LIQUID PHASE ADSORPTION EQUILIBRIA WITH MOLECULAR SIEVES

by

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PURPOSE

The purpose of this work is to study liquid phase adsorption equilibrium in systems containing a molecular sieve as adsorbent, one adsorbable component, and one non-adsorbable component; and to test the applicability of a proposed method of predicting equilibrium relationships in such systems.

NOMENCLATURE

A	amount of molecular sieves in grams.
$\underline{a}$	amount (in grams) of adsorbate per gram of adsorbent.
a_∞	asymptotic value of $\underline{a}$.
b	constant.
C_1	Langmuir constant.
C_2	Langmuir constant.
L_0	amount of liquid mixture charged in grams.
p	partial pressure.
t	temperature.
w	final weight fraction of adsorbable component in liquid mixture.
w_0	initial weight fraction of adsorbable component in liquid mixture.
x	final mole fraction of adsorbable component in liquid mixture.
x_0	initial mole fraction of adsorbable component in liquid mixture.
X_w	mole fraction of water in liquid mixture.
γ	Activity coefficient.

INTRODUCTION AND THEORETICAL BACKGROUND

Molecular sieves is the name of a class of crystalline zeolites manufactured by the Linde Company under composition of matter and manufacturing process patents (1). These zeolites are metal aluminium silicates and have the property of selectivity adsorbing compounds based on molecular dimensions.

The pore size of molecular sieves depends on the form of zeolite which in general is represented as $M_{\frac{2}{n}}$: Al_2O_3 : X SiO_2 : Y H_2O where M represents a metal cation and n its valence. A particular X and Y along with M form particular size sieve. Listed below are the chemical formulas and nominal pore sizes of the three most common molecular sieves (1,2).

Type sieve	Formula	Nominal pore size (Angstroms)
4 A	$Na_{12}(AlO_2)_{12}(SiO_2)_{12} \cdot 27H_2O$	4
5 A	$Ca_6(AlO_2)_{12}(SiO_2)_{12} \cdot 27H_2O$	5
13 X	$Na_{86}(AlO_2)_{86}(SiO_2)_{106} \cdot 27H_2O$	10

Molecular sieves differ from other gel-type adsorbents in respect to the uniform pore size formed by the holes in the crystal lattice. Consequently instead of having a range of pore sizes, a given type of molecular sieves has pores all of the same dimension, thus permitting quantitative separation between molecules small enough to enter the pores and those too large to enter. In addition to this property of selectivity based on molecular sizes, molecular sieves also show strong selectivity for unsaturated and polar compounds (1). Molecular sieves also show the property of regenerability, hence the adsorption is reversible.

When a gas or liquid is exposed to a porous adsorbent, a certain amount of gas or liquid is adsorbed at equilibrium at a given temperature and pressure. The amount of gas or liquid adsorbed and the composition of adsorbed phase and fluid phase are a function of the adsorbent and the adsorbate, temperature and pressure. Lower temperature, higher pressure, and higher concentration favor more adsorption.

In dealing with the adsorption of pure gases, there are only three variables to correlate, so the adsorption equilibrium data is represented in three ways: Adsorption isobars ($\underline{a}$ vs t at constant p), adsorption isotherms ($\underline{a}$ vs p at constant t), adsorption isosteres (p vs t at constant $\underline{a}$).

Adsorption of gases on molecular sieves has been shown generally to follow the Langmuir isotherm (1) where the amount of material adsorbed per gram of adsorbent asymptotically approaches a limiting value (a_∞) as the pressure increases. The mathematical expression of the Langmuir isotherm is

$$\underline{a} = \frac{C_1 C_2 p}{1 + C_1 p} \qquad (1)$$

As p increases $\underline{a}$ approaches its limiting value a_∞. For large p, Equation 1 reduces to

$$\underline{a} = C_2$$

hence

$$C_2 = a_\infty$$

Equation 1 can then be written

$$\frac{\underline{a}}{a_\infty} = \frac{C_1 p}{1 + C_1 p} \qquad (1a)$$

where $\frac{a}{a_\infty}$ is termed the fractional loading.

Corresponding Langmuir equations for liquid phase adsorption are

$$a = \frac{C_1 C_2 x}{1 + C_1 x} \qquad (2)$$

and

$$\frac{a}{a_\infty} = \frac{C_1 x}{1 + C_1 x} \qquad (2a)$$

The Langmuir equations can be rearranged and put into the linear form to facilitate the correlation of experimental data.

$$\frac{p}{a} = \frac{1}{C_1 C_2} + \frac{p}{C_2} \qquad (1')$$

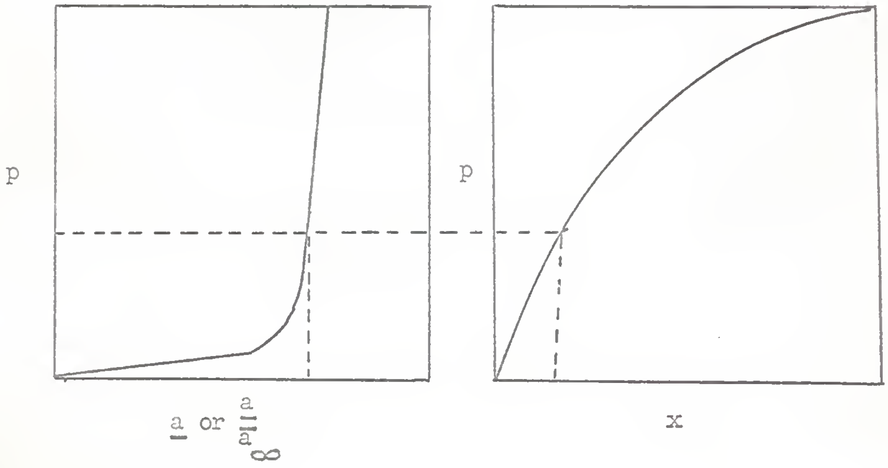
$$\frac{x}{a} = \frac{1}{C_1 C_2} + \frac{x}{C_2} \qquad (2')$$

If the data follow the Langmuir isotherm a plot of $\frac{p}{a}$ vs p or $\frac{x}{a}$ vs x will yield a straight line and the constants C_1 and C_2 may be obtained from the slope and the intercept. The evaluation of these constants allows one to plot a normalized curve of fractional loading vs x.

Kipling and Wright (3) have studied adsorption on 5A molecular sieves from four binary liquid mixtures each of which contained one adsorbable and one large non-adsorbable component. They attempted to correlate and explain their results on the assumption that the amount of adsorbable component held by the adsorbent was constant at all concentrations. This assumption leads to the conclusion that the liquid phase isotherm for any particular adsorbable component is always the same regardless of the type of non-adsorbable component present in the liquid phase. Kipling and Wright further stated "...the sorbent can completely remove water from an aqueous mixture if the volume of water present is less than is required to fill the pore space in the sample of sorbent used."

For this thesis the proposed method of explaining liquid phase adsorption equilibrium in binary mixtures containing only one adsorbable component is based on the concept that corresponding to each fractional loading of the adsorbent there is a definite fugacity of the adsorbable component. In essence this neglects the influence of the other non-adsorbable component upon the adsorbed phase. This is believed to be a reasonable assumption because the adsorbed phase resides in the interior of the adsorbent which is inaccessible to the non-adsorbed component.

With this approach liquid phase adsorption equilibrium can be easily calculated if the vapor isotherm of the adsorbable component is available and if the partial pressure of the adsorbable component is known at various liquid phase concentrations. The calculation procedure is best illustrated graphically as shown below:

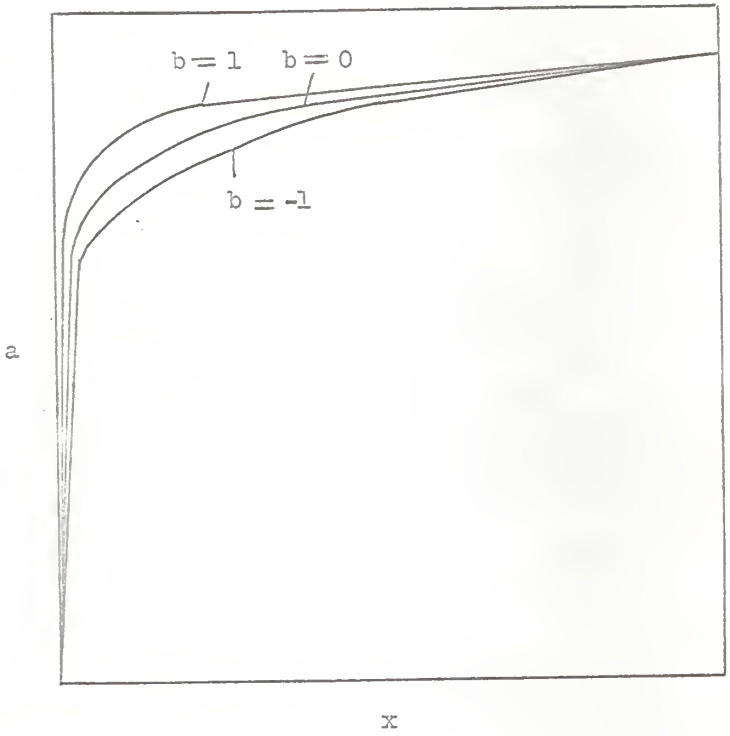


For every fractional loading of the adsorbent there is an equilibrium partial pressure p of the adsorbable component as given by the left hand figure (vapor isotherm). Also in the liquid phase there is an equilibrium partial pressure p of the adsorbable component corresponding to each mole fraction as given by the right hand figure. The adsorbed phase and the liquid phase are in equilibrium when the partial pressure of the adsorbable component is the same in both phases; hence, reading the two figures at the same value of p allows one to obtain equilibrium values of $\underline{a}$ or $\frac{a}{a_{\infty}}$ and x. These values are used to construct the liquid phase isotherm.

This method of calculating liquid phase adsorption equilibrium takes the solution effect in consideration which Kipling and Wright (3) failed to consider. Due to solution effects, the loading $\underline{a}$ varies with the type of deviation from ideal behavior. This effect is illustrated in the following figure where liquid phase isotherms for water on 5A Molecular Sieves at 25°C are plotted for three types of solution behavior. The isotherms were calculated for hypothetical systems where the activity coefficient of water was assumed to follow the simple relation

$$\ln \gamma_W = b(1 - x_W)^2$$

The three systems correspond to ideal solutions ($b = 0$), solutions which deviate positively ($b = 1$), and solutions which deviate negatively ($b = -1$) from ideal behavior.


b = 1
b = 0
b = -1
a
x

EXPERIMENTAL PROCEDURE AND CALCULATIONS

The apparatus used in this work was a 20 x 13 x 11 inch water bath equipped with cooling coils and electric heater. The bath temperature was regulated at 25°C by means of a relay which controlled the heater input. Temperature control was quite good as no fluctuation could be observed in the thermometer reading. The bath also had a rocker plate which was driven eccentrically by an electric motor. The rocking motion of the plate provided agitation for the bath as well as for the contents of flasks which were attached to the plate by means of spring clips.

The experimental procedure consisted of contacting weighed amounts of adsorbent and liquid mixture of known composition until equilibrium was established. A 125 ml. screw cap flask was weighed empty and then with 12 to 25 grams of molecular sieves and then with 50 to 70 grams of liquid mixture of known initial composition. The flask was then capped and further sealed with plastic tape, then placed in the constant temperature bath. The liquid phase composition was checked after two days and daily thereafter until a constant final composition was approached.

Refractive index was used as the measure of compositions in all three systems except for the ethylene-diamine--water system in the range of 0 to 50 mole percent of water. All the systems were calibrated for refractive index versus composition by finding the refractive indices of mixtures of known composition. All the refractive indices were read at 25°C and to an accuracy of ±0.0001. Calibration curves for all three systems are given in the appendix.

For the ethylene-diamine--water mixtures in the range 0 to 50 mole percent water analyses were performed by titrating a known weight of mixture against one normal hydrochloric acid with methyl orange as an indicator. Hydrochloric acid forms a di-chloride with ethylene-diamine (4), so that knowing the amount of hydrochloric acid used the amount of ethylene-diamine in the known weight of mixture could be determined.

Type 5A molecular sieves were used to adsorb water from the liquid mixture of p-dioxane and water; type 4A sieves were used to adsorb water from a mixture of ethylene-diamine and water and to adsorb methyl alcohol from a mixture of methyl alcohol and methyl-ethyl-ketone.

The expected non-adsorbable components in all three systems namely p-dioxane, ethylene-diamine and methyl-ethyl-ketone were tested for non-adsorptivity by mixing them individually with benzene, a known non-adsorbable compound, and by contacting this mixture with molecular sieves. If after a period of 3 or 4 days there was no change in the refractive index of the mixture it was assumed that the component was non-adsorbable on the molecular sieves.

The calculation of adsorption per gram of adsorbent is based on a material balance over the adsorbed component.

The amount of non-adsorbable component in liquid mixture is $L_0(1 - w_0)$

The amount of total liquid phase at end of adsorption is $\dfrac{L_0\,(1 - w_0)}{(1 - w)}$

The quantity adsorbed is then $L_0 - \dfrac{L_0(1 - w_0)}{(1 - w)} = \dfrac{L_0(w_0 - w)}{(1 - w)}$

The quantity adsorbed is also $A\,\underline{a}$

therefore,

$$\underline{a} = \frac{L_0 (w_0 - w)}{A \ (1 - w)} \qquad (3)$$

Experimental errors can be classified as random and systematic. Random errors depend upon the precision with which the measurements are made and can be analysed through the use of the calculus. The maximum possible error in $\underline{a}$ can be obtained from equation 3 and is given by

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

where $\underline{a} = f\,(A, L_0, w, w_0)$

$$d\,\underline{a} = \left[\frac{w_0 - w}{A(1 - w)}\right] dL_0 - \left[\frac{L_0 (w_0 - w)}{A^2 \ (1 - w)}\right] dA + \left[\frac{L_0}{A \ (1 - w)}\right] dw_0$$

$$+ \left[\frac{L_0 \ (1 - w_0)}{A \ (1 - w)^2}\right] dw \qquad (4)$$

The experimental error in a is due to uncertainties in determining weights ($dL_0 = dA = \pm 0.0002$ gm) and initial and final compositions. Errors in the composition (dw and dw_0) result from limitations of the analytical procedure. The refractive index can be determined to ±0.0001, however, the resulting error in composition depends upon the refractive index-composition calibration curve.

RESULTS AND DISCUSSION

P-Dioxane--Water:

Water is known to be an adsorbable component on type 5A molecular sieves. P-Dioxane mixed with benzene, a known non-adsorbable compound on 5A sieves, showed no change in composition when kept in contact with 5A sieves, hence showing that it was neither adsorbable on 5A sieves nor had any adsorbable impurities which would effect the measurements.

The experimental data are shown in Table 1 in which the last column, a, is calculated by Equation 3. Values a are plotted versus x in Figure 1 and values of $\frac{x}{a}$ are plotted versus x in Figure 2. The Langmuir constants, C_1 and C_2 of equation 2 were evaluated graphically from Figure 2 and also by a computer program (5) for least square fit of the data to Equation 2'. The graphically determined constants were used to draw a Langmuir isotherm through the experimental points in Figure 1.

Most of the scattering of the points in Figure 1 can be accounted for by the random errors as calculated by Equation 4. This shows that the error in the region $x < 0.1$ is about ±0.01 and in the region $x > 0.9$ is about ±0.001.

The vapor-liquid equilibrium data for the p-dioxane--water system at 25°C was taken from the literature (6) and was found to be thermodynamically consistent. Using this data and the vapor isotherms for water on 5A sieves at 25°C (7) the curve of a versus x was determined by the proposed method. The experimental data are compared with the predicted isotherm in Figure 3 where it is apparent that the agreement is quite good and within the experimental errors.

The regenerability of molecular sieves and hence the reversibility of the adsorption operation was tested by using regenerated adsorbent to determine several points on the isotherm. These points agreed with points taken with fresh adsorbent. The molecular sieves were regenerated by heating at 650°F for 36 hours in a furnace purged with dry air.

Table 1. Data for the system p-dioxane--water at 25°C.

A	L_0	x_0	x	$\underline{a}$
15.9455	50.3822	0.2110	0.0100	0.1635
21.3465	55.7301	0.2620	0.0200	0.1385
21.0616	60.6633	0.3000	0.0490	0.2034
12.6103	57.5448	0.2110	0.0500	0.1898
19.6228	61.3110	0.2620	0.0755	0.1992
8.9960	75.9490	0.2900	0.0975	0.2082
16.5905	60.6190	0.3000	0.1140	0.2057
18.2394	74.7793	0.2945	0.1225	0.2145
12.8741	61.1710	0.2910	0.1500	0.2000
12.6342	60.7663	0.3000	0.1625	0.2118
14.8169	74.7632	0.2955	0.1840	0.1950
20.0868	75.0422	0.4025	0.2630	0.2111
18.1245	76.1949	0.4025	0.2910	0.2112
18.7320	74.7890	0.4225	0.3050	0.2115
14.9318	75.3898	0.4440	0.3580	0.2137
10.1533	76.2772	0.4440	0.3900	0.2101
19.9369	75.2434	0.5440	0.4575	0.2168
12.0019	76.7073	0.5440	0.4975	0.2131
10.0035	75.6235	0.5440	0.5050	0.2146
20.2354	75.6056	0.7520	0.7220	0.2101
21.3544	64.5244	0.7525	0.7250	0.2135
20.9697	75.0486	0.8875	0.8750	0.2167
16.1721	74.6912	0.8875	0.8780	0.2109
17.8530	59.7757	0.9540	0.9501	0.2163

Table 2. Langmuir constants for the system p-dioxane--water.

Langmuir constants as obtained graphically from figure 2:

$C_1 = 232.500$

$C_2 = 0.215$

Langmuir constants as obtained by least squares computer program:

$C_1 = 194.4000$

$C_2 = 0.2140$

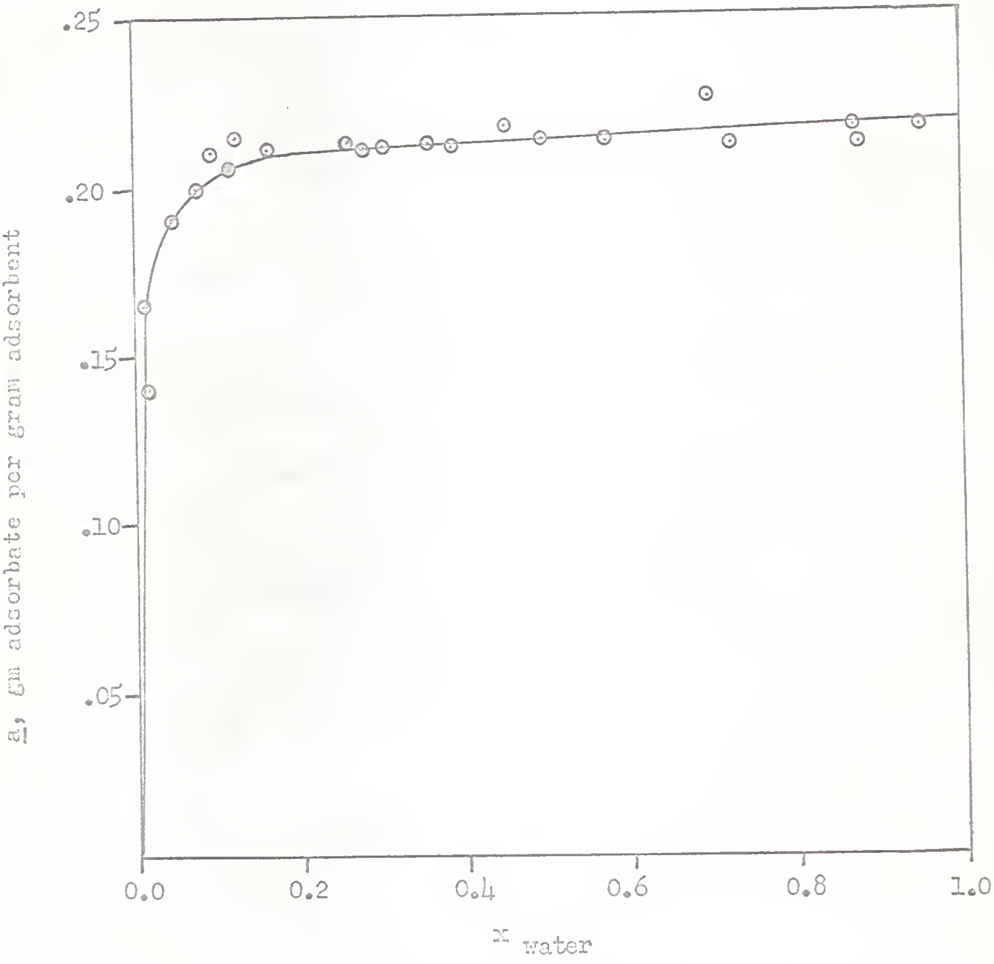


Fig. 1. Amount of adsorbate per gram adsorbent versus mole fraction of water in liquid at 25°C in p-dioxane--water system.

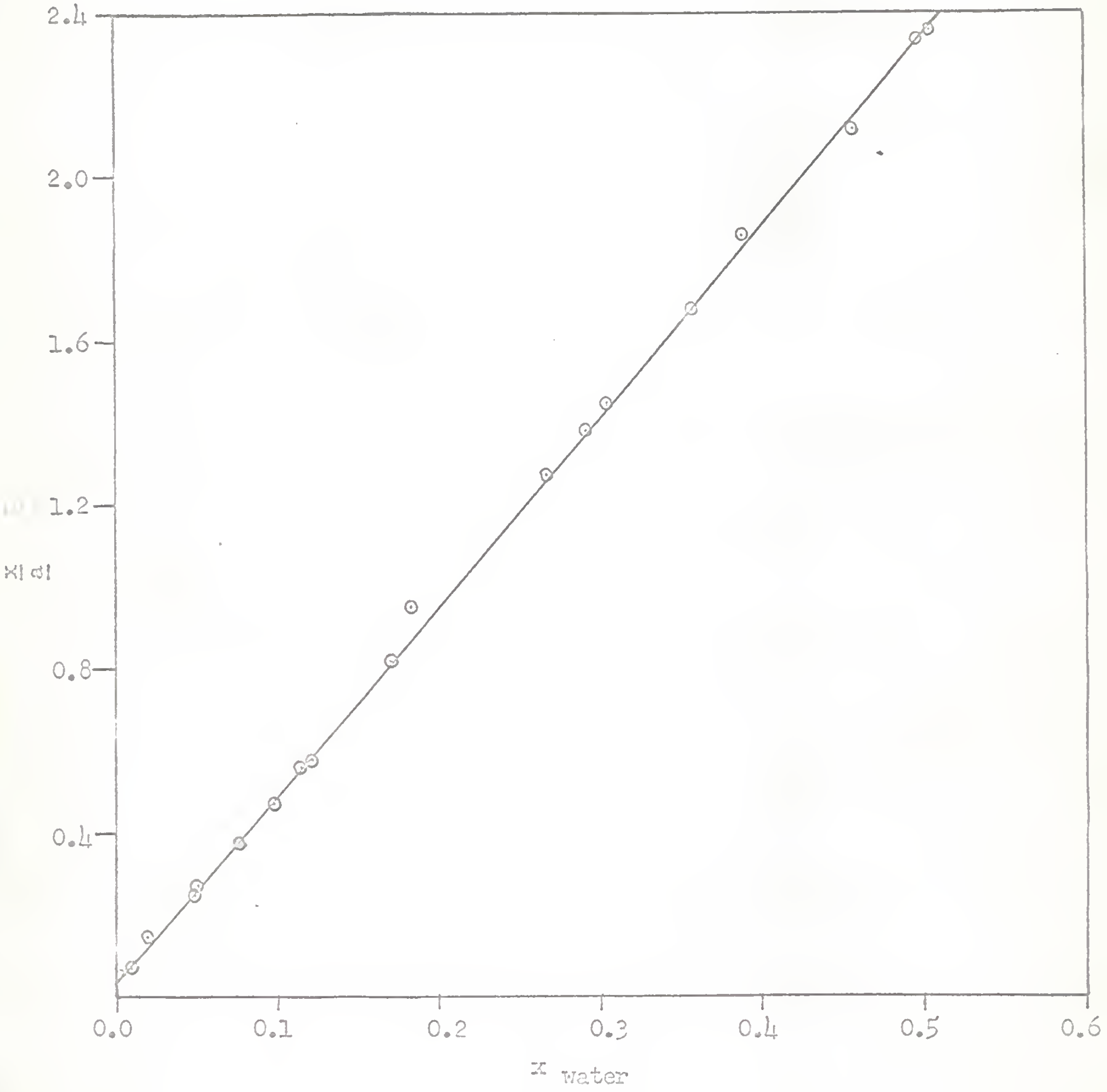


Fig. 2. $\frac{x}{a}$ versus mole fraction of water in liquid at 25°C in p-dioxane--water system.

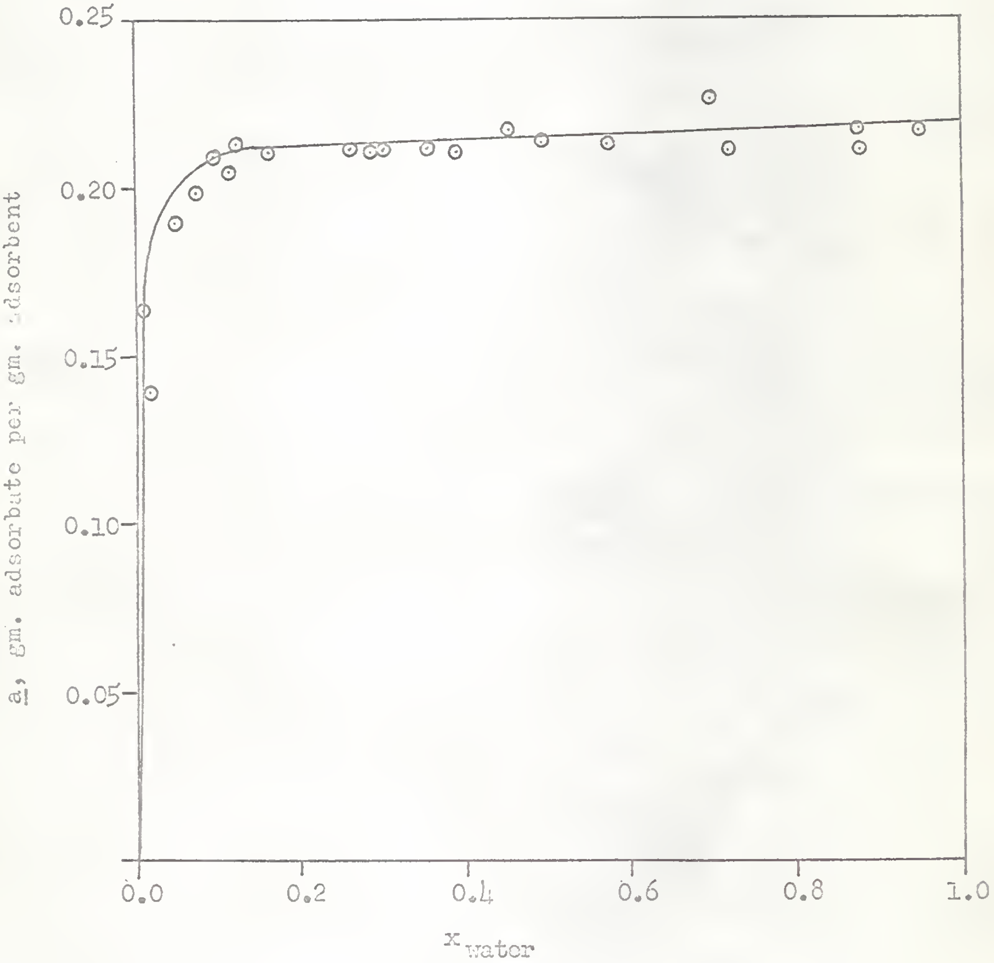


Fig. 3. Comparison of experimental points with predicted a versus x curve for water in p-dioxane--water system.

Methyl Alcohol--Methyl-Ethyl-Ketone:

Methyl alcohol is known to be adsorbable on 4A molecular sieves (8). Methyl-ethyl-ketone mixed with benzene, a known non-adsorbable component on 4A sieves, showed no change in composition when kept in contact with 4A sieves hence showing that it was neither adsorbable on 4A sieves nor had any impurities that would effect the measurements.

The data taken are shown in Table 3 where the last column was calculated by Equation 3. Values of $\underline{a}$ are plotted versus x in Figure 4 and the values $\frac{x}{a}$ are plotted versus x in Figure 5. The Langmuir constants, C_1 and C_2 of Equation 2 were evaluated graphically from Figure 5 and also by a computer program (5) for least square fit of the data in Equation 2'. The graphically determined constants were used to draw a Langmuir isotherm through the data in Figure 4.

Figure 4 reveals considerable scattering of data points. An analysis of the experimental error by means of Equation 4, however, shows that the random error in $\underline{a}$ in the region $x < 0.08$ is about ± 0.013 (± 0.1 in $\frac{a}{a_\infty}$) and in the region $x > 0.9$ is about ± 0.0024 (± 0.02 in $\frac{a}{a_\infty}$). Thus when viewed in the light of the expected random error the data are reasonably good.

The partial pressure of methyl alcohol over methyl alcohol--methyl-ethyl-ketone solutions at 25°C was calculated from activity coefficients evaluated from vapor-liquid equilibrium data reported in the literature (6). These reported isobaric data (100 mm Hg) covered the temperature range 18°-23°C and were found to be thermodynamically consistent. The assumption that activity coefficients did not change over the small temperature interval seems reasonable.

Since the asymptotic value of a for the liquid phase isotherm was not the same as the asymptotic value of a in the vapor phase isotherm for methyl alcohol (8), the ratio $\frac{a}{a_\infty}$ for both the vapor and the liquid were used to verify the proposed method. The value a_∞ for the vapor phase isotherm was determined by a Langmuir plot of the literature data (8). The a_∞ for the liquid isotherm was determined from the constants in Table 4.

Using the calculated partial pressure data and the $\frac{a}{a_\infty}$ versus p isotherm for methyl alcohol at 25°C, the curve $\frac{a}{a_\infty}$ versus x (Figure 6) was determined by the proposed method. The experimental data is compared with the predicted isotherm in Figure 6 where it is apparent that the agreement is good and the scattering is within the random errors of measurement.

Table 3. Data for the system methyl alcohol--methyl-ethyl-ketone at 25°C.

A	L_0	x_0	x	<u>a</u>
19.7419	39.2633	0.1045	0.0100	0.0895
15.6257	38.2935	0.1095	0.0140	0.1123
13.2022	48.3820	0.1045	0.0450	0.1066
10.3844	55.4585	0.1095	0.0635	0.1221
17.8079	46.7718	0.2010	0.1180	0.1268
12.3747	55.1427	0.2010	0.1550	0.1269
18.4946	40.0595	0.3100	0.2300	0.1208
15.5529	52.9948	0.3100	0.2650	0.1120
21.0570	39.4199	0.3640	0.2690	0.1355
14.1365	35.6424	0.3640	0.3250	0.1267
20.7845	41.3456	0.5095	0.4550	0.1233
15.3455	51.9003	0.5510	0.5200	0.1399
11.3588	58.3990	0.5510	0.5320	0.1334
23.1276	38.4240	0.6775	0.6338	0.1292
14.4278	55.8529	0.6775	0.6610	0.1343
21.7756	42.5321	0.8010	0.7800	0.1493
16.0273	54.3373	0.8010	0.7900	0.1422
21.3128	35.1443	0.8835	0.8715	0.1409
13.5820	54.5819	0.8835	0.8790	0.1344

Table 4. Langmuir constants for the system methyl alcohol--methyl-ethyl-ketone.

Langmuir constants as obtained graphically from Figure 5:

$C_1 = 370.1$

$C_2 = 0.1351$

Langmuir constants as obtained by least squares computer program:

$C_1 = 326.3$

$C_2 = 0.1331$

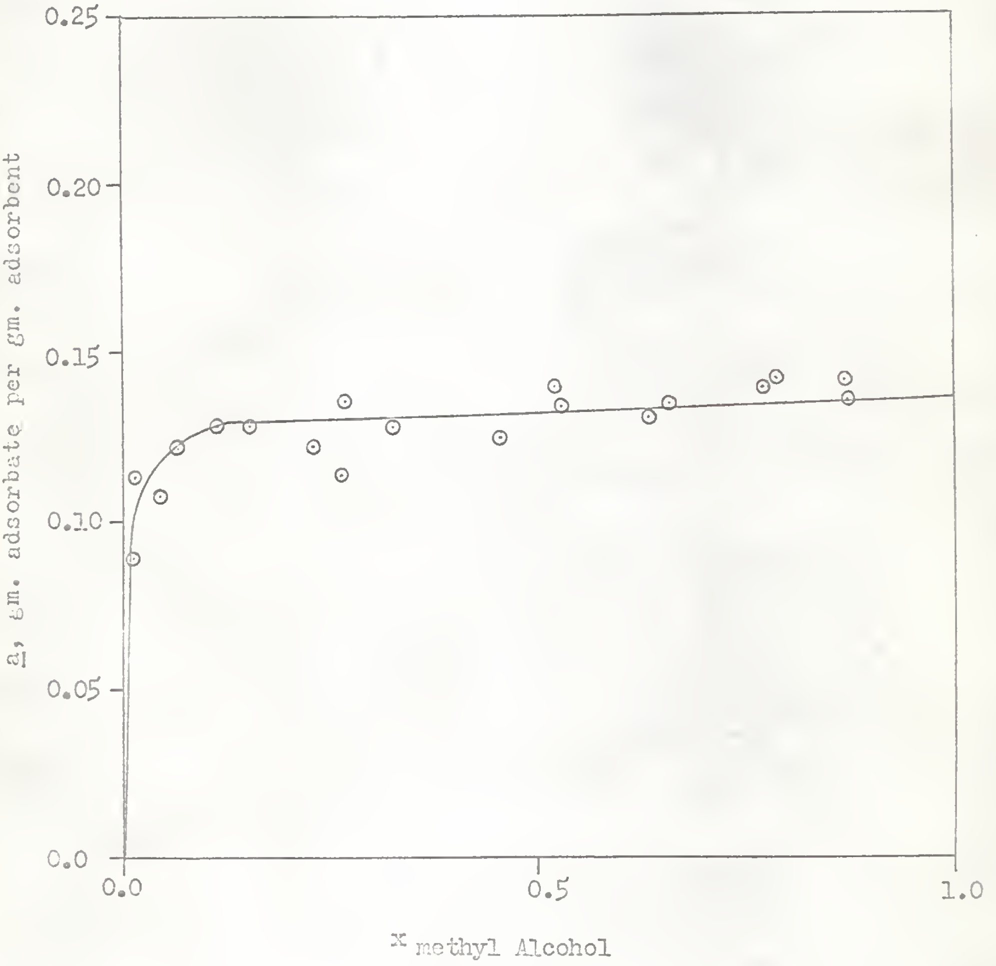


Fig. 4. Amount of adsorbate per gram adsorbent a versus mole fraction of Methyl Alcohol in liquid at 25°C in Methyl alcohol--Methyl-ethyl-ketone system.

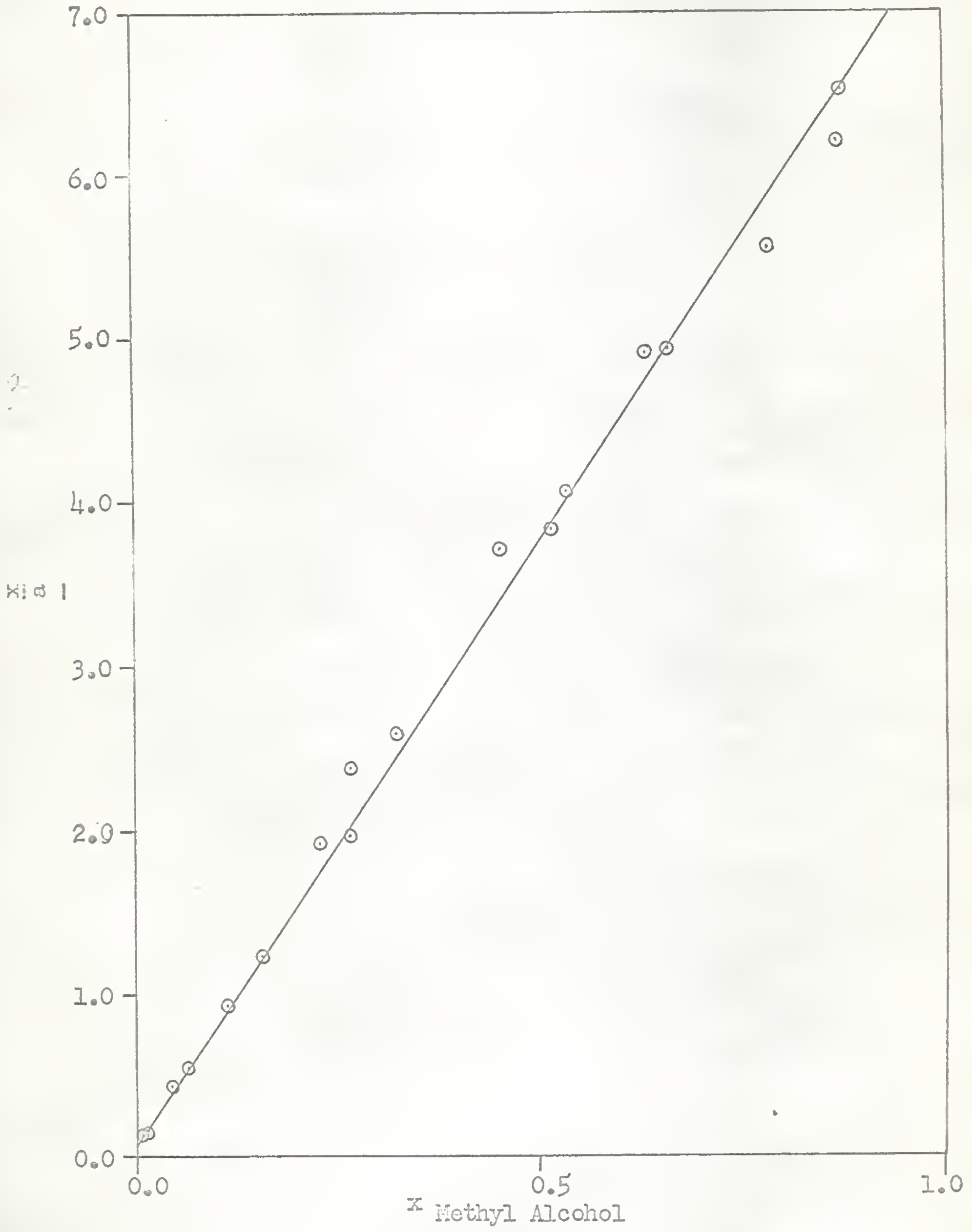


Fig. 5. $\frac{x}{a}$ versus mole fraction of Methyl alcohol in liquid at 25°C in methyl alcohol--methyl-ethyl-ketone system.

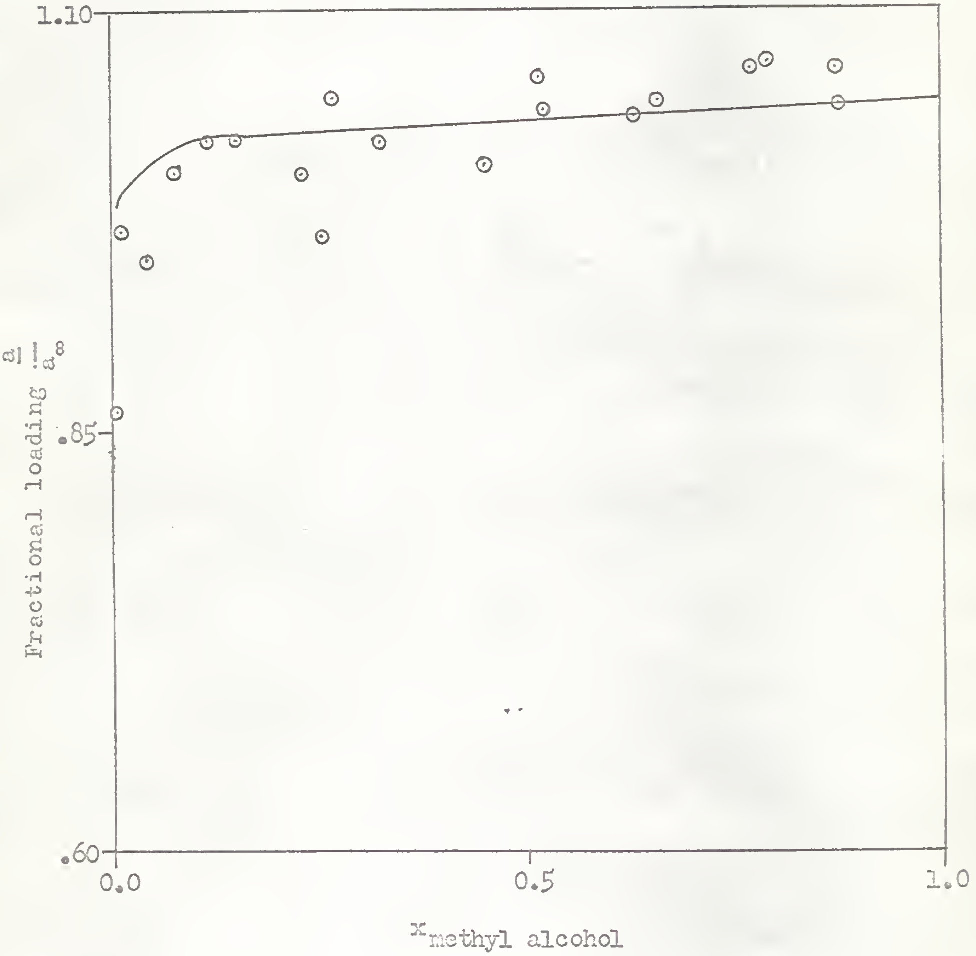


Fig. 6. Comparison of experimental points with predicted fractional loading $\frac{a}{a_\infty}$ versus mole fraction curve for Methyl alcohol in liquid at 25°C in methyl alcohol--methyl-ethyl-ketone system.

Ethylene-Diamine--Water:

Ethylene-diamine when mixed with a non-adsorbable component, benzene, and tested for adsorbability on 4A molecular sieves showed no adsorption and no adsorbable impurities.

The data taken are shown in Table 5 with the last column being calculated by Equation 3. The error in calculation as introduced by the experimental errors evaluated by Equation 4 in the range $x < 0.5$ is about ± 0.020 (assuming an error of ± 0.05 c.c. in burette readings during titrations), and is about 0.045 in the range $x > 0.8$. Considering these errors, a best possible curve was drawn through the experimental points in Figure 7.

Since no adequate vapor-liquid equilibrium data for the system were available, a predicted curve was not drawn. However, there are several indications of strong negative deviations, viz., maximum boiling azeotropes in the range 45°-175°C (9), hydrate formation at freezing point, 5°C (4) and an extremely large exothermic heat effect on mixing (4). The distorted shape of the adsorption isotherm, Figure 7, illustrates the importance of solution effects in determining liquid phase adsorption equilibrium.

This data also represents a contradiction to Kipling and Wright's statement (3) which assumes that the amount of adsorbable component held by the adsorbent is constant at all concentrations. This data shows that the amount of adsorbable component held depends strongly on concentration.

Table 5. Data for the system ethylene-diamine--water at 25°C.

A	L_0	x_0	x	a
24.3335	32.4945	0.2766	0.2179	0.0378
20.3987	44.9407	0.2766	0.2448	0.0345
21.4652	54.6548	0.2706	0.2486	0.0276
14.8796	68.2975	0.2706	0.2514	0.0436
25.6946	43.7257	0.3421	0.2913	0.0464
21.4177	58.9906	0.4298	0.4100	0.0429
25.3593	41.5371	0.4423	0.4160	0.0326
15.8477	68.2974	0.4298	0.4222	0.0242
26.9148	40.2040	0.5550	0.5137	0.0569
18.1808	51.1204	0.5550	0.5350	0.0593
22.1351	47.5779	0.5910	0.5735	0.0451
15.1133	56.8397	0.5910	0.5805	0.0482
22.0550	49.0890	0.7500	0.7390	0.0588
16.6589	58.7820	0.7500	0.7425	0.0645
21.6095	39.4197	0.8290	0.8130	0.1112
15.2859	50.0720	0.8290	0.8200	0.1167
25.3135	45.4143	0.9300	0.9236	0.1292
18.6554	52.9730	0.9300	0.9247	0.1722
23.0998	49.3795	0.9460	0.9420	0.1305
13.9007	60.5479	0.9460	0.9440	0.1397

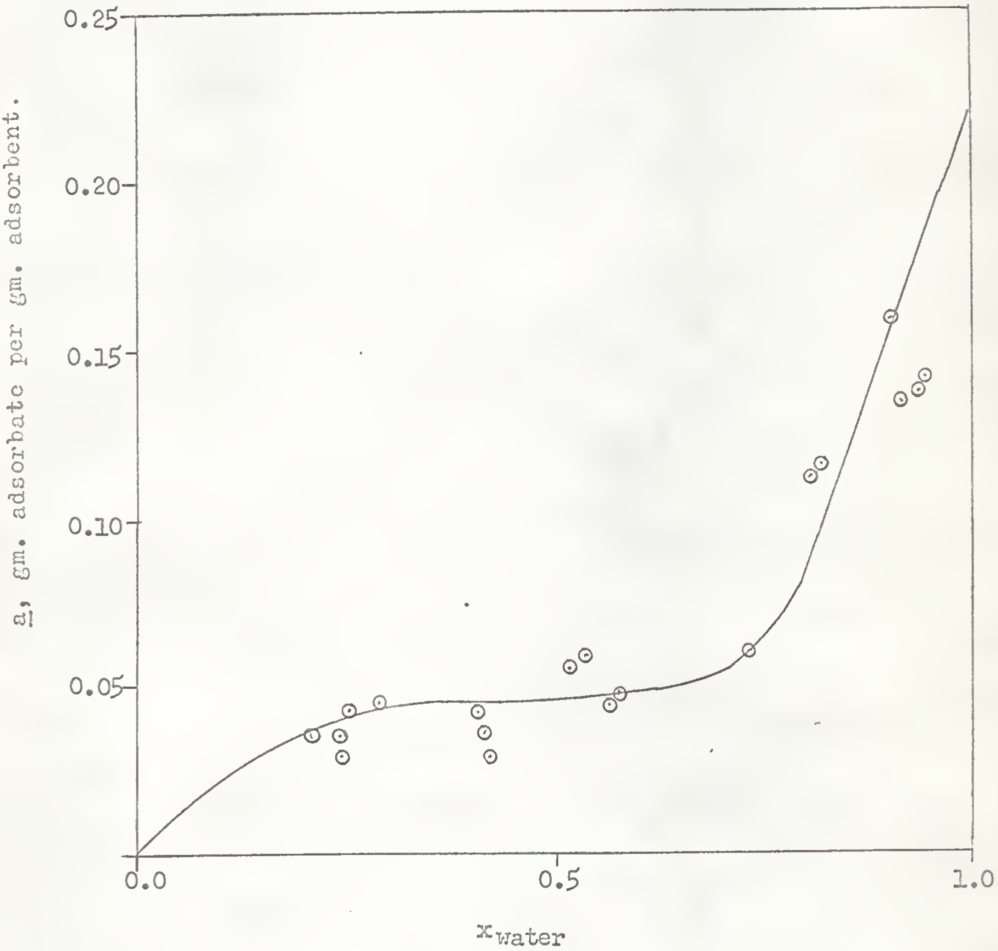


Fig. 7. a adsorbate per gram adsorbent versus mole fraction of water in liquid at 25°C in ethylene-diamine--water system.

CONCLUSIONS

The proposed method of explaining and predicting the liquid phase adsorption equilibria 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. This evidence substantiates the concept that the equilibrium partial pressure of the adsorbable component in the adsorbed phase is determined only by the fractional loading of the adsorbent and that the non-adsorbable component exerts its influence only in the liquid phase.

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APPENDIX

PROPERTIES OF CHEMICALS

The p-dioxane and ethylene-diamine used in this work were Eastman Chemical Industries' research grade products. Methyl alcohol and methyl-ethyl-ketone used were Fisher Scientific Company's products. The water used was laboratory distilled water. The non-adsorbable components p-dioxane, ethylene-diamine and methyl-ethyl-ketone showed no adsorbable impurities, hence they were not further purified. The literature values of vapor pressures at 25°C as used in calculations and experimental and literature refractive indices of the chemicals are listed in Table 6.

Table 6. Physical properties of the chemicals.

Chemicals	Vapor Pressure at 25°C. (Literature) mm. Hg.	Refractive Index at 25°C. (Experimental)	Refractive Index at 25°C. (Literature)
Ethylene-diamine	12.000 (4)	1.4541	1.4540* (4)
Methyl Alcohol	126.890 (10)	1.3251	1.3265 (10)
Methyl-ethyl-ketone	90.387 (10)	1.3750	1.3764 (10)
P-Dioxane	39.900 (11)	1.4200	1.4197 (12)
Water	23.756 (11)	1.3325	1.3333 (11)

*: at 26°C.

Table 7. Refractive index and composition for the three systems at 25°C.

p-Dioxane--Water		Methyl Alcohol--Methyl-ethyl-ketone		Ethylene-diamine--Water	
Mole Fraction dioxane	Refractive Index	Mole Fraction methanol	Refractive Index	Mole Fraction water	Refractive Index
0.0000	1.3325	0.0000	1.3750	0.0000	1.4541
0.0132	1.3375	0.0196	1.3748	0.0698	1.4540
0.0275	1.3483	0.0469	1.3742	0.1399	1.4537
0.0642	1.3560	0.0696	1.3741	0.1526	1.4536
0.0766	1.3600	0.1137	1.3729	0.2420	1.4534
0.1309	1.3740	0.3322	1.3671	0.3770	1.4531
0.1480	1.3752	0.4583	1.3630	0.5350	1.4475
0.3015	1.3960	0.6055	1.3564	0.6674	1.4367
0.3580	1.4006	0.7405	1.3486	0.7329	1.4244
0.4900	1.4075	0.8219	1.3424	0.8069	1.4061
0.5570	1.4100	0.9120	1.3330	0.8614	1.3897
0.5610	1.4103	0.9744	1.3275	0.8992	1.3761
0.6010	1.4115	1.0000	1.3251	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
0.0910	1.4187			0.9885	1.3376
1.0000	1.4200			1.0000	1.3323

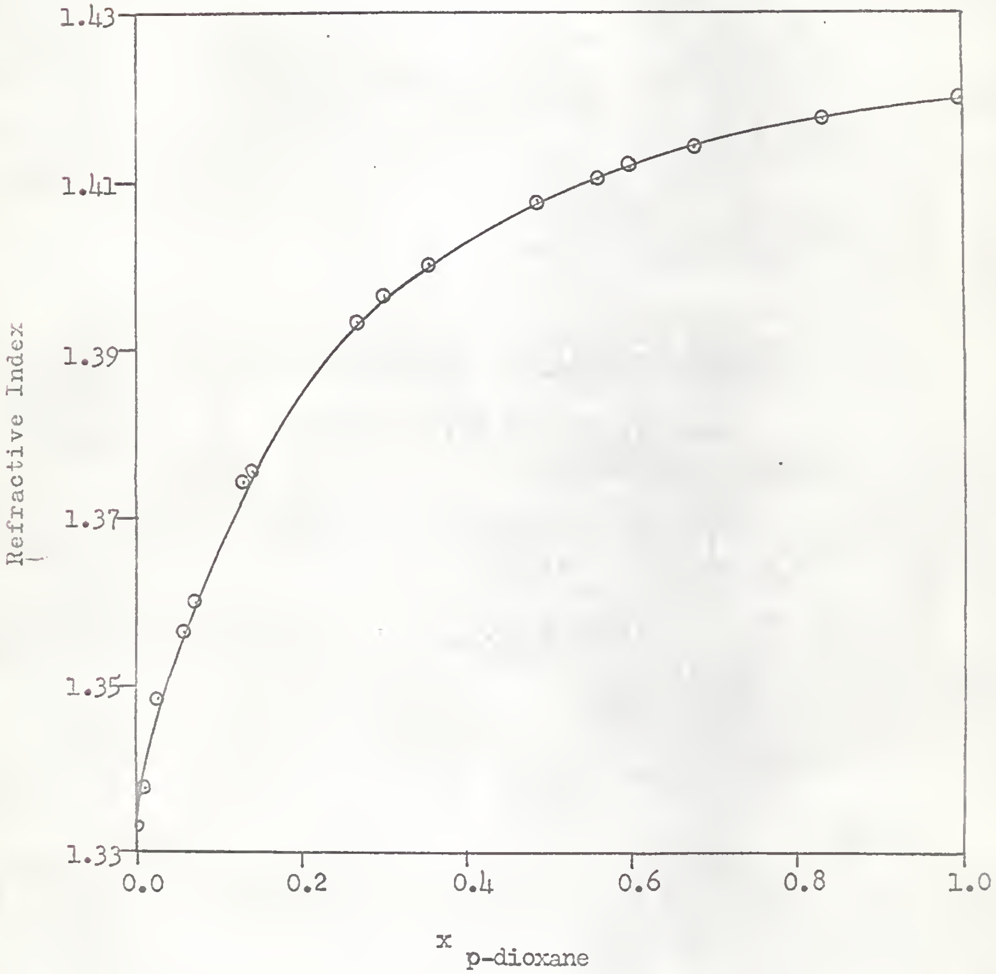

Fig. 8. Refractive index versus mole fraction of p-dioxane in water--p-dioxane system.

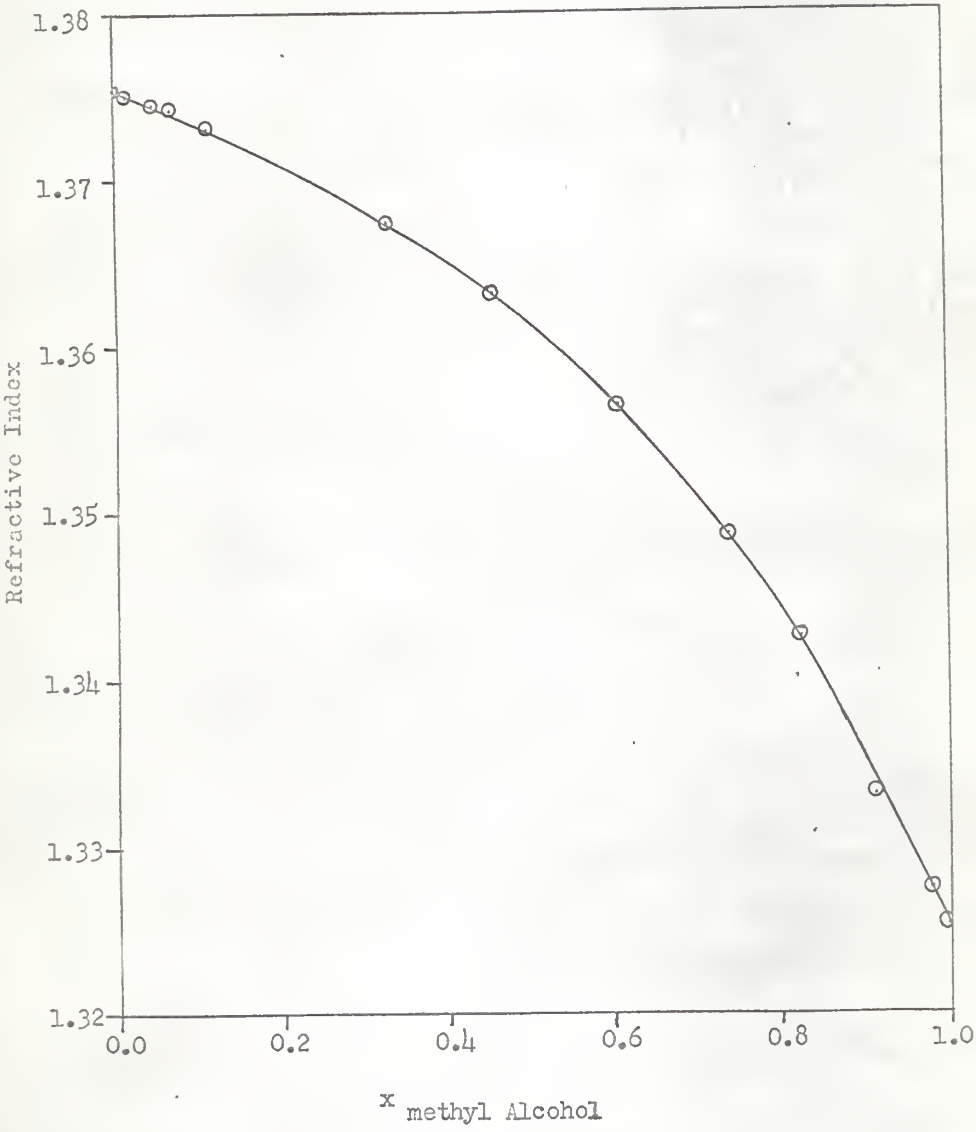

Fig. 9. Refractive index versus mole fraction of methyl alcohol in methyl alcohol--methyl-ethyl-ketone system.

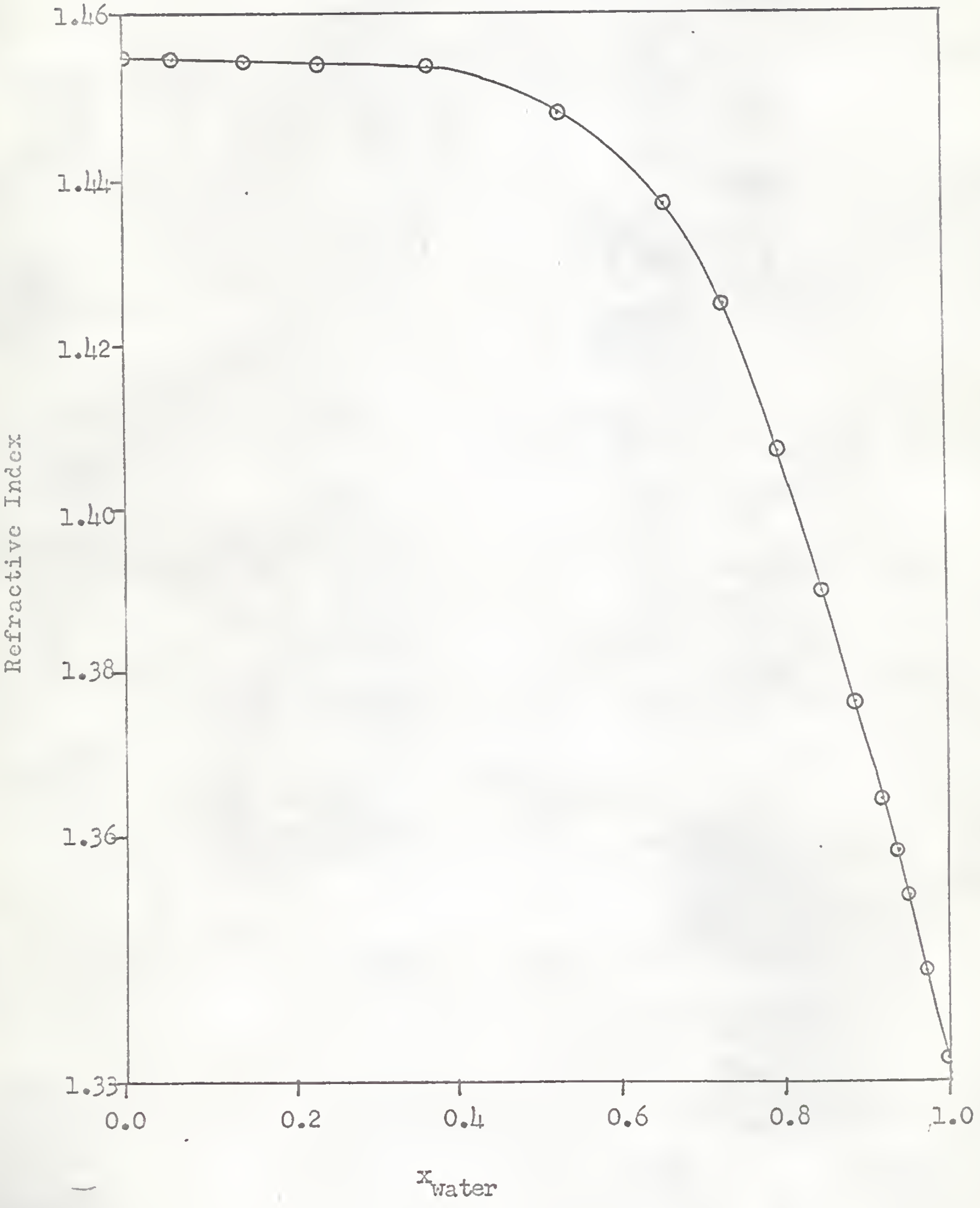

Fig. 10. Refractive index versus mole fraction of water in ethylenediamine--water.

LIQUID PHASE ADSORPTION EQUILIBRIA WITH MOLECULAR SIEVES

by

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B. S. Tri-State College, Angola, Indiana, 1963

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Liquid phase adsorption of water from p-dioxane--water and ethylene-diamine--water mixtures, and of methyl alcohol from methyl alcohol--methyl-ethyl-ketone mixtures on molecular sieves was studied in this work. The data are represented in graphical form as the loading of the adsorbed component on the adsorbent versus the liquid phase composition of the same component. The p-dioxane--water and methyl alcohol--methyl-ethyl-ketone systems were well fitted by a Langmuir isotherm.

A proposed method of explaining and correlating liquid phase adsorption equilibrium from binary mixtures containing only one adsorbable component was tested. This method is based on the concept that corresponding to each fractional loading of the adsorbent there is a definite fugacity of the adsorbable component which is uninfluenced by non-adsorbable components.

Predicted isotherms for water and methyl alcohol in the mixtures p-dioxane--water and methyl alcohol--methyl-ethyl-ketone compared well and within the experimental errors to the experimental data. No predicted isotherm for water in ethylene-diamine--water was drawn because of the unavailability of necessary physical data. However, this system strikingly shows the effect of solution behavior on liquid phase adsorption and lends support to the proposed method in a qualitative manner.