Adsorption 5, 169–176 (1999)

Measurement of Excess Functions of Binary Gas Mixtures* Adsorbed in Zeolites by Adsorption Calorimetry

FLOR SIPERSTEIN, RAYMOND J. GORTE AND ALAN L. MYERS
Department of Chemical Engineering, University of Pennsylvania, Philadelphia, PA, 19104, USA
amyers@seas.upenn.edu

Abstract. Adsorption equilibria and heats of adsorption were measured for mixtures of ethylene and ethane on NaX at 298 K. The pure-component isosteric heat of adsorption of ethane increases with loading due to gas-gas interactions; the heat of adsorption of ethylene is approximately constant with loading because of a balance between cooperative interactions and gas-solid energetic heterogeneity. This mixture, which is nearly ideal on carbon, exhibits moderate negative deviations from ideality on NaX. The nonideality is explained by a difference in the polarities of the molecules: ethylene has a quadrupole moment but ethane is nonpolar. The infinite-dilution activity coefficients are unity in the Henry's law region and decrease exponentially to a value of 0.56 at high loading. Regular-solution theory fails to agree with experiment. All three excess functions (free energy, enthalpy, and entropy) are negative; thus, activity coefficients are less than unity and the enthalpy of mixing in the adsorbed phase is exothermic. These results are consistent with an adsorbed solution in which the molecules are segregated into regions of different composition.

Keywords: activity coefficients, selectivity, adsorption equilibrium, excess functions, calorimetry, gas mixtures

Introduction

Although PSA processes are usually operated at ambient temperature, the adsorption and desorption steps in the cycle operate under approximately adiabatic conditions. The magnitude of the temperature change induced by adsorption or desorption is determined by the individual heats of adsorption of the components of the mixture through an energy balance. Since loading is highly sensitive to temperature, the selectivity is closely coupled to the magnitudes of the individual heats of adsorption. Therefore accurate design calculations require values for the heats of adsorption as well as selectivities.

Isosteric heats of adsorption (q_i) are directly related to the temperature coefficient of selectivity at fixed loading:

$$R\left[\frac{\partial \ln s_{1,2}}{\partial(1/T)}\right]_{n_1,n_2} = q_1 - q_2 \tag{1}$$

where $s_{1,2} = (x_1 y_2)/(x_2 y_1)$ is the selectivity of component 1 relative to component 2 in a binary mixture. The heats of adsorption in Eq. (1) refer to mixture heats, which differ from single-component heats as shown below. The integrated form of Eq. (1), the derivation of which contains no assumption other than ideal-gas behavior in the bulk gas phase, can be used to calculate the selectivity as a function of temperature. Therefore, the complete equilibrium behavior of a multicomponent mixture in terms of its three independent variables (T, P, and composition) can be derived from simultaneous volumetric-calorimetric measurements at a single reference temperature.

---

*Presented at AIChE Annual Meeting, Los Angeles, November 18, 1997, Section 4, Experimental Methods in Adsorption.

Vapor-liquid equilibria (VLE) are described in terms of thermodynamic excess functions (Smith et al., 1996). The excess Gibbs free energy gives the activity coefficients at a particular temperature; the excess enthalpy (heat of mixing) gives the variation of the Gibbs free energy function with temperature through the Gibbs-Helmholtz equation. This concise and elegant thermodynamic description of liquid mixtures has never been applied to nonidealities in the adsorbed phase because of the lack of experimental data for mixture heats. This paper reports a first step in that direction.

Heat of Mixing in Adsorbed Phase

The normal procedure in VLE is to measure the excess Gibbs free energy from isothermal measurements of activity coefficients and the excess enthalpy from calorimetry. Then, the excess entropy is given by the relation $\Delta g^e = \Delta h^e - T\Delta s^e$. The same procedure is followed here.

The isosteric heat of adsorption (q) measured calorimetrically or from the Clapeyron equation is a differential heat. q is actually a differential enthalpy but the "heat" terminology is widely accepted. Define a molar integral enthalpy of vaporization by:

$$\Delta h = \left(\frac{1}{n}\right)\int_0^n q\,dn \tag{2}$$

For a binary mixture:

$$\Delta h = \left(\frac{1}{n_1+n_2}\right)\int_0^{n_1}\int_0^{n_2}(q_1\,dn_1 + q_2\,dn_2) \tag{3}$$

The excess enthalpy or heat of mixing (Δh^e) in the adsorbed phase is:

$$\Delta h^e = \Delta h - \sum_i x_i \Delta h_i^\circ \tag{4}$$

The standard-state enthalpies of vaporization of the pure components (Δh_i°) are measured at the surface potential (ϕ) of the mixture. The excess enthalpy is related to excess Gibbs free energy by the Gibbs-Helmholtz equation:

$$\Delta h^e = -T^2\left[\frac{\partial(\Delta g^e/T)}{\partial T}\right]_{\psi,x} \tag{5}$$

The excess Gibbs free energy is

$$(\Delta g^e/RT) = x_1 \ln\gamma_1 + x_2\ln\gamma_2 \tag{6}$$

Equations (5) and (6) are the key equations for handling adsorbed-phase nonidealities; they are identical to the equations for bulk liquid mixtures. The difference between a bulk liquid solution and an adsorbed solution is an additional independent variable for the latter. The isothermal activity coefficients of a bulk liquid solution depend only upon its composition, since the effect of pressure is normally ignored. The isothermal activity coefficients of an adsorbed solution are strongly dependent upon the loading as well as the composition.

Regular Solution Theory

The simplest composition dependence for the excess functions is quadratic and a system with $\Delta g^e = Cx_1x_2$ is called a *quadratic mixture* (Rowlinson and Swinton, 1982). If in addition C is independent of temperature, then the excess entropy is zero, a definition close to that of a regular solution (Hildebrand et al., 1970). For an adsorbed quadratic mixture (Valenzuela and Myers, 1989; Talu et al., 1995):

$$\Delta g^e = \Delta h^e = Cx_1x_2(1 - e^{-B\psi}) \tag{7}$$

where the exponential factor with $\psi = -\phi/RT$ accounts for the dependence of the excess functions upon loading. For single-gas adsorption:

$$\psi = \int_0^P \frac{n}{P}\,dP = \int_0^n \frac{d\ln P}{d\ln n}\,dn \tag{8}$$

The two constants (C, B) are determined from experiment. The assumption that the excess free energy is independent of temperature is tested in this paper by calculating mixture heats from the model and comparing them with experiment.

The following equations in this section are derived from Eq. (7) with no further assumptions. The adsorbed-phase activity coefficients are:

$$\begin{aligned}\ln\gamma_1 &= Cx_2^2(1 - e^{-B\psi})\\ \ln\gamma_2 &= Cx_1^2(1 - e^{-B\psi})\end{aligned} \tag{9}$$

The change in total loading (n_t) upon mixing is given by:

$$\frac{1}{n_t} - \frac{x_1}{n_1^\circ} - \frac{x_2}{n_2^\circ} = \frac{CB}{RT}x_1x_2\,e^{-B\psi} \tag{10}$$

where the superscript $\circ$ refers to the standard states for single-gas adsorption at the same ψ and T as the

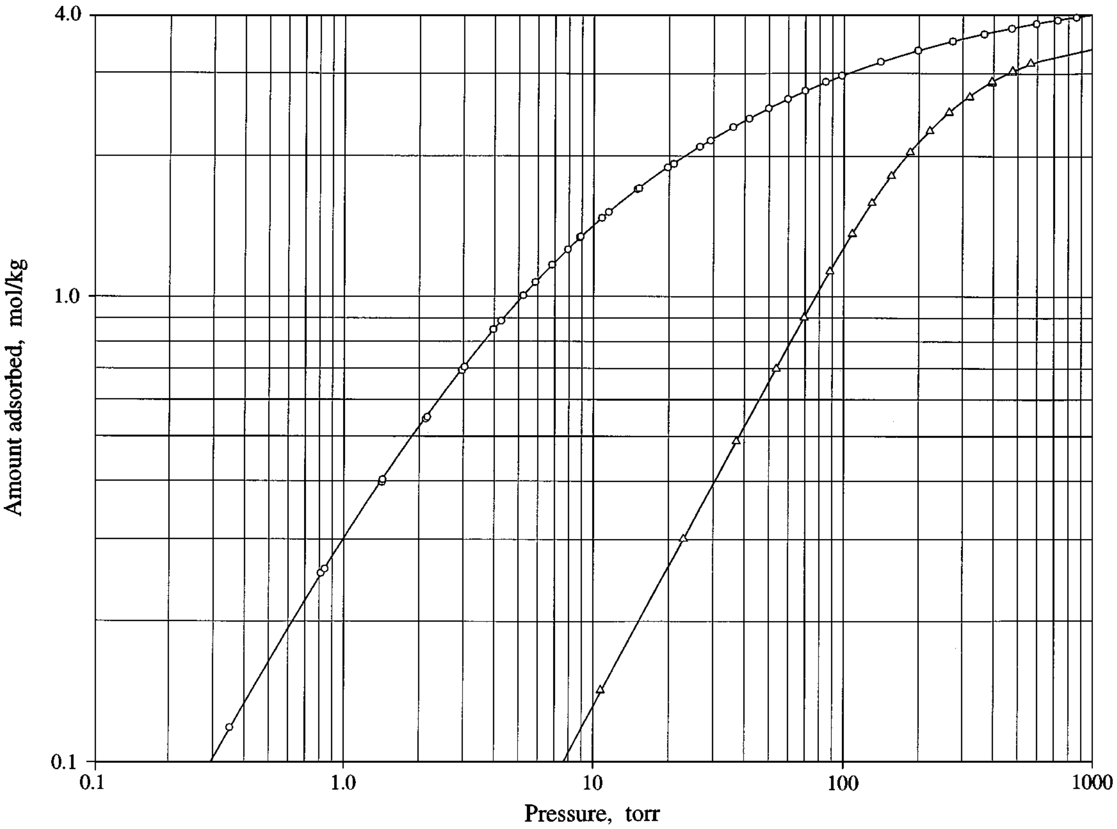

Figure 1. Single-gas adsorption isotherms of C_2H_4 (○) and C_2H_6 (△) on NaX at 305.55 K. Solid lines are a best fit of the experimental data using the virial equation.

mixture. The condition for phase equilibrium (ideal gas phase) is:

$$\begin{aligned} Py_1 &= P_1^\circ \gamma_1 x_1 \\ Py_2 &= P_2^\circ \gamma_2 x_2 \end{aligned} \tag{11}$$

For an ideal adsorbed solution (IAS), $C = B = 0$ and $\gamma_1 = \gamma_2 = 1$. The IAS prediction of mixture heats is (Karavias and Myers, 1992):

$$\begin{aligned} q_1 &= \Delta h_1^\circ + \frac{1}{n_1^\circ}\left[\frac{\sum_i x_i G_i^\circ n_i^\circ (q_i^\circ - \Delta h_i^\circ)}{\sum_i x_i G_i^\circ}\right] \\ q_2 &= \Delta h_2^\circ + \frac{1}{n_2^\circ}\left[\frac{\sum_i x_i G_i^\circ n_i^\circ (q_i^\circ - \Delta h_i^\circ)}{\sum_i x_i G_i^\circ}\right] \end{aligned} \tag{12}$$

where $G_i^\circ = (d \ln n / d \ln P)^\circ / (n_i^\circ)^2$. Nonideal behavior in the adsorbed phase introduces correction terms in Eq. (12); comparison of the experimental and calculated heats provides a stringent test of the regular-solution assumption that the excess entropy is zero.

Experimental Method

The 20 cm^3 pyrex sample cell of the mixture calorimeter is surrounded by thermopiles and embedded in an aluminum heat sink. The incremental dosing of each gas is calculated from a mass balance using the volumetric technique. The composition of the gas phase is measured with a residual gas analyzer connected to the sample cell by a leak valve (Dunne et al., 1997).

Incremental dosings to the sample cell are alternated between both components so that the total loading increases while the loading of one component remains approximately constant. The total heat released (Q) is measured by integrating the voltage signal from the thermopiles until the signal returns to baseline and the pressure and composition of the gas phase have

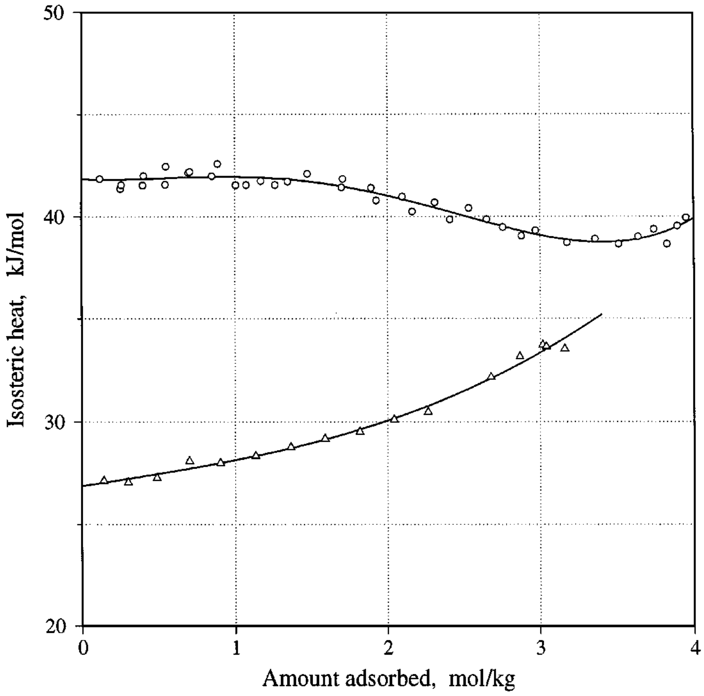

Figure 2. Isosteric heats of adsorption of C_2H_4 (○) and C_2H_6 (△) on NaX at 305.55 K. Solid lines are a power-series fit of the experimental data.

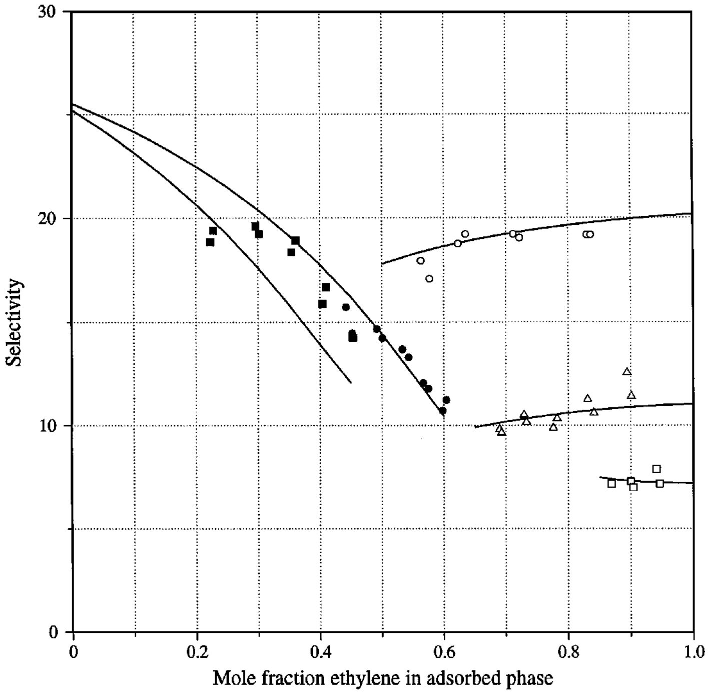

Figure 3. Selectivity of NaX for C_2H_4 relative to C_2H_6. Open symbols for constant loading of C_2H_4: (○): 0.967 mol/kg, 297.65 K. (△): 2.062 mol/kg, 297.85 K. (□): 3.025 mol/kg, 297.25 K. Closed symbols for constant loading of C_2H_6: (●): 1.250 mol/kg, 298.85 K. (■): 1.850 mol/kg, 294.75 K. Solid lines calculated from regular solution model.

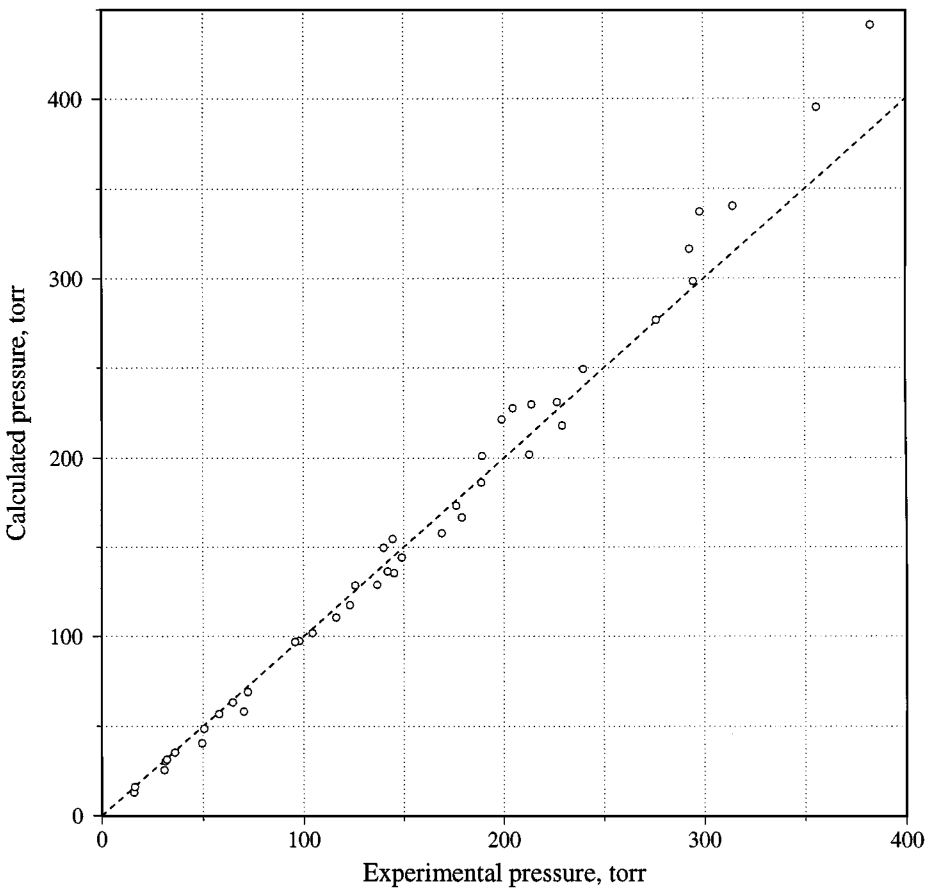

Figure 4. Comparison of calculated and experimental pressure for adsorption of mixtures of C_2H_4 and C_2H_6 on NaX. Pressure calculated from regular solution model at experimental values of temperature and loading (T, n_1, n_2). Standard deviation of error in calculated pressure is 5%.

equilibrated with the adsorbed phase at constant temperature. The heat (Q) released by incremental adsorption of both components $(\Delta n_1, \Delta n_2)$ is related to their individual heats of adsorption by:

$$Q^A = q_1 \Delta n_1^A + q_2 \Delta n_2^A \tag{13}$$

$$Q^B = q_1 \Delta n_1^B + q_2 \Delta n_2^B \tag{14}$$

The individual heats of adsorption (q_1 and q_2) are obtained from two experiments (A and B) as the solution of two linear Eqs. (13) and (14). Mixture heats and mixture equilibria are measured simultaneously.

Details about the design criteria, construction, and operation of the calorimeter, the calibration of the thermopiles, the spurious heat of compression in the sample cell, the RGA calibration, the (negligible) error associated with using finite increments of gas to measure a differential heat, and the verification of adsorption equilibrium are reported elsewhere (Siperstein et al., 1999).

Results

Pure-component adsorption isotherms and isosteric heats for C_2H_4 and C_2H_6 on NaX are shown on Figs. 1 and 2. In VLE, the accurate determination of activity coefficients demands accurate values of vapor pressure. The same principle applies to adsorption; accurate measurements of "vapor pressures" or adsorption isotherms are essential, especially in the Henry's law region.

For mixtures of C_2H_4 and C_2H_6 on NaX, the two parameters extracted from our experimental data are $C = -1.437$ kJ/mol and $B = 0.200$ (mol/kg)$^{-1}$. The activity coefficient at the limit of high loading and

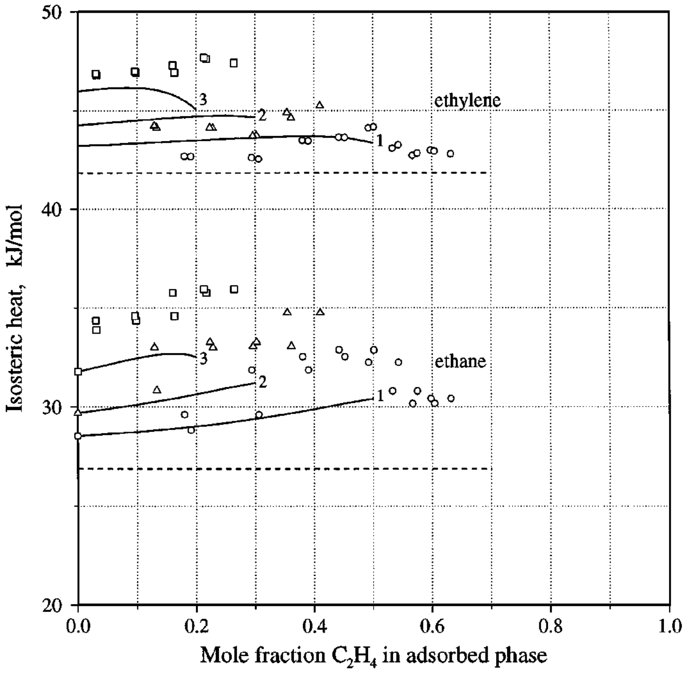

Figure 5. Experimental and calculated isosteric heats of adsorption from mixtures of C_2H_4 and C_2H_6 on NaX for constant loading of C_2H_6. (○ and line 1): 1.250 mol/kg, 298.85 K. (△ and line 2): 1.850 mol/kg, 294.75 K; (□ and line 3): 2.590 mol/kg, 298.15 K. Solid lines calculated from regular solution model. Dashed lines are pure-component isosteric heats at limit of zero loading.

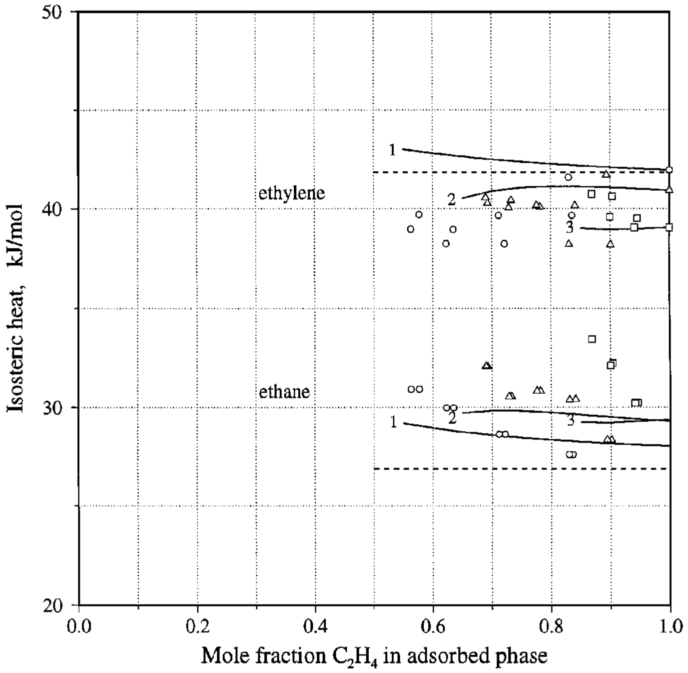

Figure 6. Experimental and calculated isosteric heats of adsorption from mixtures of C_2H_4 and C_2H_6 on NaX for constant loading of C_2H_4. (○ and line 1): 0.967 mol/kg, 297.65 K; (△ and line 2): 2.062 mol/kg, 297.85 K; (□ and line 3): 3.025 mol/kg, 297.25 K. Solid lines calculated from regular solution model. Dashed lines are pure-component isosteric heats at limit of zero loading.

infinite dilution is $\gamma^{\infty} = e^{C/RT} = 0.56$ at 25°C. The two constants B and C were derived by minimizing the sum-of-squares difference between experimental and calculated values of selectivity.

The selectivity of NaX for the mixture is plotted on Fig. 3. The solid lines calculated from the model, Eqs. (7)–(11), show that the fit of the selectivity is excellent over a wide range of composition and loading. Furthermore, the agreement of experiment with a two-constant model supports the validity of the quadratic composition factor and exponential spreading-pressure factor built into Eq. (7).

Figure 4 compares the experimental and calculated total pressure. Since these data were not used to derive the constants, the excellent agreement provides additional support for Eq. (7) and confirms the thermodynamic consistency of the experiment (because it agrees with a model which is thermodynamically consistent).

Figures 5 and 6 show that the heat of adsorption of either component increases with loading of the other component. However, the agreement of regular-solution theory with experiment is unsatisfactory for the mixture heats. Eq. (7) describes isothermal data but breaks down for heats of adsorption, which are sensitive to the temperature dependence of C. The mixture is quadratic but the excess entropy in the adsorbed phase is appreciable.

Conclusions

A regular solution model with two constants provides an excellent representation of the isothermal adsorption equilibria for mixtures of C_2H_4 and C_2H_6 on NaX. The excess free energy in the adsorbed phase at 298 K has a limit of −359 J/mol at high loading. The activity coefficients exhibit the usual negative deviations from Raoult's law associated with adsorbed solutions: the infinite-dilution activity coefficients vary from unity in the Henry's law region to 0.56 at high loading. Thus the quadratic approximation for composition dependence in Eq. (7) agrees with experiment. However, the regular-solution assumption that the excess free energy is equal to the excess enthalpy and that both functions are temperature-independent fails, as evidenced by unsatisfactory agreement between experimental and calculated heats. The next higher-order approximation is to let C in Eq. (7) be a linear function of temperature, in which case the excess free energy varies linearly with temperature but the excess enthalpy is temperature-independent. The additional constant can be obtained by minimizing the difference between the experimental and theoretical mixture heats. We will report on the accuracy of this three-constant model of binary adsorption in future work.

Disk followed

Nomenclature

B	constant in Eq. (7)	mol/kg^{-1}
C	constant in Eq. (7)	J/mol
G	quotient $d \ln n/d \ln P/n^2$ for single-gas isotherm in Eq. (12)	—
Δg^e	excess Gibbs free energy	J/mol
Δh	enthalpy of vaporization	J/mol
Δh^e	excess enthalpy	J/mol
n	amount adsorbed	mol/kg
Q	heat measured by calorimeter	J
q	isosteric heat of adsorption	J/mol
P	pressure	Pa
R	gas constant	8.3145 J/mol-K
$s_{1,2}$	selectivity for component No. 1 relative to No. 2	—
T	temperature	K
x	mole fraction in adsorbed phase	—
y	mole fraction in gas phase	—

Greek Letters

γ	activity coefficient	—
ϕ	surface potential	J/mol
ψ	$-\phi/RT$	mol/kg

Superscripts

$\circ$	refers to standard-state property of pure adsorbate	—

Subscripts

i	refers to ith component	—

Acknowledgments

This work was supported by the National Science Foundation (NSF CTS 9610030).

References

Dunne, J.A., M. Rao, S. Sircar, R.J. Gorte, and A.L. Myers, "Calorimetric Heats of Adsorption and Adsorption Isotherms. 3. Mixture of CH_4 and C_2H_6 in Silicalite and Mixtures of CO_2 and C_2H_6 in NaX," *Langmuir*, **13**, 4333–4341 (1997).

Hildebrand, J.H., J.M. Prausnitz, and R.L. Scott, *Regular and Related Solutions*, Van Nostrand Reinhold, New York, 1970.

Karavias, F. and A.L. Myers, "Isosteric Heats of Multicomponent Adsorption: Thermodynamics and Computer Simulations," *Langmuir*, **7**, 3118–3126 (1991).

Rowlinson, J.S. and F.L. Swinton, *Liquids and Liquid Mixtures*, 3rd edition, p. 135, Butterworth Scientific, London, 1982.

Siperstein, F., R.J. Gorte, and A.L. Myers, "A New Calorimeter for Simultaneous Measurements of Loading and Heats of Adsorption from Gaseous Mixtures," *Langmuir* **15**, 1570–1576 (1999).

Smith, J.M., H.C. Van Ness, and M.M. Abbott, *Introduction to Chemical Engineering Thermodynamics*, 5th edition, pp. 349–352, McGraw-Hill, New York, 1996.

Talu, O., J. Li, and A.L. Myers, "Activity Coefficients of Adsorbed Mixtures," *Adsorption*, **1**, 103–112 (1995).

Valenzuela, Diego P. and Alan L. Myers, *Adsorption Equilibrium Data Handbook*, pp. 216–217, Prentice-Hall, Englewood Cliffs, NJ, 1989.