 20 μm (that is, 1–2%). For alumina, the majority of particles have a size between 10 and 20 μm.

Figure 1 shows some typical experimental results. The addition of activated carbon increases the total amount of carbon dioxide in the slurry significantly. Table III shows the volume

0021-9568/89/1734-0263$01.50/0

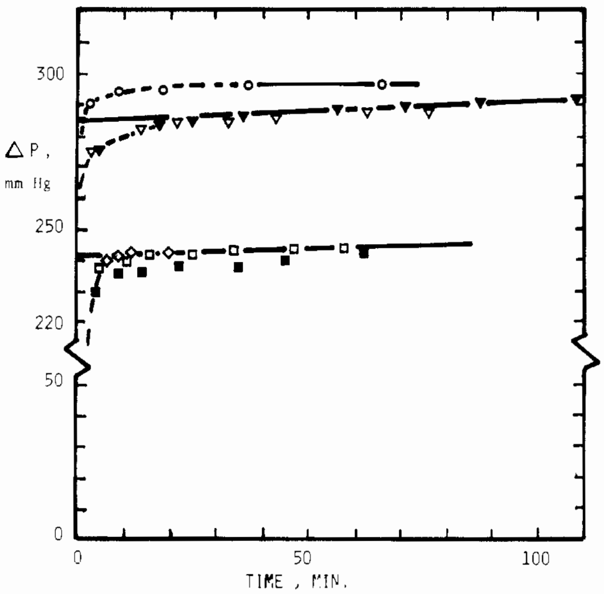

Figure 1. Typical experimental results in the isocratic solubility equipment as pressure drop against time for clear solution and slurries at 298 K (◇, water; ○, 1.5 M $NaNO_3$ solution containing 53 g/L activated carbon, ▽ and ▼, aqueous slurry of 115.3 g/L alumina; □ and ■, aqueous slurry of 115.3 g/L kieselguhr).

Table III. Volume of Gas Adsorbed per 1 g of Solid Suspended in Water or 1.5 M $NaNO_3$ Solution

solid	equilib press., kPa	CO_2 adsorbed, $cm^3{}_N/g^a$	
		H_2O	1.5 M $NaNO_3{}^b$
alumina	60.8	1.39	
	61.1	1.37	
	63.7		1.77
kieselguhr	67.4	0.13	
	66.6	0.31	
	70.8		0.53
	70.6		0.51
activated carbon	59.7	5.20	
	59.3		5.56

[a] 1 $cm^3{}_N$ = 1 cm^3 of gas at 273 K and 101.3 kPa. [b] Suspension medium.

of carbon dioxide (reduced to 273 K and 101.3 kPa) that is adsorbed on 1 g of solid when the solids were suspended in water or in the 1.5 M $NaNO_3$ solutions. From Table III it is seen that 1 g of kieselguhr adsorbs about the same amount of carbon dioxide that dissolves in 1 g of water at 298 K. That is, the addition of kieselguhr does not increase the capacity of the slurry to any measurable extent. For alumina, the increase in the adsorption capacity is considerable, to the extent that the amount of carbon dioxide that is adsorbed on 1 g of alumina is about 3 times that which dissolves in 1 g of water at 298 K. This is even more significant for activated carbon with an adsorption capacity which is roughly 3–4 times that of the alumina. The presence of $NaNO_3$ in the solution does not seem to change the observed effects.

When the slurry reaches equilibrium with the pure gas, the amount of gas in the slurry is in free and adsorbed forms. This combined equilibrium quantity of carbon dioxide in the slurry, C^*, may then be expressed in terms of the Bunsen adsorption coefficient, (Schumpe et al. (*11*)):

$$C^* = P(101.3V_m)^{-1} \qquad (1)$$

where V_m is the molar volume and P is the equilibrium pressure of the gas phase in kilopascals. These Bunsen coefficients were corrected for the portion of slurry volume that is occupied by the solids. When there is no or negligible adsorption by the solid particles, the value of the Bunsen coefficient for the slurry will be the same as that of the solution and they will lie on the diagonal line in Figure 2. For kieselguhr particles, this is nearly the case showing that the adsorption is negligible. For alumina or activated carbon slurries at high loadings the significant amount of carbon dioxide in the slurry is in the adsorbed state. It is expected that the equilibrium adsorption capacities of slurries are related to the surface areas of the particles; the latter depends, of course, not only on the type of the material but also on the mode of preparation.

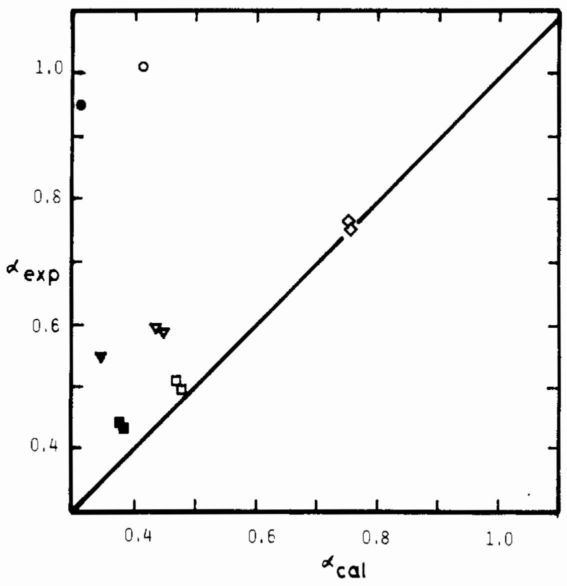

Figure 2. Comparison of experimentally determined and calculated (based on no adsorption) Bunsen coefficient for aqueous slurries at a loading of 115.3 g/L and at 298 K with final equilibrium pressure range of 60–70 kPa (◇, water; ○, aqueous slurry of activated carbon; ▽, aqueous slurry of alumina; □, aqueous slurry of kieselguhr; ●, ▼, and ■, 1.5 M $NaNO_3$ solution containing activated carbon, alumina, and kieselguhr, respectively).

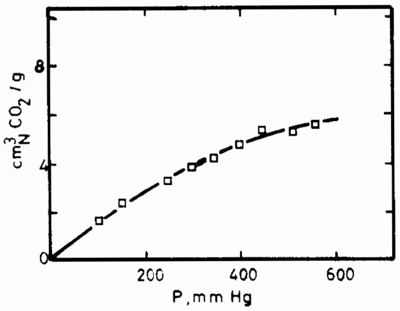

Figure 3. Equilibrium adsorption data of carbon dioxide for an aqueous slurry of 36.3 g/L activated carbon at 298 K.

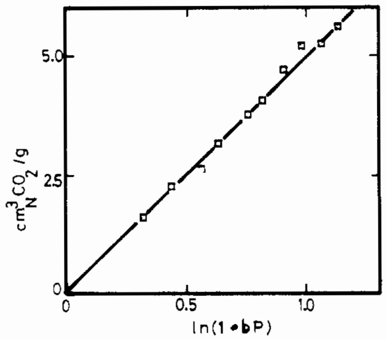

Figure 4. Experimental adsorption data corresponding to Figure 3 according to eq 1.

Figure 3 shows the adsorption isotherm of one activated carbon slurry which shows that the relationship is not linear.

Therefore, it was not possible to correlate data with isotherms of established theories such as Langmuir, Freundlich, Brunauer, Emmett, and Teller. However, the following linear relationship, which has been proposed by Li and Deckwer (*8*), can be used to describe the experimental results (see Figure 4):

$$n_v = K \ln (1 + bP) \qquad (2)$$

Here n_v is the adsorbed gas volume (reduced to 273 K and 101.3 kPa) in centimeters per gram of activated carbon and K and b are temperature-dependent constants. In this case, they were found to be $K = 5.02$ cm/g and $b = 2.72 \times 10^{-2}$ kPa^{-1} for 298 K. Li and Deckwer (*8*) have examined various other activated carbons of different sources. They found that although eq 2 was valid in each case the values for K and b differed considerably, showing the adsorption capacity of activated carbon depended also on the source and the method of preparation, which affects, of course, the surface area.

The results here show that the slurried porous materials, such as alumina and activated carbon, adsorb dissolved carbon dioxide appreciably. The effect is more pronounced for the activated carbon, which is to be expected—to some extent—due to its nonpolar and hydrophobic nature and its large surface area. These results indicate that although the dissolved carbon dioxide competes with water for adsorption on alumina or activated carbon, the equilibrium adsorption is significant to the extent that the total amount of carbon dioxide in the slurry is increased considerably. It is further noted that the presence of $NaNO_3$ in the solution does not alter the trend in the adsorption capacities.

Registry No. CO_2, 124-38-9; Al_2O_3, 1344-28-1; C, 7440-44-0.

Literature Cited

(1) Alper, E. *Mass Transfer with Chemical Reaction in Multiphase Systems*: *Vol. 2*: *Three Phase Systems*; Martinus-Nijhoff: The Hague, 1983.
(2) Alper, E.; Wictendahl, B.; Deckwer, W. D. *Chem. Eng. Sci.* **1980**, *35*, 217-223.
(3) Alper, E.; Ozturk, S. *Chem. Eng. Commun.* **1986**, *46*, 147-153.
(4) Quicker, G.; Alper, E.; Deckwer, W. D. Gas absorption rates for carbon dioxide in a stirred cell with plane interface in the presence of solid particles. *Can. J. Chem. Eng.* **1989**, *67*, 33-38.
(5) Alper, E.; Deckwer, W. D. Some aspects of gas absorption mechanism in slurry reactors. In *Mass Transfer with Chemical Reaction in Multiphase Systems*: *Vol. 2*: *Three Phase Systems*; Alper, E., Ed.; Martinus-Nijhoff: The Hague, 1983; pp 199-224.
(6) Myers, A. I.; Moses, F. *Chem. Eng. Sci.* **1977**, *32*, 529-533.
(7) Kars, R. L., Best, R. J.; Drinkenburg, A. A. M. *Chem. Eng. J.* **1979**, *17*, 201-210.
(8) Li, Z.; Deckwer, W. D. *Chem. Ing. Tech.* **1982**, *54*, 669-671.
(9) Haul, R.; Dumbgen, G. *Chem. Ing. Tech.* **1961**, *32*, 349-356.
(10) Haul, R.; Dumbgen, G. *Chem. Ing. Tech.* **1963**, *35*, 586-589.
(11) Schumpe, A.; Quicker, G.; Deckwer, W. D. *Adv. Biochem. Eng.* **1982**, *24*, 1.

Received for Review August 19, 1987. Accepted February 13, 1989.

Determination of the Diffusion Coefficients of Catecholamines by Potential Step Chronoamperometry

Stuart A. Nowinski[†] **and Dennis M. Anjo***
Department of Chemistry, California State University, Long Beach, California 90840

The diffusion coefficients for a number of catecholamines and a related compound have been determined at 20 °C by use of potential step chronoamperometry at a planar platinum electrode. All of the compounds behaved well with no sign of polymerization or filming. The diffusion coefficients were in the region of 0.6 × 10^{-5} cm^2 s^{-1}, which is typical for molecules of this size. The results had a ±6% average coefficient of variation.

Introduction

The use of electrochemical techniques for the detection and analysis of catecholamines both in physiological systems and with chromatography has seen a great increase in activity (*1*, *2*). A need for accurately determined diffusion coefficients of these compounds exists both for calibration of electrochemical instruments and for the study of their transport in biological systems. We therefore have measured the diffusion coefficients of a group of catecholamines and a related compound using potential step chronoamperometry at a platinum button electrode.

Potential step chronoamperometry at a planar electrode is a well-established standard method for the determination of both electrode areas and diffusion coefficients of electrochemically active compounds. This method has been reviewed in *Treatise in Analytical Chemistry* (*3*) and is covered in many electrochemistry texts (*2*, *4*, *5*). An especially helpful treatment on this topic is given in a monograph by R. N. Adams (*6*).

Experimental Section

The chronoamperometry and cyclic voltammetry experiments were carried out with a Princeton Applied Research Model 362 scanning potentiostat and a Linear strip-chart recorder. The working electrode was an unshielded Beckman platinum button electrode with a geometric area of 0.24 cm^2. The platinum buttom electrode was held such that the electrode surface was horizontal. The reference electrode was a Corning saturated calomel electrode. The auxiliary electrode was a 20-cm spiral coil of 24 gauge platinum wire. The cell container employed was a standard Princeton Applied Research conical voltammetry cell. A potassium nitrate salt bridge was employed between the reference electrode and the test solutions.

The following chemicals were from Sigma Chemical Co.: (±)-arterenol (norepinephrine), L-dihydroxyphenylalanine (DOPA), L-β-dihydroxyphenylalanine methyl ester (methyl-DOPA), (−)-epinephrine, 3-hydroxytyramine hydrochloride (dopamine), and (±)-isoproterenol hydrochloride. The 3,4-dihydroxyhydrocinnamic acid, (−)-3,4-dihydroxynorephedrine, and (−)-3-(3,4-dihydroxyphenyl)-2-methyl-L-alanine were from Aldrich Chemical Co. The potassium ferrocyanide, potassium chloride, potassium dichromate, potassium nitrate, and sulfuric acid were analytical reagent grade from Mallinckrodt. The catecholamine solutions were prepared fresh daily with deionized water from a Barnstead Bantam demineralizer (S-27781) which was fed distilled water.

The platinum button working electrode was cleaned by placing it in a stirred solution of sulfuric acid saturated with

---

[†] Present address: Department of Chemistry, Pasadena City College, Pasadena, CA 91106.

0021-9568/89/1734-0265$01.50/0