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Liquid-Phase Adsorption of a Benzene + Heptane Mixture on NaHY Zeolites

Jeong-Wan Choi,[†] Ko-Yeol Choi,[‡] and Baik-Hyon Ha[*]

Department of Chemical Engineering, Hanyang University, 17 Haengdangdong, Sungdongku, Seoul 133-791, Korea

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In liquid-phase adsorption of benzene + heptane on NaHY zeolites containing sodium, surface excesses were measured at 15, 30, and 45 °C. Maximum surface excesses appeared within the range of benzene mole fractions between 0 and 0.2 and increased with the sodium content. The total adsorption amount, separation factor, and difference between heats of immersion in two pure adsorbates were determined by using Everett's adsorption model. These thermodynamic parameters increased with the sodium content, especially rapidly above 27 sodium ions per unit cell.

Introduction

Synthetic faujasites X and Y have been studied not only as catalysts but also as adsorbents of selective adsorption separation from a gas and liquid mixture. Compared with gas-phase adsorption, however, little attention has been paid to liquid-phase adsorption on zeolites, especially at various cation contents.

The purpose of this investigation is to understand the characteristics of liquid-phase adsorption on NaHY zeolites with various cation contents. In the characterization of the liquid-phase adsorption, there are several models including Schay and Nagy's model (*1–3*), Sircar and Myers' model (*4–5*), and Everett's model (*6*). In this study, we employed Everett's model to determine the total adsorption amount, the separation factor, and the difference ($\Delta H_1° - \Delta H_2°$) between the enthalpies of immersion in two pure liquids.

Experimental Section

Materials. NaY (Union Carbide LZY-5) was used as a starting adsorbent for this research. The adsorbates were benzene and *n*-heptane. They were used after dehydration with metallic sodium and distillation.

Decationization of NaY. The NH_4NaY which have different sodium contents were obtained by ion exchange with 0.2, 0.4, 1, and 3 N NH_4Cl aqueous solutions for 1 h. The treated zeolites were filtered and washed completely with distilled water. After preliminary drying at 100 °C for 15 h, the zeolites were pelletized and crushed to 40–60-mesh size. The zeolite powder was further calcined at 500 °C for 16 h to obtain decationized NaHY.

The degrees of decationization of the prepared adsorbents were 12, 41, 51, 71, and 100%, determined by atomic absorption spectroscopy. The zeolites were named to be NaHY-12, NaHY-41, NaHY-51, NaHY-71, and HY, on the basis of the decationization degree. The sodium levels of decationized zeolites are shown in Table I.

Measurement of Adsorption Equilibria. Adsorption experiments were performed at 15, 30, and 45 °C. Zeolite (0.1 g) was placed in glass ampules. The samples were preliminarily dried in air at 350 °C for 3 h, and then degassed at 10^{-3} Torr and 350 °C for 16 h. The ampules were then cooled to room temperature in a stream of nitrogen gas. The ampules were then filled with about 0.15–0.17 g of a binary solution of a known composition, and sealed by using a torch lamp. The ampules were placed in a constant-temperature bath controlled within ±0.1 °C deviation. To ensure complete equilibrium during adsorption, the ampules were stirred frequently for 24 h. The composition of the equilibrium mixture was analyzed by using gas chromatography.

Table I. Results of Decationization

type	formula	solid	degree of decationization (%)	number of cations per unit cell
NaY	$(NaAlO_2)_{56}(SiO_2)_{136}\cdot H_2O$	NaY	0	56
		NaHY-12	12	49
		NaHY-41	41	33
		NaHY-51	51	27
		NaHY-71	71	16
		HY	100	0

Results and Discussion

Surface Excess. The pertinent experimental variable for the liquid–solid interface is the surface excess. The surface excess (*7*) is defined as the difference between the amount adsorbed and the hypothetical amount adsorbed when the composition of the adsorbed phase is equal to the composition of the bulk liquid.

The surface excess for component 1 (n_1^e) based on unit mass can be described as

$$n_1^e = n^\sigma(x_1^\sigma - x_1^l) \tag{1}$$

where n^σ is the total adsorption amount, x_1 is the mole fraction of component 1 (benzene), and superscripts σ and l represent the adsorbed phase and the bulk phase, respectively.

The surface excess can also be described with parameters that can be measured easily. The total number of moles of binary solution based on the unit mass of solid adsorbent, n^t, can be distributed to the bulk and adsorbed phases when equilibrated:

$$n^t = n^\sigma + n^l \tag{2}$$

where n^l is total amount of liquid phase. The material balance for component 1 is

$$n_1^\sigma = n^t x_1° - n^l x_1^l \tag{3}$$

where $x_1°$ is the initial mole fraction of component 1 of the

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[*] To whom correspondence should be addressed.

[†] Present address: Ssangyong Research Center, Daejeon, Korea.

[‡] Present address: Department of Chemical Engineering, Seoul National Polytechnic University, Seoul, Korea.

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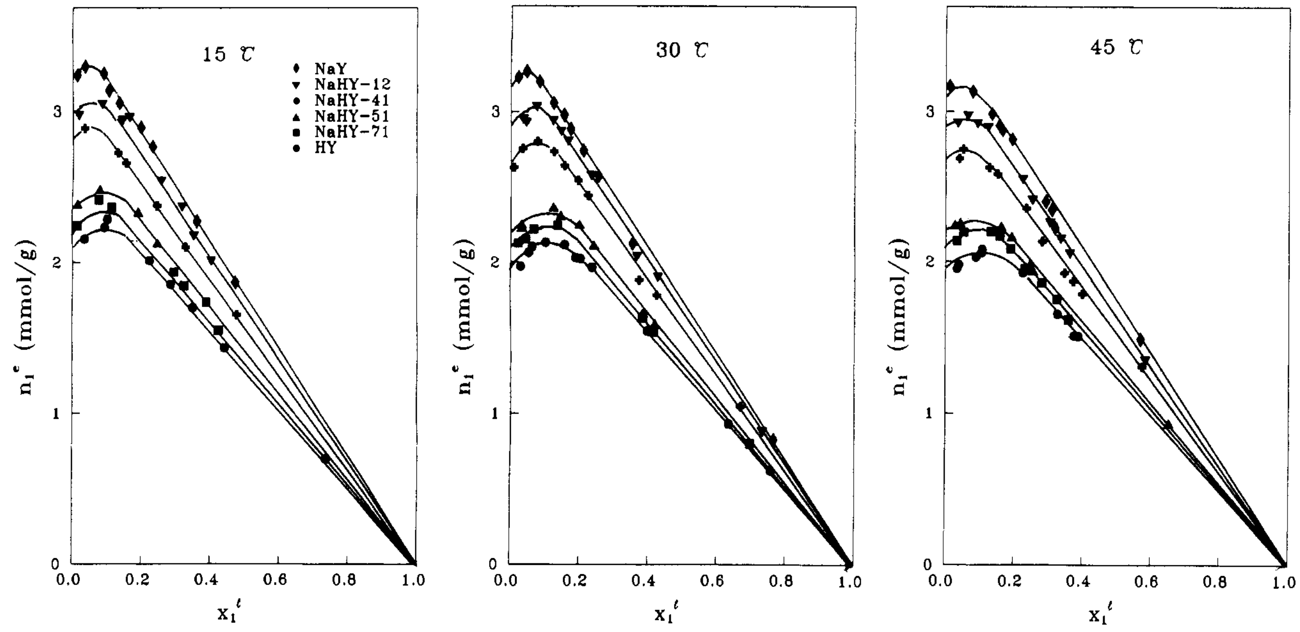

Figure 1. Surface excess of the benzene + *n*-heptane mixture.

binary solution. From eqs 2 and 3, eq 1 becomes

$$\begin{aligned} n_1^e &= n_1^\circ - n^\sigma x_1^l \\ &= n^t x_1^\circ - n^l x_1^l - (n^t - n^l) x_1^l \\ &= n^t (x_1^\circ - x_1^l) \end{aligned} \qquad (4)$$

From eq 4, therefore, we can determine the surface excess with the values of n^t, x_1°, and x_1^l. In our experiments we performed liquid-phase adsorption of benzene + heptane mixtures on NaHY zeolites with different degrees of decationization at 15, 30, and 45 °C. Figure 1 and Table II show the surface excess isotherms and their values obtained from eq 4, respectively. The excess isotherm curves that are concave downward indicate that benzene is the preferential adsorbed component. All the excess isotherms are type II of Schay's classification (*2*).

The surface excess gradually increases with increasing sodium content, especially rapidly between NaHY-41 and NaHY-51 (Figure 1). As the number of sodium ions in the zeolites increases, the maximum point of the excess isotherms shifts toward the lower concentration of the benzene in the bulk phase between 0.1 and 0.2. This means strong adsorption of benzene on the sodium ions, and the electrons of the benzene nuclei may have a specific interaction with sodium ions.

At all temperatures the types of surface excess isotherms have similar shapes regardless of the adsorption temperature. However, the value of the surface excess decreases slightly with increasing adsorption temperature.

We only obtained a few data points at the high benzene mole fraction because of the experimental difficulties due to the very small difference between x_1° and x_1^l.

Total Adsorption Amount and Separation Factor. Everett (*6*) discussed the "phase exchange reaction" model for the perfect solution of components 1 and 2 in contact with a Langmuir-type adsorbing surface:

$$(1)^\sigma + (2)^l \leftrightarrow (1)^l + (2)^\sigma \qquad (5)$$

At equilibrium, this leads to the following relationship:

$$\ln \frac{x_1^\sigma x_2^l}{x_1^l x_2^\sigma} = \left(\frac{\mu_1^* - \mu_{a,1}^*}{RT}\right) - \left(\frac{\mu_2^* - \mu_{a,2}^*}{RT}\right) \qquad (6)$$

where μ_1^* and $\mu_{a,1}^*$ are the Gibbs free energy per mole of pure component 1 in the liquid and zeolite-adsorbed phases, respectively.

Sorption selectivity is usually presented in terms of a separation factor (*K*) or relative adsorptivity (x_1^σ/x_1^l) as follows:

$$K = x_1^\sigma x_2^l / x_1^l x_2^\sigma$$

or

$$\frac{x_1^\sigma}{x_1^l} = \frac{K}{1 + (K-1)x_1^l} \qquad (7)$$

Combination of eqs 1 and 7 gives eq 8 which is known to be Everett's equation for a perfect system. Equation 8 is only

$$\frac{x_1^l x_2^l}{n_1^e} = \frac{x_1^l}{n^\sigma} + \frac{1}{n^\sigma (K-1)} \qquad (8)$$

valid when the following assumptions are satisfied: (1) The adsorption is Langmuir type (*8*). (2) *K* remains constant over the entire concentration range. (3) The ratio of the activity coefficients $\gamma_1^i\gamma_2^\sigma/\gamma_1^\sigma\gamma_2^i$ can be approximated to unity. (4) The adsorbed components have similar molecular sizes in the adsorbed phase or the selective component covers the surface, even at low concentrations.

For the behavior of a perfect solution in contact with a Langmuir-type adsorbing surface, we can obtain the total adsorption amount and the separation factor by Everett's equation. Figure 2 and Table II show the plots of the experimental data for the benzene + heptane system and their values according to eq 8, respectively. The good linear relationships indicate that the above assumptions are satisfied in this study. From the intercepts and the slopes of these linear plots, the separation factor and the total adsorption amount were obtained by least-squares analysis. The obtained values are listed in Table III.

The dependence of the total adsorption amount on the number of sodium ions per unit cell is shown in Figure 3. It shows that the total adsorption amount increases with the sodium ion content per unit cell and decreases with the adsorption temperature. Especially, the total adsorption amount increases rapidly near 27 sodium ions per unit cell, while the increasing tendency is not rapid when $x_1^l > 27$. This

Table II. Values of x_1^l, n_1^e, and $1000x_1^lx_2^l/n_1^e$ on NaHY at 15, 30, and 45 °C

15 °C

NaY			NaHY-12			NaHY-41		
x_1^l	n_1^e	$1000x_1^lx_2^l/n_1^e$	x_1^l	n_1^e	$1000x_1^lx_1^l/n_1^e$	x_1^l	n_1^e	$1000x_1^l/x_1^l/n_1^e$
0.013	3.225	4.62	0.017	2.974	5.75	0.034	2.887	11.37
0.035	3.283	10.80	0.085	3.049	24.85	0.131	2.724	41.79
0.089	3.236	25.97	0.144	2.945	41.42	0.154	2.655	49.09
0.105	3.124	30.47	0.165	2.864	47.42	0.246	2.378	78.00
0.136	3.042	39.17	0.265	2.542	74.92	0.330	2.105	105.03
0.198	2.881	56.59	0.319	2.373	91.54	0.478	1.651	151.13
0.232	2.754	66.14	0.354	2.185	104.66			
0.363	2.263	102.94	0.405	2.018	119.14			
0.474	1.855	134.12						

NaHY-51			NaHY-71			HY		
x_1^l	n_1^e	$1000x_1^lx_2^l/n_1^e$	x_1^l	n_1^e	$1000x_1^lx_2^l/n_1^e$	x_1^l	n_1^e	$1000x_1^lx_2^l/n_1^e$
0.015	2.388	6.18	0.015	2.246	6.57	0.036	2.157	16.08
0.078	2.485	28.94	0.077	2.415	29.42	0.094	2.235	38.10
0.193	2.335	66.43	0.114	2.366	42.68	0.102	2.289	40.01
0.248	2.133	87.43	0.295	1.937	107.36	0.224	2.014	86.30
			0.324	1.845	118.71	0.285	1.853	109.97
			0.389	1.733	137.14	0.350	1.698	133.98
			0.425	1.547	157.96	0.443	1.433	172.19
						0.736	0.699	277.97

30 °C

NaY			NaHY-12			NaHY-41		
x_1^l	n_1^e	$1000x_1^lx_2^l/n_1^e$	x_1^l	n_1^e	$1000x_1^lx_2^l/n_1^e$	x_1^l	n_1^e	$1000x_1^lx_2^l/n_1^e$
0.022	3.214	6.690	0.036	2.954	11.440	0.009	2.663	3.340
0.046	3.253	13.460	0.045	2.933	14.650	0.034	2.756	11.910
0.083	3.186	23.880	0.075	3.037	22.840	0.078	2.804	25.640
0.124	3.045	35.670	0.123	2.945	36.620	0.125	2.738	39.940
0.155	2.967	44.140	0.146	2.876	43.350	0.156	2.645	49.770
0.174	2.874	50.100	0.167	2.813	49.490	0.196	2.547	61.870
0.212	2.736	61.170	0.234	2.584	69.360	0.224	2.446	71.060
0.255	2.564	74.090	0.367	2.044	113.650	0.374	1.883	124.330
0.354	2.111	108.320	0.428	1.905	128.510	0.426	1.783	137.140
0.766	0.828	221.180	0.733	0.891	219.650	0.669	1.050	210.890

NaHY-51			NaHY-71			HY		
x_1^l	n_1^e	$1000x_1^lx_2^l/n_1^e$	x_1^l	n_1^e	$1000x_1^lx_2^l/n_1^e$	x_1^l	n_1^e	$1000x_{1l}x_2^l/n_1^e$
0.032	0.236	13.850	0.021	2.127	9.660	0.025	1.972	14.270
0.051	1.154	21.470	0.043	2.154	19.100	0.052	2.064	23.880
0.123	2.369	45.530	0.066	2.222	27.240	0.062	2.102	27.660
0.144	2.321	53.330	0.135	2.247	51.960	0.101	2.132	42.580
0.199	2.254	70.710	0.384	1.634	144.760	0.056	2.117	62.190
0.241	2.115	86.480	0.416	1.541	157.650	0.188	2.031	75.160
0.385	1.664	142.290	0.696	0.805	262.830	0.202	2.025	79.600
0.420	1.595	152.720				0.236	1.966	91.720
						0.397	1.546	154.840
						0.634	0.935	248.170
						0.757	0.628	292.910

45 °C

NaY			NaHY-12			NaHY-41		
x_1^l	n_1^e	$1000x_1^lx_2^l/n_1^e$	x_1^l	n_1^e	$1000x_1^lx_2^l/n_1^e$	x_1^l	n_1^e	$1000x_1^lx_2^l/n_1^e$
0.011	3.155	3.44	0.035	2.926	11.54	0.04	2.682	14.31
0.078	3.121	23.04	0.064	2.975	20.13	0.051	2.746	17.62
0.134	2.971	39.05	0.092	2.921	28.59	0.127	2.624	42.25
0.156	2.892	45.52	0.113	2.896	37.24	0.152	2.578	49.99
0.165	2.861	48.15	0.224	2.548	68.21	0.234	2.355	76.11
0.193	2.799	55.64	0.252	2.411	78.18	0.281	2.135	94.63
0.291	2.384	86.54	0.303	2.262	93.36	0.346	1.927	117.42
0.309	2.331	91.59	0.335	2.157	103.28	0.372	1.871	124.86
0.318	2.214	97.95	0.361	2.058	112.08	0.399	1.788	134.11
0.569	1.480	165.7	0.583	1.359	178.88	0.574	1.314	186.09

NaHY-51			NaHY-71			HY		
x_1^l	n_1^e	$1000x_1^lx_2^l/n_1^e$	x_1^l	n_1^e	$1000x_1^lx_2^l/n_1^e$	x_1^l	n_1^e	$1000x_1^lx_2^l/n_1^e$
0.026	2.244	11.3	0.033	2.137	14.93	0.033	1.955	16.21
0.042	2.258	17.81	0.052	2.195	22.45	0.038	1.982	18.44
0.161	2.236	60.41	0.132	2.201	52.05	0.088	2.031	32.51
0.192	2.167	71.59	0.157	2.172	60.93	0.104	2.059	45.25
0.244	1.983	93.02	0.188	2.087	73.49	0.106	2.082	45.51
0.254	1.942	97.57	0.231	1.955	90.86	0.225	1.928	90.44
0.652	0.936	242.41	0.281	1.861	108.56	0.326	1.658	132.52
			0.324	1.755	124.8	0.374	1.516	154.43
			0.358	1.621	141.78	0.386	1.512	156.73

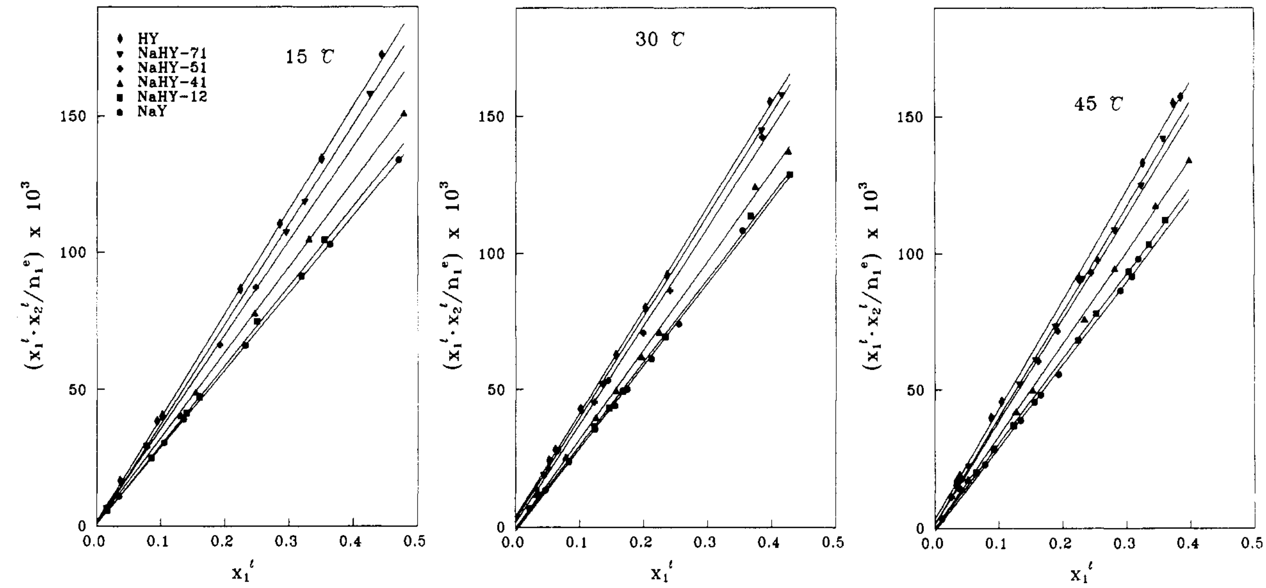

Figure 2. Everett plots of $x_1^l x_2^l/n_1^e$ vs x_1^l.

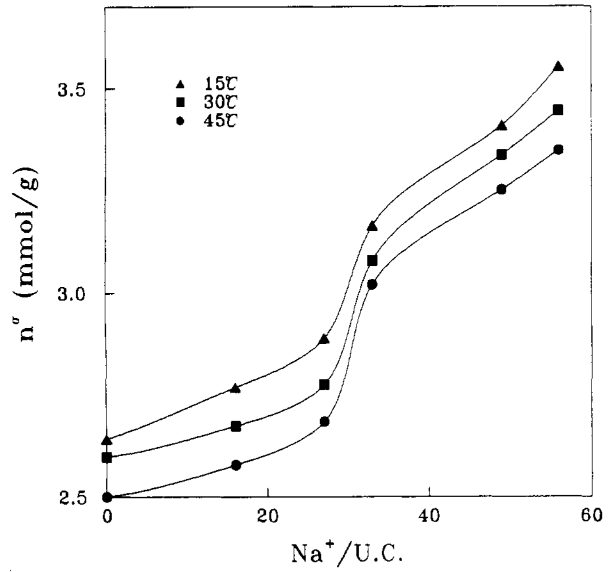

Figure 3. Total adsorption amount as a function of the number of sodium ions per unit cell.

behavior is because of the limiting pore space. It has been reported that the adsorption centers can be cation connected to structural atoms (*9, 10*). Therefore, it can be accepted that the number of cations plays an important role in adsorption. For the system in which the separation factor (>800) is so large, one species (preferentially adsorbed species) exclusively occupies the pores of the zeolites (*11*). In this work, therefore, we can guess from the separation factors in Table III that benzene is the only strongly adsorbed species for NaY and NaHY-12.

Bosacek and Beran (*12*) investigated the occupations of cationic sites per unit cell of Y zeolite with different degrees of decationization. They reported that the population of sodium ions in the site S_{II} decreases linearly with increasing decationization. Mortier et al. (*13*) reported, however, that the distribution of the site population of CaY zeolites could be varied by adsorption of a hydrocarbon such as benzene. Because of the admolecular size in this study, the cations in S_I and S_I' should not act as adsorption centers. If we assume that the cations in site S_{II} have a strong influence on the adsorption properties, a linear increase of sodium cation in site S_{II} should be connected with a linear increase of the total adsorption amount. However, the total adsorption amount in our study rapidly increases near 27 sodium ions per unit cell, which can be explained by the fact that, above 27 sodium ions per unit cell, the sodium ions in sites S_I and S_I' migrate toward site S_{II} in the supercage by the attraction force of benzene as reported by Mortier et al. (*13*).

Figure 4 shows the dependence of the separation factors on the number of sodium ions. The separation factor, obtained by eq 8, rises rapidly beyond 27 sodium ions per unit cell. This rapid increase could also be because of the increased number of sodium ions at site S_{II}. Schoonheydt and Uytterhoeven (*14*) reported that the conductivity of NaHY as a function of the Na⁺ ion content is plotted for the series of NaX and NaY. They found that the Na⁺ ions contribute to the conductivity due to the mobility of exchangeable cations in the supercage. This conductivity variation is similar to that of the our separation factor change.

Difference of Heat of Immersion in Two Pure Components. At constant pressure, differentiating eq 6 with respect to temperature and substituting the Gibbs–Helmholtz equation, i.e.,

$$[\partial(\mu_i^*/T)/\partial T]_p = -H_i/T^2 \qquad (9)$$

Table III. Determined Adsorption Parameters

	T/°C	NaY	NaHY-12	NaHY-41	NaHY-51	NaHY-71	HY
total adsorption amount (mmol/g)	15	3.56	3.42	3.17	2.9	2.77	2.65
	30	3.44	3.34	3.09	2.78	2.68	2.6
	45	3.36	3.25	3.03	2.69	2.59	2.5
separation factor	15	3649	1498	534	290	207	144
	30	1815	845	373	234	169	119
	45	901	507	254	174	139	99
$\Delta H_1° - \Delta H_2°$ (kcal/mol)		8.6	6.7	5.2	3.4	2.6	2.1

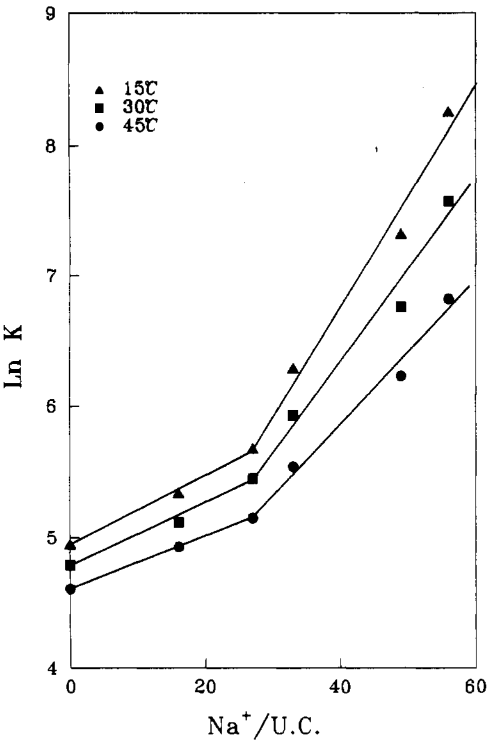

Figure 4. Separation factor as a function of the number of sodium ions per unit cell.

gives

$$\frac{\partial \ln K}{\partial T} = \frac{1}{RT^2}[(H_{a,1} - H_1) - (H_{a,2} - H_2)] \qquad (10)$$

where H_1 is the enthalpy per mole of pure component 1 at the temperature T. The term $H_{a,1} - H_1$ is the change in the enthalpy of the pure component 1 from its liquid state to its zeolite adsorbed state. Upon integration of eq 10, the following relationship is obtained:

$$\ln \frac{K_2}{K_1} = -(\Delta H_1^\circ - \Delta H_2^\circ)\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (11)$$

The difference between heats of immersion in two pure components can be obtained from the slope of the linear plot. Figure 5 shows that the plots of ln K versus $1/T$ are linear for all systems. Thus, the differences ($\Delta H_1^\circ - \Delta H_2^\circ$) between the enthalpies of immersion of the unit mass adsorbate in the two pure liquids can be evaluated.

Figure 6 represents $\Delta H_1^\circ - \Delta H_2^\circ$ as a function of the sodium ion content, which shows the same trend as the case of the separation factor. The difference in heats of immersion in two pure components increased rapidly near 27 sodium ions per unit cell. The reason for this rapid increase at higher concentrations of benzene could also be described as the increase of sodium ions at site S_{II}, the same as the result for the separation factor.

Conclusion

The objective of this study is to understand the characteristics of liquid-phase adsorption in NaHY zeolite with different degrees of decationization. The conclusions are as follows: (1) The thermodynamic analysis of liquid-phase adsportion of benzene + heptane mixtures on NaHY zeolites is correlated by Everett's model. (2) The attractive force of benzene induces the migration of sodium ions in sites S_I and S_I' toward the sites in the supercage beyond about 27 sodium ions per unit cell. (3) An increase of the total adsorption amount, separation factor, and heat of immersion with increasing sodium content is attributed to the specific interaction of benzene on increased sodium ions at site S_{II}.

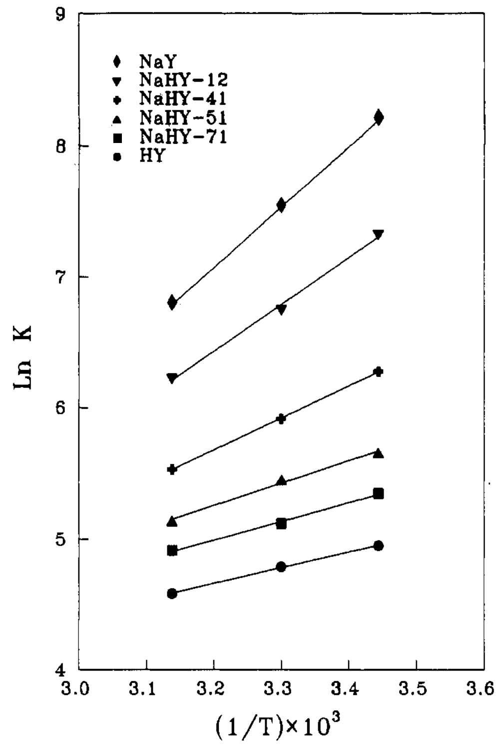

Figure 5. ln K as a function of reciprocal temperature.

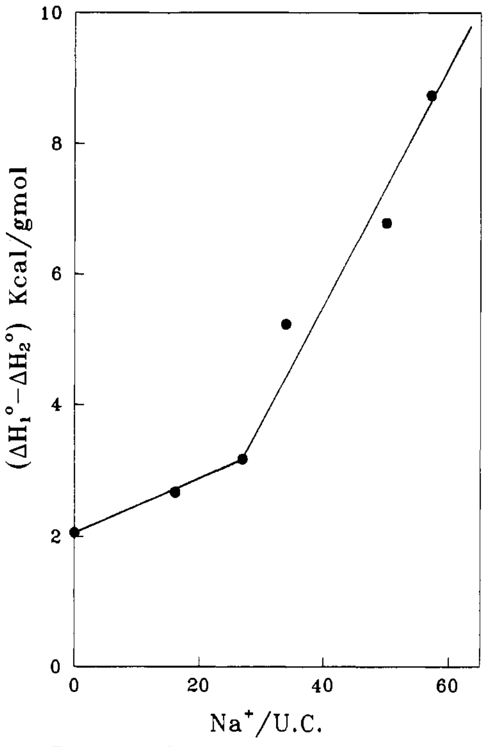

Figure 6. Difference between heat immersions as a function of the number of sodium ions per unit cell.

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