Measurement and Prediction of High-Pressure Phase Equilibria with a Dilute Component in the Gas Phase: The Methane-n-Hexane System

The design of vapor recovery processes requires very accurate vapor-liquid equilibria data. In this work the problem is attacked from both an experimental and a correlational viewpoint, and the methane-*n*-hexane system is chosen for study. A predictive model for vapor-liquid equilibrium aids in the interpretation of the experimental measurements, and data acquired in this study agree closely with the theoretical predictions. Maximum deviation between calculated and experimental equilibrium ratios (y_i/x_i) is 8.5% with average absolute deviations of 3% for *n*-hexane and 0.1% for methane. Several procedures are described for checking the accuracy of experimental VLE data when a heavy vapor is present at low concentrations in the gas phase. Several potential sources of experimental error are also identified and discussed.

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SCOPE

The recovery of high molecular weight vapors from lighter gases is important in a number of industrial processes especially with respect to the recovery of natural gasoline, butane, and propane from natural gases. The design of high pressure processes of this type requires accurate vapor-liquid equilibria data because the components to be recovered are normally present in low concentrations.

Experimental vapor-liquid equilibrium studies, however, normally show deviations of 1 mole % or more in the compositions measured by different investigators for the same system and for the same conditions of temperature and pressure. This accuracy is satisfactory for many purposes, but for the design of vapor recovery processes a 1 mole % error in the experimental data can be serious if only 2 to 5 mole % of the component or components to be recovered are present. In fact, this error can completely distort the apparent economic viability of the desired process.

Binary systems comprise the majority of high-pressure vapor-liquid equilibrium studies in the literature, whereas most mixtures of industrial interest contain many components. Nevertheless, this fact in no way demeans the importance or the need for good binary equilibrium data. Such data have, in recent years, played a central role in the development of correlations for calculating multicomponent phase equilibria (Chueh and Prausnitz, 1968; Prausnitz et al., 1967; Hudson and Van Winkle, 1970; Adler et al., 1966).

In this work vapor-liquid equilibria up to a pressure of 17 atmospheres are measured for the methane-*n*-hexane system between 38° and 138°C. This investigation has three main objectives: (1) to provide VLE data which may be used in the development of correlations; (2) To determine major sources of experimental error for phase equilibria involving a heavy and a very light component such as the methane-*n*-hexane system; (3) To delineate computational methods for evaluating experimental accuracy.

CONCLUSIONS AND SIGNIFICANCE

Sampling of the vapor phase poses a major obstacle in the measurement of accurate vapor-liquid equilibrium data. A simple graphical procedure used here aids in the evaluation of experimental gas phase compositions. Two other procedures are also used in evaluating the accuracy of experimental results. The VLE data for the methane-*n* hexane system obtained in this work are consistent with these computational methods. This consistency between theory and experimental results indicates that the data are accurate to within a few percent and may be used with confidence for correlational development and design.

The methane-*n*-hexane system was selected for the experimental part of this work because this system has been studied already by several investigators, and a considerable body of thermodynamic data is available for it. Poston and McKetta (1966) measured the vapor-liquid equilibrium compositions at temperatures of 38° to 170°C and at pres-

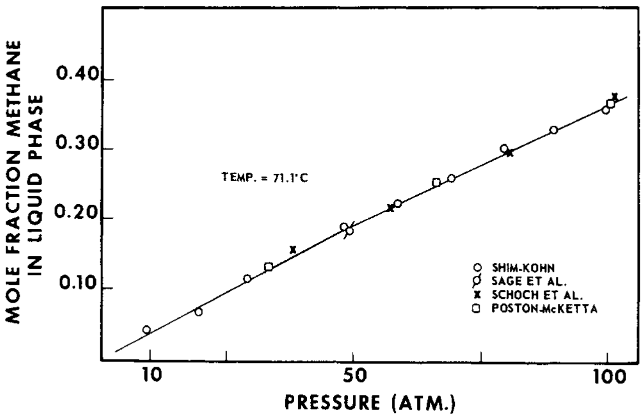

Fig. 1. Experimental methane concentrations in saturated liquid methane-n-hexane mixtures at 71.1°C.

sures from 34 atmospheres to the critical pressure. Shim and Kohn (1962) made measurements from −110° to 150°C and at pressures between 10 and 160 atmospheres. Schoch et al. (1941) determined the solubility of methane in liquid hexane at 37.8°, 71.1°, and 104.4°C at pressures of 38.6 atmospheres to the critical point. Sage et al. (1936) also reported measurements for the same temperature and pressure range. Frolich et al. (1931) carried out similar measurements at 25°C up to a pressure of 88 atmospheres. Finally, Stepanova and Vybornova (1962) reported equilibrium data for this system between 0° and 60°C. These latter investigators, however, did not have a true binary system because the methane used contained 1.0% nitrogen and 0.5% carbon dioxide as impurities.

Figure 1 shows a plot of the experimental saturation concentrations of methane in liquid n-hexane at 37.78°C. With the exception of the data of Stepanova and Vybornova which are not for a true binary and which are not shown on the graph, all investigations show good agreement for liquid phase compositions.

Only Poston and McKetta (1966) and Shim and Kohn (1962) have obtained vapor phase equilibrium data. Both groups indicate a precision of about 0.2 mole % in measured compositions. The absolute accuracy of these measurements is difficult to estimate; however, Poston and McKetta report that the differences in composition between the two investigations is generally less than + 0.5 mole % at equivalent conditions. Poston (1966) also reports maximum discrepancies between chromatograph and mass spectrometer analyses of about ± 1.0 mole %. Therefore, the absolute errors of recorded gas phase compositions are expected to be in the range of 1 mole % or less. This estimate is consistent with the findings of Won and Prausnitz (1973) who have developed a method, based on the Gibbs-Duhem equation, for estimating the accuracy of experimental measurements. For the more accurate sets of experimental results examined, Won and Prausnitz (1973) found average deviations of the data from thermodynamic consistency of about 0.35 mole %. This indicates that experimental error is less than ± 1 mole % with a 95% confidence level for the most consistent sets of data.

Errors of this magnitude normally cause little problem. For dilute components, however, a 1 mole % deviation may represent 50 or even 100% of the amount of that component present. An uncertainty of this magnitude may substantially affect the design of a vapor recovery process or the accuracy of a correlation.

These difficulties, which are also encountered in the data for many other systems, delineate a major problem in vapor-liquid equilibrium investigations of this type, that is, small errors in measured vapor mole fractions lead to very large percentage errors in the heavy component concentration in the gas phase. On the contrary corresponding errors for the light component in the liquid phase appear to be far less prominent. An experimental investigation in this work was initiated in order to study specifically the difficulties involved in measuring vapor-liquid equilibria with very dilute amounts of the heavy components in the vapor phase.

EXPERIMENTAL MEASUREMENTS

The experimental apparatus consisted of a 400-cc equilibrium cell maintained at isothermal conditions in an electrically heated constant temperature air bath. To achieve and maintain thermodynamic equilibrium vapors circulated from the top of the cell to the bottom through a magnetic pump. Temperatures were determined both from thermocouple measurements and from calibrated mercury thermometers graduated in divisions of 0.1°C. Pressures were measured with a bourdon gage calibrated to within 0.03 atmospheres by means of a dead weight gage. Compositions of the vapor phase were determined by means of a Beckman GC-2A gas chromatograph with a thermal conductivity detector and an automatic recorder. Calibration of the chromatograph was carried out before and after each isotherm. For a single isotherm as many as 20 independent measurements of the composition were made at each pressure. These measurements varied at most ±5% from the mean for the dilute component and generally varied much less. The individual measurements were averaged to obtain the final result. Equipment and experimental procedures were discussed in greater detail by Ata (1972). Gases used were research grade methane and n-hexane with a specified purity of better than 99.9%. Neither gas exhibited levels of impurity detectable with the GC-2A chromatograph.

Some of the experimental difficulties encountered are discussed later. Table 1 reports final experimental results. The equilibrium ratios (y_i/x_i) in Table 2 are calculated from the vapor compositions reported here and from a least squares fit of liquid compositions reported in the literature. Table 2 also reports equilibrium ratios calculated with a theoretical model.

THEORY

A theoretical model serves as an invaluable aid in confirming the validity of experimental data. Rigorous models with no adjustable parameters apply only to a restricted range of conditions. More versatile semi-theoretical models require interaction parameters which are curve fitted to experimental results. Because these interaction parameters

TABLE 1. EXPERIMENTAL SATURATED VAPOR PHASE COMPOSITIONS FOR THE METHANE-n-HEXANE SYSTEM

Temp., °C	Press., atm.	Vapor phase composition mole fraction Methane	n-Hexane
37.78	3.40	0.8923	0.1077
37.78	6.80	0.9451	0.0549
37.78	10.21	0.9606	0.0394
37.78	13.61	0.9696	0.0304
37.78	17.01	0.9728	0.0272
71.11	3.40	0.6791	0.3209
71.11	6.80	0.8281	0.1719
71.11	10.21	0.8830	0.1170
71.11	13.61	0.9097	0.0903
71.11	17.01	0.9257	0.0743
104.4	6.80	0.5583	0.4417
104.4	10.21	0.6877	0.3123
104.4	13.61	0.7531	0.2469
104.4	17.01	0.7961	0.2039
137.8	13.61	0.5185	0.4815
137.8	17.01	0.5999	0.4001

Table 2. Comparison of Experimental and Calculated Equilibrium Ratios for the Methane-n-Hexane System

				Equilibrium ratios			
			Methane,			n-Hexane	
Temp., °C	Press., atm.	Exp.	Calc.	% dev.*	Exp.	Calc.	% dev.*
37.78	3.40	58.59	58.64	0.09	0.1094	0.1098	0.36
37.78	6.80	29.63	29.65	0.07	0.0567	0.0590	4.05
37.78	10.21	19.95	19.97	0.10	0.0414	0.0422	1.93
37.78	13.61	15.10	15.12	0.13	0.0324	0.0340	4.94
37.78	17.01	12.19	12.21	0.16	0.0295	0.0292	−1.02
71.11	3.40	63.64	63.70	0.09	0.3244	0.3412	5.18
71.11	6.80	32.31	32.35	0.12	0.1764	0.1818	3.06
71.11	10.21	21.80	21.81	0.05	0.1220	0.1286	5.41
71.11	13.61	16.52	16.52	0.00	0.0955	0.1022	7.02
71.11	17.01	13.34	13.34	0.00	0.0799	0.0867	8.51
104.4	6.80	33.96	33.92	−0.12	0.4491	0.4504	0.29
104.4	10.21	23.03	23.01	−0.09	0.3219	0.3185	−1.06
104.4	13.61	17.48	17.46	−0.11	0.2580	0.2522	−2.25
104.4	17.01	14.13	14.10	−0.21	0.2161	0.2126	−1.62
137.8	13.61	16.00	15.94	−0.38	0.4976	0.5047	1.43
137.8	17.01	13.04	12.99	−0.38	0.4194	0.4261	1.60
Ave. abs. dev., %				0.13			3.11

* % dev. = $\dfrac{K_{CALC} - K_{EXP}}{K_{EXP}} \times 100.$

must come from VLE measurements, the engineer in general cannot make concrete estimates concerning the absolute accuracy of the experimental information but can assess to some degree the relative accuracy or thermodynamic consistency of the data.

The model used in this work parallels in many aspects the method developed by Chueh and Prausnitz (1968). Basis for the model is the fundamental relationship for phase equilibrium

$$f_{iG} = f_{iL} \tag{1}$$

Equation (1) is usually written in terms of activity and fugacity coefficients.

$$y_1 \phi_1 P = x_1 \gamma_1^* H_{12} \tag{2}$$

$$y_2 \phi_2 P = x_2 \gamma_2 f_2^0 \tag{3}$$

Subscripts 1 and 2 refer to methane and n-hexane, respectively. In Equation (3) the activity coefficient is normalized in the usual way. In Equation (2), however, the activity coefficient is normalized with the Henry's constant, because methane, which is above its critical temperature, cannot exist in the usual standard state, that is, pure liquid component. Prausnitz (1969) discusses further this convention for the normalization of activity coefficients. The equilibrium ratios used in engineering design follow directly from Equations (2) and (3).

$$K_1 = \frac{y_1}{x_1} = \frac{\gamma_1^* H_{12}}{\phi_1 P} \tag{4}$$

$$K_2 = \frac{y_2}{x_2} = \frac{\gamma_2 f_2^0}{\phi_2 P} \tag{5}$$

The quantities H_{12} and f_2^0 are obtained from experimental data and include the effect of pressure through a Poynting correction. The fugacity coefficients ϕ_1 and ϕ_2 are calculated from the virial equation by the method described by Gunn et al. (1971).

The activity coefficients are calculated from second-order van Laar equations.

$$\ln \gamma_1^* = A\, V_{c1} \,(z_2^2 - 1) \tag{6}$$

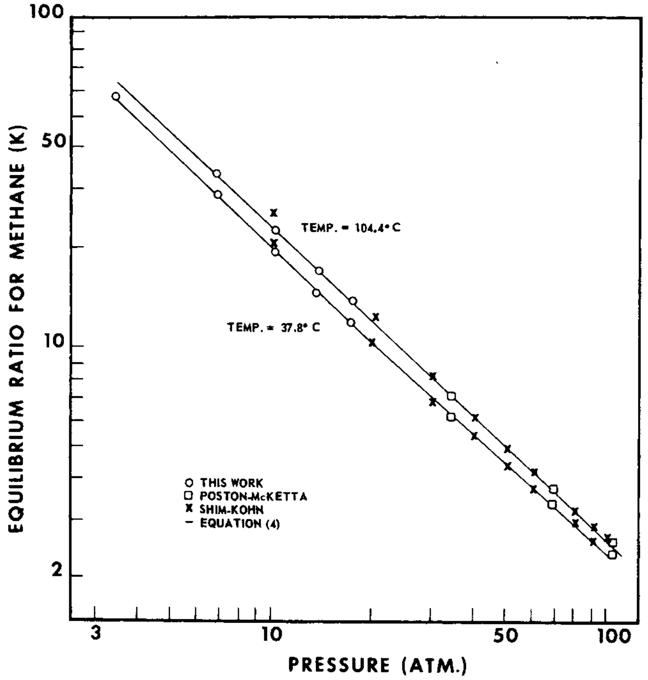

Fig. 2. Equilibrium ratios (y_1/x_1) for methane in methane-n-hexane mixtures.

$$\ln \gamma_2 = A\, V_{c2}\, z_1^2 \tag{7}$$

The volume fraction z has the following general form for a binary mixture:

$$z_i = \frac{x_i V_{ci}}{x_i V_{ci} + x_j V_{cj}} \tag{8}$$

The constant A in Equations (6) and (7) is obtained from experimental vapor-liquid equilibrium data.

Table 2 records equilibrium ratios calculated from Equations (4) and (5). Average absolute deviation between calculated and experimental data for this work is only 0.13% for methane and 3.1% for n-hexane.

Figure 2 compares experimental methane equilibrium ratios from three separate investigations with values pre-

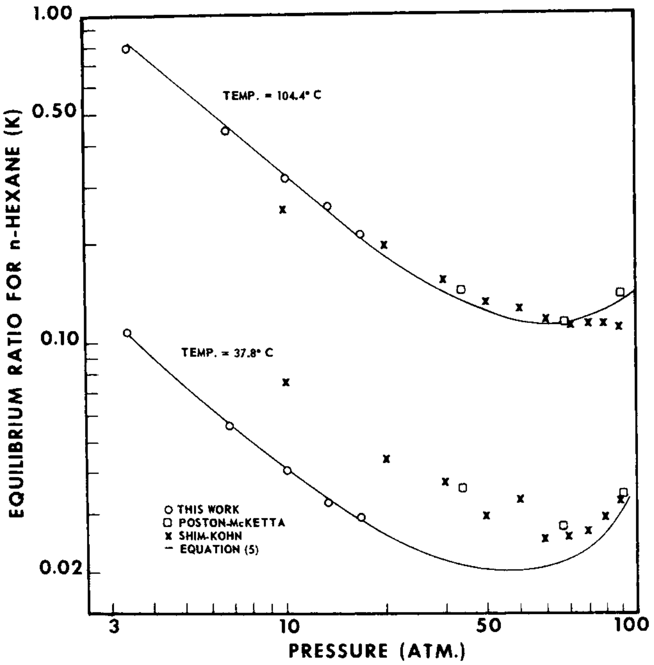

Fig. 3. Equilibrium ratios (y_2/x_2) for *n*-hexane in methane-*n*-hexane mixtures.

dicted by Equation (4). Figure 3 shows a similar comparison for *n*-hexane. At all temperatures experimental methane data agree well with the theoretical values. Methane is concentrated in the gas phase at all conditions; but it is fairly dilute, especially at low pressures and temperatures, in the liquid phase. Liquid phase compositions, however, are consistent among all investigators; and for this reason there is good agreement for the data illustrated in Figure 2.

At 104.4°C the vapor phase contains 10 to 20 mole % *n*-hexane. Because it is not very dilute in either phase the equilibrium ratios (K values) show good agreement for all investigators at this temperature. Figure 3, however, reveals a pronounced divergence between different sets of data at 37.78°C. At this temperature there is only 2 to 4% hexane in the gas phase.

To predict K values Equations (4) and (5) require two parameters, the Henry's constant and the van Laar constant, which are calculated from experimental phase equilibrium data; and methane equilibrium ratios are used for this purpose. Because methane K values agree among all investigators, as shown in Figure 2, all sets of experimental data produce about the same values for the two parameters.

ANALYSIS OF LOW-PRESSURE DATA

A number of investigators have studied extensively the problem of measuring accurately gas phase compositions in which one component has a very low vapor pressure (Hiza, 1970; Prausnitz, 1969; Prausnitz and Keeler, 1961). The theoretical calculations used to analyze those experimental data may also be applied to the problem here. For example, it is instructive to examine the experimental datum of Shim and Kohn (1962) shown in Figure 3 at 10 atmospheres pressure and 37.78°C from this theoretical viewpoint. The computational procedure is summarized in Table 3.

These calculations are quantitatively and theoretically rigorous subject to three conditions. First, the pressure must be sufficiently low so that third virial coefficients contribute only negligibly to gas phase nonideality. Second, the quantity of light component dissolved in the liquid phase should be sufficiently small so that the Lewis fugacity rule remains applicable. Third, although second virial coefficients can be calculated with reasonable confidence, experimental values are preferable. The authors have verified that all three conditions are met for results presented in Table 3.

Basically the procedure employed in this table is to use vapor-liquid equilibrium data to calculate a cross second virial coefficient B_{12}. For consistency, the calculated coefficient must agree with that obtained from direct volumetric measurements. As shown in the table the calculated B_{12} is -954 cc/g-mole. The B_{12} obtained by Dantzler et al. (1968) from volumetric measurements is -243.3 cc/g-mole. The larger B_{12} is inconsistent with the theory of second virial coefficients; and it exceeds, by more than a factor of 50, the estimated error (± 10 cc) of the volumetrically determined B_{12}.

What then is the probable major source of error for the cross virial coefficient obtained from phase data? Temperature and pressure measurements are seldom subject to large error. Similarly, for the conditions shown in Table 3, γ_2 and f_2^0 are known with substantial accuracy. The liquid phase composition x_2 is consistent to within less than 0.5% with three other experimental investigations. Only the gas phase composition y_2 can be seriously in error.

A y_2 of 0.0415 is calculated from Equation (3) when volumetrically determined virial coefficients are used. This value agrees well with the value for y_2 of 0.0404 measured in this work.

DISCUSSION

The fact that accurate vapor-liquid equilibrium data of the type discussed are very difficult to measure raises two important questions. What are the major sources of ex-

Table 3. Calculations Showing the Inconsistency between Vapor-liquid Equilibrium Data of Shim and Kohn (1962) and Volumetrically Determined Second Virial Coefficients

General relationship for phase equilibria

$$y_2\phi_2P = x_2\gamma_2f_2^\circ \tag{3.1}$$

f_2° = 0.349 atm. at 37.78°C and 10 atm. (with Poynting correction)
γ_2 = 1.00
x_2 = 0.9555, P = 10 atm. } Data of Shim and Kohn
y_2 = 0.0725 } (1962)
ϕ_2 = 0.460 from Equation (3.1)

$$\ln \phi_2 = -\ln z + \frac{2}{V}(y_1B_{12} + y_2B_2) \tag{3.2}$$

$$z = 1 + \frac{y_1^2B_1 + 2y_1y_2B_{12} + y_2^2B_2}{V} \tag{3.3}$$

$$V = \frac{zRT}{P} \tag{3.4}$$

B_{11} = -39 ± 1 cc/mol, $B_{22} = -1680 \pm 30$ cc/mol, experimental data (Dymond and Smith, (1969).

Solving Equations (3.2), (3.3), and (3.4) simultaneously gives
z = 0.9279
V = 2367 cc/mol
B_{12} = -954 cc/mol
B_{12} = -243.3 ± 10 cc/mol, experimental volumetric measurements of Dantzler et al. (1968).

perimental errors? What calculational methods can be used by experimentalists to detect the presence of unexpected errors? Both questions are difficult and can be answered only partially here.

Two major sources of experimental difficulties are analytical and sampling errors. The analytical instrument most commonly employed in vapor-liquid equilibrium studies is the chromatograph. This apparatus has the ultimate capability of detecting dilute components in extremely small concentrations. The chromatograph, unfortunately, is a secondary rather than a primary standard. Frequent recalibration is essential, and in addition calibration curves are often surprisingly nonlinear even in the dilute range. Instrument calibration is also extremely sensitive to small fluctuations in many different variables such as the power line voltage, sample temperature, room temperature, and carrier gas flow rate.

Sampling of the vapor phase is probably the largest single source of experimental inaccuracies. Adsorption and condensation in the sample container often produce very large errors. In this work consistent vapor compositions were attained only when the sampling line and valve were heated ½° to 1½°C above the temperature of the equilibrium cell by means of heating tapes. The investigators discovered that significantly larger temperature differentials also led to erratic results and that sampling procedures had to be regulated to minimize thermal diffusion effects. Such effects were detected in the early phases of the experimental work. For the system studied the thermal diffusivity is large because of the large mass difference between methane and *n*-hexane molecules.

Computational methods for checking experimental measurements for errors are recommended at two different levels of sophistication. First three empirical plotting techniques provide the simplest procedures for binary mixtures. To check vapor phase accuracy, some investigators (Kidnay et al., 1971) use a plot of the enhancement factor versus the pressure difference ($P - P_j^0$). The enhancement factor is defined as the heavy component partial pressure divided by its vapor pressure y_jP/P_j^v. Physical behavior dictates that for a plot of this type the experimental data should fall along a smooth curve (not necessarily a straight line) which extrapolates to a value of one at the ordinate. Figure 4 illustrates such a plot for the results obtained in this study and for the results of Shim and Kohn (1962). For the liquid phase a graph is made of the total pressure versus the mole fraction of the light component. Figure 1 shows a graph of this type. The extrapolated curve must have an intercept equal to the vapor pressure of the heavy component at x_i equal to 0. Finally a plot of the product $K_j P$ for the heavy component versus the pressure P also produces a curve which should pass through a point equal to the vapor pressure of the heavy component on both axes. The important aspect in each of these graphical tests is that the curve should extrapolate to the correct limit. To make these tests successfully measurements must be extended to sufficiently low pressures such that the vapor phase contains a large percentage of the heavy component. Low pressure measurements are frequently made only with difficulty in an apparatus designed for high pressures. A maximum effort should be made to make these low pressure measurements, however, because they provide an excellent test of sampling procedures which are usually least accurate at low pressures. These low pressure measurements also provide valuable fundamental information concerning the activity of the light component in the liquid phase.

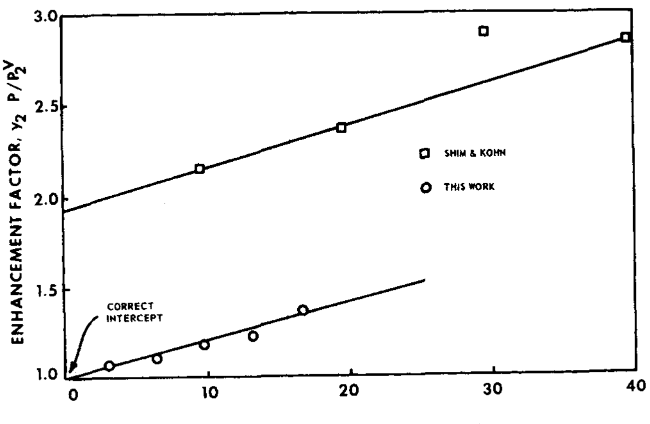

Fig. 4. Enhancement factor for *n*-hexane in methane-*n*-hexane mixtures at 37.78°C.

The more sophisticated method discussed earlier, which is outlined in Table 3, should also be employed in testing experimental results in addition to the plotting procedures.

Several authors (Chueh et al., 1965; Thompson and Edmister, 1965; Adler et al., 1960; Won and Prausnitz, 1973; Samuels et al., 1972) have described thermodynamic consistency tests for experimental data at moderate pressures. For isothermal measurements the general relationship for an integral test of an N component mixture is

$$\sum_{i=1}^{N} \int x_i \, d \ln \gamma_i = \frac{1}{RT} \int V^E \, d P \qquad (9)$$

The integral on the right-hand side of Equation (9) can be neglected over moderate ranges of pressure because, except in the critical region, the excess volume is always small (usually less than 5% of the total volume). The activity coefficients are calculated from Equation (4) for components above their critical temperature and from Equation (5) for components below their critical temperature. In Equations (4) and (5) the pressure and the equilibrium ratios are obtained from experimental measurements. At moderate pressures the gas phase fugacity coefficients can be calculated accurately from the virial equation. The standard state fugacity is readily calculated from the vapor fugacity (fugacity of the pure compound at its vapor pressure) with an appropriate Poynting correction. Chueh and Prausnitz (1968) have discussed methods for obtaining Henry's constants from experimental data.

Both the thermodynamic consistency tests and the method outlined in Table 3 require the use of the virial equation. Experimental virial coefficients for pure compounds have been compiled by Dymond and Smith (1969). Brewer (1967), Mason and Spurling (1969), and Hiza (1970) have compiled numerous references of experimental mixture second virial coefficients. In addition, the theory of second virial coefficients (Prausnitz, 1969) is sufficiently well developed that these can be estimated with reasonable accuracy if experimental data are lacking.

SUMMARY AND CONCLUDING REMARKS

Vapor-liquid equilibria data are reported for the methane-*n*-hexane system at four different temperatures and are shown to agree very well with the predictions of a theoretical model. These data are obtained from saturated liquid phase compositions reported in four previous investigations and from vapor phase compositions determined in this work.

Table 2, which records deviations between experimental and calculated equilibrium ratios, indicates approximately the absolute accuracy of the experimental data. The semi-theoretical computational model used reduces automatically at the appropriate conditions to the rigorous method outlined in Table 3. Much of the experimental data extend into the region that may be tested with this rigorous model which permits a fairly good estimate of the accuracy of the data. This estimate is considered valid for all of the data because the deviations are roughly the same at all pressures even beyond the pressure limit of the rigorous method. For this reason the experimental results can be used confidently for correlational development and design.

Acquisition of accurate vapor-liquid equilibria data is much more difficult than is generally recognized and is especially difficult for systems involving a noncondensable gas with small concentrations of a relatively high molecular weight vapor. A few of the sources of experimental error are discussed. Especially emphasized is the need for vapor-liquid equilibria measurements at low pressures as well as at the higher pressures. Also emphasized is the need for great care in sampling the vapor phase and in the calibration and use of the chromatograph, a secondary standard.

Several methods are recommended for checking the accuracy of experimental results. These techniques, of course, are not new, but their importance cannot be overemphasized.

The gap between predictive capabilities and experimental expertise is rapidly closing. However, all of the more accurate predictive methods require parameters calculated from experimental binary data. The ultimate goal, prediction of vapor-liquid equilibria from pure component parameters only, appears to be many years away. Therefore, the need for still more accurate experimental results is a challenge as great as ever. The value of good binary data for the development of better predictive techniques is perhaps greater now than at any previous time.

ACKNOWLEDGMENT

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NOTATION

A = van Laar constant, defined by Equations (6) and (7)
B = second virial coefficient
f = fugacity
f^0 = fugacity in the standard state, pure component at the temperature and pressure of the mixture
H_{ij} = Henry's constant for a solute i in a solvent j
K = y/x = equilibrium ratio
P = pressure
P^0 = vapor pressure
T = temperature
V = volume
V^E = excess volume
x = mole fraction in liquid phase
y = mole fraction in gas phase
z = volume fraction, defined by Equation (8)
γ = activity coefficient, symmetric normalization, defined by Equation (2)
γ^* = activity coefficient, unsymmetric normalization, defined by Equation (3)
$\phi = \dfrac{f}{yP}$ = gas phase fugacity coefficient

Subscripts

1 = methane
2 = n-hexane
c = property in critical state
i, j = components i and j respectively
G = gas
L = liquid

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Fast Fluxes with Supercritical Solvents

Measurements of iodine dissolution rates in supercritical carbon dioxide and other supercritical fluids show when the iodine flux in these systems can be made fast. For these systems, the dominant factor in achieving this fast flux is the solubility; increases in diffusion coefficient have less effect. An approximate guide for estimating these fluxes is developed and compared with the experimental results.

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SCOPE

This work investigates mass fluxes in supercritical fluids. These fluids, an important class of solvents, are gases or liquids compressed above their critical pressures and heated above their critical temperatures. Their study is another of the projects in this laboratory which aim at making mass transfer fast and selective.

Fast fluxes are desirable in most areas of mass transfer. The expectation that fluxes in supercritical fluids can be increased depends primarily on the increase in diffusion coefficient in going from liquid to gas. This increase is big, about 10^5. However, in dissolution or extraction, the magnitude of the solute flux depends both on the diffusion coefficient and on the solubility of the solute in the solvent. The solubility can decrease sharply in going from a liquid to a gas. Thus whether a supercritical fluid can engender a high flux depends on the product of the increased diffusion coefficient and the decreased solubility. One hopes that such a fluid will prove the ultimate solvent, with transport properties analogous to those of a gas and solubility properties like those of a liquid.

The unique feature of this study is this concern with flux, in contrast with earlier studies which emphasize measurements of diffusion coefficients. These earlier studies have used a variety of experimental methods, for example, interferometry, NMR, and radioactive tracers (Robinson and Stewart, 1968; Woessner et al., 1969). The data are used as checks for kinetic theories or are collected in more general correlations (Slattery and Bird, 1958; Ramanan and Hamrin, 1972). The work most similar to ours does measure the flux, but primarily in the region of the critical point (Tsekhanshaya, 1971; Krichevskii et al., 1971). Since the flux at the critical point goes to zero, this is not a region of great practical interest.

CONCLUSIONS AND SIGNIFICANCE

We have found that the flux of a solute in a supercritical fluid will be fast if its solubility is large. The flux is less affected by the increases in the diffusion coefficient. Such increases in diffusion coefficient are offset by decreases in solubility.

Measurements of iodine dissolution using a spinning disk show that the iodine flux in supercritical carbon dioxide does increase about 5% per °C at constant density. However, this change with temperature is considerably less at constant pressure. In all cases, the increases in flux can be estimated from available methods for calculating solubilities in supercritical fluids.

Thus our experiments suggest that extreme temperatures and pressures are necessary to achieve increases in flux of several orders of magnitude. Whether a solute's flux in a supercritical fluid is significantly greater than in an ordinary liquid depends primarily on the relative solubilities in the specific case. Whether the flux in a supercritical fluid is of practical importance depends both on the possibility of increased mass transfer and on the economic restraints involved.

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