On Thermodynamics of Mixed-Gas Adsorption

THOMAS L. HENSON and ROBERT L. KABEL
Pennsylvania State University, University Park, Pennsylvania

A significant development in the prediction of mixed-gas adsorption behavior has been accomplished by Myers and Prausnitz (*1*). By thermodynamic analysis analogous to that commonly used for vapor-liquid equilibria, they extended the familiar concepts leading to the use of activity coefficients in expressions of Raoult's law to the case of mixed-gas adsorption. Most encouraging about their paper was not the fact that one could now calculate activity coefficients for the adsorbed phase; rather it was that all of their examples demonstrated that the assumption of an ideal adsorbed solution (activity coefficients = unity) led to excellent agreement between experimental mixed-gas adsorption data and data calculated by their method from pure component adsorption data. The purposes of this paper are: (1) to extend the Myers and Prausnitz method to the limiting case of adsorption from gas mixtures at saturation conditions; (2) to obtain and interpret adsorbed phase activity coefficients for a system quite different from those treated by Myers and Prausnitz; and (3) to enhance the perspective on the possibilities and limitations of the thermodynamic method.

Reeds and Kammermeyer (*2*) investigated the simultaneous adsorption of methanol and benzene on a porous glass and observed the existence of adsorption azeotropes at 15°, 25°, and 35°C. The data at 15°C. were fewer and the data at 35°C. were more erratic than the data at 25°C. and therefore are not treated in this paper. Reeds and Kammermeyer estimate a maximum error of 7% in the vapor composition for a given adsorbed phase composition. Figure 1 shows their 25°C. data. Simply, their apparatus can be described as an adsorption chamber, a liquid reservoir, and a vapor path connecting them. The vapor from which adsorption was to occur was merely the equilibrium vapor over the liquid mixture in the reservoir. Thus when the adsorption process achieved equilibrium all three phases were in equilibrium at saturation conditions.

Consider a vapor-liquid system in equilibrium. If one introduces a slight encouragement toward condensation (for example, a minute temperature drop) at some point in the vapor space, vapor will condense out at nearly the same composition as the liquid in the reservoir. In the work of Reeds and Kammermeyer this encouragement was the rather neutral adsorbent, porous glass. Methanol and benzene exhibit vapor-liquid azeotropes of approximately equimolar concentrations at the experimental temperatures of 15° to 35°C. Over a range of liquid mixture compositions, including the vapor-liquid azeotrope, then, the observed compositions of the adsorbed (condensed) phase also would be expected to display azeotropic characteristics. The differences in the vapor-liquid and vapor-adsorbate equilibrium curves of Figure 1 attest to a varying selectivity of the adsorbent with concentration. But it would require a much more selective adsorbent to avoid the azeotrope altogether. Another example of similar behavior but with a somewhat different explanation is given by Young and Crowell (*3*).

The Myers and Prausnitz method is derived for the case of adsorption from an unsaturated vapor and is not directly applicable to the Reeds and Kammermeyer data. The phase rule for adsorption is

$$\text{(degrees of freedom)} = \text{(number of components)} - \text{(number of phases)} + 3 \quad (1)$$

where the adsorbent is considered to be thermodynamically inert and therefore is not counted as a component (*1*). The calculational method presumes only two phases and hence three degrees of freedom for the binary system. The three-phase system of Reeds and Kammermeyer has only two degrees of freedom. Thus when the entire system is maintained at a single temperature and liquid of a given composition is introduced into the reservoir, all vapor and adsorbed phase properties become fixed. By using the notation of Myers and Prausnitz, the chemical potential of one of two components in the adsorbed phase is

$$\mu_i (T, \pi, x_i) = g_i^o (T) + RT \ln P_i^o (\pi) + RT \ln \gamma_i x_i \quad (2)$$

In the three-phase case the temperature T is the same for the liquid phase as for the adsorbed phase; the composition of the adsorbed phase x_i is fixed by the composition of the liquid phase; the spreading pressure π cannot be independently specified as shown by the phase rule; and hence $P_i^o(\pi)$ is fixed at a value which merely corresponds to the fixed value of the spreading pressure. Thus Equation (2) should be written

$$\mu_i (T, x_i) = g_i^o (T) + RT \ln P_i^o(\pi) + RT \ln \gamma_i x_i \quad (3)$$

The chemical potential for the same component in the liquid phase with the same standard state as used by Myers and Prausnitz for Equation (2) is written exactly as Equation (3) only with liquid parameters in place of adsorbed phase parameters. Equating the chemical potentials for the two phases in equilibrium and simplifying, one obtains

$$\gamma_{i,\,\text{ads.}} = \gamma_{i,\,\text{liq.}} \frac{x_{i,\,\text{liq.}}}{x_{i,\,\text{ads.}}} \frac{P_i^o}{P_i^o(\pi)} \quad (4)$$

The liquid phase activity coefficients can be calculated from Equation (5):

$$\gamma_{i,\,\text{liq.}} = \frac{P\, y_i}{x_{i,\,\text{liq.}}\, P_i^o} \quad (5)$$

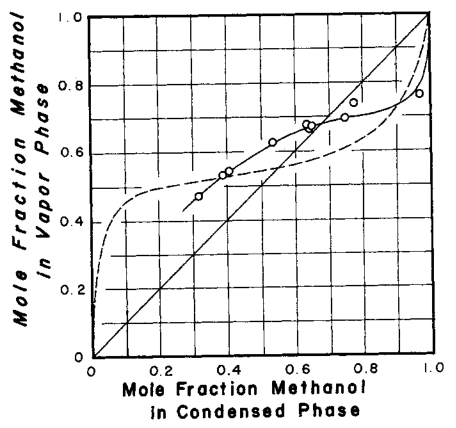

Fig. 1. Phase equilibrium diagram for methanol-benzene-porous glass system at 25°C. - - - - represents vapor-liquid equilibrium. –O– represents experimental vapor-adsorbate equilibrium (2).

Thomas L. Henson is at the University of Wisconsin, Madison, Wisconsin.

In general the vapor pressure of any adsorbed pure component $P_i^o(\pi)$ will increase with increasing spreading pressure. However it cannot exceed the pure component liquid phase vapor pressure P_i^o. Just as P_i^o is a function only of the temperature and not of the number of components in the liquid phase, so $P_i^o(\pi)$ is a function only of the temperature and total spreading pressure and not on whether the adsorbed phase is single- or multicomponent. As adsorption proceeds, the spreading pressure of the multicomponent adsorbed phase increases. At the appropriate levels of spreading pressure, the corresponding values of $P_i^o(\pi)$ for the individual adsorbed components become constant at respective values of P_i^o. In Reeds and Kammermeyer's experiment the liquid and adsorbed phases are in equilibrium with the same vapor. For this case, adsorption must continue until both condensed phases exert the same vapor pressure (or the liquid phase disappears). For a system containing pure methanol or pure benzene $P_i^o(\pi) = P_i^o$ at equilibrium. Note from Equation (4), then, that the pure component adsorbed phase activity coefficients must be unity.

The spreading pressure for a constant-temperature, variable pressure system is calculated by graphically integrating the following equation (*1*):

$$\frac{A}{RT}\,d\pi = n_B d\,\ln Py_B + n_M d\ln Py_M \tag{6}$$

The mixture spreading pressure thus obtained is used with pure component adsorption isotherms of spreading pressure vs. adsorbate vapor pressure to obtain values of $P_i^o(\pi)$ for use in Equation (4). Such a computation was attempted but rendered meaningless in this case by the erratic total adsorption data and by the lack of accurate adsorbed phase composition data at both ends of the composition range.

By solving Equation (6) for $\dfrac{d\left(\dfrac{A\pi}{RT}\right)}{dP}$ and by setting this derivative equal to 0, one can show that the spreading pressure reaches a maximum at the azeotropic composition of the adsorbed phase. Thus both pure component vapor pressures for adsorbed phase conditions will be at their maximum values at that point. Since there are no minima in the mixture spreading pressure vs. pressure curve, the spreading pressure will be at its lowest value for the case of pure benzene. Hence $P_B^o(\pi) = P_B^o$ over the entire concentration range. For methanol $P_M^o(\pi) = P_M^o$ from pure methanol to some point below the composition of the adsorption azeotrope of 0.68. Clearly $P_M^o(\pi) < P_M^o$ at some point $0 < x_{M,\,\text{ads.}} < 0.68$. Since $P_M^o(\pi)$ cannot be calculated without better data, it is assumed to be constant at P_M^o over the range of the mixture adsorption data $0.3171 \leqq x_{M,\,\text{ads.}} \leqq 0.9661$. Where not valid, this assumption will yield the smallest possible value for $\gamma_{M,\,\text{ads.}}$ [see Equation (4)]. Thus in order to calculate the adsorbed phase activity coefficients, vapor-liquid equilibrium data and pure component and mixture vapor pressure data at the constant temperature of interest were needed in addition to the available adsorption equilibrium data.

Scatchard, Wood, and Mochel (*4*) made highly precise measurements of vapor-liquid equilibria and vapor pressure for mixtures of elaborately purified methanol and benzene. Their work covered the entire range of concentrations at temperatures of 35° and 55°C. with single observations for approximately equimolar concentrations at 25° and at 45°C. Kretschmer and Wiebe (*5*) correlated the 35° and 55°C. data of Scatchard et al. with a three-constant equation for relative volatility as a function of liquid concentration. Since the variation of the constants with temperature was not great, a linear extrapolation of their values to 25°C. was made in this work. The resulting equation made possible the calculation of the vapor-liquid equilibrium data at 25°C. shown in Figure 1.

$$\alpha_{MB} = \frac{(1.041 - 0.869\,x_M)}{(x_M + 0.036)\,(1 - 2 \times 0.036 + 0.036\,x_M)} \tag{7}$$

The single datum at 25°C. of Scatchard et al. is in close agreement with the corresponding point in Figure 1. Reeds and Kammermeyer presented a vapor-liquid equilibrium curve which also passes through the 25°C. datum of Scatchard et al. At other points, however, their curve differs considerably from the curve calculated from Equation (7). Since the source of their curve was not reported, the curve predicted here has been used in all subsequent calculations. Kretschmer and Wiebe quote an agreement of Equation (7) with the data of Scatchard et al. within a few tenths of a mole percent. An error estimate of 2 mole % for the predicted curve at 25°C. over the range of compositions of the experimental adsorption data seems reasonable.

The required vapor pressure data were measured as a function of liquid mixture composition for use in this work. Accurately proportioned liquid mixtures were introduced into a previously evacuated isothermal chamber at 25.0°C. The methanol and benzene used here were of comparable purity to the analytical reagent grade material used by Reeds and Kammermeyer, but less pure than the highly refined materials used by Scatchard et al. In a crude but effective degassing operation, the vapor over the liquid mixture was twice removed by very brief evacuation. The very slight alteration in the liquid phase composition was calculated from the predicted vapor-liquid equilibrium data and the amounts and properties of the two phases. An additional very small correction was made to account for the slight cooling of the contents of the chamber due to the two evacuations. This was necessary because a slow air leak into the system made it undesirable to wait until absolute thermal equilibrium had been achieved before reading the vapor pressure. The resulting vapor pressure data are shown in Figure 2. The values indicated by the solid curve are believed to be accurate within ± 2 mm. Hg. The linearity of semilogarithmic plots of vapor pressure vs. reciprocal absolute temperature for these data at 25°C. and those of Scatchard et al. at 35° and 55°C. showed the two sets of data at each composition to be consistent within the above estimate of maximum error. These consistency plots and the single datum of Scatchard et al. at 25°C. indicated that the additional purification of their materials resulted in an increase of about 1 mm. in observed vapor pressure. This seems quite

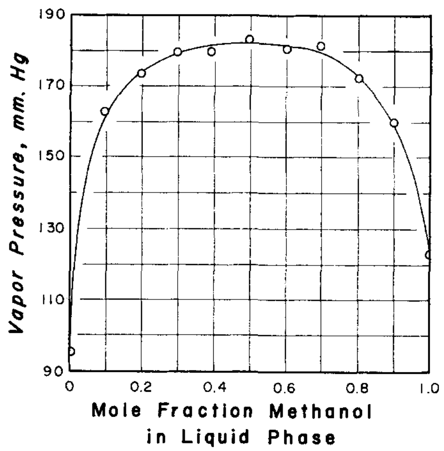

Fig. 2. Vapor pressure of methanol-benzene mixtures at 25°C.

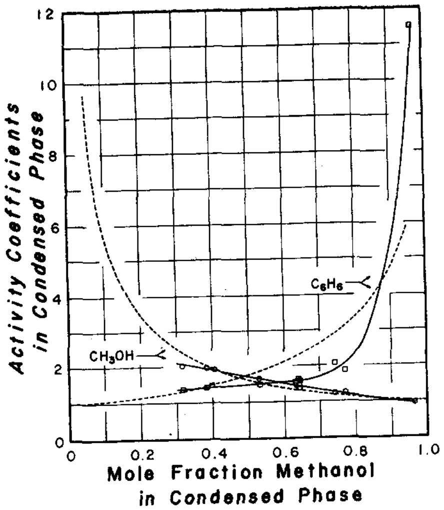

Fig. 3. Condensed phase activity coefficients for the methanol-benzene-porous glass system at 25°C. - - - - - - - - - represents liquid phase. ——— represents adsorbed phase.

reasonable. While these data should not be used recklessly in the derivation of thermodynamic properties, they are adequate and valuable for direct use as in the present work.

By combining Equations (4) and (5) and by assuming the adsorbed phase activity coefficient to be unity and $P_i^o(\pi) = P_i^o$, one can calculate the composition of the hypothetical ideal adsorbed solution for comparison to the experimental data of Figure 1. When the calculation was done by using benzene parameters, the vapor was predicted to be richer in methanol than the adsorbate over the entire concentration range. When methanol parameters were used, the vapor was poorer in methanol than the adsorbate. This inconsistency must be the consequence of adsorbed phase nonideality.

It is of interest then to calculate activity coefficients for the adsorbed phase and to compare them to the liquid phase activity coefficients. The results of these calculations for the actual data points reported by Reeds and Kammermeyer are shown in Figure 3. As far as can be seen the activity coefficients behave similarly for liquid and adsorbed phases. The fact that the point calculated at the highest methanol concentration gave an activity coefficient less than one is probably due to experimental error rather than thermodynamic activity of the adsorbent.

CONCLUSIONS

The theoretical and experimental work discussed here actually represent a limiting case within the realm of the Myers-Prausnitz analysis. As such it points up a major reason for the success of the ideal adsorbed solution assumption in the cases discussed by Myers and Prausnitz, summarized in Table 1.

Table 1. Binary Gas Adsorption Conditions

Binary mixture	Temp., °C.	Pressure, atm.	Adsorbent
Methane-ethane	20	1	Activated carbon
Carbon monoxide-oxygen	100	1	Silica gel
Carbon monoxide-oxygen	0	1	Silica gel
Propane-propylene	25	1	Silica gel
Ethylene-carbon dioxide	25.4	0.066 to 0.33	Activated carbon

In each instance the vapor is far removed from its saturation condition. Even for the propane-propylene mixture the vapor pressure is only one-tenth of the saturation pressure. Thus there will be little multilayer adsorption occurring, and the dominant forces will be interactions between the adsorption sites and individual molecules. For less than monolayer adsorption the ideal adsorbed solution assumption should not be crucial even for mixtures of considerable liquid phase nonideality. Also the adsorbent-adsorbate interaction should be well accounted for by pure component adsorption data, as shown by Myers and Prausnitz for the special case of very low surface coverage. In contrast, for adsorption near saturation conditions multilayer adsorption often can occur. When it does the great majority of the adsorbed molecules will be interacting with one another largely in the manner of the liquid phase, making the ideal adsorbed solution assumption untenable except of course when an ideal liquid solution is obtained.

This study indicates that activity coefficients may behave similarly in adsorbed and liquid phases. Certainly the assumption of an ideal adsorbed solution has been shown to be unsuccessful in predicting mixed gas adsorption behavior for the methanol-benzene-porous glass system at saturation conditions. However the Myers and Prausnitz approach should be useful in many cases of practical and theoretical interest.

NOTATION

A = specific area of adsorbent
$g_i^o(T)$ = standard state molar Gibbs free energy of component i at the perfect gas state and a pressure of 1 atm.
n_i = number of moles of component i in adsorbed phase per unit mass of adsorbent
P = total pressure
P_i^o = vapor pressure of pure component i in liquid phase at the temperature of interest
$P_i^o(\pi)$ = vapor pressure of pure component i in adsorbed phase at the temperature and spreading pressure of interest
R = gas constant
T = absolute temperature
x_i = mole fraction of component i in either condensed phase
y_i = mole fraction of component i in vapor phase

Greek Letters

α_{MB} = relative volatility of methanol with respect to benzene = $(y_M/y_B)/(x_B/x_M)$
γ_i = activity coefficient of component i in condensed phase
μ_i = chemical potential of component i
π = spreading pressure

Subscripts

ads. = adsorbed phase
B = benzene
i = component i
liq. = liquid phase
M = methanol

LITERATURE CITED

1. Myers, A. L., and J. M. Prausnitz, *A.I.Ch.E. J.*, **11**, 121 (1965).
2. Reeds, J. N., and Karl Kammermeyer, *Ind. Eng. Chem.*, **51**, 707 (1959).
3. Young, D. M., and A. D. Crowell, "Physical Adsorption of Gases," pp. 397-398, Butterworths, London (1962).
4. Scatchard, G., S. E. Wood, and J. M. Mochel, *J. Am. Chem. Soc.*, **68**, 1957 (1946).
5. Kretschmer, C. B., and R. Wiebe, *ibid.*, **71**, 1793 (1949).