Liquid Phase Adsorption Equilibria With Molecular Sieve Adsorbent

LAXMICHAND K. JAIN,[1] HENRY M. GEHRHARDT,[2] and B. G. KYLE
Department of Chemical Engineering, Kansas State University, Manhattan, Kan.

Liquid phase adsorption equilibria have been determined at 25° C. for three systems each containing Molecular Sieve adsorbent, water, and a nonadsorbable second component. The systems studied were *p*-dioxane–water–5A Molecular Sieve, benzyl alcohol–water–5A Molecular Sieve, and ethylenediamine–water–4A Molecular Sieve. In this type of system, liquid phase adsorption equilibria can be accurately predicted if the adsorption isotherm of the pure adsorbable component is available and if the partial pressure of the adsorbable component is known at various liquid phase concentrations. Contrary to the conclusions of Kipling and Wright, these results show that liquid phase adsorption equilibria strongly depend on liquid phase solution behavior.

LIQUID PHASE adsorption equilibria on Molecular Sieves has been previously studied by Kipling and Wright (*2*). These workers investigated systems which contained one adsorbable component and one nonadsorbable component, and their results were explained on the basis that the adsorbent holds the maximum amount of adsorbable component regardless of liquid phase concentration. When the amount of adsorbable component originally present in solution is less than that required to saturate the adsorbent, it was further concluded that the adsorbable component can be completely removed from solution (*2*). An approach such as this also implies that liquid phase solution effects can be neglected, and hence the liquid phase isotherm for any particular adsorbable component is always the same regardless of the type of nonadsorbable component present in the liquid phase.

An analysis is proposed here for liquid phase adsorption equilibria in systems containing Molecular Sieve adsorbent, one adsorbable component, and one or more nonadsorbable components. These systems are analogous to the partitioning of a solute between two immiscible solvents as the adsorbent will have no effect on the liquid phase, and the nonadsorbable components are assumed to have no influence on the adsorbed phase. This assumption seems quite reasonable because the adsorbed phase resides in the interior of the adsorbent which is inaccessible to nonadsorbable components.

Thermodynamic equilibrium between phases is attained when each component has the same fugacity in every phase in which it exists. As the only component common to both phases is the adsorbable component, equilibrium is established when the fugacity of this component is the same in the liquid phase and in the adsorbed phase.

The assumption regarding the independence of the liquid and adsorbed phases allows each phase to be treated separately. The adsorbed phase consists only of the adsorbable component, therefore, the fugacity of the adsorbable component in this phase depends only on temperature and adsorbent loading (a). At any given temperature, this relationship between the fugacity of the adsorbable component and the adsorbent loading can be obtained from the experimentally determined adsorption isotherm of the pure adsorbable component. In the liquid phase, the fugacity of the adsorbable component depends upon temperature and composition. This liquid phase composition–fugacity relationship may be determined experimentally or, in certain cases—e.g., ideal solutions—may be computed.

Because the adsorbed phase consists only of the adsorbable component, adsorption equilibria in these systems can be represented completely by expressing adsorbent loading as a function of liquid phase composition. This equilibrium data can be estimated from the liquid phase composition–fugacity relationship and the adsorbent loading–fugacity relationship at equal values of the fugacity.

For a given adsorbable component, the adsorbent loading–fugacity relationship will not depend on the nature of nonadsorbable components present in the liquid phase. Liquid phase adsorption equilibria, however, will be determined by the liquid phase composition–fugacity relationship which is strongly affected by the nature of the nonadsorbable components.

EXPERIMENTAL

The experimental procedure consisted of contacting weighed amounts of adsorbent and liquid mixture of known composition until equilibrium was established. Approximately 12 to 25 grams of adsorbent and 50 to 70 grams of

Table I. Refractive Index–Composition Data at 25° C.

p-Dioxane–Water		Benzyl Alcohol–Water		Ethylenediamine-Water	
M. f. dioxane	Refractive index	M. f. water	Refractive index	M. f. water	Refractive index
0.0000	1.3325	0.0	1.5383	0.0000	1.4541
0.0132	1.3375	0.0977	1.5347	0.0698	1.4540
0.0275	1.3483	0.2322	1.5280	0.1399	1.4537
0.0642	1.3560	0.2580	1.5268	0.1526	1.4536
0.0766	1.3600	0.3379	1.5217	0.2420	1.4534
0.1309	1.3740			0.3770	1.4531
0.1480	1.3752			0.5350	1.4475
0.3015	1.3960			0.6674	1.4367
0.3580	1.4006			0.7329	1.4244
0.4900	1.4075			0.8069	1.4061
0.5570	1.4100			0.8614	1.3897
0.5610	1.4103			0.8992	1.3761
0.6010	1.4115			0.9306	1.3640
0.6190	1.4125			0.9580	1.3520
0.6800	1.4145			0.9785	1.3422
0.8310	1.4174			0.9872	1.3382
0.9410	1.4187			0.9885	1.3376
1.0000	1.4200			1.0000	1.3323

---

[1] Present address: The Ceilcote Company, Inc., 4832 Ridge Road, Cleveland, Ohio

[2] Present address: Department of Chemical Engineering, University of New Hampshire, Durham, N. H.

Table II. Adsorption Equilibrium Data

p-Dioxane-Water-5A Molecular Sieve at 25° C.		Benzyl Alcohol-Water-5A Molecular Sieve at 25° C.		Ethylenediamine-Water-4A Molecular Sieve at 25° C.	
Nominal m.f. water in liquid phase	Adsorbent loading (g. water per 100 g. adsorbent)	Nominal m.f. water in liquid phase	Adsorbent loading (g. water per 100 g. adsorbent)	Nominal m.f. water in liquid phase	Adsorbent loading (g. water per 100 g. adsorbent)
0.010	16.4	0.011	17.2	0.218	3.78
0.049	20.3	0.040	19.0	0.245	3.45
0.050	19.0	0.057	19.0	0.251	4.36
0.076	19.9	0.065	19.7	0.291	4.64
0.098	20.8	0.104	19.8	0.410	4.29
0.114	20.6	0.105	21.3	0.514	5.69
0.123	21.5	0.125	20.2	0.535	5.93
0.163	21.2	0.128	21.2	0.574	4.51
0.263	21.1	0.155	21.4	0.581	4.82
0.291	21.1	0.177	20.8	0.739	5.88
0.305	21.2	0.190	21.2	0.743	6.45
0.358	21.4	0.202	22.1	0.813	11.12
0.390	21.0	0.204	21.3	0.820	11.67
0.458	21.7	0.216	22.3	0.924	12.92
0.498	21.3			0.925	17.22
0.505	21.5			0.942	13.05
0.725	21.4			0.944	13.97
0.875	21.7				
0.950	21.6				

liquid mixture were weighed into 125-ml. screw cap Erlenmeyer flasks using an analytical balance. The capped flasks were further sealed with plastic tape and were fastened to a rocking plate mounted inside a water bath maintained at a constant temperature of 25° C. Liquid phase compositions were determined after two days and daily thereafter until a constant final composition was approached. Readings on the second and third day were almost always in agreement. Refractive index was used to determine the composition in all three systems except the ethylenediamine-water system in the range 0 to 50 mole % water. All systems were calibrated for refractive index *vs.* composition by determining the refractive indices at 25° C. of mixtures of known composition. Refractive index-composition data for the three systems are tabulated in Table I. For the ethylenediamine-water system, the refractive index changed only slightly over the range 0 to 50 mole % water; hence, analyses in this range were performed by titration with 1*N* hydrochloric acid with methyl orange indicator.

The expected nonadsorbable components—namely, *p*-dioxane, benzyl alcohol, and ethylenediamine—were tested for nonadsorptivity by mixing them individually with benzene, a known nonadsorbable compound on 4A and 5A Molecular Sieves (*3*), and by contacting this mixture with the appropriate Molecular Sieve adsorbent. After a period of 3 or 4 days, no change in the refractive index of the mixture was observed. Thus, the nonadsorptivity of these compounds was considered established.

The organic compounds used in this work were obtained commercially with a reasonable degree of purity. Since their refractive indices agreed with literature values, and the nonadsorptivity test indicated that no adsorbable impurites were present, they were not subjected to further purification. The Molecular Sieve adsorbent used was in the form of $\frac{1}{16}$-inch pellets and was given no special treatment before use.

Table III. Partial Pressure Data for Benzyl Alcohol-Water Mixtures

Aqueous Phase	Water, Partial Pressure, Mm. of Hg (*5*)	M.F. Water in Alcohol Phase
Sat. K_2CO_3 sol.	10.0	0.093
Sat. NaBr sol.	13.4, 13.7	0.157
Sat. NaCl sol.	17.7, 17.8, 18.0	0.229
Water	23.8	0.384

The calculation of the adsorbent loading, *a*, is based on a material balance over the adsorbed component.

$$a = \frac{100\, L_0(w_0 - w)}{A(1 - w)}$$

The equilibrium data for all three systems are presented in Table II as adsorbate loading *vs.* nominal liquid phase mole fraction (m. f.) of water.

Partial pressure data for water in benzyl alcohol-water mixtures were needed in order to calculate the liquid phase adsorption isotherm. These data were obtained by equilibrating benzyl alcohol and various saturated salt solutions at 25° C., then measuring the refractive index of the alcohol phase. Water mole fractions were determined from the refractive index calibration curve. The salts used for this work were all reagent grade. The maximum solubility of water in benzyl alcohol was estimated by measuring the refractive index of a benzyl alcohol phase saturated with water at 25° C. The refractive index calibration curve was extrapolated to obtain the corresponding mole fraction.

Table III contains the composition of the alcohol phase and the reported water partial pressure (*5*) corresponding to each partition measurement. The solubility of water in benzyl alcohol was much greater than the value reported in the literature. Seidell and Linke (*4*) report the weight fraction of alcohol to be 0.0398 and 0.9473 in the saturated phases at 25° C., whereas the authors found the alcohol-rich phase to contain 90.5 wt. % alcohol. The partial

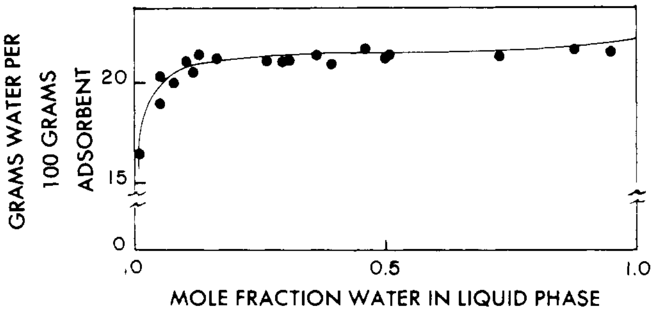
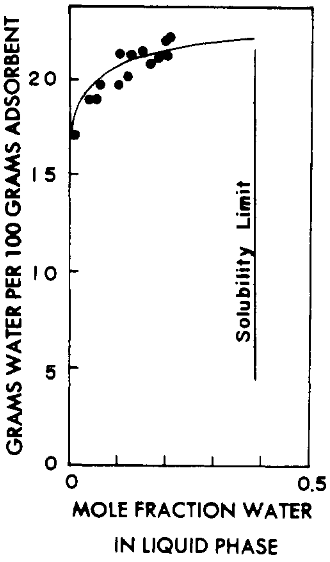


Figure 1. Comparison of calculated isotherm with experimental data for *p*-dioxane-water-5A Molecular Sieves

— Calculated isotherm

● Experimental data



←
Figure 2. Comparison of calculated isotherm with experimental data for benzyl alcohol–water–5A Molecular Sieves
— Calculated isotherm
● Experimental data

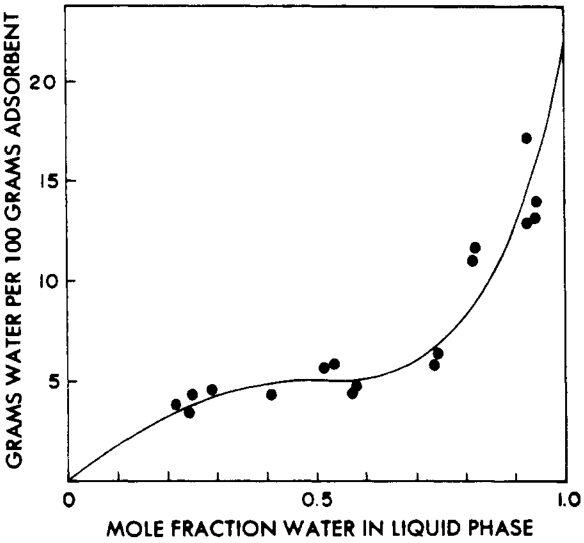


Figure 3. Liquid phase isotherm for ethylenediamine–water–4A Molecular Sieves

pressure of water over the two-liquid phase, benzyl alcohol-water system was assumed to be equal to the vapor pressure because of the low solubility of benzyl alcohol in water reported by Seidell and Linke. The four data points listed in Table III lie on a smooth curve and are considered to be reliable.

RESULTS

The calculation procedure described previously was used to calculate liquid phase isotherms for comparison with experimental data. For these systems, the pressure is low enough so that fugacities may be replaced by partial pressures.

p-Dioxane–Water–5A Molecular Sieve at 25° C. Using the published vapor isotherm for water on 5A Molecular Sieves (*3*), and vapor-liquid equilibrium data for the *p*-dioxane-water system at 25° C. (*1*), the liquid phase isotherm was calculated and is plotted on Figure 1 along with the experimental data points. The calculated isotherm agrees quite well with the experimental data points.

Benzyl Alcohol–Water–5A Molecular Sieve at 25° C. The partial pressure data of Table III were used along with the vapor isotherm for water on 5A Molecular Sieve (*3*) to calculate the liquid phase isotherm for this system. The calculated isotherm and the experimental data points are plotted on Figure 2 which shows that the agreement is good.

Ethylenediamine–Water–4A Molecular Sieve at 25° C. The system ethylenediamine-water shows evidence of large negative deviations from ideal behavior as witnessed by maximum boiling azeotropes in the range 45° to 175° C. (*6*), an extremely large exothermic heat effect on mixing, and compound formation in the solid-liquid phase diagram (*7*). No vapor-liquid equilibrium data are available for this system at 25° C., and the partitioning technique employed for the benzyl alcohol–water system was not workable hence no liquid phase isotherm could be calculated. The experimental data are plotted in Figure 3. The distorted shape of the isotherm illustrates the importance of solution effects in determining liquid phase adsorption equilibria.

CONCLUSIONS

The proposed analysis of liquid phase adsorption equilibria in systems containing Molecular Sieve adsorbent, and one adsorbable component has been quantitatively tested for two systems and was found reliable. Although a quantitative test was not possible, the third system strikingly illustrates the effect of solution behavior on liquid phase adsorption equilibria.

NOMENCLATURE

A = weight of adsorbent, grams
a = adsorbent loading, grams per 100 grams adsorbent
L_0 = initial weight of liquid solution, grams
w = weight fraction of adsorbable component in liquid phase
w_0 = initial weight fraction of adsorbable component in liquid phase

LITERATURE CITED

(1) Chu, Ju Chin, Wang, S.L., Levy, S.L., Paul, R., "Vapor-Liquid Equilibrium Data," J.W. Edwards Publishers Inc., Ann Arbor, Mich., 1956.
(2) Kipling, J.J., Wright, E.M., *Trans. Far. Soc.* **55**, 1185 (1959).
(3) Linde Company, Trade Literature on Molecular Sieves, Form 9690 E, 1962.
(4) Seidell, A., Linke, W.F., "Solubilities of Inorganic and Organic Compounds," Supplement to 3rd ed., Van Nostrand Co., New York, 1952.
(5) Timmermans, J., "Physico-Chemical Constants of Binary Systems," Vol. **3**, Interscience, New York, 1960.
(6) Union Carbide Chemicals Company, Trade Literature.
(7) Wilson, A.L., *Ind. Eng. Chem.* **27**, 867 (1935).

RECEIVED for review September 24, 1964. Accepted February 10, 1965.

CORRECTION:

In the article "Refractive Index of Phosphoric Acid Solutions at 25° C.," [J. CHEM. ENG. DATA **9**, 508 (1964)] there are two errors. The second and third sentences of the paragraph following Equation 3, page 509, should read "This precision of Δn corresponds to an uncertainty in j_m of 0.22 fringe. Throughout the entire range of concentration, . . . " The second sentence of the paragraph following Equation 7, page 509, should read "This requirement is met for phosphoric acid, within the accuracy of Equation 3, for all except the most dilute solutions in Table I of reference (*4*)—that is, when the top solution of the diffusion cell is water."
