Sorption of Normal Paraffins by Molecular Sieves Type 5A

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MOLECULAR SIEVES offer excellent opportunities for separations which are otherwise difficult to achieve. Particularly, the isolation of normal paraffins—a classical problem in petroleum chemistry—can be very efficiently carried out by Molecular Sieves Type 5A. The similarity to separations by complexes with urea is obvious. The two separation methods are similar also in some details important in technical applications: The amount of reagent required is high, and the regeneration of the reagent is rather complicated.

The further development of uses for Molecular Sieves makes desirable an extensive set of pertinent data. The object of the present work, like that of a previous investigation of urea complexes (*15*), was a systematic description of the sorption of normal paraffins as a function of temperature, concentration, and molecular size. Reasonable completeness was considered to be more important than high accuracy.

For the representation, interpolation, and limited extrapolation of the experimental results a recently proposed sorption isotherm (*16*) has been found more useful than previously suggested relations. It leads to some crude conclusions concerning the mechanism of sorption in Molecular Sieves. A comparison with the theory of multilayer sorption of Brunauer, Emmett, and Teller furnishes interesting information.

The general characteristics of sorption on zeolites have been elucidated by Barrer (*1*). Molecular Sieves Type 5A have been investigated in the laboratories of Linde Co. (*3*). More recently, some other experimental studies (*5, 9*) and reviews (*7, 8*) concerned with this zeolite have been published.

EXPERIMENTAL

McBain Balance. Most of the equilibrium measurements reported here and all observations of kinetics were made on a quartz helix balance (*13*). The helix measures 17 mm. in diameter and 180 mm. in length, and has a capacity of about 2 grams. Its sensitivity is 8.21 ± 0.04 mg. per mm. at 50°, is constant over at least a 5° temperature range, and does not vary in time. About a gram of sorbent is contained in a stainless steel mesh bucket with an aluminum foil bottom, the bucket being suspended by a 400-mm. quartz fiber as a means of isolating the helix from a furnace which surrounds a tube containing the bucket. Samples were routinely dehydrated for 1 hour in vacuo at 400°. Kinetic observations were made with buckets of widely different shapes and sizes in order to ascertain the absence of staging within the sample. Halftimes of sorption and desorption (expressed approximately by first-order kinetics) below about 5 seconds were unobservable because of oscillation of the bucket in the case of sorption, and because of pumping speed limitations in the case of desorption. High desorption rates were measured under essentially adiabatic conditions, but were not corrected for the temperature decrease. Separate measurements suggest this might have been as much as 20° in extreme cases.

Volumetric Method. The McBain balance is inconvenient for measurements at equilibrium pressures much exceeding the vapor pressure at room temperature. Such measurements were made in a compact volumetric apparatus which, having been necessarily designed for larger quantities, also served as a check on the semimicro quartz helix measurements in the overlap region. The apparatus consists simply of a large tubular vessel accommodating about 70 grams of sorbent connected directly to a thermostated, calibrated tube at right angles to each other. After the sorbent is dried and the hydrocarbon sample frozen in the calibrated tube, the whole is sealed off and thermostated at an arbitrary temperature except for the calibrated arm, whose (lower) temperature determines the equilibrium pressure over the sorbent so long as liquid remains. Attainment of equilibrium was speeded by a rocking motion of the vessel.

Flow Method. Neither of the above methods is suitable for superatmospheric or multicomponent equilibria. Measurements of these kinds were carried out with the aid of a stainless steel tube containing the sorbent. A liquid charge is continuously pumped into the tube under pressures of up to 600 p.s.i.a., completely vaporized into a constant flow of helium, and thermostated to the temperature of the tube. Attainment of equilibrium throughout the tube is ascertained by constancy of the thermal conductivity of the effluent gas. The hydrocarbon feed is then interrupted and the sorbate stripped with helium, condensed, and weighed. Appropriate corrections are made for the interstitial volume in the column and for the volume of appurtenances. Multicomponent sorbates were analyzed by means of refractive index measurements.

Liquid Mixtures. The sorption of liquid binary mixtures was studied experimentally by the conventional method of observing the change in the value of some concentration-dependent property (refractivity in the present case) of a known amount of a liquid binary mixture on the addition of a definite amount of sorbent (*6*). The derivation of absolute sorption data from the results is made fairly definite by the characteristic geometry of the active surface of Molecular Sieves, which sets definite bounds on the pore volume. The more familiar case in which these bounds are necessarily more arbitrarily defined has been discussed (*2, 10, 11*). Sorption equilibria at room temperature and at equilibrium pressures as low as 5×10^{-7} mm. for cetane were measured by contacting varying amounts of 0.005 molar solutions of paraffins in carbon tetrachloride with sorbent. Equilibrium paraffin concentrations were determined by the measurement of infrared absorption in the 3.45-micron band. A correction was applied to account for failure of Raoult's law.

The sorbent in these studies is Linde's Molecular Sieves, Type 5A, $\frac{1}{16}$-inch pellets, containing 20 ± 0.5% bentonite or kaolin (*14*) binder as supplied, or crushed and screen-graded derivatives. Normal paraffins of 99% purity were further purified by passage through columns containing Type 4A Molecular Sieves and silica gel. Storage bottles normally contained some Type 4A pellets for the purpose of eliminating water. The carbon tetrachloride was used as supplied, but blanks were run because some impurities absorb at 3.45 microns. The most prominent impurity of this kind is probably chloroform, which is not sorbed by Type 5A Molecular Sieves.

RESULTS AND DISCUSSION

The Isotherm. The sorption cavity in the Type A Molecular Sieve is sufficiently large to accommodate about four *n*-pentane molecules. The estimated maximum number of

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molecules of different size which will fit into one cavity is shown by the broken line in Figure 1. The figure also contains observed saturation values at three temperatures. Taken together with the thickness of a paraffinic chain, about 4A., and the diameter of the roughly spherical cavity, 11.4A. (*17*), it might be thought that only a monolayer would be sorbed. Indeed, sorption invariably approaches Langmuir's isotherm in a limited range of low pressures.

At high coverage, however, increased sorption was observed, although multilayer sorption in the usual sense is hardly possible. Indeed, the sorption invariably follows Freundlich's equation with notable accuracy at high pressures. If q is the amount of sorbate expressed as weight per unit weight dehydrated sorbent, p is the equilibrium pressure, and A, B, and g are parameters varying with the temperature and the nature of the sorbate, the equation

$$q = Ap/(1 + Bp^{g}) \qquad (1)$$

with

$$0 < g < 1 \qquad (2)$$

has the desired properties. The sorption isotherm is linear at low pressures. At high pressures the sorption values of Equation 1 exceed those of Langmuir's equation by increasing amounts, and Equation 1 approaches Freundlich's relation

$$q = (A/B)p^{1-g} \qquad (3)$$

Equation 1 is a purely empirical relation and cannot furnish a basis for strict interpretation. But if we introduce the vapor pressure p° and the saturation sorption value

$$q_s = Ap^{\circ}/(1 + Bp^{\circ g}) \qquad (4)$$

we may write Equation 1 as

$$q = q_s(p/p^{\circ})^{1-g} \times (B/p^{1-g}) \times p/[1 + (B/p^{1-g}) \times p] \qquad (5)$$

in superficial analogy with Langmuir's equation. From Equation 5 we may crudely conclude that the number of sites with increasing pressure slowly increases to its final value q_s while the standard free energy of sorption decreases to the final value $RT \ln [Bp^{\circ g}]$. Such a conclusion fits very well the structure of Molecular Sieves: While at low pressures only a monolayer of sites is practically available, moderately more (but slightly weaker) sorption sites become available with increasing coverage.

One may ask whether the theory of multilayer sorption of Brunauer, Emmett, and Teller will represent sorption on Molecular Sieves reasonably well. Two equations (*4*) are to be considered. The first, expressed with the aid of the vapor pressure p°, the relative pressure

$$x = p/p^{\circ} \qquad (6)$$

and the monolayer value of q, q_m, furnishes for sorption in two layers

$$q = q_m c[x/(1-x)][1 + (h-2)x - (2h-1)x^2 + hx^3]$$
$$/[1 + (c-1)x + (0.5\,h - 1)cx^2 - 0.5\,chx^3]. \qquad (7)$$

The second gives for sorption in N layers

$$q = q_m c[x/(1-x)][1 - (N+1)x^N + Nx^{N-1}]$$
$$/[1 - (c-1)x - cx^{N-1}] \qquad (8)$$

Each of the equations 1, 7, and 8 contains three parameters.

The fit of the three equations was tested by means of a least squares program written by Henry Stone. Altogether 155 observations were available for pentane, heptane, decane, and hexadecane at one to five temperatures. The data had to furnish 42 parameters for any of the three equations. The over-all standard deviations were

5.0% for Equation 1
8.0% for Equation 7
6.8% for Equation 8

Some detailed comparisons for *n*-pentane are shown in Table I and Figures 2 and 3.

The experimental data favor Equation 1 slightly over 8 and more definitely over 7. Moreover, only Equation 1 shows the close approach near saturation to Freundlich's equation (straight line in a diagram such as Figure 3), which is very characteristic of the data (Figures 4 through 7). The neglect of intrasorbate and extramonolayer-sorbent interactions, implied in the BET relations, appears not to be very satisfactory in describing sorption in the close quarters of the Type 5A zeolitic cavity. Indeed, the general two-parameter BET equation is entirely inadequate.

In addition, Equation 1 is considerably more convenient. The experimental data and curves derived for Equation 1

Table I. Comparison of *n*-Pentane Isotherms

Isotherm	Quantity	Temp., ° C. 60	 198
Empirical (Eq. 1)	A	0.459	0.00380
	B	6.08	0.0890
	g	0.945	0.914
	Std. error, %	3.4	1.6
BET (Eq. 7)	q_m	0.0489	0.0531
	c	18,960	1,884
	h	1,556	66.4
	Std. error, %	8.6	3.0
BET (Eq. 8)	q_m	0.0878	0.0698
	c	5,040	1,030
	N	1.917	1.945
	Std. error, %	3.8	2.8

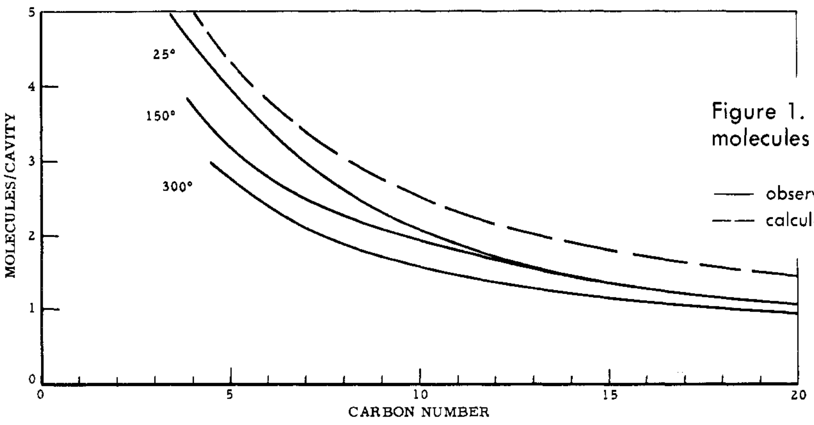

Figure 1. Number of normal paraffin molecules occupying one cavity at saturation,

—— observed
– – calculated from dimensions of cavity (*17*).

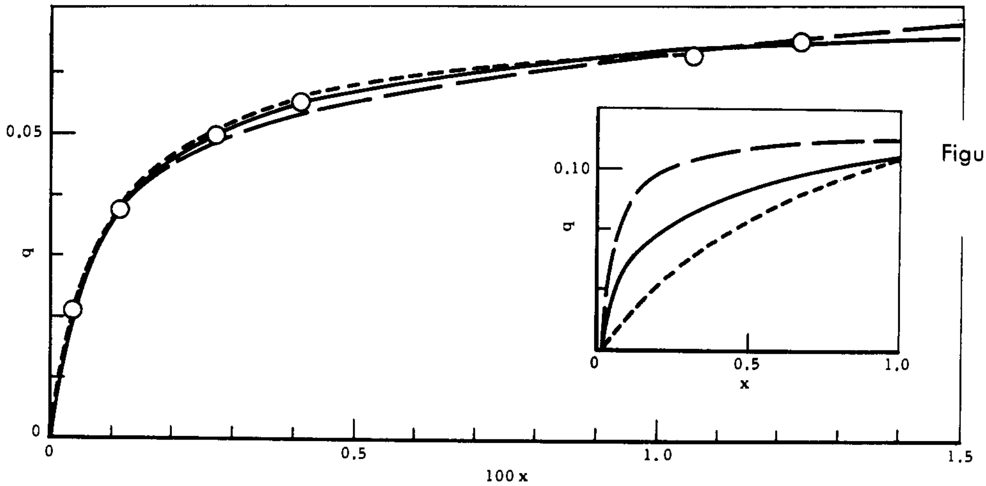

Figure 2. Least squares fit to *n*-pentane equilibrium data at 198°
—— Equation 1
— — Equation 7
---- Equation 8
○ observed data

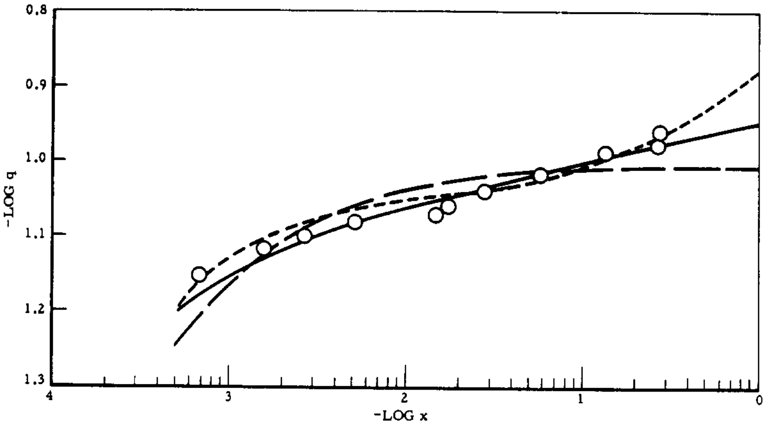

Figure 3. Least squares fit to *n*-pentane equilibrium data at 60°
—— Equation 1
— — Equation 7
---- Equation 8
○ observed data

are shown in Figures 4 through 7. (A few points with high deviations are omitted from the diagrams for clarity.)

GENERAL REPRESENTATION OF DATA

For an exhaustive representation of the results for normal paraffins, suitable for interpolation and extrapolation, the three coefficients of Equation 1 must be given as functions of the temperature and the molecular size. Suitable functions are

$$\begin{aligned}
\log A &= 0.176n - 8.588 + 5.211\, T_c/T && (T_c/T \leqq 1.6)\\
\log A &= 0.176n - 4.090 + 2.400\, T_c/T && (T_c/T \geqq 1.6)\\
\log q_s &= -1.2309 + 0.2356\, T_c/T && (T_c/T \leqq 1.6)\\
q_s &= 0.140 && (T_c/T \geqq 1.6)\\
g &= 1 - 0.0266n + 0.00160\, n^2T_c/T && (nT_c/T \leqq 16.6)\\
g &= 1 && (nT_c/T \geqq 16.6) \qquad (9)
\end{aligned}$$

The molecular weight dependence is introduced through the carbon number n and the critical temperature T_c of a general normal paraffin. The observations lie within the following ranges

$$\begin{gathered}
0.8 \leqq T_c/T \leqq 2.5\\
4 \leqq nT_c/T \leqq 40\\
0.9 \leqq g \leqq 1\\
10^{-5} \leqq x \leqq 0.7
\end{gathered}$$

While this method of expression permits some extrapolation of n outside the experimental limits of $5 \leqq n \leqq 16$, an extrapolation becomes highly uncertain outside the range $3 \leqq n \leqq 20$. Isotherms at supercritical temperatures were included in the correlation through the simple expedient of a hypothetical supercritical vapor pressure obtained by extrapolation. The curves drawn in Figures 4 through 7 are based on the correlation Equations 9.

The present data lead to an approximate value of 165 cal. per gram for the isosteric heat of sorption of a normal paraffin on Molecular Sieves Type 5A. This value is in reasonable agreement with other observations (*12*).

MIXTURES

In analogy with Langmuir's equation, one will expect that Equation 1 can be extended to the sorption q_i of a component i at the mole fraction y_i in a mixture at total pressure P

$$q_i = A_i y_i P/[1 + \sum_j B_j (y_j P)^{g_j}] \qquad (10)$$

The parameters should be the same as for the pure components. Figure 8 shows a comparison of Equation 10 with observations for pentane-heptane mixtures. It illustrates the pronounced selectivity of Molecular Sieves according to the molal weight M in sorption from a gaseous phase.

The sorption of component i at mole fraction x_i in the liquid phase should be given by

$$-q_i = A_i x_i p_i^\circ/[1 + \sum_j B_j (x_j p_j^\circ)^{g_j}] \qquad (11)$$

if, as before, deviations from ideality in the equilibrium fluid are disregarded. Equation 11 predicts, under certain conditions, reversals of the relative sorbability as compared with the gaseous phase. According to Equations 10 and 11, and to the usual definitions of the relative sorbability α_{ij}, we have

$$\alpha_{ij}^G = q_i y_j M_j/(q_j y_i M_i) = A_i M_j/(A_j M_i) \qquad (12)$$

and

$$\alpha_{ij}^L = q_i x_j M_j/(q_j x_i M_i) = A_i p_i^\circ M_j/(A_j p_j^\circ M_i) \qquad (13)$$

in gaseous and liquid phases, respectively. While the gaseous phase sorbability A/M always increases with increasing M, the sorbability in the liquid phase Ap°/M not only increases in general less rapidly, but it actually decreases with increasing M at low temperatures for light paraffins. Its variation with carbon number n expected from the general correlation is shown in Figure 9. The tendency toward reversal disappears rapidly with increasing temperature and is expected to be absent for $n < 20$ above 100°.

Heptane-decane mixtures are shown in Figure 10 as an example of the agreement of experimental results with Equation 11. The curvatures (positive deviation from a straight line for heptane, negative deviation for decane) demonstrate the expected and actually observed selectivity reversal.

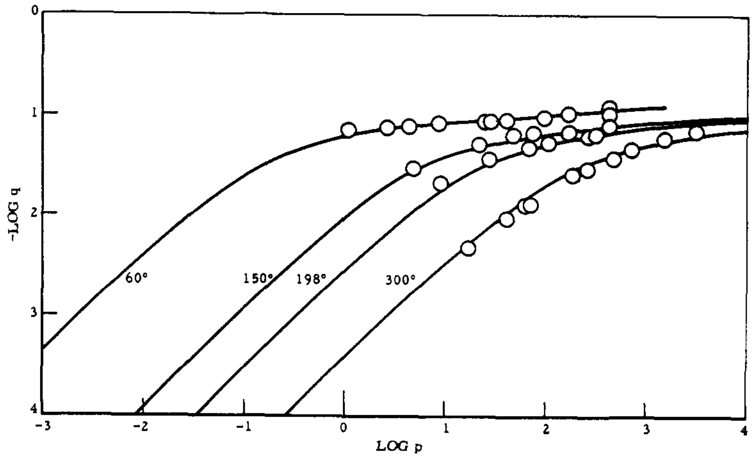

Figure 4. Observed *n*-pentane equilibrium data and correlated isotherms

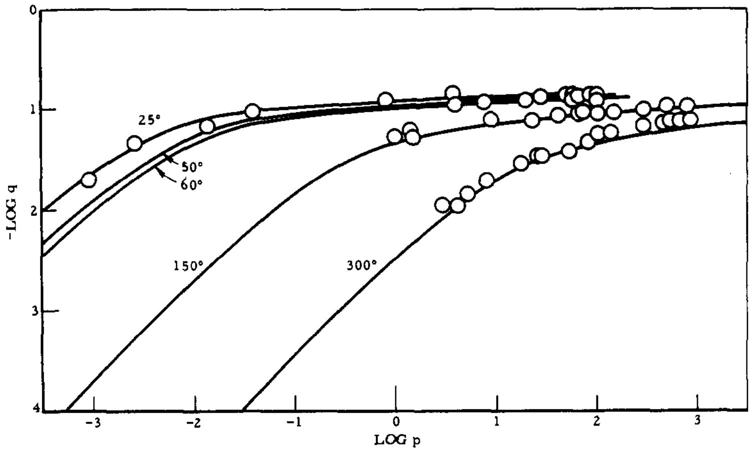

Figure 5. Observed *n*-heptane equilibrium data and correlated isotherms

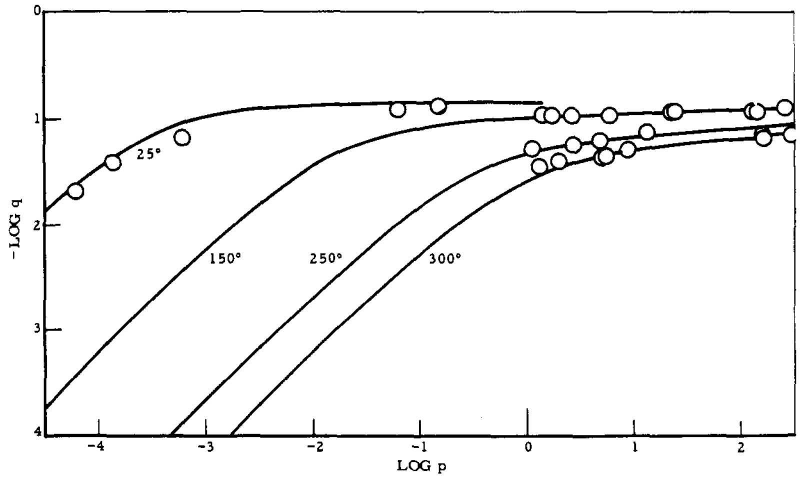

Figure 6. Observed *n*-decane equilibrium data and correlated isotherms

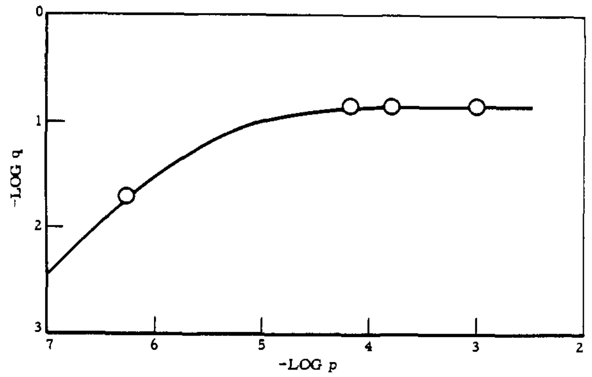

Figure 7. Observed *n*-hexadecane equilibrium data at 25° and correlated isotherm

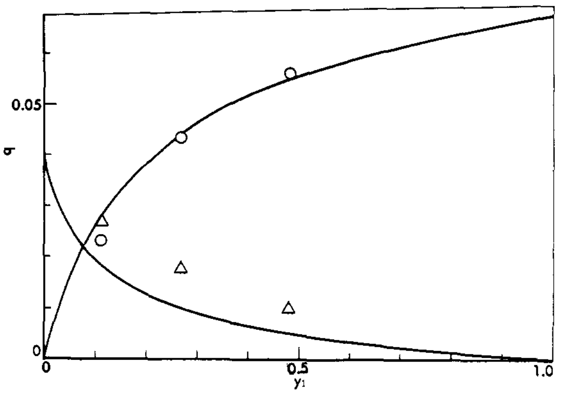

Figure 8. Observed equilibrium data for the heptane-pentane gaseous binary system at 300° and 550 mm. total pressure

O heptane, component 1

△ pentane

—— Equation 10

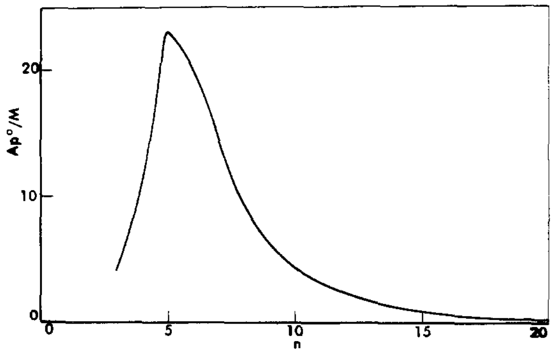

Figure 9. Variation of the liquid-phase sorbability with carbon number at 25°

KINETICS

The sorption of normal paraffins from the gaseous phase on Type 5A proceeds rapidly. In less than 20 seconds, one-half of the equilibrium value is reached at room temperature even for as large a molecule as decane. It appears that steps other than intrazeolitic diffusion are responsible for the lower sorption rates observed in the liquid phase.

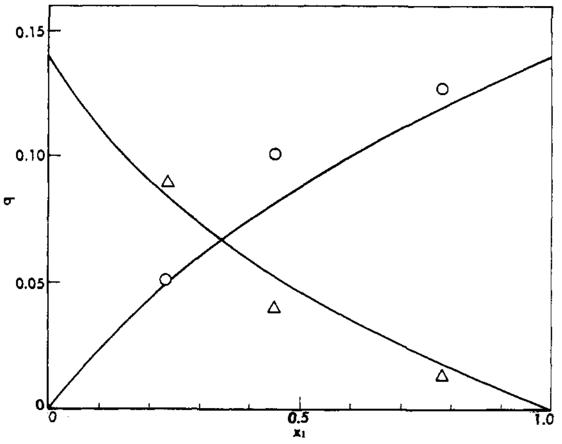

Figure 10. Observed equilibrium data for the heptane-decane liquid binary system at 25°

○ heptane, component 1

△ decane

—— Equation 11

In harmony with the present description of the sorption equilibrium, desorption into a vacuum proceeds in two distinct steps of which the later, slower one is of first order with an activation energy of the magnitude of the sorptive heat. The early, more rapid, portion of the desorption is of an indefinite order and involves an amount of sorbate roughly equivalent to the excess over monolayer sorption. If the early desorption is crudely approximated by a first-order term, the progress of desorption may be expressed as

$$q(t) = q_2(0)e^{-k_2 t} + [q(0) - q_2(0)]e^{-k_1 t} \qquad (14)$$

in which k_1 and k_2 are first-order rate constants characterizing the more rapid and the less rapid processes, respectively, and $q_2(0)$ is the amount of sorbate desorbed at the lower rate. These quantities are approximately given by

$$\begin{aligned} \log k_1 &= 0.5 - 1.7\,T_c/T \\ \log k_2 &= 2.5 - 0.1n - 4.0\,T_c/T \\ \log q_2' &= -4.48 + 2.29\,T_c/T \end{aligned} \qquad (15)$$

with q_2' defined by

$$q_2 = Apq_2'/(q_2' + Ap) \qquad (16)$$

The coefficient A is given by Equations 9. The rate constants are measured in inverse seconds. The limits of validity are the same as for the equilibrium correlation with the exception of the lower temperature limit, $T_c/T \leq 1.5$. Over-all rates of desorption become approximately equal to sorption rates in the neighborhood of the critical temperature.

ACKNOWLEDGMENT

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NOMENCLATURE

A = parameter in Equation 1, weight sorbate/weight sorbent-mm. Hg
B = parameter in Equation 1, (mm. Hg)$^{-g}$
c = temperature-dependent parameter in BET Equations 7 and 8, dimensionless
g = parameter in Equation 1, dimensionless
h = second temperature-dependent BET parameter, Equation 7, dimensionless
k = first order rate constant, inverse seconds
M = molecular weight, grams
n = number of carbon atoms in a normal paraffin
N = number of layers in BET Equation 8
p = pressure, mm. Hg
q = quantity sorbed, weight sorbate/weight dehydrated sorbent
R = molar gas constant
t = time, seconds
T = absolute temperature
x = relative pressure, Equation 6 or liquid phase mole fraction
y = gas phase mole fraction
α = relative sorbability, Equations 12 and 13

Superscripts

G = gas phase
L = liquid phase
^{c} = vapor-liquid equilibrium

Subscripts

$i, j, 1, 2$ = component designation or identification of rapidly or slowly desorbed sorbate
c = critical point
m = monolayer valve
s = saturation value

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