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High Pressure Phase Equilibria for Vapour Phase Extraction Processes

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ABSTRACT

For the design of separation processes with supercritical dense gases, referred to as vapour phase extraction processes, high-pressure vapour-liquid equilibria have to be known. In the present investigation the Redlich-Kwong equation of state has been applied to a parametric study of high-pressure phase equilibria. The study has developed a generalized description of the phase behaviour of binary and multicomponent systems and provided general rules for the design of vapour phase extraction processes.

INTRODUCTION

During the last few years separation processes referred to as "extraction with dense gases", "extraction with supercritical gases" or "gas extraction" have grown more and more important. They are especially suitable for the separation of low volatile substances which decompose before reaching their boiling points. These processes are based on the phenomenon that supercritical gases can dissolve substances of low volatility. Compared with normal pressures a large increase in volatility can be obtained at high pressure under favourable conditions.

Various applications of supercritical gases for separating mixtures have been discussed by Ellis (1), Paul and Wise (2), Peter, Brunner and Riha (3), Pilz (4), Riha (5), Zosel (6), Stahl and Schilz (7), Whitehead and Williams (8) and Gangoli and Thodos (9).

A knowledge of phase equilibria at high pressures is essential for the understanding of vapour phase extraction processes. By considering the typical behaviour of binary mixtures consisting of a supercritical gas and a heavy component, one can explain the dissolving phenomenon of the supercritical gas. Such systems have been investigated by several authors in the last few years (3, 10 - 16). However, to investigate technical processes for separating two or more low volatile components by means of a supercritical gas, the behaviour of multicomponent mixtures has to be considered.

The purpose of the present investigation is to develop a systematic description of the behaviour of multicomponent mixtures by means of a simple and well suited equation of state. It will be shown that the phase behaviour of binary and multicomponent mixtures can be characterized by a few dimensionless parameters and that general correlations for vapour phase extraction processes can be derived.

METHOD

The Redlich-Kwong equation of state has been applied to a parametric study of high-pressure phase equilibria. At present good results in predicting phase compositions are being obtained using certain modifications of this equation of state both in the vapour phase and in the liquid phase (10 - 16, 23).

With the Redlich-Kwong equation of state (18)

$$p = \frac{RT}{\overline{V} - b} - \frac{a}{\sqrt{T}\,\overline{V}(\overline{V} + b)} \qquad (1)$$

(p = pressure, $\overline{V}$ = molar volume, T = temperature) and the mixing rules for the coefficients a and b

$$a = \sum_i \sum_j x_i x_j a_{ij}; \quad a_{ij} = \sqrt{a_{ii} a_{jj}}\,(1 - \Theta_{ij});$$
$$b = \sum_i x_i b_i \qquad (2)$$

(x_i = mole fraction; a_{ii}, b_i = Redlich-Kwong coefficients of pure component i; Θ_{ij} = interaction parameter between two components i and j), the fugacities f_i of component i can be calculated for the liquid (') and vapour phases (") (17)

$$RT \ln \frac{f_i}{x_i p} = \int_V^{\infty} \left[\left(\frac{\partial p}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - RT \ln \frac{pV}{RT} \qquad (3)$$

The application of the condition for phase equilibria

$$f_i' = f_i''; \quad i = 1,2...K \qquad (4)$$

yields a system of equations which has to be solved by trial and error (10). For binary systems (K = 2) the mole fractions x_1' of component 1 (supercritical component) in the liquid phase and x_1'' in the vapour phase can be estimated if the pressure (p), the temperature (T), the four coefficients (a_{11}, b_1, a_{22}, b_2) and the interaction parameter (Θ_{12}) are known:

$$x_1', x_1'' = f(T, p, a_{11}, a_{22}, b_1, b_2, \Theta_{12}). \qquad (5)$$

In Equation (5) the composition of a binary isotherm is described by five parameters. On the other hand it is obvious that the behaviour of a binary mixture depends principally on the different physical behaviour of the pure components. That means that the shape of a binary isotherm must be principally characterized by the ratios of the pure component parameters and not by their absolute values. This is the basic idea for introducing ratios of coefficients and dimensionless parameters in Equation (5) and for reducing the number of parameters.

Using the original Redlich-Kwong equations (18)

$$a_{11} = 0.4278R^2T_{c1}^{2.5}/p_{c1}; \quad b_1 = 0.0867\,RT_{c1}/p_{c1} \tag{6}$$

(T_{c1} = critical temperature and p_{c1} = critical pressure) to evaluate the coefficients a_{11} and b_1 of the supercritical carrier gas, the system of Equations (5) can be written with the dimensionless parameters

$$\tilde{p} = p/p_{C1} \quad ; \quad \tilde{T} = T/T_{C1} \quad ; \quad \tilde{V} = V/V_{C1} \tag{7a}$$

and with the ratios of the pure component coefficients

$$A_i = a_{ii}/a_{11} \quad \text{and} \quad B_i = b_i/b_1 \tag{7b}$$

in the following generalized form:

$$\begin{aligned}
&\ln \frac{(\tilde{V}'-B')}{(\tilde{V}''-B'')}\,\frac{x_i''}{x_i'} + B_i\left(\frac{C_1}{\tilde{V}''-B''} - \frac{C_1}{\tilde{V}'-B'}\right) + \frac{Z_{C1}\tilde{P}}{\tilde{T}B'}\ln\left(\frac{\tilde{V}'+B'}{\tilde{V}'}\right) \times \\
&\times \left[2C_2\left(\sum_{j=1}^{K} x_j'\sqrt{A_iA_j}\,(1-\Theta_{ij})\right) - \frac{A'B_iC_1}{B'}\right] - \frac{Z_{C1}\tilde{P}}{\tilde{T}B''}\ln\frac{\tilde{V}''+B''}{\tilde{V}''} \times \\
&\times \left[2C_2\left(\sum_{j=1}^{K} x_j''\sqrt{A_iA_j}\,(1-\Theta_{ij})\right) - \frac{A''B_iC_1}{B''}\right] + \\
&+ B_iC_1\frac{Z_{C1}\tilde{P}}{\tilde{T}}\left[\frac{A'}{B'(\tilde{V}'+B')} - \frac{A''}{B''(\tilde{V}''+B'')}\right] = 0,
\end{aligned} \tag{8a}$$

$$A' = C_2\sum_{i=1}^{K}\sum_{j=1}^{K} x_i'x_j'\sqrt{A_iA_j}\,(1-\Theta_{ij}),(\Theta_{ii} = 0);$$

$$A'' = C_2\sum_{i=1}^{K}\sum_{j=1}^{K} x_i''x_j''\sqrt{A_iA_j}\,(1-\Theta_{ij});$$

$$B' = C_1 \sum_{i=1}^{K} x_i' B_i ; \qquad B'' = C_1 \sum_{i=1}^{K} x_i'' B_i ;$$

$$C_1 = 0.0867/Z_{C1} \quad \text{and} \quad C_2 = 0.4278/(Z_{C1}^2 \sqrt{\tilde{T}}\ p).$$

$\overline{V}_{C1}$, T_{C1} and p_{C1} are critical values and $Z_{C1} = p_{C1}\overline{V}_{C1}/RT_{C1}$ is the critical compressibility factor of the supercritical component (1). The value of Z_{C1} can be calculated from Equation (1). The dimensionless volumes $\tilde{V}'$ and $\tilde{V}''$ are given by the dimensionless Redlich-Kwong equation of state.

$$\tilde{V}^3 - \frac{\tilde{T}}{Z_{C1}\tilde{p}} \tilde{V}^2 + \tilde{V}\left(A - B^2 - \frac{\tilde{T}}{Z_{C1}\tilde{p}} B\right) - AB = 0 \qquad (8b)$$

$\tilde{V}'$ must be calculated with the parameters A' and B', and $\tilde{V}''$, with parameters A'' and B''. The system of Equations (8) is solved by trial and error*.

For binary systems Equations (8) can be written:

$$x_1', x_1'' = f(\tilde{T}, \tilde{p}, A_2, B_2, \Theta_{12}). \qquad (9)$$

Compared with Equations (5) the shape of a binary $\tilde{p}$-x isotherm ($\tilde{T}$ = const) can be described by only three parameters A_2, B_2 and Θ_{12}.

BINARY SYSTEMS

All important types of binary isotherms can be generated by variation of the parameters A_2, B_2 and Θ_{12}. Only isotherms such as

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*Due to a well suited numerical method based on Newton-Raphson-Iteration it is possible to compute multicomponent systems with two and three phases using little CPU-time. Furthermore, the computer program allows one to calculate phase equilibria with any low concentrations of heavy components.

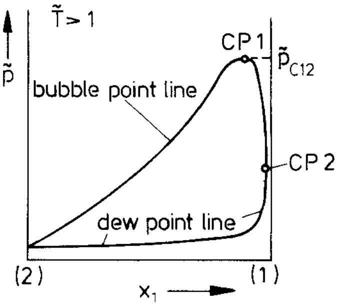

FIGURE 1. Normal isotherm.

that in Fig. 1 are normally considered in connection with vapour phase extraction processes. This isothermal line, with one critical point CP1 and a second critical point CP2 $(d\tilde{p}/dx_{2\ CP2} = \infty)$ is referred to as a normal isotherm. Between the second critical point and the first critical point the solubility of component 2 in the supercritical gas increases with increasing pressure.

Computer evaluation shows that the ratio A_2/B_2 determines the mole fraction at the second critical point and the range of the dew-point mole fractions. Hence, it is convenient to introduce the ratio $A_2/B_2 = AB_2$ as a new parameter. Subsequently, binary isotherms can be described by means of three parameters, AB_2, B_2, Θ_{12}. At constant values of AB_2 and Θ_{12} the parameter B_2 is a measure of the critical pressure (CP1). A high value of B_2 results in a low critical pressure and in a boiling curve situated in the region of large mole fractions x_1' as shown in Fig. 2. A variation of the interaction parameter Θ_{12} at constant values of B_2 and AB_2 produces similar results. With increasing values of Θ_{12} the critical pressure increases and the boiling curve becomes displaced towards low mole fractions x_1' of the supercritical component in the liquid phase (Fig. 2).

In addition to these normal isotherms there are two other important types of isotherms for vapour phase extraction processes.

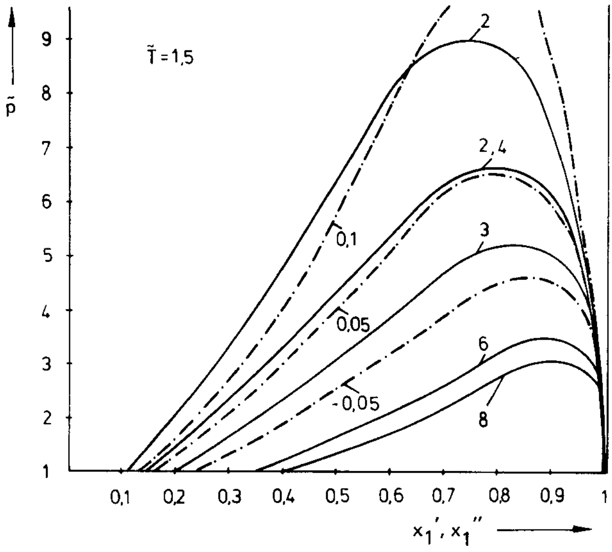

FIGURE 2. Isotherms at a constant value of $AB_2 = 5$.

——— variation of B_2 (B_2 = 2 to 8); $\Theta_{12} = 0$.

-.-.- variation of Θ_{12} (Θ_{12} = -0.05 to 0.1); $B_2 = 3$.

One type is characterized by a maximum solubility (MS) of the low volatility component in the vapour phase as shown in Fig. 3. At pressures above the maximum solubility pressure, the solubility of a low volatility component in the vapour phase decreases with increasing pressure. It is possible that there exists a critical point at very high pressures, but this high pressure range is of no interest for industrial separation processes (24). A few systems of this type like CO_2 - $C_{30}H_{62}$, N_2 - NH_3, or CO_2 - H_2O are discussed by Schneider (26), Rowlinson (20) and Tödheide and Franck (27).

The third important type of isotherm is characterized by a three phase region, Fig. 4. At a certain pressure p''' two liquid phases (l_1, l_2) and a gaseous phase are formed. This type of isotherm only occurs at temperatures near $\tilde{T}$ = 1 (20). A parametric

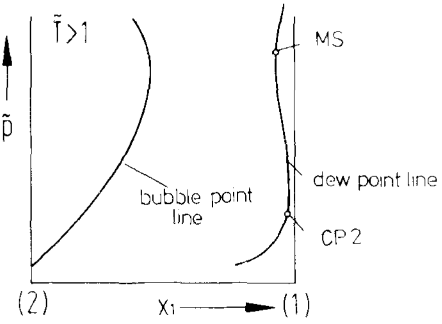

FIGURE 3. Isotherm with maximum solubility (MS).

study yields a limit for the values of the parameters AB_2, B_2 and 0_{12}, beyond which three phase equilibria occur. This limit is shown in Fig. 5. Above the dashed line the values of the parameters AB_2 and B_2 characterize three phase equilibria for $0_{12} = 0$. To demonstrate good conformity of experimental experience and the parametric study in Fig. 5 two points are marked, which represent the binary systems methane-pentane and methane-hexane. The method to estimate the values AB_2 and B_2 for these systems is discussed in the following section. As found experimentally (20) three phase equilibria occur in the binary system methane-hexane but not in the system methane-pentane.

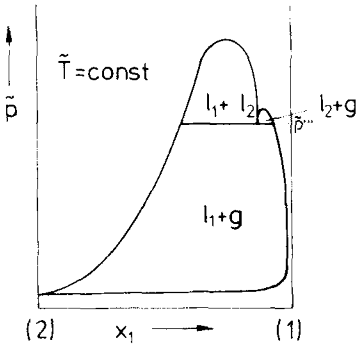

FIGURE 4. Three phase isotherm.

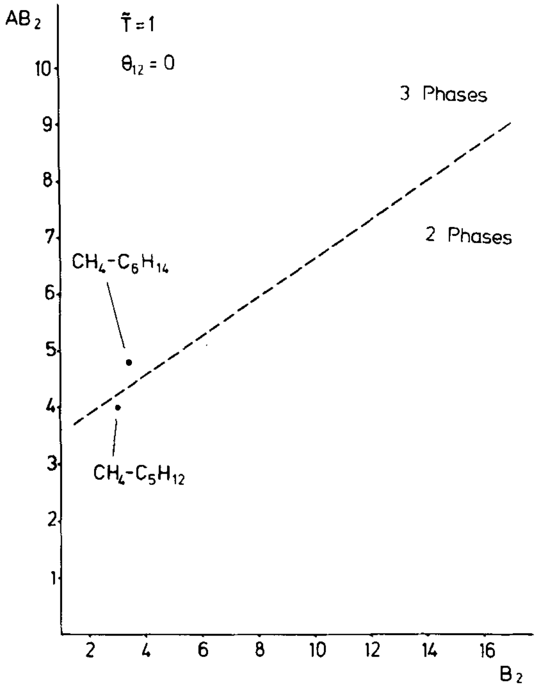

FIGURE 5. Limit of binary parameters AB_2 and B_2 for three phase isotherms.

DETERMINATION OF PARAMETERS AB_2, B_2 and Θ_{12}

The values of parameters AB_2, B_2 and Θ_{12} of binary systems are chosen to obtain satisfactory agreement with experimental data. Since practically all the industrial vapour phase extraction processes are carried out within a temperature range $1<\tilde{T}<2$ and a pressure range $0.5<\tilde{p}<15$, the task is simplified in that it is not necessary to describe the behaviour of binary mixtures outside these ranges with parameters AB_2, B_2 and Θ_{12}.

The parameters AB_2 and B_2 depend on the properties of the pure components. The coefficients a_{11} and b_1 can be calculated with reasonable accuracy by means of Eqs. (6). Hence, for the estima-

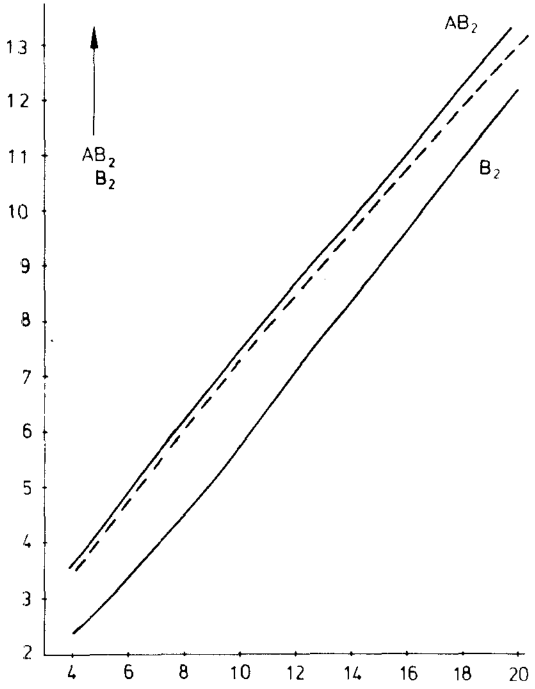

FIGURE 6. Smoothed parameters AB_2 and B_2 of the binary systems methane-alkanes with $\Theta_{12} = 0$. (References of experimental data see Table 1.)

——— t = 100°F (37.8°C)

------ t = 300°F (148.9°C)

tion of AB_2 and B_2, the coefficients a_{22} and b_2 are required. To determine these coefficients for a low volatility component at a temperature far below its critical temperature, Equations (6) cannot be applied since they are only valid in the critical region. Several authors have suggested that these coefficients (a_{22} and b_2) should be determined by fitting Equation (1) to experimental saturation data of pure components and they developed methods for this purpose (10-14). These methods produce temperature dependent coefficients.

In the present study a simple method, as proposed by Joffe, Zudkevitch and Schroeder (13), has been used. In this method coefficients a_{22} and b_2 are obtained from experimental vapour pressures and liquid densities. With parameters AB_2 and B_2 calculated from these coefficients it is normally possible to obtain a reasonable accuracy in describing an isothermal dew point line (24). However, a better conformity can be obtained by fitting the parameters AB_2 and B_2 to experimental isotherms. For a couple of binary systems, AB_2 and B_2 have been fitted at various temperatures (24).

These parameters were found to be roughly directly proportional to the number of carbon atoms within the homologous series of alkanes with methane as supercritical component (Fig. 6). Based on these results, the unknown parameters AB_2 and B_2 of a system within a homologous series can be easily estimated if values for a few systems within these series are known. If methane as a supercritical component is replaced by another gas, e.g., carbon dioxide, the parameters AB_2 and B_2 of the homologous series methane-alkanes must be multiplied by the ratios b_{CH_4}/b_{CO_2} and $(a/b)_{CH_4}/(a/b)_{CO_2}$ respectively. Good agreement with experimental data can be obtained with these new values of AB_2 and B_2, provided that the estimated interaction parameter Θ_{12} differs from zero.

This parameter Θ_{12} can be fitted to experimental bubble point data for the mixture. The parameter is characteristic for the interaction between the supercritical gas and other components of an homologous series and does not vary within such a series. For systems with carbon dioxide and alkanes, a value of $\Theta_{12} = 0.11$ was obtained. For systems with ethane and alkanes the interaction parameter is $\Theta_{12} = -0.01$.

Especially binary systems with alkanes have been investigated since a large number of experimental data are available for these systems. Investigations of other systems, however, yield similar results. For all investigated systems, it has been found that the parameter AB_2 can be estimated with good accuracy from experimental

TABLE 1

Investigated Binary Systems (24)

System	Temperature Range °C	Interaction Parameter Θ_{12}	Ref
methane-butane	4.5 - 71.1	0	(28)
" -pentane	37.8 - 104.4	0	(29)
" -hexane	25 - 171.1	0	(30)
" -heptane	4.5 - 204.4	0	(31)
" -octane	25 - 50	0	(32)
" -nonane	75 - 150	0	(33)
" -decane	37.8 - 237.8	0	(19)
" -hexadecane	100 - 300	0	(34)
" -cyclohexane	21.1 - 171.1	0	(36)
" -benzene	65.6	0	(37)
" -water	150 - 200	0.2 - 0.3	(35)
carbon dioxide			
" -butane	37.8	0.11	(38)
" -pentane	37.8 - 71.1	0.11	(39)
" -decane	37.8 - 104.4	0.11	(40)
" -eicosane	37.8	0.10	(41)
" -water	50 - 200	0.2	(27)
ethane -pentane	37.8	0	(42)
" -heptane	65.6 - 121.1	0	(43)
" -octane	40 - 75	-0.01	(44)
" -decane	37.8 - 104.4	-0.01	(45)
" -dodecane	50 - 100	-0.01	(46)
" -eicosane	36	-0.01	(47)
propane-decane	71.1 - 137.8	-0.025	(48)
" -benzene	71.1 - 137.8	0	(49)
hydrogen sulfide-decane	104.4 - 171.1	0.045	(50)
nitrogen -decane	37.8 - 71.1	0.08	(51)
" -hexadecane	250	0.1	(52)
" -benzene	75	0.17	(53)
" -ammonia	4.5 - 37.8	0.1	(54)
hydrogen-heptane	151	-0.3	(55)
ethylene-dodecane	25 - 75	0	(56)
" -ethanol	75	0	(57)
" -benzene	75	0.01	(57)
R13-tetradecane	33	0.04	(58)

vapour pressure and liquid density data, but the parameters B_2 and Θ_{12} must be fitted to the experimental bubble point line of the mixture. Table 1 gives a summary of the investigated binary systems. This result is valid even for a binary system consisting of water and a supercritical component at high pressure. The system carbon dioxide-water, for instance, has maximum-solubility isotherms (22).

TERNARY SYSTEMS

According to the phase rule of Gibbs a two-phase ternary system has three degrees of freedom. If the pressure, the temperature and mole fraction of one component are fixed, the following relationship for dimensionless parameters is valid:

$$x_1', \; x_1'', \; x_2' = F(x_2'', \tilde{T}, \tilde{p}, AB_2, B_2, \Theta_{12}, AB_3, B_3, \Theta_{13}, \Theta_{23}); \quad x_1 + x_2 + x_3 = 1. \tag{10}$$

The shape of a ternary bubble point line or dew point line at constant temperature $\tilde{T}$ and constant pressure $\tilde{p}$ in triangular coordinates depends on two sets of binary parameters (AB_2, B_2, Θ_{12} and AB_3, B_3, Θ_{13}, which characterise the binary systems (1) - (2) and (1) - (3)) and on an interaction parameter Θ_{23} for the two low-volatile components (2) and (3).

Before providing general rules for the design of separation processes it is appropriate to discuss various types of ternary systems in triangular coordinates especially with regard to the problem of how the vapour composition changes by increasing the mole fraction of one component. In Figure 7 b - f five important types of ternary vapour liquid equilibria with supercritical components are shown. The shapes of these various dew and bubble point lines in triangular coordinates can be explained in a first approach by considering the corresponding six binary systems in Figure 7a. The ternary systems, shown in Figure 7 b - f, are generated, if the com-

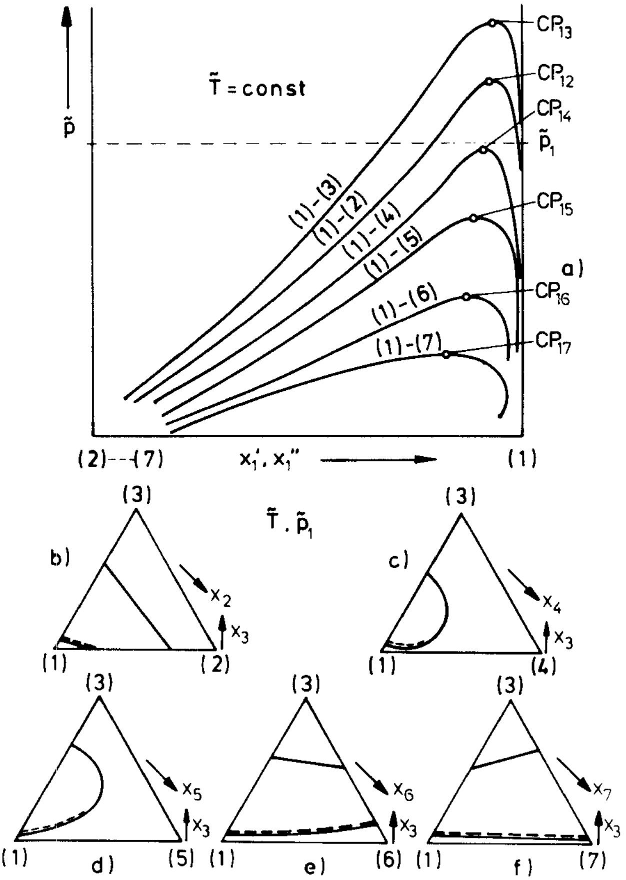

FIGURE 7. Types of ternary system.

——— bubble point lines

- - - - dew point lines

CP_{1i} = critical pressures

ponents (2), (4), (5), (6), or (7) are added to the binary system (1) - (3) at a constant temperature $\tilde{T}$ and a constant pressure $\tilde{p}_1$.

If component (2) is added to the binary system (1) - (3) at a constant pressure $\tilde{p}_1$ and a constant temperature $\tilde{T}$, a ternary system with separated dew and bubble point lines as shown in Fig. 7b is obtained. The start and end points of these lines correspond to the binary phase compositions at a pressure $\tilde{p}_1$ and a temperature $\tilde{T}_1$ in Fig. 7a. These systems in which both binary critical pressures (CP_{12} and CP_{13}) are higher than the pressure $\tilde{p}_1$ of the ternary system are characterized by decreasing mole fractions x_3 of component (3) in the vapour phase with increasing mole fraction x_2 of component (2).

The critical pressure of the binary system (1) - (4) at a constant temperature $\tilde{T}$ (CP_{14} in Fig. 7a) is lower than the pressure $\tilde{p}_1$ of the ternary system. At this pressure no binary phase equilibrium (1) - (4) exists, and a ternary system shown in Figure 7c is obtained with joining dew and bubble point lines. Increasing the mole fraction x_4 of component (4), the mole fraction x_3 of component (3) in the vapour phase decreases until a certain limit with a minimum mole fraction x_3 in the vapour phase.

In comparison to that, the mole fraction x_3 of component (3) in the vapour phase only increases by adding component (5) to the binary system (1) - (3) as shown in Figure 7d. This behaviour occurs if the critical pressure of the binary system (1) - (5) is low enough. By means of these components the vapour phase mole fractions of the low volatile components can be enhanced enormously as a parametric study shows. In this investigation these components are called extraction support components.

If a component (6) with a critical pressure CP_{16} still lower than the critical pressure CP_{15} is added to the binary system (1) - (3), a miscibility gap (3) - (6) occurs in the ternary system as shown in Fig. 7e. This means that there exists a binary phase equilibrium in a system (3) - (6) at a temperature $\tilde{T}$ and a pressure $\tilde{p}_1$.

Component (6) is an extraction support component, too, but the concentration of the heavy component (3) cannot be enhanced so much as in the system (1) - (3) - (5). Thus, component (5) is better suited as an extraction support component. If the binary critical point CP_{17} of a system (1) - (7) in Fig. 7a is situated very low and far away from the pressure $\tilde{p}_1$ of the ternary system, the miscibility gap (3) - (7) in the ternary system in Figure 7f increases so much that the vapour phase concentration x_3 of the heavy component essentially does not change by addition of component (7) to the binary system (1) - (3). Such a component (7) can be considered as a second supercritical carrier gas.

These above discussed results are obtained by varying the characteristic parameters AB_2, B_2, O_{12}, AB_3, B_3, O_{13} and O_{23} of ternary systems. The method of varying these generalized parameters within certain ranges is well suited to study the general behaviour of ternary and multicomponent mixtures, because experimental data of ternary and multicomponent systems with supercritical components are hardly available.

For the design of separation processes two important problems-- the separation of two low volatile components and the choice of a suitable extraction support component -- are discussed in the following sections.

SEPARATION OF TWO LOW VOLATILE COMPONENTS

In order to deduce rules for estimating the effectiveness of separating two components of low volatility, ternary systems consisting of a supercritical gas (1) and two low-volatile components (2) and (3), as shown in Fig. 7b, have to be considered. (Component (2) is referred to as the extractive component and component (3) as the refined product component.)

A convenient measure of the effectiveness of a separation process is the relative volatility α:

$$\alpha = (x_2''x_3')/(x_2'x_3''). \tag{11}$$

Values of the relative volatility α for generalized systems have been computed using the above parameters at various temperatures and pressures (Fig. 8).

An important result of this parametric study can be obtained by considering the behaviour of such a ternary system with the components (1), (2) and (3) shown in Fig. 7b. This system has two miscibility gaps at a given pressure $\tilde{p}_1$ and temperature $\tilde{T}$; that means the binary mixtures (1) - (2) and (1) - (3) form vapour liquid equilibria at the pressure $\tilde{p}_1$. If the pressure $\tilde{p}$ increases and exceeds the critical pressure of one of the binary systems (CP_{12} or CP_{13} in Fig. 7a), a ternary system like that in Fig. 7c is formed and the relative volatility between the components (2) and (3) decreases considerably. Therefore, the operating pressure selected for a vapour phase extraction process at a given temperature should be lower than either of the critical pressures. This implies that investigations of ternary systems can be restricted to those ternary systems such as shown in Fig. 7b, with two miscibility gaps (1) - (2) and (1) - (3), where the starting points and the end points of the dew point and bubble point lines are determined by mole fractions of the binary systems (1) - (2) and (1) - (3).

Further studies of the relative volatility indicated that at constant temperature and pressure this parameter chiefly depends on the parameter ratios AB_3/AB_2 and B_3/B_2 (Fig. 8). Nevertheless, the relative volatility α is also strongly affected by the interaction parameter Θ_{23}, increasing with rising values of Θ_{23}.

In order to determine favourable conditions for separating two low-volatile components (2) and (3), the effects of temperature and pressure on the relative volatility must be known. These effects are indicated by mole fractions of the low-volatile components in vapour phases of the binary systems (1) - (2) and (1) - (3) at the pressure and temperature of the ternary system. In order to obtain

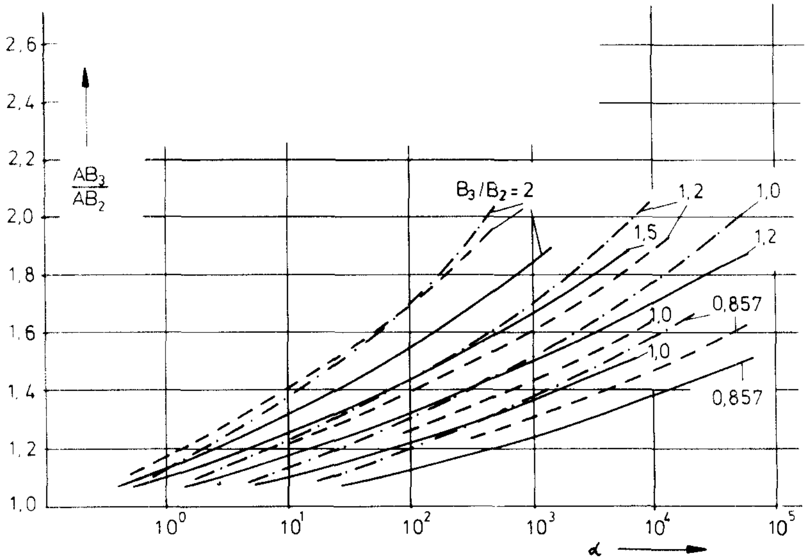

FIGURE 8. Relative volatility α as a function of the ratios AB_3/AB_2 and B_3/B_2 and various values of parameters AB_3 and B_3 at a constant temperature $\tilde{T} = 1.1$ and a constant pressure $\tilde{p} = 2$; $\Theta_{23} = 0$.

——— $B_3 = 12$, $AB_3 = 15$
–·–·–· $B_3 = 10$, $AB_3 = 12$
------ $B_3 = 16$, $AB_3 = 15$.

large values of the relative volatility α, the mole fraction of the extract component (2) in the vapour phase of the binary system (1) - (2) should be significantly larger than the mole fraction of the refined product component (3) in the vapour phase of the binary system (1) - (3). Consequently, in order to determine favourable conditions for the separation of two components (2) and (3) by a supercritical gas (1), the dew point lines of the binary systems (1) - (2) and (1) - (3) must be known.

TERNARY SYSTEMS WITH TWO LIQUID PHASES

If the parameter Θ_{23} which characterizes the interaction between two components (2) and (3) is greater than $\Theta_{23} = 0.05$, a second liquid phase is formed in the ternary system (1) - (2) - (3), Fig. 9. These three-phase equilibria can also be described by the Redlich-Kwong equation of state. For these systems the above defined relative volatility has normally high values and component (2) can easily be separated from component (3). The phenomenon of a ternary three phase equilibrium shown in Fig. 9 is always connected with the existence of a binary liquid miscibility gap in the system (2)-(3). A binary liquid-liquid equilibrium occurs at certain values of the parameters AB_2, AB_3, B_2, B_3, and Θ_{23}. The parametric study yields the result shown in Fig. 10. The existence of a phase equilibrium can be mainly characterized by the ratios AB_3/AB_2 and B_3/B_2. Figure 10 is valid for a temperature range of $1<\tilde{T}<1.5$, a pressure range of $0.5<\tilde{p}<10$ and for the interaction parameter $\Theta_{23} = 0$. With increasing values of Θ_{23}, the homogenous region decreases.

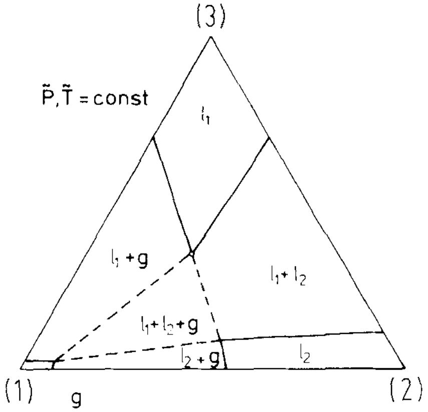

FIGURE 9. Three phase equilibrium in a ternary system.

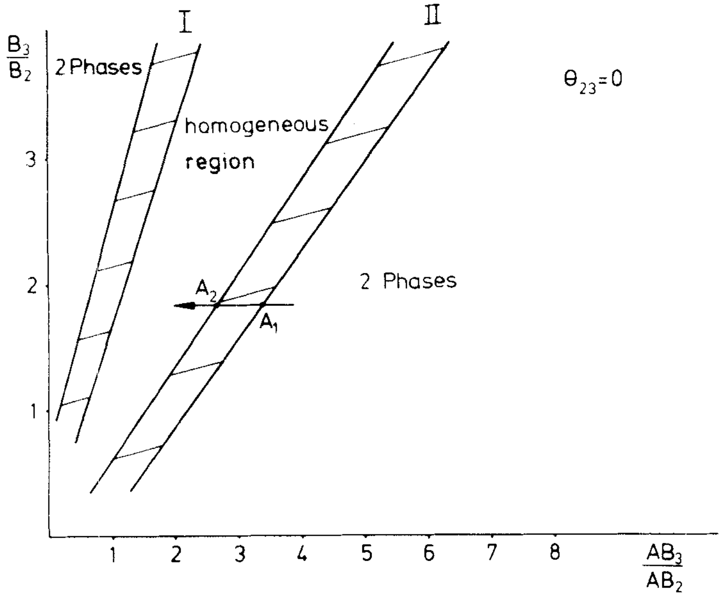

FIGURE 10. Ranges for phase equilibria.

Both of the two "2 Phases" regions are characterized by vapour-liquid and liquid-liquid equilibria. The cross-hatched regions labeled I and II are the spread in the calculated values.

MULTICOMPONENT SYSTEMS

Mixtures containing a carrier gas and more than two low-volatile components can be considered as ternary systems if the low-volatile components are divided into extractive and refined product component groups. Thus, in triangular coordinates, multicomponent dew point and bubble point ranges, which are limited by ternary dew and bubble point lines, can be plotted. Hence, rules similar to those for ternary systems are valid.

A knowledge of the dew point lines of binary systems consisting of a carrier gas and low-volatile components (1) - (2), (1) - (3), ... , (1) - (K) is sufficient for the determination of favourable values of operating pressure and temperature for separating multicomponent mixtures.

APPLICATION OF EXTRACTION SUPPORT COMPONENTS

To get favourable separation conditions, the relative volatility α of the extractive product component has to be as large as possible. Furthermore, the mole fraction of the extractive product component in the vapor phase should not be too small, because then too much carrier gas has to be compressed to dissolve this component. To avoid this disadvantage, extraction support components can be used to increase the mole fraction of the extractive component in the gaseous phase. Then, later in a second stage of this separation process, the extraction support component has to be separated from the extract (5).

An extraction support component has to be chosen similar to component (5) or (6) in Fig. 7d and e. To select a suitable extraction support component, Fig. 10 can be used. It is favorable to select a component which yields no miscibility gap in a binary system consisting of the extractive component and the extraction support component. The parametric study shows that for those two components values of parameter ratios in the homogenous region near transition zone II are suitable. In order to estimate the effectiveness of such processes with extraction support components, systems with four components consisting of two low volatile components, a carrier gas, and an extraction support component have been investigated. The parametric study yielded the following result: it is possible to increase the relative volatility between the refined and extractive product components only if the interaction parameter between these two components has a large value--i.e., if these two components are very different in their chemical structure and physical properties. On the contrary, if similar heavy components have to be separated, it can be expected that the relative volatility decreases enormously by using an extractive support component.

SUMMARY

Fluid phase equilibria with one supercritical component have been investigated in order to establish general rules governing vapour phase extraction processes. A parametric study with the Redlich-Kwong equation of state, reduced to characteristic dimensionless parameters, shows that rules for establishing favourable operating pressures and temperatures can be derived without knowing the exact values of the mixture parameters.

For the classification of binary systems three parameters are used and methods for estimating these parameters are discussed. The results of the parametric study of binary systems indicate some rules for characterizing various types of binary isotherms. In order to estimate the effectiveness of separating two or more low-volatile components by a supercritical carrier gas, ternary and multicomponent mixtures have been investigated. Types of ternary systems that are important for separation processes are discussed in general and two applications, the separation of two low volatile components and the use of an extraction support component, are discussed in detail. The results of the parametric study of multicomponent mixtures show that a knowledge of binary supercritical isotherm behaviour is sufficient for selecting the operating conditions for vapour phase extraction processes.

SYMBOLS

$'$	liquid
$''$	vapour phase
a	Redlich-Kwong coefficient of a mixture
a_{ii}	Redlich-Kwong coefficient of a pure component

a_{11}		Redlich-Kwong coefficient of a supercritical gas
A		$= a/\bar{V}_{K1}^2 \sqrt{\tilde{T}}\, \tilde{p}$
A_i		$= a_{ii}/a_{11}$
AB_i		$= A_i/B_i$
b		Redlich-Kwong coefficient of a mixture
b_i		Redlich-Kwong coefficient of a pure component
b_1		Redlich-Kwong coefficient of a supercritical gas
B		$= b/\bar{V}_{K1}$
B_i		$= b_i/b_1$
f_i		fugacity of a component i in a mixture
K		number of components
n_i		number of moles of component i
p	(bar)	pressure
p_s	(bar)	vapour pressure
$\tilde{p}$		p/p_{K1}
$\tilde{p}_M$		minimum pressure
p_{K1}		critical pressure of supercritical gas
R		molar gas constant
t, T	($^\circ$C or K)	temperature
t_{K1}, T_{K1}		critical temperature of supercritical gas
V	(m^3)	volume
$\bar{V}$		molar volume
$\bar{V}_{K1}$		critical molar volume of supercritical gas
$\tilde{V}$		$= \bar{V}/\bar{V}_{K1}$
x_1		mole fraction of component i
Z_{C1}		critical compressibility factor of supercritical gas
α		relative volatility
Θ_{ij}		interaction parameter between two components i and j

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