Adsorption From Binary Immiscible Liquid Mixture

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The surface excess isotherms for adsorption of binary liquid mixtures are governed by (a) the difference in the sizes (molar volumes) of the adsorbate molecules; (b) the nonideality of the bulk liquid phase; (c) the energetic heterogeneity of the adsorbent; and (d) lateral interactions of adsorbed molecules (Sircar, 1986). An extreme case of bulk liquid phase nonideality is where the liquid mixture becomes unstable and forms two immiscible liquid phases in equilibrium with each other over a certain composition range. This article reports the adsorption characteristics of such a binary liquid mixture and provides a thermodynamic analysis of the data.

Experimental Systems and Surface Excess Isotherms

Water (1) + methyl acetate (2) binary liquid mixture exhibits immiscibility over a large range of water concentration at 30°C. The mole fraction of water in the methyl acetate rich (x_1^*) and the water rich (x_1^{**}) phases are, respectively, 0.282 and 0.929 (*International Critical Table*, 1928). The liquid mixtures are miscible ($0 \leq x_1 \leq x_1^*$ and $x_1^{**} \leq x_1 \leq 1$) elsewhere. Furthermore, the liquid mixture exhibits an azeotrope at an x_1 value of 0.06 at 30°C.

We measured the binary surface excess isotherm over the miscible concentration ranges of water (1) + methyl acetate (2) liquid mixture on NaX zeolite using the conventional method at 30°C (Sircar and Myers, 1971). n^0 moles of liquid mixture was contacted with m grams of adsorbent in a flask contained in a thermostated shaker-bath. The mole fraction of component 1 before contact (x_1^0) and after attainment of equilibrium (x_1) were measured using a gas chromatograph. The equilibrium surface excess of component 1 (n_1^e) at the corresponding bulk liquid phase composition (x_1) was calculated by

$$n_1^e = (n^0/m)(x_1^0 - x_1) \tag{1}$$

The NaX zeolites were obtained (1/8 in. diameter bead form) from UOP. They were regenerated by heating in dry N_2 at 350°C for 8 h before contacting with the liquid mixture. The liquid mixture-adsorbent composite in the flask was agitated for 16 h to facilitate mass transfer into the zeolite pores during the equilibration process.

In order to check the integral thermodynamic consistency of the data (Sircar and Myers, 1971), we also measured the binary surface excess isotherms of two more liquid mixtures (which were completely miscible) on the NaX zeolite beads at 30°C. They were (a) Water (1) + Methanol (2) and (b) Methanol (1) + Methyl acetate (2) liquid mixtures.

Figures 1 to 3 show the three binary surface excess isotherms where n_1^e values are plotted against x_1. The experimental data (circles) are also tabulated in Tables 1 to 3 for easy access. Component 1 represents the more selectively adsorbed component of the liquid mixture. These data were measured by contacting different amounts of liquid mixture (n^0) having various initial compositions (x_1^0) with different amounts (m) of adsorbent. Experiments were carried out several times to cover the entire composition range of the equilibrium bulk liquid mixture in order to check the data reproducibility. The scatter in the data demonstrates a maximum uncertainty of ±0.5 mmol/g in the measurement of the absolute value of the surface excess. The solid lines in the figures represent smooth curves through the data points.

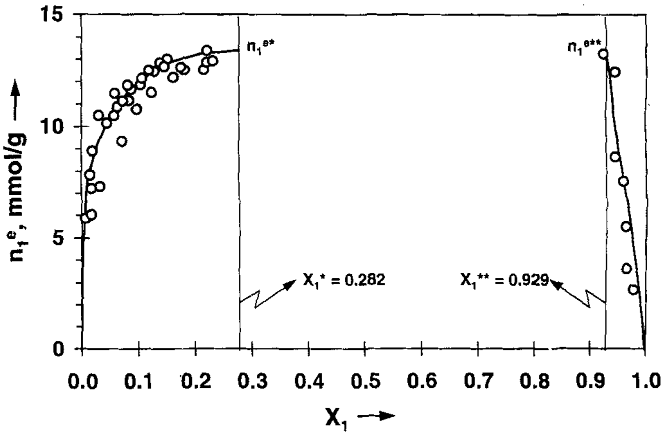

Figure 1. Binary adsorption isotherm of water (1) + methyl acetate (2) on NaX zeolite at 30°C.

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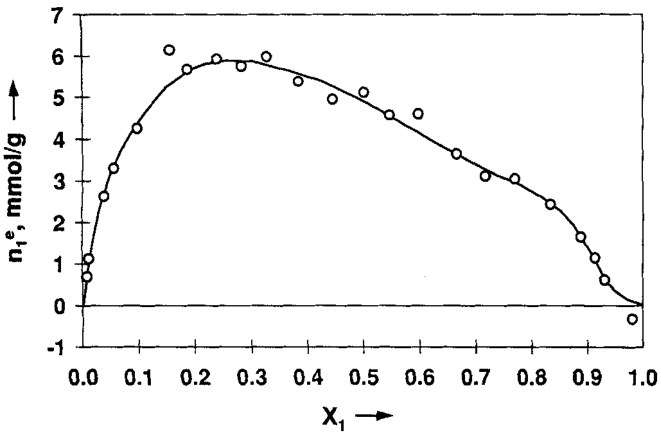

Figure 2. Binary adsorption isotherm of water (1) + methanol (2) on NaX zeolite at 30°C.

Table 1. Surface Excess Isotherm for Adsorption of Binary Water (1) + Methyl Acetate (2) Liquid Mixture on NaX Zeolite at 30°C

x_1	n_1^e mmol/g	x_1	n_1^e mmol/g	x_1	n_1^e mmol/g
0.004	2.92	0.069	11.32	0.175	12.78
0.006	6.10	0.076	9.41	0.180	12.56
0.006	6.68	0.080	11.93	0.214	12.63
0.015	6.26	0.084	11.78	0.217	13.03
0.015	8.02	0.095	10.89	0.220	13.49
0.019	7.52	0.103	12.07	0.231	12.99
0.019	9.07	0.106	12.24	0.920	13.31
0.028	10.58	0.117	12.59	0.940	12.60
0.029	7.48	0.120	11.66	0.947	8.86
0.044	10.22	0.126	12.64	0.955	7.80
0.057	10.63	0.140	13.90	0.962	5.80
0.057	11.63	0.142	12.82	0.962	5.92
0.060	11.73	0.153	13.15	0.975	2.90
0.067	11.07	0.166	12.31		

The Water (1) + Methyl acetate (2) surface excess isotherm of Figure 1 has two sections covering the two miscible ranges. The positive values of n_1^e in both sections indicate that water is selectively adsorbed over methyl acetate at all compositions in these sections. The surface excess isotherms for the miscible Water (1) + Methanol (2) and Methanol (1) + Methyl acetate (2) liquid mixtures described by Figures 2 and 3, respectively, are *U* shaped indicating that component 1 is more selectively adsorbed over component 2 over the entire composition range (Sircar, 1986).

Water, methanol, and methyl acetate are highly polar molecules having permanent dipole moments of 1.8, 1.7 and 1.7 debye, respectively (Reid et al., 1977). The polarizabilities ($\times 10^{25}$ cm^3) of water, methanol and methyl acetate are 14.5, 32.3 and 69.4, respectively (Lide, 1990). The pure liquid molar volumes (v_i^o) of water, methanol and methyl acetate at 30°C are, respectively, 18, 40.9 and 80.5 cm^3/mol. Thus, the adsorbate sizes for the binary liquid mixtures of the present work differ by a factor of 2–4.5. The liquid mixtures exhibit moderate to very high nonideality.

Vapor-Liquid Equilibrium (VLE)

The published VLE data indicated that the bulk liquid phase nonidealities were strikingly different at 30°C for the three liquid mixtures studied in this work (Gmehling and Onken, 1977a,b,c). Water (1) + Methanol (2) mixtures were modestly nonideal. The activity coefficients at infinite dilutions for water (γ_1^∞) and methanol (γ_2^∞) were 1.54 and 1.86, respectively. Methanol (1) + methyl acetate (2) mixtures were very nonideal. The activity coefficients at infinite dilutions for methanol (γ_1^∞) and methyl acetate (γ_2^∞) were 3.2 and 3.1, respectively. This mixture actually formed an azeotrope at a liquid phase methanol mole fraction of 0.285 (Figure 4b). Water (1) + methyl acetate (2) mixture was extremely nonideal causing immiscibility as described earlier. The activity coefficients of water (γ_1^∞) and methyl acetate (γ_2^∞) at infinite dilutions were, respectively, 8.78 and 21.9. The pure liquid vapor pressures (P_i^0) of water, methanol and methyl acetate at 30°C were, respectively, 31.4, 162.6 and 267.5 torr.

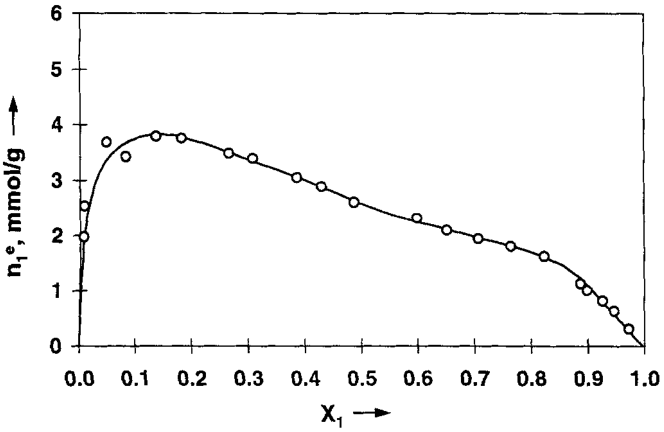

Figure 3. Binary adsorption isotherm of methanol (1) + methyl acetate (2) on NaX zeolite at 30°C.

The VLE data at 30°C for (a) water-methanol and (b) water-methyl acetate liquid mixtures were interpolated from the published isothermal data at 25 and 35°C (System a) and 25, 50, 60, 70 and 80°C (System b) by assuming that $[\{\partial \ln \gamma_i / \partial (1/T)\}_{x_i}]$ were independent of temperature (T). γ_i is the liquid-phase activity coefficient of component i when its mole fraction is x_i. The published isothermal data for water-methyl acetate system were limited to the water-rich miscible portion of the system only. The VLE data for methanol-methyl acetate system were available at 30°C.

The liquid-phase activity coefficients (γ_i) for all three systems could be correlated as functions of liquid phase mole fractions (x_i) by the two Suffix Margules equations

Table 2. Surface Excess Isotherm for Adsorption of Binary Water (1) + Methanol (2) Liquid Mixture on NaX Zeolite at 30°C

x_1	n_1^e mmol/g	x_1	n_1^e mmol/g	x_1	n_1^e mmol/g
0.006	0.71	0.278	5.79	0.720	3.31
0.009	1.16	0.324	5.92	0.770	3.10
0.036	2.73	0.386	5.51	0.832	2.44
0.053	3.28	0.448	5.12	0.887	1.73
0.094	4.27	0.499	5.13	0.914	1.26
0.157	6.19	0.553	4.62	0.934	0.70
0.190	5.74	0.599	4.59	0.956	0.28
0.241	5.96	0.667	3.74	0.983	−0.25

Table 3. Surface Excess Isotherm for Adsorption of Binary Methanol (1) + Methyl Acetate (2) Liquid Mixture on NaX Zeolite at 30°C

x_1	n_1^e mmol/g	x_1	n_1^e mmol/g	x_1	n_1^e mmol/g
0.008	1.96	0.308	3.32	0.768	1.80
0.008	2.56	0.385	2.99	0.822	1.60
0.050	3.70	0.428	2.83	0.888	1.12
0.080	3.41	0.491	2.58	0.903	1.03
0.134	3.78	0.602	2.29	0.927	0.84
0.178	3.70	0.653	2.13	0.950	0.62
0.265	3.39	0.712	1.96	0.973	0.35

$$\ln \gamma_1 = [A_{12} + 2(A_{21} - A_{12})x_1]x_2^2 \tag{2a}$$

$$\ln \gamma_2 = [A_{21} + 2(A_{12} - A_{21})x_2]x_1^2 \tag{2b}$$

The Margules constants for the binaries at 30°C were: water (1) + methanol (2) [$A_{12} = 0.4291$, $A_{21} = 0.6230$]; methanol (1) + methyl acetate (2) [$A_{12} = 1.1626$, $A_{21} = 1.1364$]; water (1) + methyl acetate (2) [$A_{12} = 2.1725$, $A_{21} = 3.0870$].

Figures 4a–4c shows the equilibrium vapor (y_1) and liquid phase (x_1) mole fractions of component 1 for the three binaries at 30°C.

Thermodynamic Analysis of Surface Excess Isotherms

The two immiscible bulk liquid phases of water (1) + methyl acetate (2) mixtures, which are in equilibrium with each other and which have water mole fractions of x_1^* and x_1^{**}, must produce the same equilibrium adsorption system when equilibrated separately with the same adsorbent at the same temperature. The bulk liquid phase activities (a_i^* and a_i^{**}) of component $i (= 1,2)$ corresponding to the liquid phase mole fractions x_i^* and x_i^{**} are equal due to thermodynamic equilibrium. Thus, the surface excess of water (n_1^{e*} and n_1^{e**}) must have the same value when the water mole fractions of the bulk equilibrium liquid phases are x_1^* and x_1^{**}. That is indeed the case as shown by Figure 1. Consequently, the data of Figure 1 obey the basic thermodynamic requirement for adsorption of an immiscible binary liquid mixture.

For the same reason, the surface potential (ϕ^*) of the adsorbed phase in equilibrium with the bulk liquid mixtures of compositions x_1^* and x_1^{**} must be identical. Using the thermodynamic relationships (Sircar and Myers, 1986), the methyl acetate-rich portion ($0 \leq x_1 \leq x_1^*$) of the surface excess isotherm can be used to calculate

$$\frac{(\phi_2^0 - \phi^*)}{RT} = \int_0^{a_1^*} \frac{n_1^e}{a_1 x_2} da_1 \tag{3}$$

and the water-rich portion ($x_1^{**} \leq x_1 \leq 1$) of the surface excess isotherm can be used to calculate

$$\frac{(\phi^* - \phi_1^0)}{RT} = \int_{a_1^{**}}^1 \frac{n_1^e}{a_1 x_2} da_1 \tag{4}$$

where ϕ_i^0 is the surface potential for adsorption of pure liquid i. R is the gas constant.

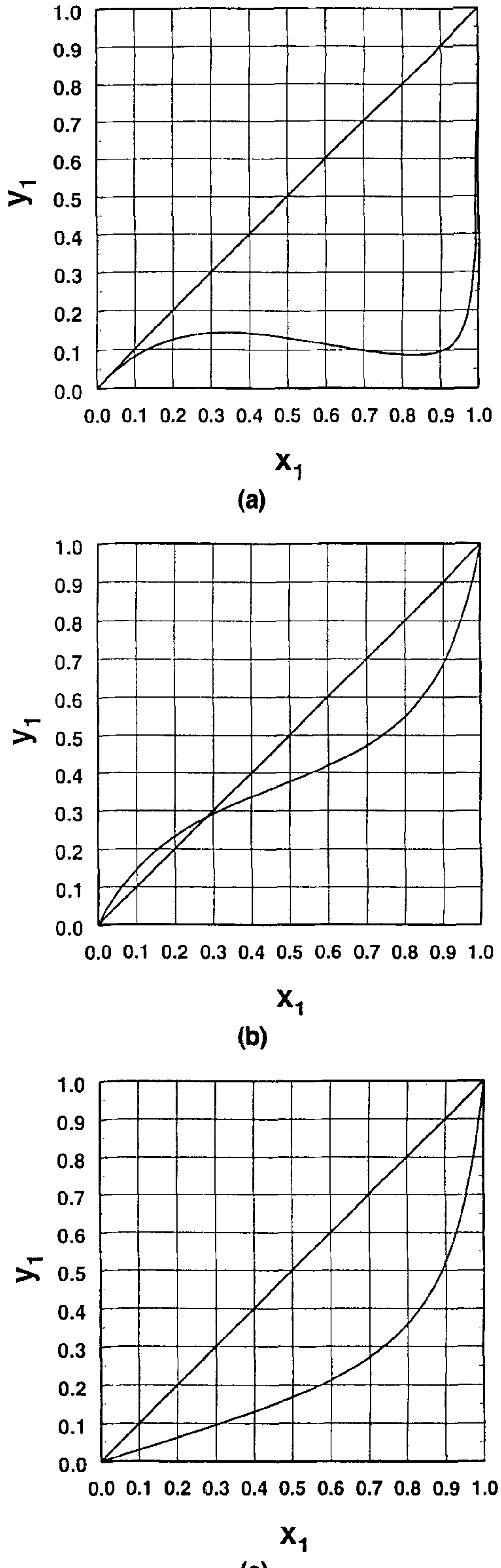

Figure 4. Vapor-liquid equilibrium data for binary systems at 30°C.

(a) Water (1) + methyl acetate (2); (b) methanol (1) + methyl acetate (2); (c) water (1) + methanol (2).

Table 4. Integral Thermodynamic Consistency Test on NaX Zeolite at 30°C

Adsorbate Mixture	*Surface Potential Differences* (mmol/g)	
Water (1) + Methyl Acetate (2)	$(\phi_2^0 - \phi^*)/RT$	35.44±0.7
	$(\phi^* - \phi_1^0)/RT$	7.69
	$(\phi_2^0 - \phi_1^0)/RT$	43.13
Methyl Acetate (2) + Methanol (3)	$(\phi_3^0 - \phi_2^0)/RT$	−18.50
Methanol (3) + Water (1)	$(\phi_1^0 - \phi_3^0)/RT$	−24.20
	SUM	0.43

The VLE data in the water-rich portion of water-methyl acetate binary mixture were used to calculate $a_i^{**}(=x_i^{**}\gamma_i^{**})$ using Eqs. 2a and 2b. The activity values of $a_1^{**} = 0.948 = a_1^*$ and $a_2^{**} = 0.905 = a_2^*$ were obtained. These limits were used to integrate Eqs. 3 and 4 using the experimental $n_1^e(x_1)$ data of Figure 1 and the activity coefficient correlations of Eqs. 2a and 2b. They are summarized in Table 4. The parameter $(\phi_2^0 - \phi_1^0)/RT$ for adsorption of the water (1) + methyl acetate (2) binary system on NaX zeolite adsorbent could be calculated by adding the integrated values of Eqs. 3 and 4.

The difference in the pure component surface potentials for adsorption of miscible binary liquid mixtures can be simply obtained by

$$\frac{(\phi_2^0 - \phi_1^0)}{RT} = \int_0^1 \frac{n_1^e}{a_1 x_2} da_1 \tag{5}$$

Equations 2a, 2b, and 5 and the experimental data of Figures 2 and 3 were used to calculate the parameters $(\phi_2^0 - \phi_1^0)/RT$ for adsorption of water (1) + methanol (2) and methanol (1) + methyl acetate (2) binaries on the NaX zeolite. They are also reported in Table 4.

The integral thermodynamic consistency test requires that for isothermal adsorption of three possible binary liquid mixtures comprising of three pure components [water (1), methanol (2) and methyl acetate (3)] on the same adsorbent, the following identity be satisfied

$$(\phi_1^0 - \phi_2^0) + (\phi_2^0 - \phi_3^0) + (\phi_3^0 - \phi_1^0) = 0 \tag{6}$$

Table 4 shows that Eq. 6 is extremely well satisfied, given the scatter in the experimental surface excess isotherms and the uncertainty in the methyl acetate rich portion of the VLE data for water-methyl acetate system. Thus, the surface excess isotherm for the immiscible water-methyl acetate system on NaX passes the integral consistency test.

The authors are not aware of any published data on adsorption of immiscible binary liquid mixtures. The present work provides a set of thermodynamically consistent surface excess isotherms for such a system. Further analysis of these systems will be interesting.

A very interesting characteristic of the surface excess isotherm of Figure 1 is that the value of limiting surface excess of water (n_1^{e*} or n_1^{e**}) at bulk liquid phase water compositions of x_1^* and x_1^{**} is 13.5 mol/kg. The vapor phase (assumed ideal) partial pressure of water ($p_1^* = P_1^0 a_1^*$) in equilibrium with the binary liquid mixture of composition $x_1^*(=x_1^{**})$ is 29.8 torr. The corresponding specific adsorption capacity of pure water vapor or NaX zeolite at 30°C is very close to 13.5 mol/kg (UOP Data Sheet). Thus, it appears that water is adsorbed from methyl acetate almost exclusively at the miscibility limits of the water-methyl acetate liquid mixture. The commonly used monolayer-pore filling (MPF) mechanism of adsorption from binary miscible liquid mixture (Sircar, 1986) cannot describe this behavior.

Another interesting feature of the water (1) + methanol (2) and methanol (1) + methyl acetate (2) surface excess isotherms is that the isotherms are not linear functions of x_1 or slightly concave toward abscissa in the high mole fraction region of component 1, which are common for most experimental surface excess data. These features can be explained by the variation in the selectivity of adsorption of component 1 over component 2 as a function of x_1 for the U-shaped isotherms using the MPF models. Both isotherms of Figures 2 and 3 show a pronounced bulge at the high concentration region of the more selectively adsorbed components. Water, methanol, and methyl acetates are very polar molecules. Their interactions with a very polar zeolite or their laterial interactions including hydrogen bonding, when they are present in high concentration in the adsorbed phase, may be the cause of such isotherm shapes. The explanation, however, is not clear.

Literature Cited

Gmehling, J., and U. Onken, *Vapor-Liquid Equilibrium Data Collection: 1*, Vol. 1, DECHEMA, Frankfurt, p. 54 (1977a).

Gmehling, J., and U. Onken, *Vapor-Liquid Equilibrium Data Collection: 2A*, Vol. 1, DECHEMA, Frankfurt, p. 95 (1977b).

Gmehling, J., and U. Onken, *Vapor-Liquid Equilibrium Data Collection: 1*, Vol. 1, DECHEMA, Frankfurt, pp. 258, 260 (1977c).

International Critical Tables, Vol. 3, McGraw-Hill, New York, p. 387 (1928).

Lide, D. R., *Handbook of Chemistry and Physics*, 71st ed., CRC Press, Boston, p. 10-198 (1990).

Reid, R. C., J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, 3rd ed., McGraw-Hill, New York, p. 629 (1977).

Sircar, S., "Thermodynamics of Adsorption from Binary Liquid Mixtures on Heterogeneous Adsorbents," *J. Chem. Soc., Faraday Trans. I.*, **82**, 831 (1986).

Sircar, S., and A. L. Myers, "A Thermodynamic Consistency Test for Adsorption from Binary Liquid Mixtures on Solids," *AIChE J.*, **17**, 186 (1971).

Sircar, S., and A. L. Myers, "Liquid Adsorption Operations: Equilibrium, Kinetics, Column Dynamics and Applications," *Sep. Sci., Tech.*, **21**, 535 (1986).

"Molecular Sieve Type 13X Pellets Water Adsorption Isotherms," UOP Molecular Sieve data sheet, F-43C-5 (1991).

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