J. Chem. Eng. Data 1991, 36, 319-321

Adsorption of Binary Liquid Mixtures of Amines on Zeolite 13X at 29 °C

Emmanuel A. Dada and Leonard A. Wenzel*

Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015

Experimental data for adsorption of binary liquid mixtures of diethylamine and dipropylamine, diethylamine and triethylamine, and dipropylamine and triethylamine on zeolite 13X at 29 °C were obtained. Diethylamine is preferentially adsorbed over both dipropylamine and triethylamine in the binaries throughout the concentration range. Also, dipropylamine is preferentially adsorbed in a dipropylamine–triethylamine system over the entire concentration region. The data are subjected to the thermodynamic consistency test.

Introduction

Zeolites are widely used in purification and separation processes. The high selectivity of the zeolites in conjunction with their "molecular sieve" action find wide applications in the processing of a wide variety of feedstocks. Zeolites are also used as a catalyst or catalyst support in the petroleum industry. Compared with other adsorbents like activated carbon and silica gel, zeolites have exceptionally high adsorptive capacities for many chemical substances. In spite of the importance of zeolites, there have been limited adsorption data of liquids on zeolites reported in the open literature. Most of the reported work has been limited to the adsorption of paraffins on zeolites (*1–4*). Thermodynamic consistency tests on the data reported on adsorption on zeolites are lacking in most of the work. The disagreements between the work of Sundstrom et al. (*4*) and Gupta et al. (*1*) and between the work of Kipling and Wright (*5*) and Jain et al. (*6*) on adsorbent capacities of some components may be difficult to resolve because the experimental variables used by these authors are not amenable to the thermodynamic consistency test (*7–9*).

The meaningful experimental variable for adsorption of liquids on adsorbents is the surface excess (*7*). With a few exceptions (*8*, *10*), the adsorption data on zeolites have not been reported in terms of the surface excess. One of the advantages of using the surface excess variable is that if the binary data are thermodynamically consistent, reasonable binary parameters for predicting adsorption of a multicomponent system can be obtained. Minka and Myers (*9*) have successfully developed and tested a theory for predicting the adsorption of ternary liquid mixtures on solids using parameters obtained from the binary data only. The theory has been simplified and extended to multicomponent systems by Dada (*11*). Our objective in this paper is to present the surface excess data on the adsorption of the constituent binaries of diethylamine, dipropylamine, and triethylamine on zeolite 13X and show that the data are thermodynamically consistent.

Experimental Section

Materials and Equipment. Zeolite 13X used in this study is a powder form of a Linde molecular sieve product of the Union Carbide Co. The chemicals used (diethylamine, dipropylamine, and triethylamine) were purchased from Eastman Kodak Co. The chemicals are of 99.8% minimum purity and were used without further purification. For each equilibrium data determination, the liquid mixture of interest and the activated zeolite were put in a 30-mL septum type screw-cap bottle. This enabled the needle of a microliter syringe to pierce the septum to withdraw liquid sample for analysis on the gas chromatograph (GC). An isotherm vacuum oven Model 281 of Fischer Scientific Co. was used to activate the zeolite 13X sample. Equilibration of the adsorption system was carried out in a temperature-controlled water bath shaker of the New Brunswick Scientific Co., New Brunswick, NJ. The water bath maintains a thermostatically controlled temperature within ±0.2 °C and with a capability of up to 500 rpm.

The composition of each of the equilibrated bulk liquid phase mixtures was analyzed on a Perkin-Elmer Model 910 GC using its thermal conductivity detector facility. A heated on-column injector packed column glass tube of dimension 6-mm o.d., 4-mm i.d., and 1.83-m length was used. The column was packed with chromosorb 103 of 80/100 mesh (Supelco).

Procedures. A 0.2-g amount of zeolite 13X was added to a weighed dry empty bottle and activated in a vacuum oven operated at 240 °C for 24 h. The oven was allowed to cool under vacuum and was purged with dry helium gas. By a weight difference technique, the weight of the activated zeolite 13X was determined by using an analytical balance with an accuracy of ±0.0002 g. Then a 1.25-mL aliquot of a standard binary liquid mixture of amines of interest was added and its weight similarly determined. The bottle was placed in a temperature-controlled water bath shaker operating at 200 rpm and 29 °C, and its contents were allowed to equilibrate for 36 h. The contents of the bottle were allowed to settle, 0.2 μL of a clear liquid sample was withdrawn, and its composition was analyzed on the GC. The GC was initially calibrated from a series of prepared standard binary liquid mixtures of the amines of interest in this study. The accuracy of the measurements of the mole fraction of the binary liquid mixtures is better than ±0.002. Further details of the experimental method are described elsewhere (*11*).

Results and Discussion

The experimentally determined adsorption variable is the surface excess, n_i^e, defined as (*11*)

$$n_i^e = n^0(x_i^0 - x_i^l) \tag{1}$$

Standard binary mixtures were prepared ranging from 0.04 to 0.96 mole fraction of component i. The surface excess, n_i^e, at 29 °C was determined by using eq 1. The results for the adsorption of diethylamine + dipropylamine, diethylamine + triethylamine, and dipropylamine + triethylamine are shown in Tables I–III, respectively.

The surface excess data are correlated by using the modified Freundlich adsorption isotherm equation defined as (*8*, *11*)

$$n_i^e = p x_i^l (x_i^l)^q x_j^l - r (x_j^l)^s x_i^l \tag{2}$$

The results are shown in Table IV and Figures 1–3. From Figures 1 and 2, diethylamine is preferentially adsorbed by zeolite 13X over both dipropylamine and triethylamine throughout the entire composition range. Of the three components, diethylamine has the smallest and most compact structure, and hence it has the best packing efficiency in the cavities of zeolite 13X. Satterfield and Cheng (*2*) and Satterfield and Smeets (*3*) reached a similar conclusion in their studies of

0021-9568/91/1736-0319$02.50/0

Table I. Adsorption of Liquid Mixtures of Diethylamine (1) and Dipropylamine (2) on Zeolite 13X at 29 °C

x_1^0	x_1^l	n_1^e, mmoles/g	x_1^0	x_1^l	n_1^e, mmoles/g
0.048	0.039	0.444	0.448	0.416	1.728
0.077	0.063	0.706	0.467	0.438	1.575
0.095	0.080	0.738	0.468	0.440	1.618
0.123	0.104	0.982	0.502	0.469	1.729
0.145	0.124	1.015	0.517	0.491	1.740
0.174	0.152	1.146	0.569	0.537	1.785
0.215	0.190	1.275	0.630	0.604	1.646
0.223	0.197	1.332	0.647	0.619	1.589
0.243	0.217	1.319	0.648	0.620	1.557
0.271	0.241	1.542	0.687	0.662	1.455
0.289	0.260	1.508	0.727	0.710	1.131
0.331	0.302	1.496	0.730	0.711	1.195
0.341	0.312	1.496	0.773	0.757	0.911
0.364	0.333	1.655	0.827	0.816	0.695
0.370	0.340	1.640	0.829	0.818	0.732
0.394	0.363	1.611	0.928	0.922	0.341
0.427	0.396	1.649	0.960	0.957	0.209

Table II. Adsorption of Liquid Mixtures of Diethylamine (1) and Triethylamine (2) on Zeolite 13X at 29 °C

x_1^0	x_1^l	n_1^e, mmoles/g	x_1^0	x_1^l	n_1^e, mmoles/g
0.047	0.024	1.060	0.427	0.384	2.300
0.053	0.029	1.197	0.473	0.434	2.058
0.075	0.045	1.500	0.572	0.539	1.985
0.122	0.085	1.787	0.574	0.543	1.825
0.140	0.097	2.047	0.601	0.568	1.708
0.176	0.138	2.135	0.733	0.708	1.340
0.225	0.177	2.401	0.777	0.759	1.122
0.253	0.203	2.526	0.877	0.867	0.644
0.341	0.286	2.655	0.910	0.901	0.544
0.335	0.287	2.469	0.961	0.957	0.204
0.369	0.322	2.476			

Table III. Adsorption of Liquid Mixtures of Dipropylamine (1) and Triethylamine (2) on Zeolite 13X at 29 °C

x_1^0	x_1^l	n_1^e, mmoles/g	x_1^0	x_1^l	n_1^e, mmoles/g
0.037	0.030	0.313	0.704	0.698	0.303
0.079	0.070	0.406	0.729	0.723	0.286
0.145	0.135	0.453	0.806	0.802	0.201
0.239	0.228	0.542	0.831	0.827	0.187
0.376	0.365	0.484	0.900	0.898	0.106
0.450	0.440	0.476	0.944	0.943	0.076
0.508	0.499	0.435			

Table IV. Modified Freundlich Isotherm Equation Parameters for Adsorption of Liquid Amines on Zeolite 13X at 29 °C

	parameters			
liquid mixtures system on zeolite 13X	p	q	r	s
diethylamine (1) + dipropylamine (2)	14.42	0.90	8.51	0.95
diethylamine (1) + triethylamine (3)	14.55	0.65	10.27	0.99
dipropylamine (2) + triethylamine (3)	1.28	0.40	0.16	0.95

the adsorption of hydrocarbons on zeolites. Because of their structural differences, dipropylamine has a better packing efficiency in the zeolite cavities than triethylamine. Therefore dipropylamine would be preferentially adsorbed by zeolite 13X over triethylamine throughout the concentration range, as confirmed in Figure 3. It should be noted that both dipropylamine and triethylamine have the same molecular weight. Thus the structural differences of the species play the significant role in the observed preferential adsorption by zeolite 13X. This is further confirmed from Figures 1 and 2 which show that diethylamine is more preferentially adsorbed in a diethylamine and triethylamine binary mixture (Figure 2) than in a diethylamine and dipropylamine binary mixture (Figure 1) throughout the entire concentration range. Here, diethylamine and dipropylamine are secondary amines whereas triethylamine is a tertiary amine. Thus the preferential adsorption of zeolite for one component

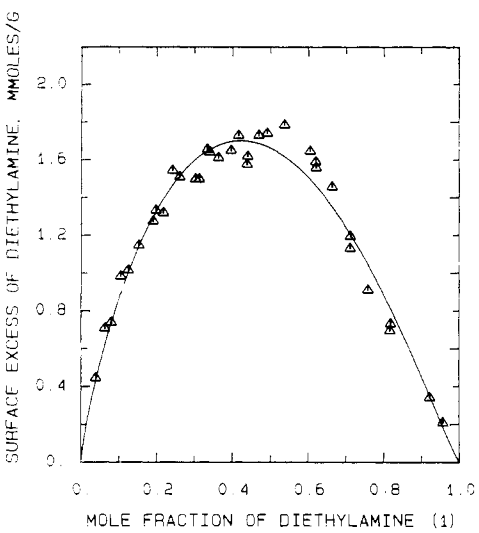

Figure 1. Adsorption of diethylamine from the binary mixture of diethylamine (1) and dipropylamine (2) on zeolite 13X at 29 °C.

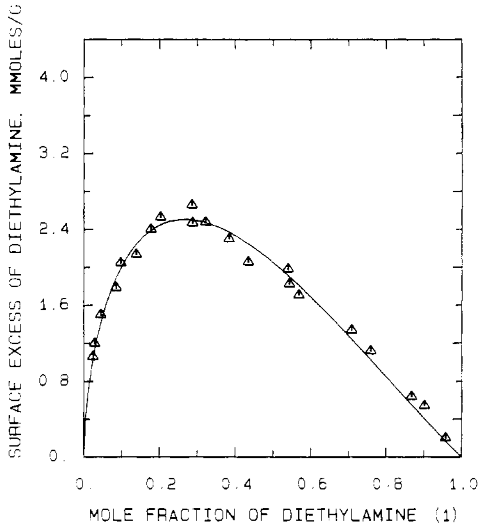

Figure 2. Adsorption of diethylamine from the binary mixture of diethylamine (1) and triethylamine (2) on zeolite 13X at 29 °C.

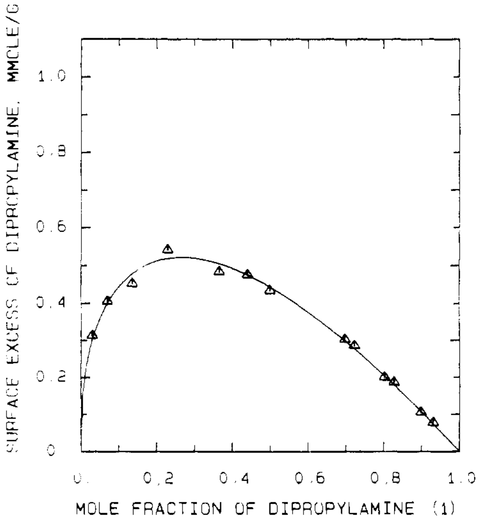

Figure 3. Adsorption of dipropylamine from the binary mixture of dipropylamine (1) and triethylamine (2) on zeolite 13X at 29 °C.

Table V. Constants of the Redlich–Kister Equation for the Binary Liquid Mixtures of Amines at 29 °C

	bulk liquid phase parameters				
components ($i + j$)	A_{ij}	B_{ij}	C_{ij}	D_{ij}	average deviation |obs − calc|
Using the UNIFAC Model Predicted Bulk Liquid Activity Coefficients					
diethylamine (1) + dipropylamine (2)	−0.0236	−0.0017	−0.0001	0.0000	0.000 20
diethylamine (1) + triethylamine (3)	0.1717	0.00943	0.0019	0.0002	0.000 03
dipropylamine (2) + triethylamine (3)	0.12058	−0.0121	0.0019	−0.0004	0.000 02
Using Literature Data (DECHEMA) Bulk Liquid Activity Coefficients					
diethylamine (1) + triethylamine (3)	0.1219	0.0174	0.0024	0.0003	0.000 02

Table VI. Integral Thermodynamic Consistency Test of Adsorption of Binary Liquid Mixtures of Amines on Zeolite 13X at 29 °C

components ($i + j$)	calculated free energy of immersion,[a] mmol/g
Using UNIFAC Model Predicted Bulk Liquid Activity Coefficients	
diethylamine (1) + dipropylamine (2)	7.08
dipropylamine (2) + triethylamine (3)	2.56
triethylamine (3) + diethylamine (1)	−11.07
sum	−1.43
Using Literature Data (DECHEMA) Bulk Liquid Activity Coefficients	
triethylamine (3) + diethylamine (1)	−11.25

[a] $(\phi_j^0 - \phi_i^0)/RT$.

over the other component will increase as the structural difference between the competing components increases.

The free energy of immersion, ϕ, of an adsorbent in a liquid solution is given by (*7*, *11*)

$$\phi_j^0 - \phi_i^0 = -RT\int_1^0 \left(\frac{n_i^e}{x_i^l x_j^l \gamma_i^l}\left(\gamma_i^l + x_i^l \frac{d\gamma_i^l}{dx_i^l}\right)\right) dx_i^l \qquad (3)$$

Binary data can be tested for the thermodynamic consistency test by using the method of Sircar and Myers (*7*). The test requires that

$$(\phi_3^0 - \phi_1^0) + (\phi_1^0 - \phi_2^0) + (\phi_2^0 - \phi_3^0) = 0.0 \qquad (4)$$

The integration required in eq 3 is very sensitive at the extremely low concentration region where the surface excess data are generally not very accurate. Therefore, the summation required in eq 4 is generally not expected to be closed due to the associated experimental errors. The integration required in eq 3 could be carried out numerically by fitting the surface excess data with a cubic spline interpolation. Because of the random errors, especially at the low concentration region, cubic spline interpolation gives undesirable oscillations at the extreme concentration regions. These random errors can be eliminated by first smoothing the data and then fitting the smoothed data with a cubic spline interpolation. These procedures have been detailed by Dada (*11*). Because the derivative of the activity coefficient of a given component with respect to its mole fraction is required in eq 3, a four-parameter Redlich–Kister activity coefficient equation (*9*, *11*, *12*) is very convenient and was used in this work.

Of the three binaries in this work, only the activity coefficient of the binary liquid mixture of diethylamine and triethylamine is available in the literature (*13*). The available activity coefficient data in terms of the NRTL equation parameters are converted to the equivalent Redlich–Kister equation parameters. The UNIFAC (universal functional activity coefficient) method (*12*) is then used to predict the binary liquid mixture activity coefficients of the three binaries as reported in Table V and detailed elsewhere (*11*). The integration required in eq 3 was carried out, and the results are shown in Table VI. From Table VI, $\phi_3^0 - \phi_1^0$, obtained by using the literature data activity coefficients of the binary mixture of diethylamine and triethylamine, compares favorably with the value obtained by using the UNIFAC predicted activity coefficients. As shown in Table VI, within the limits of experimental errors and the accuracy of the UNIFAC model used to predict the activity coefficients of the binary liquid mixtures, the obtained surface excess data satisfied the thermodynamic consistency test of eq 4.

Glossary

i, j	components i, j
n_i^e	surface excess of component i
n^0	moles of liquid per gram of the adsorbent prior to contact of liquid and adsorbent
p, q, r, s	constants defined by eq 2
R	gas constant
T	temperature
x_i^0	mole fraction of component i prior to contact of liquid mixture and the adsorbent
x_i^l	bulk liquid phase mole fraction of component i
ϕ	free energy of immersion of adsorbent in liquid solution
ϕ_i^0	free energy of immersion of adsorbent in pure ith component
γ_i^l	bulk liquid phase activity coefficient of component i

Registry No. Diethylamine, 109-89-7; dipropylamine, 142-84-7; triethylamine, 121-44-8.

Literature Cited

(1) Gupta, R. K.; Kunzuru, D.; Saraf, D. N. *J. Chem. Eng. Data* **1980**, *25*, 14.
(2) Satterfield, C. N.; Cheng, C. S. *AIChE J.* **1972**, *18*, 720.
(3) Satterfield, C. N.; Smeets, J. K. *AIChE J.* **1974**, *20*, 618.
(4) Sundstrom, D. W.; Krautz, F. G. *J. Chem. Eng. Data* **1968**, *13*, 223.
(5) Kipling, J. J.; Wright, E. H. M. *Trans. Faraday Soc.* **1959**, *55*, 1185.
(6) Jain, L. K.; Gehrhardt, H. M.; Kyle, B. G. *J. Chem. Eng. Data* **1965**, *10*, 202.
(7) Sircar, S.; Myers, A. L. *AIChE J.* **1971**, *17*, 186.
(8) Kipling, J. J. *Adsorption from Solutions of Non-Electrolytes*; Academic Press: London, 1965.
(9) Minka, C.; Myers, A. L. *AIChE J.* **1973**, *19*, 453.
(10) Eletekov, Y. A.; Kiselev, A. V. *Molecular Sieves*; Society of the Chemical Industry: London, 1968.
(11) Dada, E. A. Ph.D. Dissertation, Lehigh University, Bethlehem, PA, 1989.
(12) Prausnitz, J. M.; Litchtenthaler, R. N.; Azevedo, E. G. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1986.
(13) *DECHEMA*, *Deutsche Gesellschaft dur Chemisches Apparatewesen*, *Vapor-Liquid Equilibrium Data Collections*; Behrens, D.; Eckermann, R., Eds.; Chemistry Data Series; Schon & Wetzel Gmbh: Frankfurt/Main, FRG, 1984; Vol. 1, Part 8.

Received for review October 24, 1990. Accepted February 20, 1991.