This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Adsorption Equilibria of Normal Paraffins on 5A Molecular Sieve

Jasem A. M. Alkandary[a]; Rasheeds Al-Ammeri[b]; Abu Bakr S. H. Salem[c]
[a] CHEMICAL ENGINEERING DEPARTMENT, COLLEGE OF TECHNOLOGICAL STUDIES, KUWAIT
[b] CHEMICAL ENGINEERING DEPARTMENT, KUWAIT UNIVERSITY, SAFAT, KUWAIT [c] CHEMICAL ENGINEERING DEPARTMENT, KING FAHAD UNIVERSITY OF PETROLEUM AND MINERALS, DHAHRAN, SAUDI ARABIA

To cite this Article Alkandary, Jasem A. M. , Al-Ammeri, Rasheeds and Salem, Abu Bakr S. H.(1995) 'Adsorption Equilibria of Normal Paraffins on 5A Molecular Sieve', Separation Science and Technology, 30: 16, 3195 — 3209
To link to this Article: DOI: 10.1080/01496399508013138
URL: http://dx.doi.org/10.1080/01496399508013138

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION SCIENCE AND TECHNOLOGY, 30(16), pp. 3195–3209 (1995)

Adsorption Equilibria of Normal Paraffins on 5A Molecular Sieve

---

JASEM A. M. ALKANDARY
CHEMICAL ENGINEERING DEPARTMENT
COLLEGE OF TECHNOLOGICAL STUDIES
KUWAIT

RASHEEDS AL-AMMERI
CHEMICAL ENGINEERING DEPARTMENT
KUWAIT UNIVERSITY
13060 SAFAT, KUWAIT

ABU BAKR S. H. SALEM*
CHEMICAL ENGINEERING DEPARTMENT
KING FAHAD UNIVERSITY OF PETROLEUM AND MINERALS
DHAHRAN 31261, SAUDI ARABIA

ABSTRACT

The adsorption equilibria of normal paraffins (C_{12}, C_{16}, and C_{20}) and isooctane at three different temperatures (30, 50, and 70°C) on type 5A molecular sieve are presented. The adsorption capacity of this zeolite was found to decrease with an increase in temperature and also with an increase in the carbon number of the *n*-alkane. The calculated isosteric heats of adsorption for these binary systems are also reported.

INTRODUCTION

Adsorption involving molecular sieves is widely used in separation processes to recover *n*-paraffins from their isomers in petroleum feedstocks. The design of an effective adsorption process depends upon knowledge of the nature and characteristics of the adsorbate–adsorbent system. Anal-

---

* To whom correspondence should be addressed.

ysis of the equilibrium isotherm of the system is an important first step in design, where the general nature of the mass transfer zone is predicted entirely from equilibrium isotherms.

Several previous studies have been undertaken into the adsorption of *n*-paraffins on molecular sieves, mainly in the vapor phase (1–3). Studies in the liquid phase have been limited to the adsorption of normal paraffins in the C_{10}–C_{28} range on CaA zeolite (4); C_5, C_6, and C_8 from benzene on Linde type 5A molecular sieve (5); and C_7, C_{10}, C_{12}, and C_{19} on Linde type 5A molecular sieve (6). However, the separation of *n*-paraffins in the C_{12}–C_{20} range is commercially important since they are used for the manufacture of detergents and waxes. Therefore, the objective of this study was to develop the isotherms for liquid phase adsorption of binary systems of some of these *n*-paraffins and a solvent. The *n*-paraffins used are dodecane, hexadecane, and eicosane. Isooctane was used as the solvent in this investigation. Adsorption was performed on Linde type 5A molecular sieve.

The experimental data collected were used for estimating the isosteric heats of adsorption.

EXPERIMENTAL

Material Used

n-Dodecane, *n*-hexadecane, *n*-eicosane, and isooctane were obtained from Fluka AG. The physical properties and purities of these chemicals are given in Table 1.

Linde type 5A molecular sieve was obtained from Union Carbide Corporation. Some properties of this zeolite are given in Table 2. This zeolite

TABLE 1
Physical Properties of *n*-Paraffins and Isooctane

Item	Name	Formula	Molecular weight	Specific gravity	Description
1	*n*-Dodecane	$C_{12}H_{26}$	170.34	0.748	Purity > 98% (GC)
2	*n*-Hexadecane	$C_{16}H_{34}$	226.45	0.773	Purity > 98% (GC)
3	*n*-Eicosane	$C_{20}H_{42}$	282.56	0.791	Purity > 97% (GC), mp 36–38°C
4	Isooctane	C_8H_{18}	114.23	0.690	Purity > 99% (GC)

TABLE 2
Physicochemical Properties of Type 5A Molecular Sieves

No.	Property	Value	Unit
1	Nominal pore diameter	5	Å
2	Unit cell composition	$Ca_{4.5}Na_3[(AlO_2)_{12}\ (SiO_2)_{12}]\cdot 30H_2O$	—
3	Pellet particle size	3.175×10^{-3}	m
4	Density	690	kg/m^3
5	Water content	<1.5	wt%
6	Inert binder	20.0	wt%
7	Porosity	43	%
8	Crushing strength	5.63	kg
9	Heat of adsorption	4186.8	kJ/kg H_2O
10	Specific heat	1.09	kJ/kg·K
11	Type of crystal	Simple cubic	—
12	Adsorption capacity of water vapor	21.5	wt[a]

[a] Pounds H_2O/100 lb activated adsorbent at 17.5 mmHg and 25°C.

type was obtained in the form of 1/8 in. pellets containing 20% of an inert clay binder. Activation of the 5A sieves was achieved by heating them in crucibles in an oven at 450°C for 5 hours followed by rapid sealing and subsequent cooling in a dessicator.

PROCEDURES AND RESULTS

Binary mixtures (10 mL) composed of a *n*-paraffin and isooctane were prepared. The concentrations of these prepared solutions are given in Table 3.

Each solution was placed in a stainless steel tube of 60 mL capacity. A freshly prepared dry activated 5A molecular sieve (1 g) was added carefully and quickly into the tube which was then closed firmly.

The tubes containing the solutions and the solid adsorbent were placed in a thermostatically controlled water bath. The bath was kept at the preset temperature within ±0.1°C. The bath was provided with a shaking mechanism which allowed for continuous mixing of the contents of the tubes to enhance mass transfer rate and attainment of equilibrium between the liquid and solid phases.

Preliminary experiments were initially performed for each binary solution to determine the time required for equilibrium at different temperatures. Data obtained from these preliminary experiments are given in Table 4.

TABLE 3
Concentration Range of Original Binary Solutions of *n*-Paraffins with Isooctane

	n-Dodecane		*n*-Hexadecane		*n*-Eicosane	
No.	Wt%	Mole fraction	Wt%	Mole fraction	Wt%	Mole fraction
1	1.07	0.0072	0.570	0.0029	1.04	0.0042
2	1.62	0.0109	1.127	0.0057	1.22	0.0050
3	2.11	0.0143	1.664	0.0084	1.64	0.0067
4	3.10	0.0210	2.234	0.0114	1.99	0.0081
5	3.86	0.0262	2.680	0.1360	2.33	0.0091
6	4.37	0.0297	3.280	0.0168	2.49	0.0102
7	4.87	0.0332	3.580	0.0184	3.12	0.0128

TABLE 4
Equilibrium Time at Different Temperatures

		Equilibrium time (hours) at		
Item	Normal paraffin	303 K	323 K	343 K
1	*n*-Dodecane	40	26	15
2	*n*-Hexadecane	63	40	20
3	*n*-Eicosane	70	45	25

After allowing the equilibrium time for each system to be attained, the tubes were removed from the bath. Samples from each tube were analyzed using a digital density meter DMA 40 with a precision of $\pm 1 \times 10^{-4}$ g/mL. This instrument was first calibrated using pure isooctane at 25°C.

The amount of *n*-paraffins adsorbed was calculated for each system by using the following equation:

$$G = \frac{(X_0 - X)}{m_s} n \qquad (1)$$

where n is the total number of moles in solution, m_s is the weight of the molecular sieve in grams, X_0 is the initial concentration of *n*-paraffin (mole fraction), and X is the equilibrium concentration of *n*-paraffin (mole fraction).

A sample of typical data obtained is given in Table 5.

TABLE 5
Experimental Adsorption Data Obtained

(i) Equilibrium Loading Experiment

Sample	Wt. of C_{12} (W_1), g	Wt. of iso-C_8 (W_2), g	Mmol of C_{12} (n_1)	Mmol of iso-C_8 (n_2)	X_0 ($n_1/[n_1 + n_2]$), mole fraction	Mmol/g solution ($N = [n_1 + n_2]/[W_1 + W_2]$)
1	0.2972	27.5671	1.7447	241.3298	0.0072	8.7235
2	0.4548	27.6651	2.6700	242.1877	0.0109	8.7076
3	0.5973	27.6443	3.5065	242.0056	0.0143	8.6933
4	0.8843	27.6078	5.1914	241.6861	0.0210	8.6648
5	1.1098	27.6284	6.5152	241.8664	0.0262	8.6428
6	1.2683	27.7320	7.4457	242.7734	0.0298	8.6282
7	1.4095	27.5474	8.2746	241.1573	0.0332	8.6139

(ii) Adsorption Data Table

Sample	Wt. of solution, g	m_s, g	$n = WN$, mmol/10 mL	Instrument reading	X^a mole fraction	$G = (X_0 - X)n/m_s$, mmol/g
1	7.7106	1.1013	67.2634	39935.7	0.0001	0.4275
2	7.6387	1.1199	66.515	39936.5	0.0010	0.5862
3	7.5939	1.0708	66.0165	39938.5	0.0031	0.6863
4	7.4310	1.1182	64.2320	39943.6	0.0094	0.6651
5	7.4988	1.1136	64.8103	39948.3	0.0150	0.6536
6	7.4262	1.0683	64.0744	39951.4	0.0185	0.6764
7	7.4756	1.0943	64.3941	39954.4	0.0219	0.6634

[a] Equilibrium concentration was estimated using instrument reading with the calibration curve for the binary systems under investigation.

DISCUSSION

A model proposed by El'tekov and Kiselev (4) was used for fitting the isotherm data obtained experimentally. This model is a modification of the well-known equation of Brunauer–Emmett–Teller (BET). This model is represented by the following equation:

$$G = \frac{a_m \beta X(1 - X)(f - 1)}{1 + X(\beta f - 1)} \tag{2}$$

where a_m is the maximum amount of the component filling the cavities of 1 g zeolite, f is a function characterizing the collective interactions occurring in the zeolite–solution system, and β is a coefficient of mutual displacement of the molecules. Since the critical diameter of the isooctane molecule is greater than the effective pore diameter of 5A molecular sieve, it may be assumed that molecules of isooctane solvent are absent in the zeolites cavities in the system under investigation. Therefore, it can be assumed that $\beta = 1.0$ (4). Using Eq. (2) in a linearized form:

$$\frac{X(1 - X)}{G} = \frac{1}{a_m(f - 1)} + \frac{X}{a_m} \tag{3}$$

Values of a_m and f were estimated by linear regression analysis of the experimental data.

Figures 1, 2, and 3 show isotherms of the three systems at different temperatures. These figures indicate that the modified BET model seems to fit the experimental data very well.

In each system studied the adsorption capacity decreased with an increase in temperature. This is attributed to increased molecular mobility of the solute in the cavities and weakening of intermolecular bonds with increasing temperature. It can be noted that a decrease in the amount of

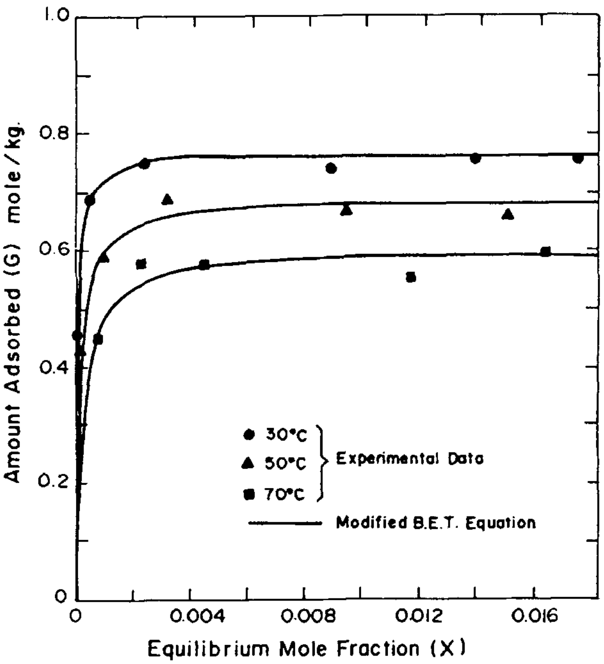

FIG. 1 Adsorption isotherms of *n*-dodecane.

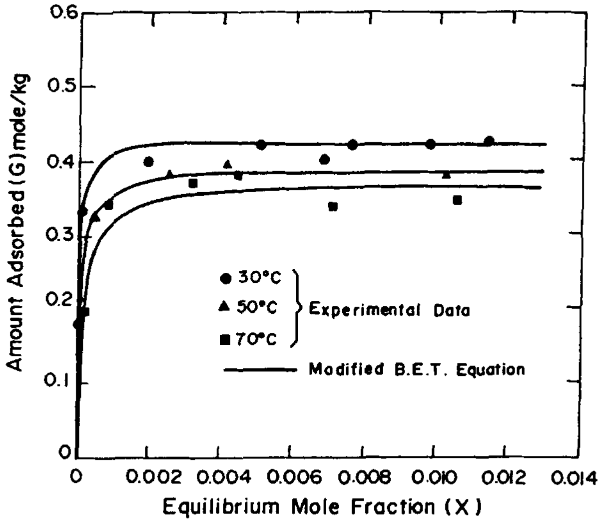

FIG. 2 Adsorption isotherms of *n*-hexadecane.

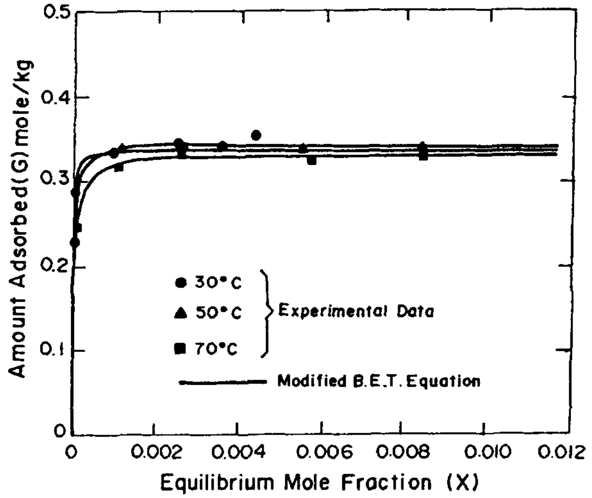

FIG. 3 Adsorption isotherms of *n*-eicosane.

the paraffins adsorbed was accompanied by an increase in the chain length of the paraffin molecule. This may be attributed to the increased viscosity of the high molecular weight *n*-alkanes resulting in decreased diffusivities in the pores of the adsorbent.

The results of equilibrium loading for normal dodecane are in good agreement with the findings of Sandstorm and Krautz (6). These authors reported a loading of 12.4 g/100 g sieve at 303 K. In this study a loading of 13.2 g/100 g sieve at the same temperature was obtained.

Figure 4 illustrates the relationship between the amounts adsorbed at saturation (maximum loading), $q_{\max}$, versus the number of carbon atoms in the *n*-alkane components at different temperatures. This figure demonstrates that the temperature effects decreased with an increase of the *n*-paraffin chain length. The percentage decrease in maximum loading from 30 to 70°C was 27, 15, and 2.6% for *n*-dodecane, *n*-hexadecane, and *n*-eicosane, respectively. At the same adsorption temperature and liquid concentration, the equilibrium loading was found to decrease with an in-

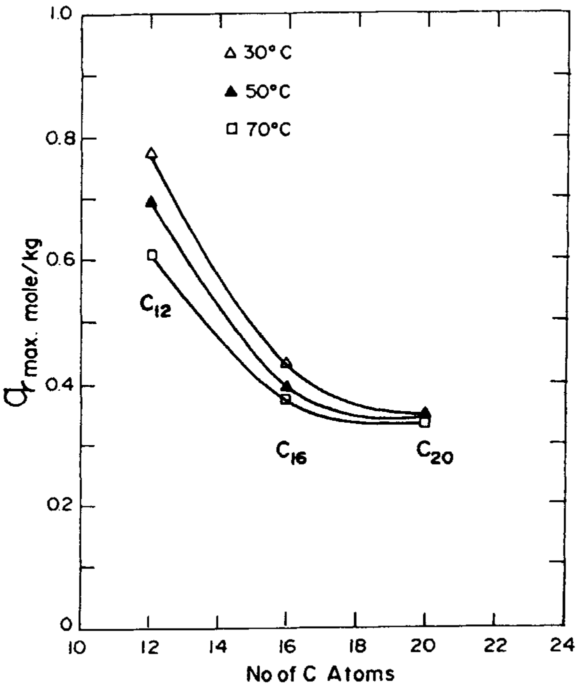

FIG. 4 Plot of maximum value adsorbed vs *n*-paraffin carbon atoms.

crease in molecular weight. This means that the lower molecular weight paraffin was preferentially adsorbed. This is clear from the data obtained at an adsorption temperature of 323 K and a solution equilibrium concentration of 0.004 mole fraction: the equilibrium loading for *n*-dodecane was 0.67 mol/kg sieve while it was 0.38 and 0.335 mol/kg sieve for *n*-hexadecane and *n*-eicosane, respectively.

Gupta et al. (5) observed a similar trend for the adsorption of normal paraffins C_5, C_6, C_7, and C_8 at 18°C and at an equilibrium concentration of 1.6 mol/L. The equilibrium loadings for the normal paraffins were 2.03, 1.62, 1.43, and 1.34 mol/kg sieve, respectively.

The preferential adsorption of lower molecular weight normal paraffins on 5A molecular sieves may arise because both physiochemical adsorption and steric effects are important in the zeolites material. Since type 5A molecular sieve has a pore opening of 5 Å and normal paraffins have a critical diameter of 4.9 Å, steric effects may play an important role in adsorption. For lower molecular weight normal paraffins, steric effects can be less in comparison to those in the larger chain compounds (5). Table 6 lists the calculated values of the limiting amount of adsorbate filling the cavities of 1 g molecular sieve (a_m), separation coefficient (f), and equilibrium adsorption time (t) for the normal paraffins under investigation at different temperatures. It can be seen that the logarithms of the separation coefficient (log f) for the three normal paraffins at different temperatures are higher than 2. This is an indication of the high selectivity of adsorption of these normal paraffins from isooctane solution by type 5A molecular sieve.

The values of a_m, f, and t decreased with an increase in the temperature due to increasing molecular mobility through weakening of bond strength in the cavity surfaces. An increase in temperature also results in more rapid diffusion of the molecules in the molecular sieve cavities with a consequent reduction in time required for physical interactions to occur.

TABLE 6
Calculated Equilibrium Adsorption Values

	n-Dodecane				*n*-Hexadecane				*n*-Eicosane			
Temperature (K)	a_m (mol/kg)	f	log f	t (h)	a_m (mol/kg)	f	log f	t (h)	a_m (mol/kg)	f	log f	t (h)
303	0.7735	16,879	4.2	40	0.428	28,775	4.5	63	0.3450	47,286	4.7	70
323	0.6936	6,161	3.8	26	0.394	10,206	4.0	40	0.3415	46,481	4.6	45
343	0.6090	3,547	3.5	15	0.372	6,612	3.8	20	0.3363	12,830	4.1	25

TABLE 7
Values of Isosteric Heat and Amount of *n*-Paraffins Adsorbed

	n-Dodecane			*n*-Hexadecane			*n*-Eicosane		
Amount adsorbed	0.30	0.40	0.55	0.20	0.30	0.35	0.25	0.30	0.31
Heat of adsorption (kcal/g·mol)	7.00	8.20	15.90	4.50	9.40	14.50	5.40	7.20	7.20
kJ/g·mol	29.10	34.40	66.60	18.80	39.30	60.70	22.60	30.10	30.10

The heat of adsorption provides a direct measure of the bond strength between the sorbate and the adsorbent surface. The adsorption isostere represents a functional relationship between the concentration of the solute in the solution and the heat of adsorption.

The isosteric heats of adsorption were derived from application of the Clausius–Clapeyron equation (7):

$$q_{\text{iso}} = -R\frac{\partial(\ln X)}{\partial(1/T)} \tag{4}$$

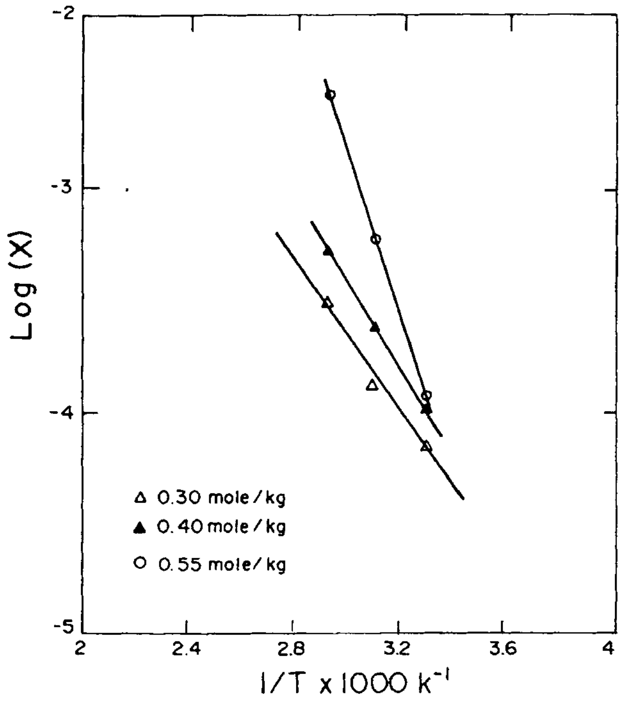

FIG. 5 Isostere of *n*-dodecane.

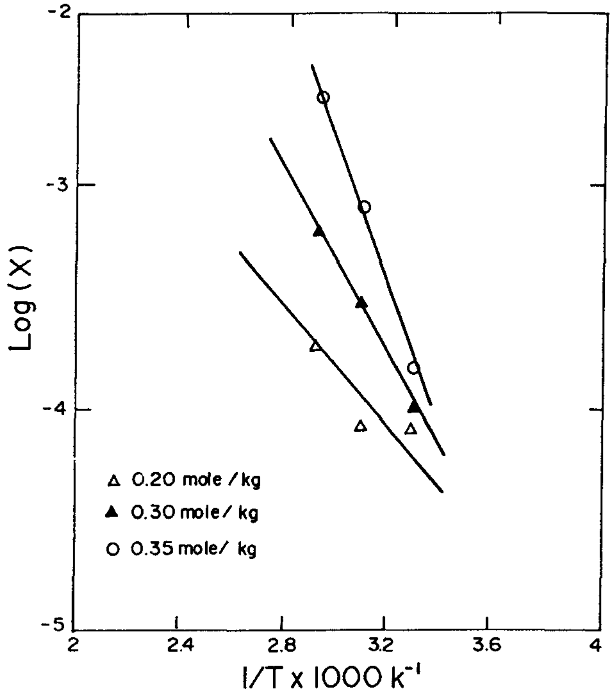

FIG. 6 Isostere of *n*-hexadecane.

where q_{iso} is the isosteric heat (kcal/g mol), X is the concentration (mole fraction), T is the absolute temperature, and R is the gas constant [kcal/(g·mol)K].

At a constant adsorbent loading G, the equilibrium concentration is plotted versus the reciprocal of the absolute temperature $1/T$ on semilogarithmic coordinates. The slopes of the straight-line isosters yield the isosteric heats.

From pairs of isotherms at different temperatures (T_1 and T_2), the isosteric heat may be calculated by the following equation:

$$q_{iso} = R\left[\frac{T_1T_2}{T_1 - T_2}\right] \ln\left[\frac{X_2}{X_1}\right] \tag{5}$$

where X_1 and X_2 are the equilibrium concentrations at temperatures T_1 and T_2, respectively.

The isosteric heats of adsorption of normal paraffins n-C_{12}, n-C_{16}, and n-C_{20} as presented in Table 7 were derived from adsorption isosteres in

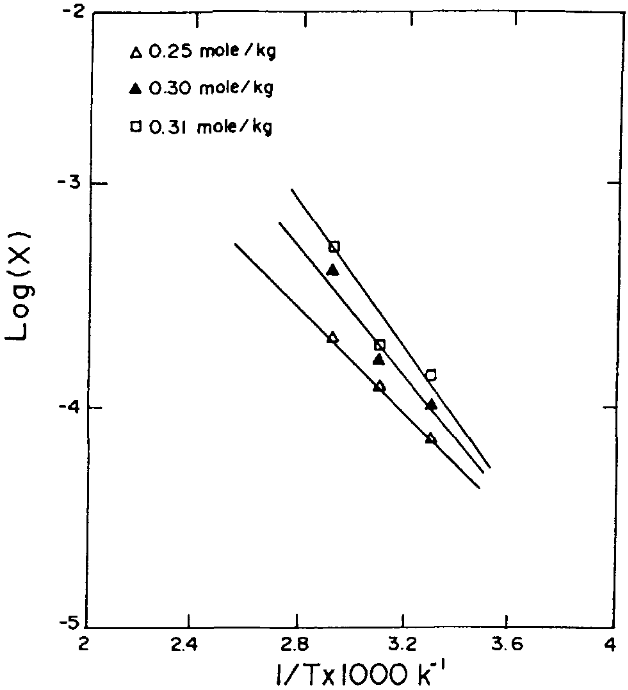

FIG. 7 Isostere of *n*-eicosane.

Figs. 5 to 7, respectively, at three different temperatures (303, 323, and 343°C).

The variation of isosteric heat with fractional loading (θ) for sorption of the *n*-paraffins under investigation is shown in Fig. 8. This figure indicates that the values of heat of adsorption of normal paraffins C_{12}, C_{16}, and C_{20} decreased with increasing molecular weight at a certain θ value (e.g., $\theta = 0.8$). A similar trend was observed by Burgess et al. (8) with a 5A sieve in the normal paraffin molecular weight region (C_{10}–C_{20}) at a temperature of 623 K.

Barrer and Ibbitson (9) discussed the effect of the molecular weight on the heat of sorption in molecular sieves. Their observation with chabazite showed that q_{iso} increased by 3 kcal/mol per CH_2 group in the lower paraffin series starting from methane up to *n*-heptane. With other types of adsorbing surfaces, the heat of sorption also rises for this *n*-paraffin series.

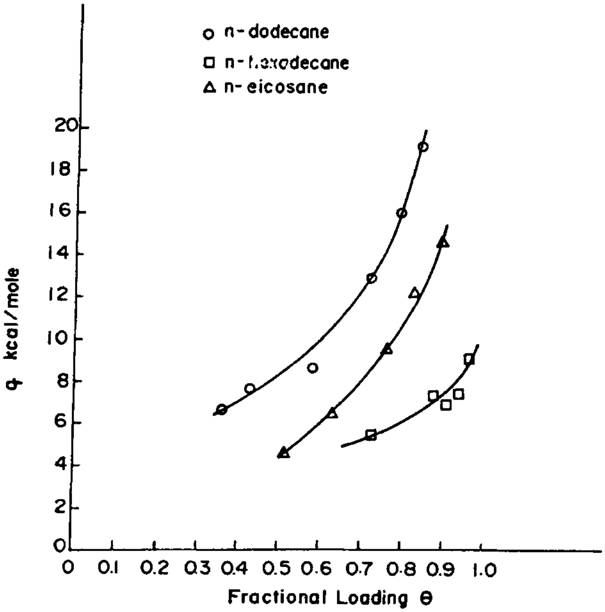

FIG. 8 Variation of q_{iso} with fractional loading for sorption of *n*-paraffins on 5A molecular sieves at 323 K.

Barrer's postulations were based on the assumption that all additional CH_2 groups would have equal access to the sieve wall. While this may be true in urea complexes, a limiting effect may be expected in zeolites. The reason for this is that the additive behavior of heat of adsorption continues as long as every part of a hydrocarbon molecule can interact without complication with a suitable sorption site on the sieve wall until the energy of stabilization is fully attained. Thus deviations are likely to be associated with the shape of the molecule itself and in particular with the coiled configuration adopted by paraffins such as C_8 and above. The carbon atoms in such a long-chain molecule can only approach the wall after a partial uncoiling, which may involve up to 0.5–1.0 kcal/mol per CH_2 group. The loss of this energy offsets the gain in stability due to the interaction with the wall. The importance of the proximity of CH_2 groups to the walls would be more marked in sieves with narrow entrances, such as 5A molecular sieves. This effect could explain why the increase in heat of adsorption with carbon number in 5A sieves does not continue beyond C_8.

CONCLUSIONS

For each of the *n*-paraffins studied, the equilibrium loading decreased as the adsorption temperature increased. The temperature effect, however, decreased with an increase in *n*-paraffin molecular size.

At any given temperature the adsorptive capacity of type 5A molecular sieves decreased with an increase in *n*-paraffin molecular size in general and, as expected, the isosteric heat of adsorption increased with an increase of the amount adsorbed.

Type 5A molecular sieve is a suitable separating agent for the purification of high molecular weight paraffins from isoparaffins at lower temperatures.

NOMENCLATURE

G	adsorbed amount of solute (mmol/g)
n	total number of moles in solution (mmol/L)
m_s	mass of molecular sieve (g)
X_0	initial concentration (mole fraction)
X	equilibrium concentration (mole fraction)
a_m	the maximum amount of components filling the cavities of 1 g of zeolite
β	coefficient of mutual displacement of the molecule of the components
f	function characterizing the collective interaction occurring in the zeolite–solution system
T	absolute temperature (K)
R	gas constant [kcal/(gram mole)·K]
q_{iso}	isosteric heat [kcal/(gram mole)]
q_{max}	maximum loading (mmol/g)
θ	fractional loading

REFERENCES

1. D. M. Ruthven and K. F. Loughlin, "Sorption of Light Paraffins in Type A Zeolites," *J. Chem. Soc., Faraday Trans.*, *68*, 696 (1972).
2. D. L. Peterson and O. Redlich, "Sorption of *n*-Paraffins by Molecular Sieves Type 5A," *J. Chem. Eng. Data*, *7*(2), 570–574 (1962).
3. C. W. Chi and H. Lec, "Separation of *n*-Tetradecane from *i*-Octane–*n*-Tetradecane Mixture by Molecular Sieves," *Chem. Eng. Prog. Symp. Ser. 96*, *65*, 65 (1969).
4. M. I. Fal'kovich, Yu. A. El'tekov, and Chernozhuov, "Adorption of Normal C_{10}–C_{28} Alkanes from Isooctane Solution by CaA Zeolite," Translated from *Khim. Tekhnol. Topl. Masel*, (2), 10–14 (February 1969).

5. R. K. Gupta, D. Kunzru, and D. N. Saraf, "Liquid-Phase Adsorption of *n*-Paraffins on Molecular Sieves," *J. Chem. Eng. Data*, *25*, 14–16 (1980).
6. D. W. Sandstorm and F. G. Krautz, "Equilibrium Adsorption of Liquid-Phase Normal Paraffins on Type 5A Molecular Sieve," *Ibid.*, *13*, 223–226 (1968).
7. D. W. Breck, *Zeolite Molecular Sieves*, Wiley, New York, 1974, p. 647.
8. Burgess, Duffet, Minkeff, and Taylor, "Sorption of Long Chain *n*-Paraffin in Molecular Sieves," *J. Appl. Chem.*, *14*, 350 (August 1964).
9. R. M. Barrer and D. A. Ibbitson "Occlusion of Hydrocarbons by Chabazite and Analcite," *Trans. Faraday Soc.*, *40*, 195–206 (1944).

Received by editor January 27, 1995