NOTATION

= concentration at coalescer input concentration at coalescer output

= experimental value of the diameter of the drop

formed as defined by equation (1a)diameter of the drop formed

= diameter of the drop still attached to the sphere

diameter of packing element = average microdrop size gravitational acceleration

mass velocity (dispersion flow rate/column sec-

 U_c critical velocity water velocity

Greek Letters

= diameter of the circle at the constriction point as defined by Equation (1b)

= interface tension

= density difference between the two phases $\Delta \rho$ Δp = pressure difference at the poles of the coalescer

= standard deviation

= kinematic viscosity of continuous phase

LITERATURE CITED

Aurelle, Y., "Contribution à l'étude du traitement des eaux polluées par des HC émulsionnés par coalescence sur résine oléophile," thèse de docteur-ingénieur, No. 144, UPS, Toulouse, France (1974). Calteau, J. P., "Contribution à l'étude hydrodynamique de la

phase dispersée dans le phénomène de coalescence en lit fixe," thèse de docteur-ingénieur, No. 593 UPS, Toulouse,

Harkins, W. D., and F. E. Brown, J. Am. Chem. Soc., 41, 499

(1919).

Hazlett, N., "An Examination of the Steps Involved in the Separation of Water from Fuel in Fibrous Bed," Jet Fuel

Quality Symposium, San Antonio, Tex. (Oct. 22-24, 1968). Scheele, G. F., and B. J. Meister, "Drop Formation at Low Velocities in Liquid-Liquid Systems," AIChE J., 14, 9

Vinson, C. G., and S. W. Churchill, "Removal of Drops from Liquid-Liquid Dispersions upon Flow Through Screens," Chem. Eng. J., 1, (1970).

Wilkinson, D., Ph.D. thesis, No. D 15008/76 Aston Birmingham, England. (1974).

Vignes, A., Génie chimique, 93, No. 5 (May, 1965).

Manuscript received March 28, 1977; revision received November 18, and accepted December 7, 1977.

Vapor-Liquid Equilibrium Measurements Through Vapor-Adsorption Chromatography

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Further understanding of the application of perturbation chromatography as applied to gas-adsorption systems enables one to study vapor-liquid equilibria at finite concentrations. The generalized relations for the determination of gas adsorption on arbitrary adsorbents using the principles of perturbation chromatography were developed by Gilmer and Kobayashi (1965). Perturbation chromatography has been successfully applied to study the adsorption of gas mixtures on several adsorbents (Gilmer and Kobayashi, 1964; Haydel and Kobayashi, 1967; Masukawa and Kobayashi, 1969).

Adsorption chromatography was used by Masukawa et al. (1968) to show that the dew point could be viewed as a limiting condition of gas adsorption. They introduced the hypothetical perfect gas perturbation to obtained adsorbed phase properties (Masukawa and Kobayashi, 1968a). They also showed that the condensed state could be defined within very narrow limits, that is, tens of Angstrom units. Kobayashi and Carnahan (1975) defined the dew point in explicit Gibbsian terms and used the earlier measurements of Masukawa and Kobayashi (1968b) as an example of the mixture dew point definition.

Through careful selection of a homogeneous adsorbent for a given type of adsorbate, Porapak P, for the methanen-butane system, the authors have found that the K value

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for adsorbent, defined by

$$K_i = \frac{y_i}{x_i} \tag{1}$$

where y_i is the mole fraction of component i in the elution gas phase, and x_i is the mole fraction of the adsorbate in the adsorbed phase, is essentially independent of the pressure, Figure 1. From the determination of the K value for the components in a mixture by methods described earlier (Masukawa and Kobayashi, 1969), from determination of the very onset of condensation from the detector signal, Figure 2, and from the behavior of the adsorption isotherm, Figure 3, it has been found possible to determine the vapor-liquid equilibrium constants for the components in the mixture (Everett, 1977). Similar results were obtained at 255.37° and 244.26°K (0° and -20°F) for the methane-3 mole % n-butane mixtures and for a methane-5 mole % n-butane mixture at 266.48°, 255.37°, and 244.26°K (+20°, 0°, and -20°F). The V-L-E K values determined by classical methods at 255.37°K (-20°F) are also shown on Figure 1 and found to agree quite satisfactorily with the V-L-E K values determined by adsorption chromatography.

A precise method for determining vapor-liquid equilibria as a limiting case of gas-adsorption chromatography is presented. The small, radioactive samples were injected into the flowing system in the gaseous state with a six-port injection and column bypass switching valves (model CV-H Pax from the Valco Instruments Co., Houston, Texas) with special rotors for low temperature work. If

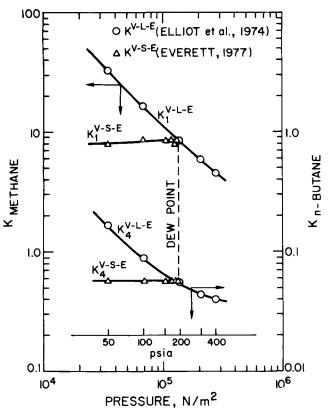


Fig. 1. K values for V-L-E and V-S-E C_1 -n- C_4 -porapak P at 255.37°K (0°F).

necessary, the radioactive *n*-butane to be injected was diluted with methane to keep the radioactive compound, for example, *n*-butane, in the gaseous state. Under the present state of the art, the method should be applicable to mixtures whose components possess relative volatilities

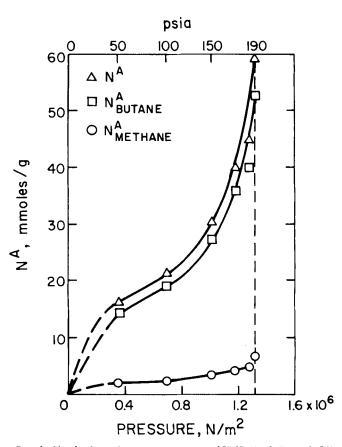
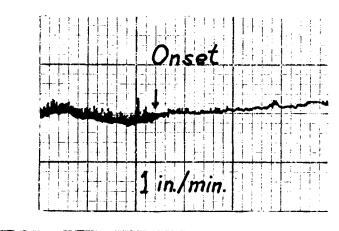
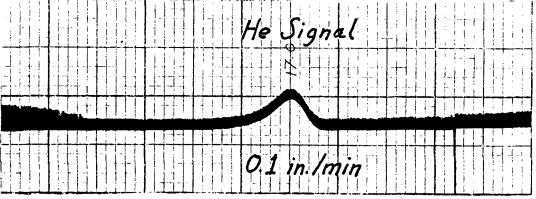


Fig. 3. Total absorption vs. pressure at 255.37°K (0°F) and 5% n-butane concentration.

less than 100 and where adsorbate-adsorbent interactions do not cause special orientation effects at the gas-liquid interface.



0.423 mm/S



0.0423 mm/s

Fig. 2. TC cell signal at the dew point.

ACKNOWLEDGMENT

The authors wish to acknowledge the support of the National Science Foundation for the support of this work and the Phillips Petroleum Company for the light hydrocarbons. Mr. Ray Martin contributed significantly to maintaining the integrity of the experimental apparatus.

LITERATURE CITED

Elliot, D. G., R. J. J. Chen, P. S. Chappelear, and R. Kobayashi, "Vapor-Liquid Equilibrium of Methane-n-Butane System at Low Temperatures and High Pressures," J. Chem. Eng. Data,

19, 71 (1974). Everett, A. K., "Demonstration of the Gibbs Definition of Dew Point Conditions of the Methane-n-Butane Mixtures on an Organic Surface," M.S. thesis, Rice Univ., Houston, Tex.

(1977).

Gilmer, H. B., and R. Kobayashi, "The Study of Gas-Solid Equilibrium at High Pressures by Gas-Chromatography: Part I. Ethane, Propane, and n-Butane at Essentially Infinite Dilutions in the Methane-Silica Gel System," AIChE J., 10, 797 (1964).

"The Study of Gas-Solid Equilibrium at High Pressures by Gas-Chromatography: Part II. Generalization of the Theory and Application to the Methane-Propane-Silica Gel System," *ibid.*, 11, 702 (1965).

Haydel, J. J., and R. Kobayashi, "Adsorption Equilibria in the Methane-Propane-Silica Gel System at High Pressures," Ind. Eng. Chem. Fundamentals, 6, 546 (1967).

Kobayashi, R., and N. F. Carnahan, "A Reasonable Gibbsian Definition of the Dew Point and Its Experimental Verification," AIChE J., 21, 158 (1975).

Masukawa, S., J. I. Alyea, and R. Kobayashi, "Applications of the Hypothetical Perfect Gas Perturbation to Study the Continuity Between Gas-Solid and Gas-Liquid Equilibrium and to Evaluate Vapor-Liquid Equilibrium," J. Gas Chrom., 6, 266 (1968).

Masukawa, S., and R. Kobayashi, "The Hypothetical Perfect Gas Perturbation and the Determination of the Volume of the Adsorbed Phase in Gas-Solid Chromatographic Col-

umns," ibid., 257 (1968a).

———, "Thermodynamics of Multilayer Adsorption Studied by Elution Gas Chromatography," ibid., 461 (1968b)

-, "Experimental Determinations of the Molar Heat and Entropy of Adsorption and the Activity Coefficient of the Adsorbed Phase for the Methane-Ethane-Silica Gel System," AIChE J., 15, 190 (1969).

Manuscript received June 2, 1977; revision received January 3, and accepted January 5, 1978.

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The Second Conference on PhysicoChemical Hydrodynamics will be held at The National Academy of Sciences, 1201 Constitution Avenue, Washington DC USA, from November 6 to 8 1978. The Conference will be conducted by way of six 4-hour sessions, each involving four presentations by experts in the field, followed by discussions. It is hoped to promote interdisciplinary understanding and collaboration among persons who approach this subject from diverse points of view. Among the scheduled speakers are S. G. Bankoff, P. L.

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cik June 28, 1978