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Supercritical Fluid Technology

Edited by

J.M.L. Penninger

M. Radosz

M.A. McHugh

and

V.J. Krukonis

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J.M.L. Penninger

AKZO Zout Chemie Nederland B.V., P.O. Box 25, 7550 GC Hengelo, The Netherlands

M. Radosz

Exxon Research and Engineering Company, Clinton Township, Annandale, NJ 08801, U.S.A.

M.A. McHugh

Department of Chemical Engineering, The Johns Hopkins University, Baltimore, MD 21218, U.S.A.

V.J. Krukonis

Phasex Corporation, No. 1 Mill, 85 Factory Street, Nashua, NH 03060, U.S.A.

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PREFACE

This book reflects the most recent progress in the area of supercritical fluid technology. The amount of research in this area has increased substantially, as indicated by the large number of publications which have appeared within the last decade. On a commercial scale, the supercritical fluid technology has been applied to energy- and food-related separation processes. These applications demonstrate a lower energy consumption and a better product purity, when compared with conventional separations. Both energy- and food-related separations are covered in this book. Also covered are extraction of organic compounds from water, polymer separations, drug separations, and chemical reactions in the presence of supercritical fluids.

Thermodynamics, particularly high-pressure phase equilibria, is the single most important discipline of chemical engineering which is used to understand and develop new supercritical fluid technologies. Phase equilibrium data are needed to evaluate and design new processes. In most cases, such data have to be measured experimentally. However, the need for experimental effort can be reduced when thermodynamic models are available for correlating and predicting phase equilibrium data.

Thermodynamic fundamentals and modeling of supercritical fluids are the subject of the first part of this book. The second part covers experimental data and techniques. However, most of the papers in both parts deal with both modeling and experiment, and the only difference between the two parts is that of emphasis. It is worth noting that in addition to the phase equilibrium studies mass transfer studies are also covered in part two.

The third part of the book discusses process development issues and energy-related applications and the fourth part discusses special applications of supercritical fluids. While these two parts suggest many new opportunities for supercritical fluids, they also indicate that more data and further improvements are needed in such areas as solids handling at high pressures, metal corrosion, gasket material compatibility, and heat and mass transfer characteristics.

Johan M.L. Penninger
Maciej Radosz
Mark A. McHugh
Val J. Krukonis

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FUNDAMENTAL THERMODYNAMICS OF SUPERCRITICAL EXTRACTION

K. E. Starling, M.A. Khan, and S. Watanasiri
School of Chemical Engineering and Materials Science, University of Oklahoma, Norman, OK 73019

ABSTRACT

Supercritical extraction phenomena in vapor-liquid and liquid-liquid systems are discussed. The effects of operating conditions and solvent to solute ratio on product separation and solvent recovery are studied for the model vapor-liquid system, solvent (methane) plus solute (n-butane plus n-decane). A similar study for the model liquid-liquid system solvent (methane) plus solute (n-hexane) leads to the general conclusions that the best operating conditions for supercritical extraction processes are as near as possible to the mixture critical point (not the pure solvent critical point). Also, it is concluded that within process constraints, high solvent to solute ratios are preferred in supercritical extraction processes.

INTRODUCTION

Supercritical extraction has been used increasingly in recent years for specialized separation processes. These processes include separation of drugs from plants, caffeine from coffee, oils from vegetable seeds, impurities from labile materials, and chemical feedstocks from coal and petroleum residua. The popularity of supercritical extraction processes stems principally from the enhanced solubility characteristics of a solvent near its critical point and the ease with which the solvent can be recovered for recycle.

In a supercritical extraction process a solvent is contacted with a solute at conditions near a critical point of the solvent plus solute mixture. The mixture may exhibit multiphase behavior involving vapor, liquid, and solid phases, depending on the mixture composition and temperature and pressure conditions.

Although multiphase equilibria have long been observed experimentally (e.g., ref.1) the effects of industrial operations near mixture critical points were not clear in early applications. For example, multiphase behavior has been used for deasphalting and refining lubricants (ref.2) and fractionation of crude oils (ref.3). Vink, et al. (ref.4) observed that when propane and other solvents were added to crude oils three phase vapor-liquid-liquid systems sometimes resulted and the precipitation of asphaltic materials was feasible.

In the case of two phase vapor-liquid systems, the fact that retrograde

condensation and vaporization phenomena occur probably has been known for over a century (ref.5). The retrograde phenomenon is quite important in petroleum reservoir fluid phase behavior (ref.6) and therefore extensive laboratory studies have been performed (ref.7, ref.8). However, only recently have the advantages of retrograde behavior been exploited extensively in industrial processing (ref.9).

The objective of the study presented here is to explain certain effects in supercritical extraction using examples for two and three component mixtures such that there is confidence that the phenomena referred to actually occur and phase splits and compositions at conditions considered are quantitatively accurate. The computations are performed using equation of state methods and have been compared with experimental data for the mixtures studied to assure accuracy of the predictions. Because interest here is in system behavior and not computation methods, discussion of the equation of state methodology is omitted; the equation of state may be considered merely to be a data interpolation tool in this application. The study is limited to vapor-liquid and liquid-liquid systems. Vapor-liquid-liquid systems were excluded because of the paucity of reliable experimental critical region data. Systems containing solids were excluded because only fluid phase effects are considered important.

The first major section of the paper deals with vapor-liquid systems. In contrast to the work of Brulé and Corbett (ref.9), which considered aromatic solvents plus heavy temperature-sensitive asphaltic materials, here relatively light, well defined systems for which more detailed experimental phase behavior data are available are studied. The methane + n-butane + n-decane ternary system was chosen for study because of the extensive data available (ref.8). This is an interesting system because it simulates petroleum fluid behavior. For high methane concentrations, the system exhibits retrograde behavior at pressures and temperatures similar to high pressure condensate gas reservoir fluids. Furthermore, it contains a light component, an intermediate component and a heavy component, analagous to the solvent and products from industrial critical solvent processes. Discussion in this section on vapor-liquid systems is focused on the choices of operating conditions and solvent to solute ratios for product separation and solvent recovery.

The second major section of the paper deals with the liquid-liquid equilibrium (LLE) behavior that occurs in the vicinity of the solvent critical point. The methane + n-hexane system studied experimentally by Lin, et al. (ref.10) is used in this part of the study. The effects of temperature and pressure on equilibrium compositions are discussed.

VAPOR-LIQUID SYSTEMS

Phase diagram

Pressure-temperature projections of the multidimensional pressure-temperature-composition surface at constant compositions of methane + n-butane + n-decane mixtures were constructed using equation of state methods; an example is shown in Figure 1. Because of the availability of extensive experimental data (ref.8) for this ternary system, the behavior shown in Figure 1 is known to approximate the experimental behavior. The mole ratio of methane to butane plus decane, hereafter referred to as solvent to solute ratio, is 49 to 1 for the mixture in Figure 1. The mole fraction of butane for this mixture is 0.09262. Because of the high concentration of methane, the critical point of the mixture, estimated to be 191 K and 48 atm, is very close to that of pure methane (Tc= 190.5 K, Pc=45.4 atm). Lines of constant fraction vaporized (V/F, where V is moles of vapor and F is moles of feed) are also shown. The feed mixture composition remains constant throughout the diagram, but the compositions of the equilibrium vapor and liquid phases change as functions of V/F, T, and P. Note the very large region in which there is retrograde behavior both isothermally and isobarically, a region which is bounded by the dew line (V/F=1.0) and the locus of temperature maxima for the V/F curves. Within this retrograde region, extraction, product separation, or solvent recovery processes can be carried out. Some general features of the retrograde region are mentioned here.

Starting at Point A on Figure 1, which is on the dew line (V/F=1.0) at 200 K, if the pressure is decreased isothermally, the dew-point fluid initially condenses (i.e., V/F decreases). Condensation continues as the pressure is reduced isothermally to point B. As the pressure is further reduced below point B, V/F increases until it reaches the value of unity at the lower dew point (not shown). The variation of the fraction vaporized (V/F) with temperature along an isobar in the retrograde region is similar to the behavior of V/F with pressure.

Product separation and solvent recovery

For consideration of operating conditions for extraction or solvent recovery, plots of the vapor mole fraction of the heavy components along constant pressure traverses (Figure 3) and constant temperature traverses (Figure 4) are valuable. The 50 atm isobar of Figure 3 has the most striking feature, the steepness of the left-hand-side of the curve. With a small increase in temperature, the mole fraction of butane plus decane in the vapor phase can be reduced by an order of magnitude. At higher pressures, the drop in composition is not as drastic. The 30 atm isobar does not show the same behavior as the higher pressure ones because it lies below the critical pressure of the mixture and therefore the low temperature phase boundary is a bubble point rather than a dew point. This demonstrates that a large change in solubility of heavy components in a solvent

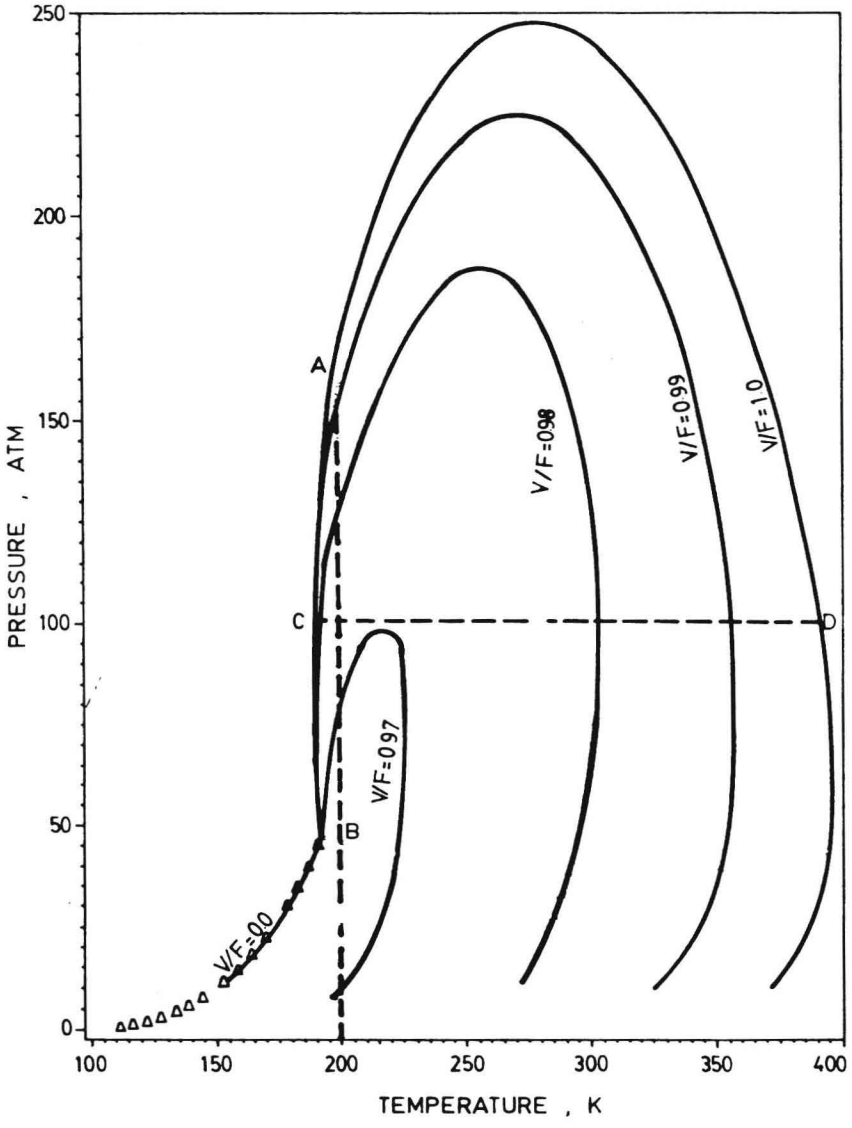

Figure 1. Pressure Temperature Phase Diagram at Constant Composition for the Methane + n-Butane + n-Decane System (Δ is Methane Vapor Pressure)

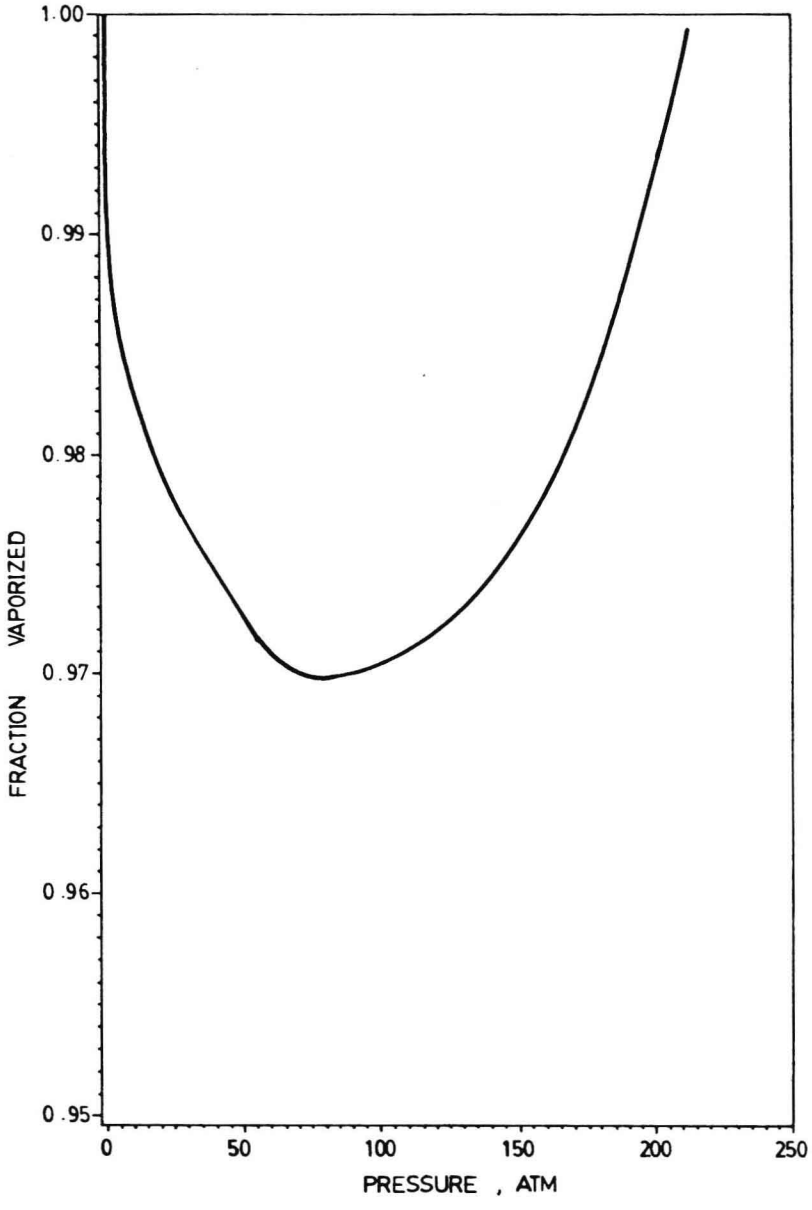

Figure 2. Behavior of Fraction Vaporized (V/F) in the Retrograde Region at 200 K.

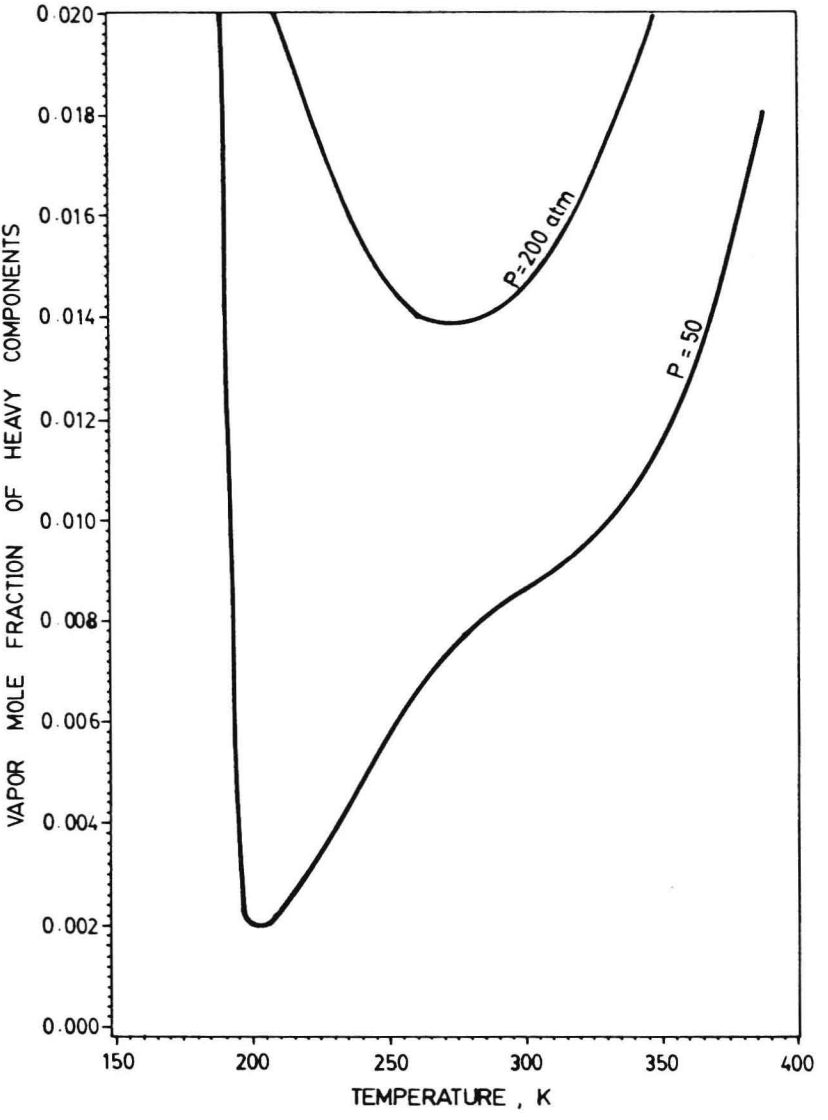

Figure 3. Effect of Temperature on Mole Fraction of Heavy Components in the Vapor Phase.

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