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Separation Science and Technology

Publication details, including instructions for authors and subscription information:
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To cite this Article Hassan, Neguib M. , Al-Ameeri, Rasheed S. and Oweysi, Fathi A.(1994) 'Adsorption of *n*-Paraffin Wax from Isooctane Solution on Crystalline Urea', Separation Science and Technology, 29: 7, 897 — 906

To link to this Article: DOI: 10.1080/01496399408006633

URL: http://dx.doi.org/10.1080/01496399408006633

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SEPARATION SCIENCE AND TECHNOLOGY, **29**(7), pp. 897–906, 1994

Adsorption of *n*-Paraffin Wax from Isooctane Solution on Crystalline Urea

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ABSTRACT

Equilibrium isotherms and kinetics of adsorption of *n*-paraffin wax from isooctane solution on crystalline urea were obtained at 50 and 70°C and at 50, 70, and 90°C, respectively. The equilibrium data were correlated according to the Polanyi potential theory, which provided a single characteristic curve of the experimental data at two temperatures. The batch kinetic data suggest that the adsorption of *n*-paraffin wax on crystalline urea is diffusion controlled. Effective diffusion coefficients derived from fractional uptake versus time were in the order of 10^{-14} to 10^{-13} cm^2/s. The apparent activation energies of diffusion decreased with increasing uptake, as expected.

INTRODUCTION

The flow properties of crude oil depend heavily on the content of high molecular *n*-paraffins (*n*-paraffin wax), which cause the petroleum indus-

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try undesirable expense and other difficulties. Today, these *n*-paraffins are suitable raw materials for the manufacture of synthetic fatty acids, industrial surfactants, single cell proteins, and various pharmaceutical products. Certain crude oil fractions are dewaxed for the purpose of obtaining *n*-paraffin wax, while the dewaxed products are cracked for the production of gasoline. One of the primary methods employed is crude oil dewaxing with urea. In this method, urea adducts are formed in aqueous or alcoholic solution. After separation of dewaxed products, the adduct slurry is washed and then decomposed into *n*-paraffin wax and urea. This method is relatively complicated and usually unreliable owing to the reversibility of the adduct formation reaction (1). In addition, the purity of the recovered *n*-paraffins is low due to nonnormal hydrocarbons participating in the adduct formation (2).

An alternative to the urea adduction method is to adsorb the *n*-paraffins on solid urea. A few studies have investigated the physicochemical characteristics of solid urea and normal hydrocarbons. For instance, McAdie and Frost (3) investigated the mechanism of *n*-octane adsorption on solid urea. Calderbank and Nikolov (4) found a large exothermic heat, similar to that of the heat of adsorption, when normal paraffins were contacted with solid urea; they suggested some form of physical adsorption had taken place between urea and normal hydrocarbons. Patrilyak (5) studied the equilibria of the urea–paraffin system and found that the heats evolved during complex formation were of the same order of magnitude as the heat of adsorption.

Recently, we pursued this approach in a series of batch studies investigating both the equilibrium and kinetics of adsorption of *n*-paraffins from isooctane solution on crystalline urea. In previous publications (6, 7) we reported the equilibrium adsorption isotherms and kinetic data of the adsorption of *n*-paraffins of small and medium chain length (C_{12}–C_{16}) on crystalline urea. The equilibrium data were correlated with several adsorption isotherm models, such as the Langmuir, Freundlich, and BET isotherm equation. The isosteric heats of adsorption of medium and long chain *n*-paraffin on crystalline urea were also determined from the experimental data.

In the present study the equilibrium adsorption isotherms of *n*-paraffin wax (C_{13}–C_{27}) on crystalline urea were measured at 50 and 70°C. The data were correlated with the Polanyi potential theory (8). The kinetic data were also obtained at 50, 70, and 90°C. The effective diffusion coefficients and apparent activation energies of *n*-paraffin wax on crystalline urea were derived from these data.

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EXPERIMENTAL SECTION

Materials

The *n*-paraffin wax used in the present study was separated from diesel oil (distillate fraction of crude oil, bp 211–370°C) obtained from Kuwait National Petroleum Company. The wax contained *n*-paraffins in the carbon range C_{13}–C_{27}; the relative amounts are shown in Table 1. Isooctane and methanol were obtained from Matheson Co. with stated purities greater than 99.3 and 99.8%, respectively. These chemicals were used without further treatment or purification. The adsorbent used in the study was crystalline urea, supplied by Hopkin and William's Co., Chadwell Heath, Essex, England. The urea had a density of 0.73 g/cm^3 and a moisture content of 0.2% by weight. Prior to use, the urea was dried at 40°C and was then stored in a vacuum desiccator.

Procedure

Equilibrium Study

The adsorption isotherm data were determined at 50 and 70°C in a batch system. The equilibrium uptake was based on the measurement of *n*-paraffin wax concentration in isooctane solution before and after contact

TABLE 1

Relative Amounts of *n*-Paraffins Present in the Wax

Hydrocarbon	Molecular weight	Weight %
n-C_{13}	184	0.63
n-C_{14}	198	1.85
n-C_{15}	212	3.79
n-C_{16}	226	7.32
n-C_{17}	240	7.66
n-C_{18}	254	12.5
n-C_{19}	268	13.2
n-C_{20}	282	11.67
n-C_{21}	296	10.66
n-C_{23}	310	9.12
n-C_{24}	338	6.44
n-C_{25}	352	5.18
n-C_{26}	366	2.53
n-C_{27}	380	0.86
Total		93.42

with known quantities of crystalline urea. In each run, 25 mL sample solutions with varying initial concentrations were added to glass tubes containing 2 g crystalline urea. The urea was wetted with about 5% by volume of methanol activator. The purpose of wetting urea with methanol was to activate the urea by freeing an increasing number of urea molecules from their tetragonal structure to aid in the formation of a hexagonal lattice upon contact with *n*-paraffin. The glass tubes were tightly sealed with Teflon-lined caps, and they were shaken in a constant temperature bath controlled to a desired temperature within ±0.2°C for a period of time sufficient to establish equilibrium. After reaching equilibrium, the sample solutions were settled for 2 hours. They were then filtered with Whitman No. 42 filter papers to ensure that urea crystals were completely removed. The *n*-paraffin wax concentration in the isooctane solution before and after adsorption was determined by a digital density meter (DM 240) from Anton Par, Graz, Austria. The density meter was calibrated prior to sample analysis.

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Kinetic Study

The batch kinetic data were obtained at 50, 70, and 90°C. After preparing 500 mL *n*-paraffin wax in isooctane solution with a known initial concentration (i.e., 40 mol/m^3), 25 mL samples were withdrawn and added to glass tubes containing about 2 g crystalline urea. The glass tubes were shaken in a constant temperature bath controlled to within ±0.2°C of the desired temperature. Periodically, a sample was withdrawn and analyzed with a digital density meter to determine the total *n*-paraffin concentration. For each sample, three analyses were performed to obtain the mean value; the average standard deviation was ±8%.

RESULTS AND DISCUSSION

Equilibrium Data

The equilibrium adsorption isotherms of *n*-paraffin wax on crystalline urea were obtained at 50 and 70°C, and the results are shown in Fig. 1. As illustrated by the data shown in the figure, we had difficulty obtaining sufficient data in Henry's law region. The equilibrium uptake decreased with increasing temperature, as expected. This indicates that the adsorption of *n*-paraffin wax on crystalline urea is like an exothermic reaction but physical in nature. The adsorption of *n*-paraffin wax from isooctane solution on urea takes place in an unusual manner. The *n*-paraffin mole-

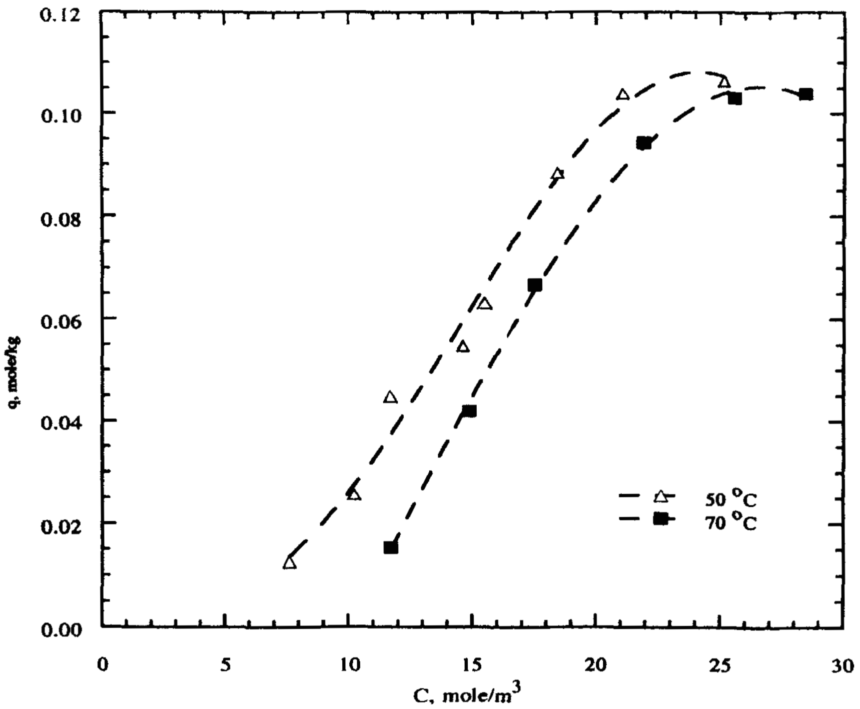

FIG. 1 Adsorption of *n*-paraffin wax from isooctane solution on crystalline urea.

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cules trigger a structural transformation of urea from planar tetragonal into hexagonal lattice. The hexagonal unit cell consists of six urea molecules forming a zigzag channel lined with oxygen atoms. The stability of the lattice structure increases with increasing chain length of the *n*-paraffin and decreases with increasing temperature. The equilibrium uptake is controlled by the packing characteristics (steric effects) as well as by the adsorbate–adsorbent interactions (interactions of the *n*-paraffin molecules with the oxygen atoms lined up on the channel walls). The *n*-paraffin molecules can only fit the urea channel in an extended planar zigzag configuration, with their long axis along the diameter of the channel. Small-sized *n*-paraffin molecules are better for satisfying the steric requirements for aligning with and entering the urea channels than are larger molecules. Once occluded in urea channels, specific interactions between methyl groups of *n*-paraffin molecules and the oxygen atoms lined up on the walls

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of urea channels contribute more significantly to the uptake capacity than do smaller molecules. Thus, a delicate balance between the steric effects and the interaction energy contribution of the *n*-paraffin molecules determines the equilibrium uptake and the shape of the isotherms of *n*-paraffin wax on crystalline urea.

The adsorption isotherm data were correlated according to the adsorption potential theory proposed by Polanyi (8), which assumes that a potential field exists at the surface of adsorbent. In this regard, the adsorption of solid solutes from solution would be analogous to the adsorption of gases. The adsorption potential, therefore, is given as

$$\epsilon = RT \ln(C_S/C) \qquad (1)$$

where C_S is the saturation concentration at equilibrium temperature and C is the equilibrium concentration. As shown in Fig. 2, a plot of the volume of *n*-paraffin wax adsorbed versus the adsorption potential yielded a single

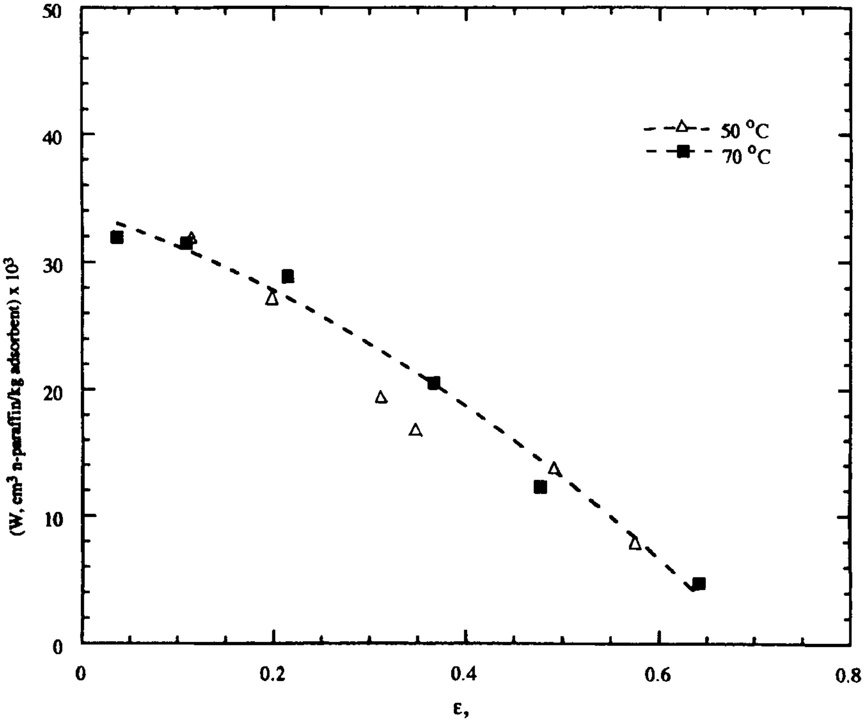

FIG. 2 Characteristic curve for adsorption of *n*-paraffin wax on crystalline urea.

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characteristic curve, as required by the potential theory. The fact that the experimental data lie close to this single curve provides a consistency check for the equilibrium adsorption data.

Kinetic Data

The kinetic data of adsorption of *n*-paraffin wax on crystalline urea were determined at 50, 70, and 90°C, and the results are presented in Fig. 3. The kinetic data follow the "$\sqrt{t}$ diffusion law" as opposed to a simple linear or exponential dependence on time. The uptake rate increases with increasing temperature. This suggests that the adsorption of *n*-paraffin wax on crystalline urea is diffusion controlled. This agrees with the results of Lathi and Manning (9), who found that the occlusion of *n*-paraffin into urea channels is due to a slow activated diffusion process. Figure 4 shows

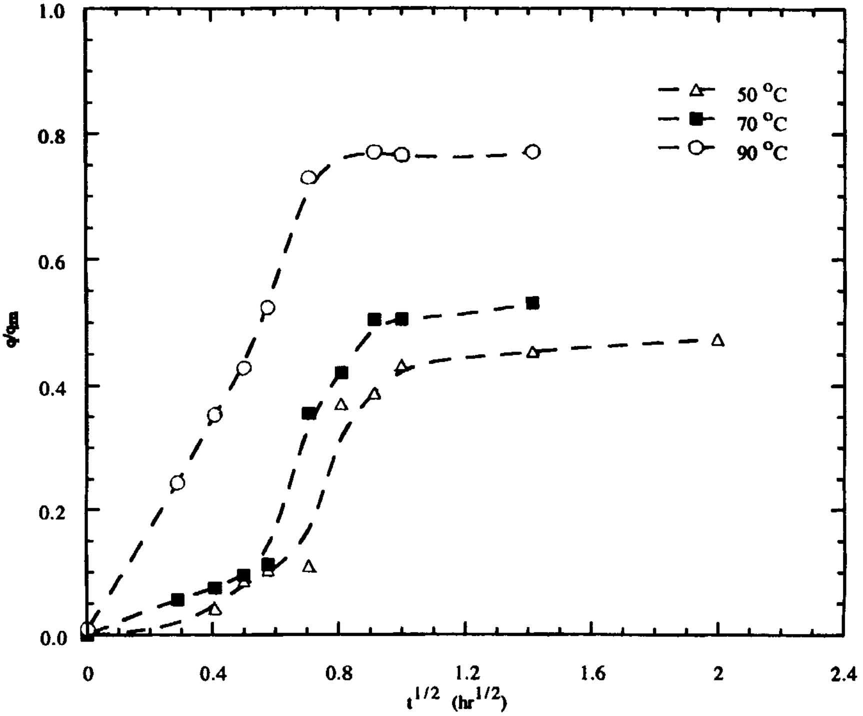

FIG. 3 Kinetics of adsorption of *n*-paraffin wax on crystalline urea.

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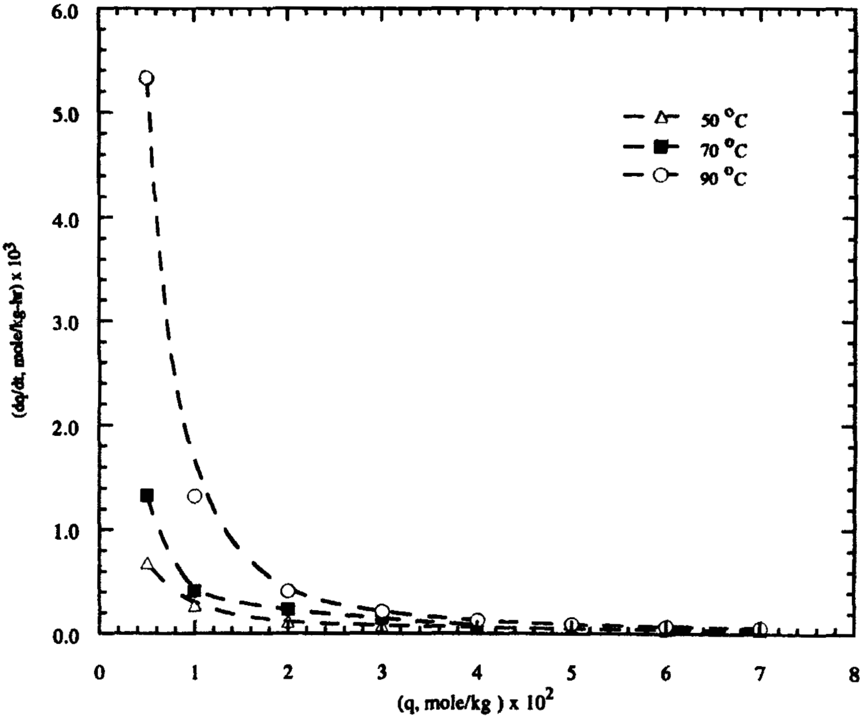

FIG. 4 Rate of adsorption of *n*-paraffin wax on crystalline urea.

a plot of the rate of adsorption versus fractional uptake of *n*-paraffin wax by crystalline urea.

The effective diffusion coefficients of *n*-paraffin on crystalline urea were derived from the kinetic data according to the expression

$$\frac{q}{q_m} = 2\left(\frac{A}{V}\right)\sqrt{\left(\frac{D_e t}{\pi}\right)} \tag{2}$$

where q and q_m are the amounts of *n*-paraffin wax adsorbed at time t and at saturation, A is the lattice surface area, V is the lattice volume, and D_e is the effective diffusion coefficient, expressed in cm²/s. A plot of the effective diffusion coefficients versus fractional uptake curves is shown in Fig. 5. As shown in the figure, the values of the diffusion coefficients were of the order of 10^{-14} to 10^{-13} cm²/s. At 50 and 70°C, the diffusion coefficients increased with increasing uptake and reached a maximum value; they tend to decrease thereafter. At 90°C, however, they decreased

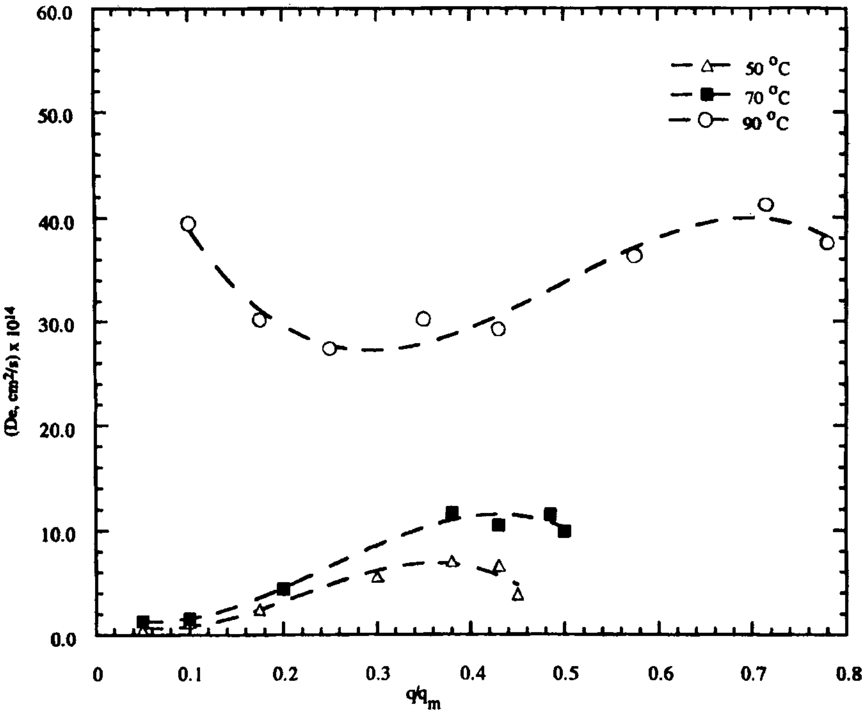

FIG. 5 Effective diffusion coefficients for *n*-paraffin wax on crystalline urea.

TABLE 2
Activation Energies of Diffusion for *n*-Paraffin Wax in Urea Channels

Fractional uptake (q/q_m)	E_a (kcal/mol) (50–70°C)	E_a (kcal/mol) (70–90°C)
0.1	7.63	39.65
0.15	4.98	30.73
0.2	3.38	24.17
0.25	3.25	20.46
0.3	3.05	14.97
0.35	—	12.74
0.4	—	12.13

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initially with increasing uptake and then followed the same trend as the other two temperatures. This may be due to undesired lattice destruction, particularly at this high temperature which approaches the melting point of urea.

The apparent activation energies of diffusion were derived from the equation

$$D_e = D_0 \exp(-E_a/RT) \qquad (3)$$

where E_a is the activation energy, D_0 is a preexponential constant, T is the temperature, and R is the universal gas constant. The calculated values of the apparent activation energies of diffusion are given in Table 2. These values represent the energy barrier for the molecules of *n*-paraffin wax to enter urea channels. The apparent activation energies decreased with increasing fractional uptake, as expected.

ACKNOWLEDGMENT

This work was supported by the Research Council of Kuwait under Grant EC 027.

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Received by editor August 9, 1993

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