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Gas Mixture Adsorption on Molecular Sieves

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The note of Myers (1973) recently published in the Journal attributes a "serious mistake . . based upon an unjustifiable procedure" as being responsible for "incorrect conclusions" in the paper of Danner and Wenzel (1969). In this latter paper the authors evaluated the ideal adsorbed solution theory (Myers and Prausnitz, 1965) as a practical method for predicting a priori binary adsorption data from the pure gas isotherms. In contrast to Myers' comments, it is claimed here that the procedure followed was both reasonable and justified and that no mistake was made in the calculations or conclusions.

Use of the Myers and Prausnitz method for predicting gas mixture adsorption data requires calculation of the spreading pressure of each pure adsorbate as a function of pressure. Accurate calculation of spreading pressures requires low surface coverage data. For strongly adsorbing systems, this in turn requires such extremely low pressures that they generally cannot be measured in standard adsorption equipment. If one cannot obtain such data, some means of extrapolating the data to low coverage is necessary if only pure gas data are to be used to predict the mixture adsorption behavior. Danner and Wenzel made the extrapolation to zero coverage by using the Langmuir equation, a procedure Myers has characterized as unjustified. The selection of this equation, however, was based on the relative accuracy of the Langmuir, *n*-layers BET, and Freundlich equations in representing the lowest portion of the experimental isotherms of oxygen, nitrogen, and carbon monoxide on molecular sieves.

Myers suggests that the solution to the low coverage extrapolation problem is the application of the Gibbs adsorption isotherm to binary mixtures at constant pressure as described by Van Ness (1971). There are two serious deficiencies in his suggestion. First, the application of this method defeats the primary goal of having a means of predicting the mixture data from the pure gas isotherms. The calculation now requires an integral of the experimental binary adsorption data over the entire composition range to derive a correction factor (integration constant). Thus, although Myers claims that this modification of the theory shows "that the theory of ideal solution predicts . . adsorption on molecular sieves"; the method, in fact, no longer predicts mixture results from pure gas data but instead simply correlates the experimental mixture data.

Second, the correlating method described by Myers still retains the deficiency of requiring the extrapolation of the isotherm data to zero coverage for at least one of the adsorbates. The calculated correction factor is a difference between the spreading pressures of the two pure gases; and in order to calculate absolute values of the spreading pressures, one of the actual spreading pressure curves must be determined. In the example given by Myers, the curve for nitrogen was calculated from the data of Danner and Wenzel. Although these nitrogen data extended down to a coverage of one-fourth the monolayer coverage rather than only to one-half coverage as in the case of carbon monoxide, this is still not a sufficiently low range of coverage to allow extrapolation with confidence. Although Myers has been quite critical of Danner and Wenzel's method of making this extrapolation, he does not report how he carried out the calculations for nitrogen. He must have relied, however, on some similar type of procedure for nitrogen that he has termed a serious mistake when used by Danner and Wenzel for the case of carbon monoxide.

In summary, although the note of Myers does suggest that the ideal adsorbed solution theory may be a useful correlating method for molecular sieve systems, the suggested modification does not allow its use as an a priori predictive method and does not remove the necessity for extrapolating the pure component data. The treatment of the data reported by Danner and Wenzel was a rational and justified attempt to compare the theory of Myers and Prausnitz with the other methods of predicting binary adsorption data using only the pure gas isotherms.

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