1.0 to 3.0 MPa with the uncertainty being less than ±0.3%. The C_p' values of saturated liquid HFC-134a were also determined from the measured data, and a correlation of C_p' was also developed.

Literature Cited

(1) Sato, H.; Sakate, N.; Ashizawa, M.; Uematsu, M.; Watanabe, K. *Proc. ASME-JSME Therm. Eng. Joint Conf.* **1987**, *4*, 350.

(2) Ashizawa, M.; Saitoh, A.; Sato, H. *Proc. 17th Cong. Refrig.* **1987**, *B*, 185.

(3) Saitoh, A.; Sato, H.; Watanabe, K. *Int. J. Thermophys.* **1989**, *10* (3), 649.

(4) Saitoh, A. M.S. Thesis, Keio University, Yokohama, Japan, 1989.

(5) Piao, C.; Sato, H.; Watanabe, K. *Proc. 9th Jpn. Symp. Thermophys. Prop.* **1988**, 235.

(6) Kabata, Y.; Tanikawa, S.; Uematsu, M.; Watanabe, K. *Int. J. Thermophys.* **1989**, *10* (3), 605.

(7) Thermodynamic Properties; FC-134a, E.I. du Pont de Nemours & Co., Inc.: Wilmington, DE, 1979.

(8) Wilson, D. P.; Basu, R. S. *ASHRAE Trans.* **1988**, *99* (Part 2), 2095.

(9) Thermophysical Properties of Refrigerants (R12); Japanese Association of Refrigeration: Tokyo, Japan, 1986.

Received for review June 19, 1989. Accepted January 17, 1990. The financial support from the Grants-in-Aid for Scientific Research Fund in 1988 (Project No. 63603025) by the Ministry of Education, Science and Culture, Japan, and the Tokyo Electric Power Co., Inc., are greatly appreciated.

Adsorption of Normal Alkanes from Isooctane Solution onto Crystalline Urea

Rasheed S. Al-Ameeri[†] **and Mohamed M. Hassan**[*]

Department of Chemical Engineering, University of Missouri—Columbia, Columbia, Missouri 65211

Experimental data are reported for the adsorption of four *n*-alkanes from isooctane solution onto crystalline urea. Equilibrium isotherms for *n*-dodecane, *n*-tetradecane, and *n*-hexadecane were obtained at 283, 295, and 303 K. The equilibrium adsorption data were correlated by the Langmuir, Freundlich, and BET isotherm equations. The kinetics of the adsorption of *n*-dodecane, *n*-tridecane, and *n*-tetradecane from isooctane solution onto crystalline urea were also studied at 283, 295, and 303 K. The kinetic data were used to calculate the diffusivities and the apparent energies of activation for the urea–*n*-alkane systems.

Introduction

Industrial applications of *n*-paraffins depend on the number of carbon atoms in the *n*-alkane chain. For instance, *n*-paraffins with a chain length of C_8 to C_{20} are used in the manufacture of surfactants and single-cell proteins, C_{10} to C_{17} are used as plasticizers, and C_{20} and higher can be used as additives for lubricating oils. At present, industrial separations of *n*-alkanes from petroleum distillates are accomplished primarily by selective adsorption on molecular sieves and urea adduction techniques. Only a few studies have been reported in which solid urea was used to adsorb *n*-paraffins. Among those studies, McAdie and Frost (*1*), Calderbank and Nikolov (*2*), Patrilyak and Motornyi (*3*), and Zimmerschield et al. (*4*) presented experimental data. Schirmer et al. (*5*) studied the adsorption of *n*-alkanes with medium chain length (C_{10}–C_{12}) on molecular sieve 5A and compared the results with the adsorption on solid urea. They found the dimensions of molecular sieve 5A and urea cavities are similar; both have critical diameters of about 5 Å. Inside the cavities, the molecules of the *n*-alkanes interact during adsorption with the oxygen atoms in the urea channels.

This study presents the adsorption of *n*-dodecane, *n*-tridecane, *n*-tetradecane, and *n*-hexadecane from isooctane solution onto crystalline urea at 283, 295, and 303 K. The data obtained are important for developing a new separation procedure based on the physicochemical aspects of the urea–*n*-alkane systems.

Experimental Section

Materials. All of the chemicals used were high-purity-grade reagents. *n*-Dodecane, *n*-tridecane, *n*-tetradecane, and *n*-hexadecane were used as adsorbates in this study. All four *n*-alkanes were obtained from Alltech Associates, Deerfield, IL, and had a stated purity greater than 99.5%. Isooctane and methanol were obtained from the Matheson Co. with stated minimum purities of 99.5%. The chemicals were used without further purification. The adsorbent used was crystalline urea supplied by Hopkin and Williams Co., Essex, England. Prior to use, the crystalline urea was dried by heating it in a vacuum desiccator for 5 h. It was then placed in a closed container until it was to be weighed for the adsorption study.

Procedure. The adsorption isotherm data were determined by adding 25 mL of sample solutions of initial concentrations ranging from 10 to 50 mol/m^3 to a carefully weighed 1 g of crystalline urea. The solutions were placed in sample bottles and sealed tightly with Teflon-lined caps. The bottles were then placed in a shaker bath, controlled at either 283, 295, or 303 K (±0.2 °C), for 24 h to reach equilibrium. After equilibration, the solutions were withdrawn and filtered twice with Whatman No. 42 filter paper to ensure that all urea crystals were removed from the solution. The filtrate samples were then analyzed with use of a digital density meter (Model DM 240) manufactured by Anton Paar, Graz, Austria.

The batch kinetic data were obtained by mixing 1000 mL of the *n*-alkane solutions (initial concentration 40 mol/m^3) with 10 mL of methanol activator. From the mixture, 25-mL samples were withdrawn and placed in sample bottles each containing a carefully weighted 1 g of crystalline urea. The bottles were tightly sealed with Teflon-lined caps and then placed in a shaker bath controlled to within ±0.2 °C of the desired temperature. Periodically, a sample solution was withdrawn and filtered twice with Whatman No. 42 filter paper to ensure that all urea crystals were removed from the solution. The analysis of the sample filtrate was performed using the digital density meter (DM 240). In order to achieve an accurate measurement, a constant

---

[*] To whom correspondence should be directed.

[†] Department of Chemical Engineering, Kuwait University, Kuwait.

0021-9568/90/1735-0110$02.50/0 © 1990 American Chemical Society

Table I. Adsorption Isotherm Data for *n*-Dodecane, *n*-Tetradecane, and *n*-Hexadecane

	283 K		295 K		303 K	
n-alkane	*C*, mol/m^3	*q*, mol/kg	*C*, mol/m^3	*q*, mol/kg	*C*, mol/m^3	*q*, mol/kg
n-C_{12}	9.25	0.07	10.0	0.01	7.50	0.15
	16.5	0.18	18.5	0.91	15.0	0.12
	17.3	0.80	25.5	1.26	27.0	0.79
	18.5	1.46	29.5	1.63	45.0	1.58
	21.3	1.78	34.2	1.75	48.0	1.72
	33.8	1.84	43.2	1.79		
	41.8	1.93	54.3	1.78		
n-C_{14}	3.00	0.35	1.50	0.22	6.50	0.12
	3.75	0.83	6.25	0.67	8.25	0.54
	4.00	1.37	6.50	1.72	10.5	0.93
	12.3	1.42	11.3	1.87	12.0	1.47
	14.5	1.59	21.0	1.92	13.0	1.90
	24.0	1.67	29.5	1.97	20.8	1.93
	34.8	1.72	40.0	1.89	39.0	1.96
n-C_{16}	2.20	0.30	1.30	0.42	1.50	0.55
	4.00	0.66	1.50	1.29	2.40	1.08
	4.20	1.25	3.00	1.72	3.00	1.72
	8.70	1.35	4.50	2.21	5.00	2.12
	12.5	1.62	13.5	2.22	14.5	2.13
	22.2	1.70	20.5	2.25	22.5	2.17
	26.5	1.72	30.5	2.31	37.8	2.17
	34.0	1.74	36.8	2.26	46.0	2.21

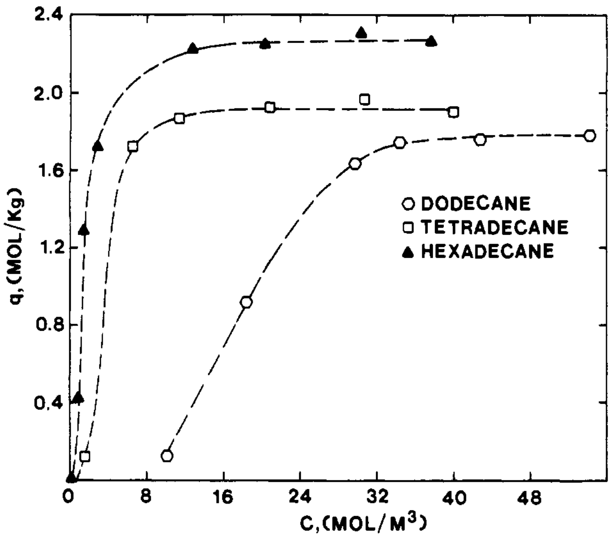

Figure 1. Adsorption isotherms of *n*-dodecane, *n*-tetradecane, and *n*-hexadecane at 295 K.

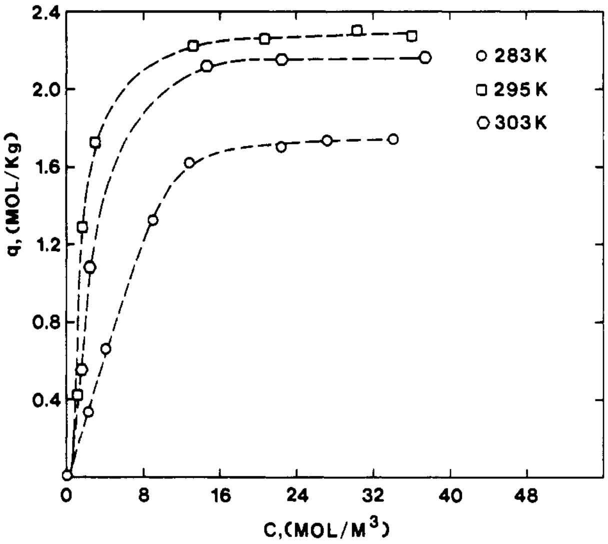

Figure 2. Adsorption isotherms of *n*-hexadecane at different temperatures.

temperature was maintained in the oscillator with a recirculating ultrathermostat with an accuracy of ±0.05 °C. The amount of each *n*-alkane adsorbed onto crystalline urea was found by comparing the final concentration of the sample solution with a calibration curve that was prepared for the *n*-alkane in isooctane solution. For each sample solution, three analyses were performed to obtain the mean value. The average absolute deviation from the mean was estimated to be 0.05% mole fraction.

Results and Discussion

Equilibrium Data. The equilibrium data for the adsorption of *n*-dodecane, *n*-tetradecane, and *n*-hexadecane onto crystalline urea at 283, 295, and 303 K are presented in Table I. Figure 1 shows the adsorption isotherms of *n*-dodecane, *n*-tetradecane, and *n*-hexadecane onto crystalline urea at 295 K. An examination of the equilibrium data revealed that the adsorption of *n*-alkanes from isooctane solution increases with increasing chain length. This result agrees with the findings of Schiessler et al. (*6*), who noted that the addition of a CH_2 group to the *n*-alkane chain length increases the interaction between the adsorbate molecules and the electrostatic field of crystalline urea. This electrostatic field is strong enough to cause shifts of bonding electrons in adsorbed molecules and strong interactions between the urea and the diffusing *n*-alkane molecules. The physicochemical interactions between the *n*-alkane molecules and the urea channels have been described by Smith (*7*). The effect of the adsorption temperature on the equilibrium uptake of *n*-hexadecane onto crystalline urea is shown in Figure 2. It is important to note that the equilibrium uptake does not decrease with an increase in the temperature of adsorption as expected theoretically. The equilibrium uptake is dependent on an optimal temperature, which is of practical interest (*8*). At temperatures higher than the optimal, the uptake is lower because of the shift of the equilibrium in the direction of dissociation.

Kinetic Data. The experimental data for the kinetics of the adsorption of *n*-dodecane, *n*-tridecane, and *n*-tetradecane onto crystalline urea at 295 K are presented in Figure 3. The plots of Figure 3 indicate that the amount adsorbed, for a given time, increases with increasing chain length of the *n*-alkane. The uptake rate data conformed to the "$t^{1/2}$ diffusion law" rather than to a simple linear (or exponential) dependence on time. This result supports and extends the conclusions reached by Lathi and Manning (*9*), who found that the *n*-alkanes are occluded in the urea channels by a slow activated diffusion pro-

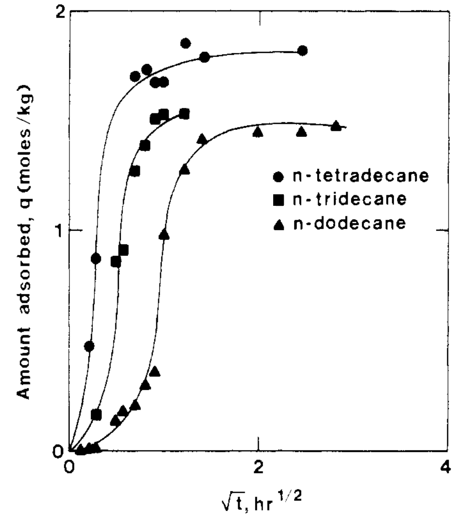

Figure 3. Kinetics of the adsorption of *n*-dodecane, *n*-tridecane, and *n*-tetradecane at 295 K.

Table II. Effective Diffusion Coefficients for *n*-Dodecane, *n*-Tridecane, and *n*-Tetradecane at 283 K

n-alkanes	fractional uptake (q_t/q_m)	$D_e \times 10^{10}$, cm^2/s
n-dodecane	0.20	0.80
	0.30	1.40
	0.40	2.60
	0.50	4.00
	0.60	5.40
n-tridecane	0.20	5.70
	0.30	9.20
	0.40	12.8
	0.50	16.0
	0.60	18.4
n-tetradecane	0.20	
	0.30	24.0
	0.40	36.0
	0.50	38.4
	0.60	37.0

cess. The diffusivities for the adsorption of *n*-dodecane, *n*-tridecane, and *n*-tetradecane were calculated from the expression

$$\frac{q_t}{q_m} = 2\frac{A}{V}\left(\frac{D_e t}{\pi}\right)^{1/2} \tag{1}$$

where q_t and q_e represent the amounts of *n*-alkane adsorbed at time *t* and at equilibrium, respectively. D_e is the effective diffusion coefficient, cm^2/s, and A/V denotes the ratio of external area to particle volume of adsorbent. The values of the effective diffusion coefficients for *n*-dodecane, *n*-tridecane, and *n*-tetradecane are presented in Table II. The diffusion coefficients derived from the uptake rate measurements do not remain constant with increasing adsorbent loading. The rate of adsorption of *n*-dodecane, *n*-tridecane, and *n*-tetradecane from isooctane solution by crystalline urea at 283 K is shown in Figure 4. The rate of adsorption tends to increase with increasing chain length of the *n*-alkane. The activation energies for diffusion of the *n*-alkanes were calculated from the equation

$$E_a = 2.303R\frac{\log D_1 - \log D_2}{\dfrac{1}{T_1} - \dfrac{1}{T_2}} \tag{2}$$

where D_1 and D_2 represent the diffusion coefficients at temperatures T_1 and T_2, respectively. The values of the activation energy for diffusion are presented in Table III. The fact that the energy of activation increases with increasing chain length of the *n*-alkane is somewhat consistent with the literature (*10*).

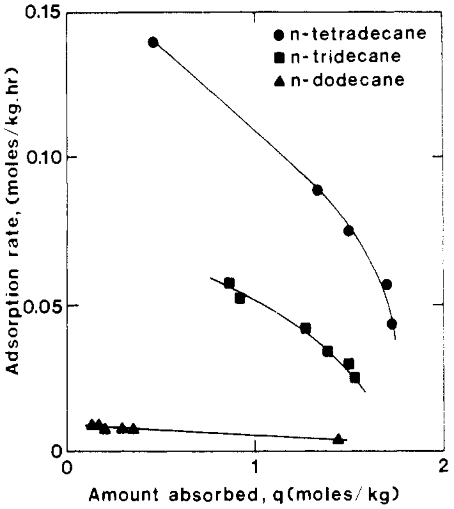

Figure 4. Adsorption rates for *n*-dodecane, *n*-tridecane, and *n*-tetradecane at 283 K.

Table III. Activation Energies for Diffusion of *n*-Dodecane, *n*-Tridecane, and *n*-Tetradecane in the Temperature Range 283–295 K

n-alkane	fractional uptake (q_t/q_m)	E_a, kcal/mol
n-dodecane	0.30	6.25
	0.40	3.30
	0.50	2.23
	0.6	1.23
	0.70	0.63
n-tridecane	0.30	7.13
	0.40	6.31
	0.50	5.26
	0.60	4.46
	0.70	4.02
n-tetradecane	0.30	16.4
	0.40	13.2
	0.50	11.0
	0.60	11.3
	0.70	12.4

Table IV. Parameters of the Freundlich Isotherm Equation

n-alkane	*T*, K	k_1	$1/n$	av abs dev, %
n-dodecane	283	0.07	0.896	18.6
	295	0.143	0.651	8.8
	303	0.048	0.898	5.4
n-tetradecane	283	0.647	0.283	9.6
	295	0.628	0.334	11.8
	303	0.324	0.507	19.2
n-hexadecane	283	0.552	0.354	5.3
	295	1.17	0.21	16.9
	303	1.09	0.207	13.1

The addition of a CH$_2$ group to the *n*-alkane chain length would be expected to increase the heat of adsorption and the activation energy as well.

Data Correlation

The equilibrium data were compared to the Langmuir, Freundlich, and BET isotherm equations. Although the Langmuir, Freundlich, and BET equations may not strictly apply to the adsorption of *n*-alkanes onto crystalline urea, they were used in this work to follow the development of the physicochemical aspects of the urea-*n*-alkane systems. The Freundlich equation (*11*) is a semiempirical expression that has been widely used to represent equilibrium data, particularly for adsorption from liquids. The Freundlich equation has the form

$$q = k_1 C^{1/n} \tag{3}$$

where *q* is the amount of adsorbate per unit weight of adsor-

Table V. Parameters of the Langmuir Isotherm Equation

n-alkane	*T*, K	a_1	a_2	av abs dev, %
n-dodecane	283	0.061	0.007	18.8
	295	0.073	0.020	7.6
	303	0.041	0.005	4.4
n-tetradecane	283	0.430	0.217	5.75
	295	0.397	0.166	10.44
	303	0.159	0.050	17.80
n-hexadecane	283	0.552	0.354	5.3
	298	1.17	0.21	16.9
	303	1.09	0.207	13.1

Table VI. Parameters of the BET Isotherm Equation

n-alkane	*T*, K	q_m	*f*
n-dodecane	283	5.29	159
	295	4.31	19
	303		
n-tetradecane	283	2.15	142
	295	2.70	91
	303	3.88	36
n-hexadecane	283	2.29	129
	295	2.81	297
	303	2.43	374

bent, mol/kg, and C is the equilibrium concentration of the *n*-alkane in the solution, mol/m^3. The constant k_1 is a measure of the adsorbent capacity, and n is constrained to be greater than 1. The parameters of the Freundlich equation were determined for each system at different temperatures by using a nonlinear least-squares curve fit to the experimental data. The values of the parameters and the average absolute deviations between the predicted and the experimental data are presented in Table IV.

The Langmuir equation (*12*, *13*), which can be derived either from the concept of dynamic equilibrium between the rates of adsorption and desorption or by using statistical thermodynamics, has the form

$$q = \frac{a_1 C}{1 + a_2 C} \tag{4}$$

where a_1 and a_2 are the first and second Langmuir constants, respectively. The best values for a_1 and a_2 were obtained by using a nonlinear least-squares curve fit to experimental data. The constants of the Langmuir equation for each system at different temperatures are presented in Table V.

The equation most widely used to obtain the surface area of solids is that derived by Brunauer, Emmett, and Teller (BET equation) for multilayer adsorption on nonporous adsorbents (*14*). The BET equation has been widely used to calculate the monolayer capacity and the surface area from the adsorption isotherm data. The expression for the BET isotherm equation may be written as

$$q = \frac{q_m\beta(f-1)X(1-X)}{1+(\beta f-1)X} \tag{5}$$

where q is the amount of adsorbate per unit weight of adsorbent, mol/kg, and X is the equilibrium concentration of the *n*-alkane in mole fraction. The parameter β is defined as a coefficient of mutual displacement of the molecules of isooctane and the *n*-alkanes, f is a function due to the difference of the molecular fields of the bulk and adsorbed phases, and q_m represents a characteristic constant of the amount of adsorption that would saturate the unit surface with a monolayer. A plot of $X(1-X)/q$ against X would be a straight line with a slope given by $(\beta f - 1)/q_m\beta(f-1)$ and an intercept defined by $1/q_m\beta(f-1)$, so that the values of q_m and f can be calculated. The coefficient β has been taken as equal to 1. The values of the parameters obtained for q_m and f are presented in Table VI. The stronger the adsorbate–adsorbent interactions, the

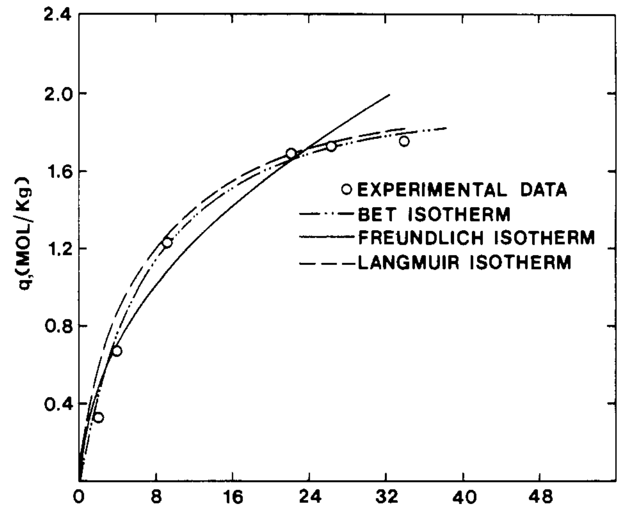

Figure 5. Comparison of experimental and predicted isotherms for *n*-hexadecane at 283 K.

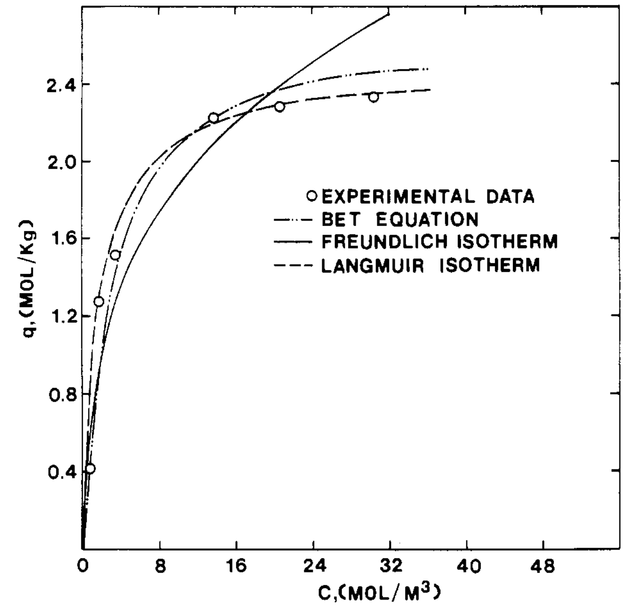

Figure 6. Comparison of experimental and predicted isotherms for *n*-hexadecane at 295 K.

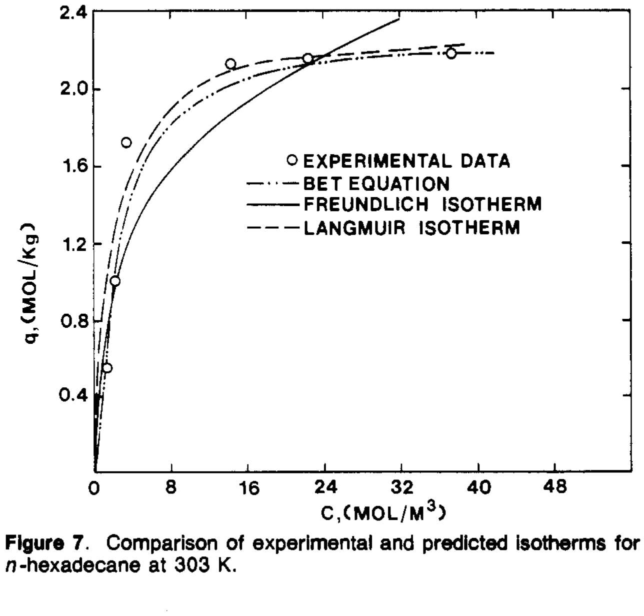

Figure 7. Comparison of experimental and predicted isotherms for *n*-hexadecane at 303 K.

higher the f values. Figures 5-7 show a comparison of the predicted and experimental data for the adsorption of n-hexadecane at 283, 295, and 303 K. The adsorption isotherms calculated from parameters determined by a nonlinear least-squares fitting procedure are in fairly good agreement with the experimental data. From the results presented, the Langmuir isotherm equation appears to provide a better fit to the experimental data than the Freundlich model. The average absolute deviations between the predicted and the experimental data range from 5.3% to 19.2% for the Freundlich isotherm and from 4.4% to 18.8% for the Langmuir isotherm equation. The poor fit of the Freundlich isotherm equation is due to systematic deviations between the predicted values and the experimental data. That is, the predicted values are higher than the experimental ones in both regions of lower and higher concentrations, while in the region of medium concentration the predicted values are lower than the experimental ones. The BET isotherm equation provides a good overall correlation of the experimental data. The values of the parameters in Tables IV-VI show a considerable scatter among the adsorbates. The temperature dependence of the parameters is also questionable. Although any two parameter model would provide a good fit to the data, there remains a problem of whether the parameters for the Langmuir, Freundlich and BET equations can be related to the adsorption process.

Glossary

a_1, a_2	parameters of the Langmuir isotherm
A	surface area
C	equilibrium concentration, mol/m^3
D_e	effective diffusion coefficient
E_a	apparent activation energy
f	separation coefficient
k_1	a parameter of the Freundlich isotherm equation
n	constant in the Freundlich isotherm equation
q_t	amount of n-alkane adsorbed at time t
q_e	amount adsorbed at equilibrium
q_m	amount adsorbed in the monolayer
R	gas constant
T	temperature
V	unit volume
X	equilibrium concentration, mole fraction
β	coefficient of mutual displacement of the components

Literature Cited

(1) McAdie, H. G.; Frost, G. B. *Can. J. Chem.* **1958**, *36*, 635.
(2) Calderbank, A. H.; Nikolov, N. S. *J. Phys. Chem.* **1956**, *60* (1), 1.
(3) Patrilyak, K. I.; Motornyi, V. G. *Rus. J. Phys. Chem.* **1975**, *49*, 649.
(4) Zimmerschield, W. J.; Dinerstein, R. W.; Weitkamp, A. W.; Marschner, R. F. *Ind. Eng. Chem.* **1950**, *42*, 1300.
(5) Schrimer, W.; Fiedrich, G. IUPAC, Tagung, Moscow, 1965.
(6) Schiessler, R. W.; Flitter, D. *J. Am. Chem. Soc.* **1952**, *74*, 1720.
(7) Smith, A. E. *Acta Crystallogr.* **1952**, *5*, 224.
(8) Dorodnova, V. S.; Korzhov, Y. A.; Martynenko, A. G. *Chem. Technol. Fuels Oils* **1982**, *18*, 395.
(9) Lathi, L. E.; Manning, F. S. *Ind. Eng. Chem. Process Des. Dev.* **1985**, *4* (3), 254.
(10) Barrer, R. M.; Ibbitson, D. A. *Trans. Faraday Soc.* **1944**, *40*, 195.
(11) Freundlich, H. *Z. Phys. Chem.* **1906**, *57*, 385.
(12) Langmuir, I. *J. Am. Chem. Soc.* **1916**, *38*, 2221.
(13) Langmuir, I. *J. Am. Chem. Soc.* **1917**, *39*, 1848.
(14) Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1936**, *60*, 309.

Received for review July 14, 1989. Accepted January 17, 1990.

Isobaric Vapor–Liquid Equilibria for the Binary Systems of Benzene/Triethylamine, Benzene/Trimethyl Phosphite, and Triethylamine/Trimethyl Phosphite[†]

N. V. K. Dutt,* A. P. Kahol, P. J. Reddy, and K. S. Raghunandanan
Indian Institute of Chemical Technology, Hyderabad 500007, India

Isobaric boiling point data for the binary liquid mixtures of benzene with triethylamine, benzene with trimethyl phosphite, and triethylamine with trimethyl phosphite are obtained at 100- and 200-mmHg pressures. The data are found to be well represented by the Wilson and the NRTL models.

Introduction

The importance of benzene, triethylamine, trimethyl phosphite, and their mixtures in plastic, detergent, drug, dye, and pesticide industries is well-known. Among the binary combination of this group of important compounds, only the isothermal VLE measurements on benzene–triethylamine system are reported in the literature (*1*, *2*). Hence, the present work on isobaric VLE measurements is undertaken. The method of fitting the experimental temperature–liquid composition (t–x) measurements to the well-tested models for predicting the liquid-phase activity coefficients is employed in this study. The advantages of this method are as follows: (i) quicker estimation and (ii) minimization of the effort as well as errors involved in the measurement of vapor composition.

Experimental Section

The apparatus consists of a Swietoslawski-type ebulliometer described by Hala et al. (*3*), a Cenco high-vacuum pump, a U-tube mercury manometer, a double surface condenser, and a 2-L capacity buffer vessel for dampening the pressure fluctuations. An externally wound nichrome wire supplies the heat to the ebulliometer so that the apparatus could be used for corrosive liquids also. Nucleation for the boiling process is provided by fine glass pieces fused inside the ebulliometer. Cold water circulated at an appropriate flow rate in the double-walled condenser ensures the complete condensation of the vapors. Temperature measurements, with use of a calibrated mercury-in-glass thermometer, are to an accuracy of 0.1 °C while the pressures are maintained and measured to an accuracy of 1 mmHg.

---

* Author for correspondence.

[†] IICT Communication No. 2096.