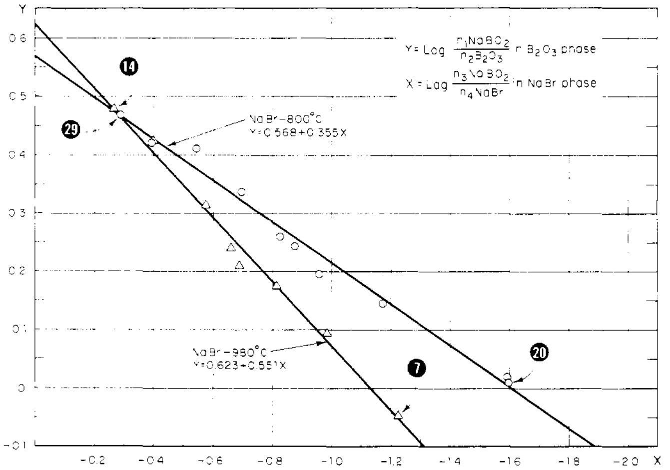

Figure 2. Log-log plots of distribution of $NaBO_2$ between $B_2O_3$ and NaBr in conjugate phases at 800° and 980° C.

jaggedness stems from formation of diverse additive compounds between disodium octaborate and sodium bromide. A more detailed tentative interpretation of the jaggedness is given in Table II.

*g.* The log-log regression lines of the molar distribution of $NaBO_2$ between the major components of the conjugate phases (Figure 2) agree with the finding (*1*) that, the ratio of $NaBO_2$-to-$B_2O_3$ in the boron oxide phase being fixed, proportionately more $NaBO_2$ (as a component) is extracted by the conjugate sodium halide phase with higher temperature.

## INTERACTION OF COMPONENTS

Metal halides tend to react additively with polyborates, forming a variety of boratohalides (*2*). Therefore the diagrams (Figure 1) were examined for possible formation of such compounds among disodium octaborate, disodium tetraborate, and sodium bromide in the equilibrated melts. Accordingly, two sets of lines were drawn on the diagrams. These lines project from the $B_2O_3$ and NaBr corners to the NaBr-$NaBO_2$ and $B_2O_3$-$NaBO_2$ composition edges, respectively, at the indicated simple stoichiometric ratios of the components. At the point on the isotherm at which such lines mutually intersect, all the components exist in exact stoichiometric combination. For example, the lines representing the ratios $1NaBr{:}3NaBO_2$, or $1NaCl : 3NaBO_2$ (*1*), and $2NaBO_2 : 3B_2O_3$ intersect precisely on each of the isotherms. This observation suggests formation of stable complexes: $2NaX \cdot 3(Na_2O \cdot 4B_2O_3)$, where $X$ stands for Cl or Br. This and additional inferences are presented in Table II.

## ACKNOWLEDGMENT

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Editor's Note: In connection with this article, read the critical comment on page 295, submitted as correspondence by M. A. Bredig.

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# Equilibrium Adsorption of Liquid Phase Normal Paraffins on Type 5A Molecular Sieves

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**Normal paraffins were adsorbed from the liquid phase on Type 5A molecular sieves to determine the effect of molecular size, temperature, and concentration on the equilibrium loadings. Single component adsorptive capacities varied irregularly with molecular size and were independent of temperature when loadings were expressed on a volume basis. In liquid phase adsorption from binary systems, the lower molecular weight normal paraffin was adsorbed preferentially. Temperature had a negligible effect on the composition of adsorbate in equilibrium with a given liquid composition. The equilibrium data for each binary system could be correlated by a single value of relative adsorptivity.**

MOLECULAR sieves are crystalline adsorbents with pore openings of fixed and uniform dimensions. The surface of adsorption is almost entirely internal and is accessible through channels penetrating the entire volume of the adsorbent (*1*). Molecular sieves are used in the petroleum industry for the efficient separation of normal paraffins from their isomers (*3, 8*). The importance of these separations has increased greatly with the introduction of biodegradable detergents requiring normal paraffins with 10 to 14 carbon atoms.

Equilibrium data for the adsorption of normal paraffins on molecular sieves are incomplete. Most of the available data are for the adsorption of pure normal paraffins from the vapor phase (*2, 5*). The purpose of this study was to provide equilibrium information for liquid phase adsorption of both pure normal paraffins and binary mixtures on Type 5A molecular sieves. The effect of molecular size,

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Present addresses: [1] The University of Connecticut, Storrs, Conn. 06268. [2] Owens-Corning Corp., Granville, Ohio 43023 concentration, and temperature on equilibrium loading was investigated.

## EXPERIMENTAL

Equilibrium measurements were made in a 200-ml., three-necked glass vessel. The necks were adapted for sampling the system, temperature measurement, and introducing materials. A water bath maintained the equilibrium vessel at a constant temperature during a run. Dry molecular sieves from a regeneration column and the hydrocarbons were charged to the vessel. Samples of liquids were withdrawn periodically with a microliter syringe and promptly analyzed with an Abbé refractometer. The run was terminated when successive refractometer readings were in agreement. Equilibrium loadings on the sieves were calculated from the change in concentration of a known amount of binary mixture (7).

The normal paraffins studied were heptane, decane, dodecane, and tetradecane. Equilibrium loadings were obtained for the single components and for six combinations of binary systems. To determine the temperature dependence, measurements were made at 30°, 60°, and 90° C. for both the single components and binary mixtures. Pressure was held constant at 1 atm. for all experimental runs.

To obtain single component loadings, a material with an effective molecular diameter larger than 5A. was added to the normal paraffin. Since this material was excluded from the adsorption cavities, refractive index measurements allowed calculation of the amount of single component adsorbed. The nonadsorbable components, carbon tetrachloride and 1,1,2,2-tetrachloroethane, were selected for their large difference in refractive index from the normal paraffins. As an independent determination of single component loadings, saturated sieves from the equilibrium vessel were dried in a vacuum oven, and the change of weight with time was measured (*4*). Binary data were obtained by contacting mixtures of known compositions and weight with known quantities of molecular sieves. Preferential adsorption of one of the components resulted in a change of composition of the liquid in contact with the sieves.

The molecular sieves used were Linde Type 5A, $^1/_{16}$-inch pellets, containing 20% inert clay binder. The normal paraffins, with minimum purity of 99 mole %, were purified further by passage through Linde Type 4A molecular sieves.

**Single Component Results.** The equilibrium loadings for the normal paraffins are listed in Table I. Volumetric loadings were calculated by assuming that the liquid density of the adsorbate is the same as the liquid density of the contacting hydrocarbon. The estimated propagated error for these data is about 0.2 gram of paraffin per 100 grams of molecular sieves.

Equilibrium loadings vary irregularly with molecular weight. The general trend is for the equilibrium loading to decrease with increasing molecular weight, with *n*-decane exhibiting an unusually low loading capacity compared with the other normal paraffins. On a weight basis, equilibrium loading capacity decreases with increasing temperature. When expressed on a volume basis, however, the equilibrium loading capacity for a given paraffin is essentially independent of temperature between 30° and 90° C. As a check on the refractive index technique, sieves were contacted with pure normal paraffins and then dried. The results at 30° C. were within 3% of the data from the refractive index method.

Table I. Single Component Adsorptive Capacities

| | G./100 G. Sieves | | | G./100 G. Sieves | | |
|---|---|---|---|---|---|---|
| | 30° C. | 60° C. | 90° C. | 30° C. | 60° C. | 90° C. |
| *n*-Heptane | 12.5 | 12.2 | 11.5 | 18.5 | 18.9 | 18.5 |
| *n*-Decane | 10.5 | 10.3 | 9.8 | 14.6 | 14.7 | 14.6 |
| *n*-Dodecane | 12.4 | 11.8 | 11.5 | 16.7 | 16.4 | 16.6 |
| *n*-Tetradecane | 11.3 | 11.2 | 10.7 | 15.0 | 15.2 | 15.1 |

The single component loadings were the same with both carbon tetrachloride and 1,1,2,2-tetrachloroethane as the nonadsorbable material. Also, the concentration level of nonadsorbable component in the contacting liquid did not affect the equilibrium loadings. Thus, the adsorptive capacity of the molecular sieves were not measurably changed by the presence of nonadsorbable material. The equilibrium loading capacity, however, can be affected by inherent variations in the molecular sieves. For example, two batch numbers of molecular sieves gave equilibrium loadings for *n*-heptane of 12.5 and 11.0 grams per 100 grams of sieve, respectively. Some of the differences between saturation values reported by different investigators may result from batch to batch variations in the adsorptive capacity of the sieves.

**Binary Adsorption Results.** The adsorption data for the six binary systems studied are presented in Table II. The data are plotted for the *n*-heptane, *n*-decane system in Figures 1 and 2. For all six binary systems, the normal

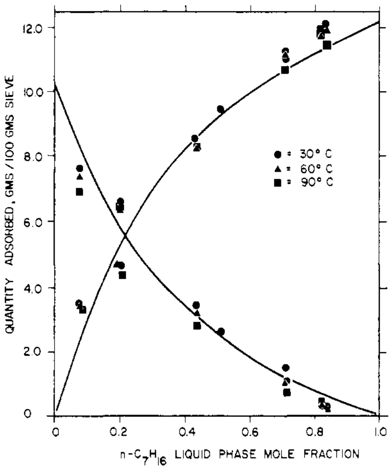

Figure 1. Adsorptive capacities for the *n*-heptane–*n*-decane system

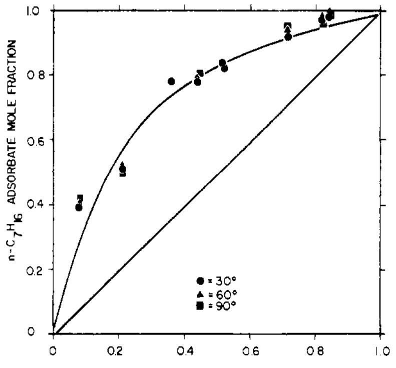

Figure 2. Equilibrium diagram for the *n*-heptane–*n*-decane system

Table II. Adsorption Data for the Six Binary Systems

| $T$, °C. | $W_L$, G./100 G. | $W_H$, G./100 G. | $X_L$ | $Y_L$ |
|---|---|---|---|---|
| | | *n*-Heptane–*n*-Decane | | |
| 30 | 3.5 | 7.6 | 0.08 | 0.39 |
| 30 | 4.7 | 6.7 | 0.20 | 0.50 |
| 30 | 4.7 | 6.6 | 0.20 | 0.51 |
| 30 | 8.6 | 3.4 | 0.35 | 0.78 |
| 30 | 8.6 | 3.4 | 0.44 | 0.78 |
| 30 | 9.5 | 2.6 | 0.51 | 0.84 |
| 30 | 9.3 | 2.8 | 0.52 | 0.82 |
| 30 | 11.1 | 1.5 | 0.72 | 0.92 |
| 30 | 11.3 | 1.0 | 0.72 | 0.94 |
| 30 | 12.3 | 0.2 | 0.77 | 0.98 |
| 30 | 12.0 | 0.4 | 0.83 | 0.98 |
| 30 | 12.2 | 0.3 | 0.84 | 0.98 |
| 60 | 3.5 | 7.4 | 0.08 | 0.40 |
| 60 | 4.7 | 6.4 | 0.20 | 0.51 |
| 60 | 8.3 | 3.3 | 0.44 | 0.79 |
| 60 | 11.2 | 0.9 | 0.72 | 0.94 |
| 60 | 11.8 | 0.3 | 0.83 | 0.98 |
| 60 | 12.0 | 0.2 | 0.84 | 0.99 |
| 90 | 3.4 | 6.9 | 0.08 | 0.41 |
| 90 | 4.4 | 6.5 | 0.21 | 0.49 |
| 90 | 8.3 | 2.8 | 0.44 | 0.90 |
| 90 | 10.7 | 0.7 | 0.72 | 0.96 |
| 90 | 11.0 | 0.4 | 0.83 | 0.97 |
| 90 | 11.5 | 0.1 | 0.84 | 0.99 |
| | | *n*-Heptane–*n*-Dodecane | | |
| 30 | 2.0 | 10.4 | 0.07 | 0.25 |
| 30 | 5.4 | 7.0 | 0.24 | 0.57 |
| 30 | 7.6 | 4.8 | 0.49 | 0.73 |
| 30 | 11.0 | 1.5 | 0.65 | 0.92 |
| 30 | 12.0 | 0.4 | 0.85 | 0.98 |
| 60 | 2.0 | 10.0 | 0.07 | 0.25 |
| 60 | 5.4 | 6.6 | 0.24 | 0.58 |
| 60 | 7.5 | 4.6 | 0.49 | 0.74 |
| 60 | 10.9 | 1.3 | 0.65 | 0.93 |
| 60 | 11.8 | 0.3 | 0.85 | 0.98 |
| 90 | 2.0 | 9.5 | 0.07 | 0.26 |
| 90 | 5.2 | 6.3 | 0.24 | 0.58 |
| 90 | 7.2 | 4.2 | 0.49 | 0.74 |
| 90 | 10.5 | 1.0 | 0.65 | 0.95 |
| 90 | 11.4 | 0.2 | 0.85 | 0.99 |
| | | *n*-Heptane–*n*-Tetradecane | | |
| 30 | 3.9 | 7.8 | 0.10 | 0.49 |
| 30 | 6.9 | 4.8 | 0.23 | 0.76 |
| 30 | 7.4 | 4.4 | 0.28 | 0.80 |
| 30 | 10.2 | 1.9 | 0.48 | 0.94 |
| 30 | 11.6 | 0.7 | 0.52 | 0.99 |
| 30 | 11.4 | 1.0 | 0.70 | 0.98 |
| 30 | 12.0 | 0.3 | 0.72 | 1.00 |
| 30 | 12.2 | 0.2 | 0.87 | 1.00 |
| 30 | 12.2 | 0.1 | 0.88 | 1.00 |
| 60 | 3.9 | 7.7 | 0.10 | 0.50 |
| 60 | 6.9 | 4.8 | 0.23 | 0.74 |
| 60 | 7.4 | 4.4 | 0.28 | 0.77 |
| 60 | 10.2 | 1.8 | 0.48 | 0.92 |
| 60 | 11.6 | 0.6 | 0.52 | 0.98 |
| 60 | 11.2 | 0.9 | 0.70 | 0.97 |
| 60 | 12.0 | 0.2 | 0.72 | 0.99 |
| 60 | 12.0 | 0.2 | 0.87 | 0.99 |
| 60 | 12.2 | 0.1 | 0.88 | 0.99 |
| 90 | 3.8 | 7.2 | 0.10 | 0.52 |
| 90 | 6.8 | 4.4 | 0.23 | 0.76 |
| 90 | 7.4 | 3.8 | 0.28 | 0.80 |
| | | *n*-Heptane–*n*-Tetradecane | | |
| 90 | 10.0 | 1.4 | 0.48 | 0.94 |
| 90 | 11.4 | 0.2 | 0.52 | 0.99 |
| 90 | 11.2 | 0.4 | 0.70 | 0.98 |
| 90 | 11.5 | 0.0 | 0.72 | 1.00 |
| 90 | 11.5 | 0.0 | 0.87 | 1.00 |
| 90 | 11.5 | 0.0 | 0.88 | 1.00 |
| | | *n*-Decane–*n*-Dodecane | | |
| 30 | 1.4 | 10.8 | 0.08 | 0.13 |
| 30 | 4.9 | 6.7 | 0.19 | 0.47 |
| 30 | 4.0 | 7.8 | 0.20 | 0.38 |
| 30 | 7.0 | 4.3 | 0.41 | 0.66 |
| 30 | 9.0 | 1.8 | 0.61 | 0.86 |
| 30 | 10.0 | 0.4 | 0.91 | 0.99 |
| 60 | 1.3 | 10.3 | 0.08 | 0.13 |
| 60 | 4.7 | 6.4 | 0.19 | 0.47 |
| 60 | 3.8 | 7.4 | 0.20 | 0.38 |
| 60 | 6.9 | 4.1 | 0.41 | 0.67 |
| 60 | 8.9 | 1.6 | 0.61 | 0.87 |
| 60 | 10.0 | 0.4 | 0.81 | 0.97 |
| 90 | 1.3 | 10.0 | 0.08 | 0.13 |
| 90 | 4.7 | 6.1 | 0.19 | 0.48 |
| 90 | 3.7 | 7.1 | 0.20 | 0.38 |
| 90 | 6.6 | 3.8 | 0.41 | 0.68 |
| 90 | 8.6 | 1.5 | 0.61 | 0.88 |
| 90 | 9.6 | 0.3 | 0.81 | 0.98 |
| | | *n*-Decane–*n*-Tetradecane | | |
| 30 | 3.1 | 8.0 | 0.06 | 0.35 |
| 30 | 5.6 | 5.4 | 0.18 | 0.59 |
| 30 | 7.7 | 2.9 | 0.43 | 0.78 |
| 30 | 9.5 | 1.1 | 0.64 | 0.92 |
| 30 | 9.8 | 0.8 | 0.83 | 0.95 |
| 60 | 3.1 | 7.8 | 0.06 | 0.36 |
| 60 | 5.5 | 5.3 | 0.18 | 0.59 |
| 60 | 7.7 | 2.8 | 0.43 | 0.79 |
| 60 | 9.4 | 1.1 | 0.64 | 0.92 |
| 60 | 9.6 | 0.7 | 0.83 | 0.94 |
| 90 | 3.1 | 7.3 | 0.06 | 0.37 |
| 90 | 5.5 | 4.8 | 0.18 | 0.62 |
| 90 | 7.6 | 2.5 | 0.43 | 0.80 |
| 90 | 9.1 | 0.9 | 0.64 | 0.94 |
| 90 | 9.2 | 0.6 | 0.83 | 0.96 |
| | | *n*-Dodecane–*n*-Tetradecane | | |
| 30 | 2.4 | 9.1 | 0.06 | 0.23 |
| 30 | 5.9 | 6.0 | 0.15 | 0.53 |
| 30 | 10.3 | 1.9 | 0.35 | 0.86 |
| 30 | 8.6 | 3.5 | 0.37 | 0.74 |
| 30 | 11.0 | 1.2 | 0.59 | 0.92 |
| 30 | 11.2 | 1.2 | 0.81 | 0.92 |
| 60 | 2.4 | 9.0 | 0.06 | 0.24 |
| 60 | 5.6 | 5.9 | 0.15 | 0.53 |
| 60 | 10.2 | 1.5 | 0.35 | 0.89 |
| 60 | 8.5 | 3.3 | 0.37 | 0.75 |
| 60 | 10.8 | 0.8 | 0.59 | 0.94 |
| 60 | 10.7 | 1.1 | 0.81 | 0.92 |
| 90 | 2.4 | 8.5 | 0.06 | 0.25 |
| 90 | 5.7 | 5.3 | 0.15 | 0.56 |
| 90 | 10.0 | 1.2 | 0.35 | 0.91 |
| 90 | 8.3 | 3.0 | 0.37 | 0.77 |
| 90 | 10.7 | 0.7 | 0.59 | 0.95 |
| 90 | 10.5 | 1.0 | 0.81 | 0.93 |

paraffin with the lower molecular weight is preferentially adsorbed. The selectivity for the lower molecular weight paraffin is determined mainly by steric factors (*1*). The shorter chains are better able to satisfy the steric requirements for aligning with and entering the cavities. The equilibrium adsorptive capacity of the molecular sieves decreases slightly with increasing temperature. Over the temperature range studied, however, temperature has a negligible effect on the composition of the adsorbate in equilibrium with a given liquid composition.

For the binary systems, accurate measurement of the total quantity of selectively adsorbed material was difficult. Wet sieves from the equilibrium vessel were placed in a vacuum oven, and the loss in weight with time was

Table III. Relative Adsorptivities for Binary Systems

| Binary System | Experimental $\alpha$ | Correlation $\alpha$ |
|---|---|---|
| *n*-Hexane-*n*-decane | 5.2 | 5.2 |
| *n*-Hexane-*n*-dodecane | 4.3 | 4.3 |
| *n*-Hexane-*n*-tetradecane | 10.0 | 10.3 |
| *n*-Decane-*n*-dodecane | 3.0 | 3.0 |
| *n*-Decane-*n*-tetradecane | 7.1 | 7.2 |
| *n*-Dodecane-*n*-tetradecane | 6.2 | 6.0 |

measured. Liquid at the external surface of the sieves evaporated at a faster rate than the internally adsorbed liquid. The change in drying rate, however, was not abrupt enough in many cases to distinguish clearly between liquid at the external surface and internally adsorbed liquid. The calculated results for the binary systems are based on the assumption that the total quantity of selectively adsorbed material is related linearly to weight fraction of adsorbate.

$$N_T = N_H + (N_L - N_H)Z_L \qquad (1)$$

This assumption gives total equilibrium loadings within about 0.3 gram of the loadings indicated by the drying runs.

Various modifications and extensions of the Freundlich, Langmuir, and Brunauer-Emmett-Teller relations have shown promise in describing vapor phase adsorption on molecular sieves (*5*, *6*). These equations however were not adequate for correlating the liquid phase data of this study. Instead, the selectivity for the lower molecular weight paraffin was described by a relative adsorptivity:

$$\alpha = \frac{Y_L X_H}{Y_H X_L} \qquad (2)$$

where $Y$ refers to adsorbate mole fractions and $X$ to liquid phase mole fractions. Since the relative adsorptivities for each binary were essentially independent of concentration and temperature, a single value of $\alpha$ was obtained for each binary by minimizing the standard deviation between calculated and experimental mole fractions. The solid lines on Figures 1 and 2 were calculated from an $\alpha$ value of 5.2 for the heptane-decane binary.

Peterson and Redlich (*5*, *6*) have proposed an equation for predicting the relative adsorptivities of liquid normal paraffins on molecular sieves. Their expression was an extension of an equation developed for vapor phase adsorption. Relative adsorptivity values calculated from their suggested equation differed significantly from the experimental values of this study, particularly at the higher temperature levels.

The relative adsorptivities for the six binary systems were correlated by the following empirical relation:

$$\alpha = \frac{C_H}{C_L}\gamma_H \qquad (3)$$

where $C_H$ and $C_L$ are the number of carbon atoms in the two components, and $\gamma_H$ is an empirical constant based on the higher molecular weight paraffin. The average values of $\gamma_H$ for tetradecane, dodecane, and decane were 5.12, 2.50, and 3.64, respectively. Table III lists the relative adsorptivities obtained for each binary system from experimental data and from the above correlating equation.

## NOMENCLATURE

$C$ = number of carbon atoms in the normal paraffin
$N$ = grams of *n*-paraffin adsorbed as pure component per 100 grams of molecular sieves
$T$ = temperature, ° C.
$W$ = grams of *n*-paraffin adsorbed from binary solution per 100 grams of molecular sieves
$X$ = mole fraction in liquid phase at equilibrium
$Y$ = mole fraction in adsorbate phase at equilibrium
$Z$ = weight fraction in adsorbate phase at equilibrium
$\alpha$ = relative adsorptivity of lower molecular weight *n*-paraffin with respect to higher molecular weight *n*-paraffin
$\gamma$ = empirical constant

### Subscripts

$H$ = higher molecular weight *n*-paraffin
$L$ = lower molecular weight *n*-paraffin
$T$ = total *n*-paraffin

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# Temperature Dependence of Volume Changes on Mixing Electrolyte Solutions

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In a previous paper (*3*) the volume changes on mixing all possible pairs of solutions of NaCl, $Na_2SO_4$, LiCl, and $Na_2SO_4$ were determined for ionic strengths of 1 and 4. The observed volume changes were used to calculate $D'$, the correction term in Young's rule (*5*), where;

$$D' = \Phi' - (E_2\phi_2' + E_3\phi_3') \qquad (1)$$

$\Phi'$ is the observed mean equivalent volume of the solutes in the mixed solutions at a given ionic strength, $\phi_2'$ and $\phi_3'$ are the equivalent volumes of the individual solutes in solutions of the same ionic strength, and $E_2$ and $E_3$ are the (weight) equivalent fractions of the two solutes.

Since $D'$ is a measure of the interaction between like-charged ions, the determination of the effect of temperature on this type of interaction is interesting.

## EXPERIMENTAL

The dilatometer used (Figure 1) was constructed of Vycor and had an internal volume of approximately 280 ml. In