Liquid-Phase Adsorption of *n*-Paraffins on Molecular Sieve

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Liquid-phase adsorption of *n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane from (nonadsorbed) benzene on Linde 5A molecular sieve was carried out to study the effect of temperature and concentration on equilibrium loading. On a mole basis, the adsorption was higher for lower molecular weight paraffins. The effect of temperature on equilibrium loading decreased with increasing molecular weight. The effect of concentration on equilibrium loading was most significant for *n*-pentane, decreasing with increase in molecular weight. The time required for the attainment of adsorption equilibrium increased with decreasing temperature.

Introduction

Molecular sieves are widely used as adsorbents as well as catalysts or catalyst supports. The use of *n*-paraffins in the manufacture of biodegradable detergents has increased the importance of the molecular sieve separation process. Although several studies (*4*-*8*) have been made on the vapor-phase adsorption of pure and binary paraffins, very little information is available on liquid-phase adsorption. Sundstrom and Krautz (*11*) have reported some data on pure component adsorption of *n*-heptane, *n*-decane, *n*-dodecane, and *n*-tetradecane on Linde 5A molecular sieve (LMS-5A) but have mainly concentrated on binary systems of these paraffins. Satterfield and Cheng (*9*) have reported sorption equilibrium studies of a wide variety of liquid binary hydrocarbon systems on NaY zeolite. Satterfield and Smeets (*10*) studied binary liquid-phase adsorption of *n*-octane with either *n*-decane, *n*-dodecane, or *n*-tetradecane on NaY zeolite.

As in vapor-phase adsorption, it should be possible to predict multicomponent adsorption with a knowledge of pure component data. With this in mind, the present investigation was carried out to study the effects of concentration and temperature on equilibrium loadings in the liquid-phase adsorption of *n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane on LMS-5A.

Experimental Section

The molecular sieves used were LMS-5A: $^1/_{16}$ in. pellets containing 20% inert clay binder. The sieves contained Ca^{2+} as the cation and were used without any further exchange. Benzene (A.R. grade, British Drug House) and *n*-paraffins (G.R. grade, E. Merk/British Drug House) had a minimum purity of 99.0%. To study the effect of liquid concentration on the adsorption, we diluted pure *n*-paraffins with benzene. Due to its critical diameter (6.8 Å), benzene is essentially excluded from the pores (equilibrium loading of benzene on LMS-5A has been reported as 0.002 g/g of zeolite by Thomas (*2*)).

The experiments were conducted in a Pyrex glass assembly shown in Figure 1 which consisted of a 100-mL adsorption cell attached to a three-way vacuum stopcock. The stopcock and other joints were lubricated with high vacuum silicon grease. The molecular sieves were heated at 450 °C in a muffle furnace for 48 h. The adsorption cell was preheated up to 150 °C and was brought inside the furnace where the sieves were transferred to the cell, and it was then stoppered. The assembly containing the molecular sieves was then evacuated to 10^{-3} torr at 200 °C for 4 h to remove any water vapor or air left in the cell. The evacuated cell was then cooled to room temperature. A weighed quantity of liquid paraffin and benzene mixture was then added to the adsorption cell under vacuum with the help of the assembly shown in Figure 1b which was connected to the cell at point A (Figure 1a). Since the cell was under vacuum, the liquid sample was almost instantaneously drawn into the cell, and the stopcock B (Figure 1a) was then closed. The adsorption cell was then transferred to a controlled-temperature water bath with a shaker (Model G-86, New Brunswick Scientific Co., N.J.) which was maintained at the desired temperature of adsorption within ±0.25 °C. Preliminary experiments were conducted with varying amounts of molecular sieves, shaker speeds, and volumes of sample. From these runs, 30 g of molecular sieves, 50 mL of liquid sample, and a shaker speed of 300 rpm were chosen as the operating conditions for the main runs.

At first the time taken to attain adsorption equilibrium (equilibration time) was established. To facilitate periodic withdrawal of liquid samples for chromotographic analysis, we attached the assembly shown in Figure 1c to the adsorption cell in place of stopper c (Figure 1a). This had a rubber septum through which the needle of a microliter syringe could be pierced to reach the liquid in the cell. These samples were subsequently analyzed on a thermal conductivity gas chromatograph (Chromatographic Instrumentation Co., Baroda). A 30 ft long column of 20% bentone on Chromosorb W was used for the analysis. Adsorption runs were terminated when the composition of two successive samples was identical. In general, equilibrium was attained in approximately 24 h. To ensure complete equilibration during adsorption studies, we continued each run for 48 h and then analyzed the liquid sample to get the final concentration of *n*-paraffin in the solution. Each reported point on the adsorption isotherm was determined by averaging the results of two experiments conducted simultaneously in two identical cells.

Results and Discussion

Dynamic Adsorption. The effect of temperature on the approach to equilibrium for *n*-heptane is shown in Figure 2. This figure shows that the time for reaching equilibrium decreases with increasing temperature. This is to be expected because adsorption is a mass transfer process and increasing the temperature increases the mass transfer coefficient, resulting in the steady state being reached earlier.

Adsorption Isotherms. Figures 3-6 show the adsorption isotherms for *n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane, respectively. Tables I-IV give equilibrium adsorption data for these hydrocarbons at different temperatures and are available as supplementary material. The general trend of the isotherms shows an initial increase in equilibrium loading with concentration followed by a relatively large range of concentration over which the equilibrium loading is nearly constant and then a further increase at still higher concentrations. This upward trend at high paraffin concentration could not be observed for *n*-octane because of some practical limitations. This upward increase in equilibrium loading is probably associated with adsorption on external surfaces and not with intracrystalline adsorption. Barrer and Lee (*1*) have also reported an upward inflection in the vapor-phase adsorption of hydrocarbons near the condensation temperature. As expected, at the same concentration, the equilibrium loading decreases with increasing temperature. A comparison of these figures shows that the effect of temperature is maximum for *n*-pentane and reduces for higher paraffins,

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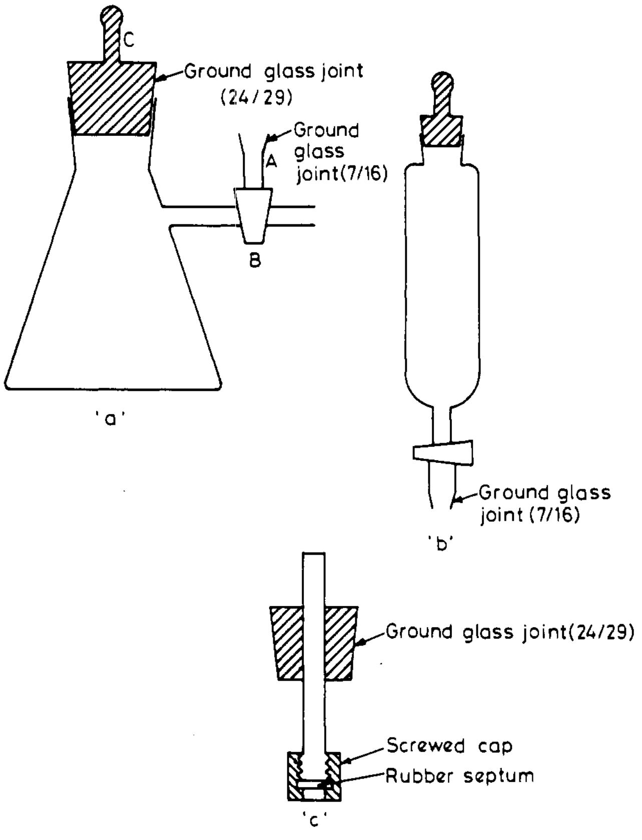

Figure 1. Assembly of adsorption cell.

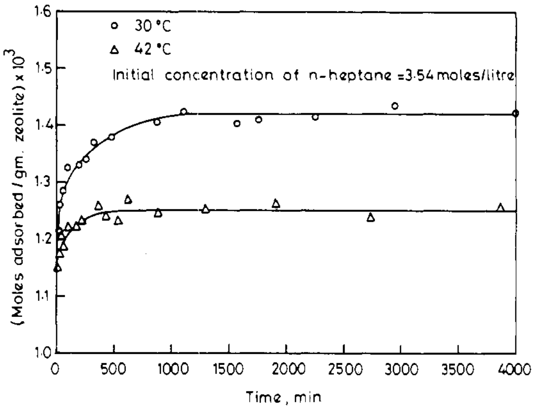

Figure 2. Dynamic adsorption of *n*-heptane.

being a minimum for *n*-octane in the present study.

For a particular temperature, the effect of concentration on the equilibrium loading is most significant for *n*-pentane and decreases with increase in molecular size. A typical plot at 30 °C is shown in Figure 7. This shows that as the liquid paraffin equilibrium concentration changes from 0.4 to 3.2 mol/L, the equilibrium loading for *n*-pentane increases from 10.9 to 13.8 g/100 g of zeolite which amounts to approximately 27%. For *n*-heptane, the equilibrium loading increases from 12.5 to 14.3 g/100 g of zeolite in the same range of concentration, which amounts to only a 14.4% increase. The results of equilibrium loading for *n*-heptane are in good agreement with those of Sundstrom and Krautz, who have reported a loading of 12.5 g/100 g of zeolite at 30 °C. These authors did not observe any change in the equilibrium loading with concentration; however, the concentration ranges have not been reported in their paper and it is possible that they did not cover as wide a concentration range.

For the same temperature and liquid concentration, the equilibrium loading decreases with increase in molecular size;

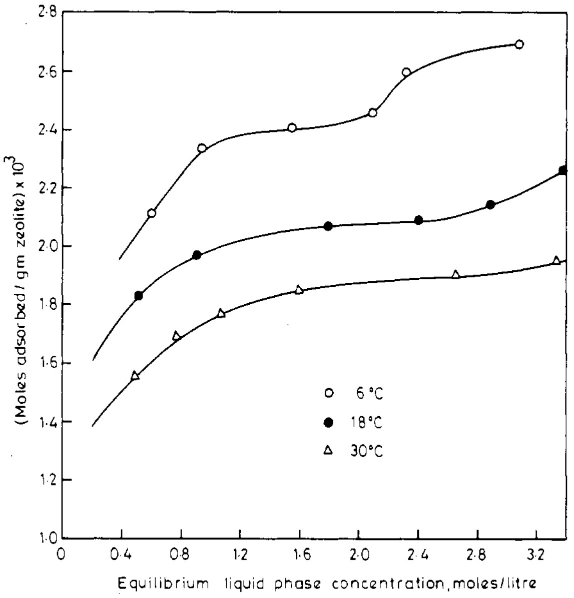

Figure 3. Adsorption isotherms of *n*-pentane.

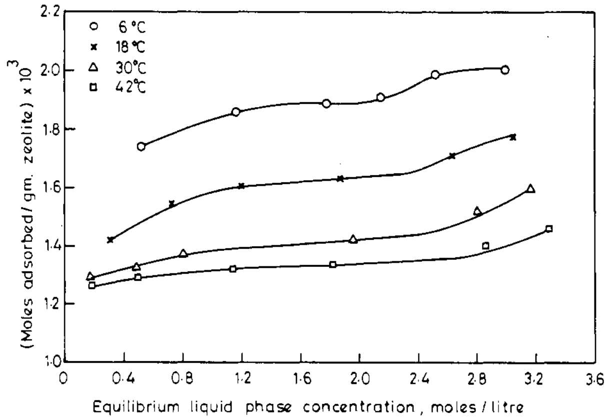

Figure 4. Adsorption isotherms of *n*-hexane.

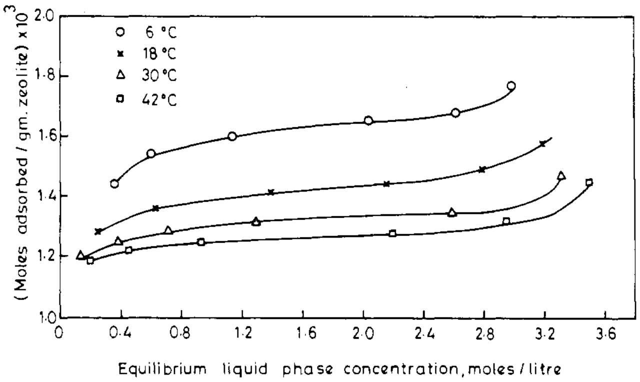

Figure 5. Adsorption isotherms of *n*-heptane.

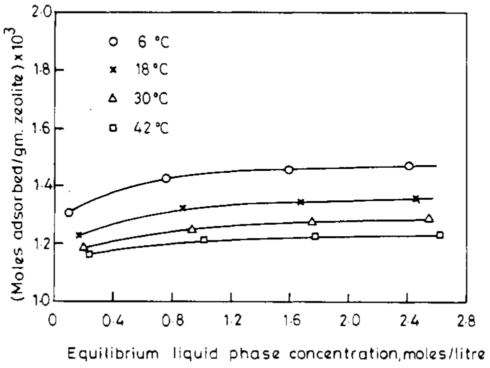

Figure 6. Adsorption isotherms of *n*-octane.

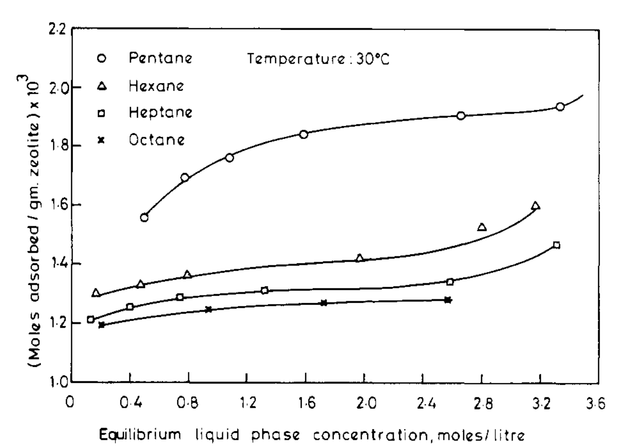

Figure 7. Adsorption isotherms of different *n*-paraffins at 30 °C.

i.e., the lower molecular weight paraffin is preferentially adsorbed. With increasing molecular weight, the effect of size diminishes. Thus, at 18 °C the equilibrium loading for *n*-pentane is 2.03 × 10^{-3} mol/g of zeolite at an equilibrium concentration of 1.6 mol/L compared to 1.62 × 10^{-3}, 1.43 × 10^{-3}, and 1.34 × 10^{-3} mol/g of zeolite for *n*-hexane, *n*-heptane, and *n*-octane, respectively. Peterson and Redlich (*3*) have also shown that liquid-phase sorbability decreases with increasing number of carbon atoms for *n*-paraffins having five or more carbon atoms. This violates Traube's rule that higher molecular weight adsorbate should be preferentially adsorbed. The reason for the preferential adsorption of lower molecular weight hydrocarbons on 5A molecular sieves is that in the zeolites both physicochemical adsorption and steric effects are important. Since type 5A molecular sieves have a pore opening of 5 Å and *n*-paraffins have a critical diameter of 4.9 Å, steric effects will play an important role. In shorter chain compounds (lower molecular weight *n*-paraffins) steric effects will be less in comparison to larger chain compounds.

Each experiment was conducted in two identical cells where initial concentration of the hydrocarbon and amount of sieves were kept same. For 95% of the runs, the deviation in the equilibrium loading between two parallel runs was less than 5%, the maximum being 9%. A few experiments were repeated somewhat separated in time and these were also found to be within 5% of each other.

In the present investigation, an experimental technique, for the liquid-phase adsorption of hydrocarbons on zeolite has been perfected. Adsorption isotherms have been measured for different liquid paraffins in the temperature range 6–42 °C. These data can be used to design single- or multiple-component adsorption plants.

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Supplementary Material Available: Tables I–IV, equilibrium adsorption data for *n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane at different temperatures (4 pages). Ordering information is given on any current masthead page.

Viscosity of the Eutectic LiF–NaF–KF Melt (FLINAK)

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The viscosity of the molten eutectic mixture of LiF–NaF–KF (FLINAK) has been measured and the result can be expressed by $\eta(\text{mPa s}) = 1.633 \exp(-2762.9T^{-1} + (3.1095 \times 10^{6})T^{-2})$.

The eutectic mixture of LiF–NaF–KF (FLINAK) is of interest as a solvent and low-pressure heat-transfer medium, because of its solvent properties, thermal stability, and extended liquid range. The present study was aimed at obtaining more reliable viscosity data for this liquid in connection with a nuclear technology program.

The experimental viscometry technique, including its application to other fluoride systems, has been described in detail elsewhere.[1-3] A specially designed high-temperature viscometer measures the period of oscillation and the damping of an oscillating Pt–Ir cylinder immersed in the liquid, using a computer-assisted digital method of timed intervals. The viscosity is calculated from fundamental viscosity equations, and no calibration against reference liquids is required.

Table I. Viscosity of FLINAK Melt Mixture, Mean Values[a]

temp, °C	viscosity, mPa s	10^3SD, mPa s
549.3	5.615	1
599.5	4.097	<1
700.3	2.535	<1
649.8	3.156	<1
497.0	8.551	1

[a] The uncertainty is given as the standard deviation (SD) of the mean.

The eutectic FLINAK mixture (29.21 wt % LiF–11.7 wt % NaF–59.09 wt % KF) was supplied by Dr. Vriesema and his group at the Laboratory for Thermal Power Engineering, Delft University of Technology (Prepared by drying under 1 Pa at 675 °C for several days after melting. The composition was thereafter checked and adjusted by using melting point determinations. The FLINAK from which the received sample was taken had been in operation for 1.5 years in Inconel-600 vessels under an argon blanket.). The sample was heated in the viscometer at 400 °C under 4 × 10^{-3} Pa prior to the measurements, which were carried out in a stream of highly purified nitrogen. The temperature was changed in a semirandom fashion in steps of 50 °C between 500 °C and 700 °C. About six determinations were made at each temperature. Results

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