meability with tritium-labeled water and water.

Conclusions

1. Much attention should be paid to the affinity of test solute for membrane materials in characterizing dialysis membranes from permeability data.

2. Pore model studies on characterization of hydrophilic membranes for dialysis give lower values of pore radius and tortuosity, and higher values of surface porosity using ^{3}H-water than using ^{14}C-urea.

3. The method using ^{3}H-water is suitable for characterizing dialysis membranes because of lack of adsorption of ^{3}H-water on fully wetted or hydrophobic dialysis membranes and determination of P_m and L_W for the same solute.

Nomenclature

A	= surface area	[m^2]
A_k	= fractional surface porosity	[—]
D	= diffusivity in free water	[m$^2 \cdot$s^{-1}]
D_m	= intramembrane diffusivity	[m$^2 \cdot$s^{-1}]
$f(q)$	= wall correction factor for diffusion	[—]
H	= fractional water content	[—]
L_W	= pure water permeability	[m$^3 \cdot$m$^{-2} \cdot$s$^{-1} \cdot$Pa^{-1}]
ΔP	= transmembrane pressure	[Pa]
P_{Bi}	= feed pressure at inlet	[Pa]
P_{Bo}	= feed pressure at outlet	[Pa]
P_F	= filtrate pressure	[Pa]
P_m	= solute permeability	[m$\cdot$s^{-1}]
q	= r_s/r_p	[—]
Q_F	= filtrate flow rate	[m$^3 \cdot$s^{-1}]
r_p	= radius of membrane pore	[m]
r_s	= Stokes radius of solute	[m]
S_D	= steric hindrance factor for diffusion	[—]
ΔX	= membrane thickness	[m]
μ	= viscosity	[Pa$\cdot$s]
τ	= tortuosity	[—]

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PRESSURE DETERMINATION OF VAPOR–LIQUID EQUILIBRIUM USING SUCCESSIVE SUBSTITUTION METHOD

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Introduction

Successive substitution is the most popular method for solving the simultaneous nonlinear equations of vapor-liquid equilibrium due to its simplicity, even though the Newton-Raphson method can also be used.

Heidemann[3] reviewed the successive substitution method used in high-pressure phase equilibrium calculation. Veeranna and Rihani[8] showed that poor initial pressure or temperature guesses can lead to a trivial solution and recommended an initial pres-

sure or temperature correlation for bubble or dew points of various mixtures.

Precise details are lacking in the open literature on algorithms to carry out these calculations. This paper concerns an iteration formula for the pressure determination of vapor-liquid equilibrium. Among the publications which deal with the computational procedures, Hanley and Rosen[2] presented the following formula:

$$P^{(k+1)} = P^{(k)} \left/ \sum_{i=1}^{N} y_i / K_i^{(k)} \right.$$ (1)

Similarly, for a bubble-point pressure,

$$P^{(k+1)} = P^{(k)} \left[2 - 1 \bigg/ \sum_{i=1}^{N} K_i^{(k)} x_i \right] \qquad (2)$$

However, some improvements should be made because Eq. (1) cannot predict both a lower dew-point and an upper retrograde dew-point.

The objectives of this work are to propose an iteration formula for the pressure determination of vapor-liquid equilibrium from the successive substitution method and to elucidate the selection algorithms for the initial pressure.

1. Pressure Iteration Formulae

Consider the calculation of vapor-liquid equilibrium at a specified temperature T, feed composition z_i, and vapor phase-to-feed mole ratio θ. Two computational iteration loops are required, one for K-values related to the composition of vapor and liquid phases and the other for pressure determination.

The iteration formula for pressure determination in this work is based on the phase equilibrium condition for each component i as follows:

$$Py_i = Px_i K_i \qquad (3)$$

where

$$K_i = \varphi_i^L(T, P, x_1, \cdots, x_N) / \varphi_i^V(T, P, y_1, \cdots, y_N) \qquad (4)$$

Presently we will treat the above equation at a constant temperature as an expression in a single variable of P, even though the K_i's are also functions of composition.

Rearranging Eq. (3) into an equivalent expression of the form

$$P = g(P) \qquad (5)$$

shows that the solution of Eq. (3) is the intersection of the right-hand and left-hand sides of the above equation. To apply the successive substitution method for solution, Eq. (5) is rewritten in the following form:

$$P^{(k+1)} = g(P^{(k)}) \qquad (6)$$

If a well-known sufficient (but not necessary) condition

$$|g'(P)| \leqq 1 \qquad (7)$$

is satisfied[1] for all P in the interval, then Eq. (6) will converge to a root.

It is quite important to select both an initial pressure and an iteration formula which satisfy the condition presented by Eq. (7). We propose the following iteration formulae for the pressure determination of vapor-liquid equilibrium. From Eq. (3), we have

$$P^{(k+1)} = P^{(k)} \sum_{i=1}^{N} x_i K_i^{(k)} \qquad (8)$$

since $\sum_{i=1}^{N} y_i = 1$. The symmetric expression with regard to $P = g(P)$ is rigorously obtained by exchanging the exponent (k) for $(k+1)$ in the above equation. The following approximate expression is employed as an iteration formula, however, by replacing $K_i^{(k+1)}$ with $K_i^{(k)}$

$$P^{(k+1)} = P^{(k)} \bigg/ \sum_{i=1}^{N} x_i K_i^{(k)} \qquad (9)$$

Either Eq. (8) or (9) will satisfy Eq. (7) because they are approximately symmetric with $P = g(P)$.

Similarly, we obtain an another iteration formula from Eq. (3):

$$P^{(k+1)} = P^{(k)} \sum_{i=1}^{N} y_i / K_i \qquad (10)$$

This approximately symmetric expression is identical with Eq. (1), derived for dew-point pressure determination on the basis of another method. The proposed four iteration formulae in this work are to be applied to any value of θ from zero to one.

2. Results of Pressure Determination

The curve $g(P)$ should pass through an intersection shown as a positive point B in **Fig. 1** as long as there is vapor-liquid equilibrium. It is possible, however, to have another root, shown as point C, if the system has, for example, an upper retrograde dew-point pressure. When the function $g(P)$ of Eq. (6) is expressed as either Eq. (1) or Eqs. (8) through (10), it is easily found that $g(P)$ also passes through the origin, shown as point A in the figure.

Considering the condition under which Eq. (7) is applicable, two paths for convergence are anticipated to be found as shown in Fig. 1: one path converges to a root C or a meaningless root A for a curve in Fig. 1(a), and the other to a root B or diverges as shown in Fig. 1(b). Numbers in the figure indicate the number of each iteration, k.

In this work, calculations are carried out using an extended BWR equation of state with 15 constants,[5,7] and our proposed mixing rules[6] with binary interaction parameters correlated by the critical molar volume ratio V_{ci}/V_{cj}. Iterations continue until Eq. (10) is satisfied within a given tolerance of pressure, i.e. an absolute average deviation of 0.3% and 0.5% for K-values.

Figure 2 shows a typical dew-point pressure calculation for the carbon dioxide-hydrogen sulfide system with an equimolar feed at 273.15 K using Eq. (1) as the pressure iteration formula. Using both 5.0 and 0.1 MPa as the initial pressure, the iteration converges to the same dew-point pressure, 1.90 MPa, indicated as point B in the figure. This feature seems to be explained by Fig. 1(b). For a higher initial pressure than 9.0 MPa, however, the calculation does not

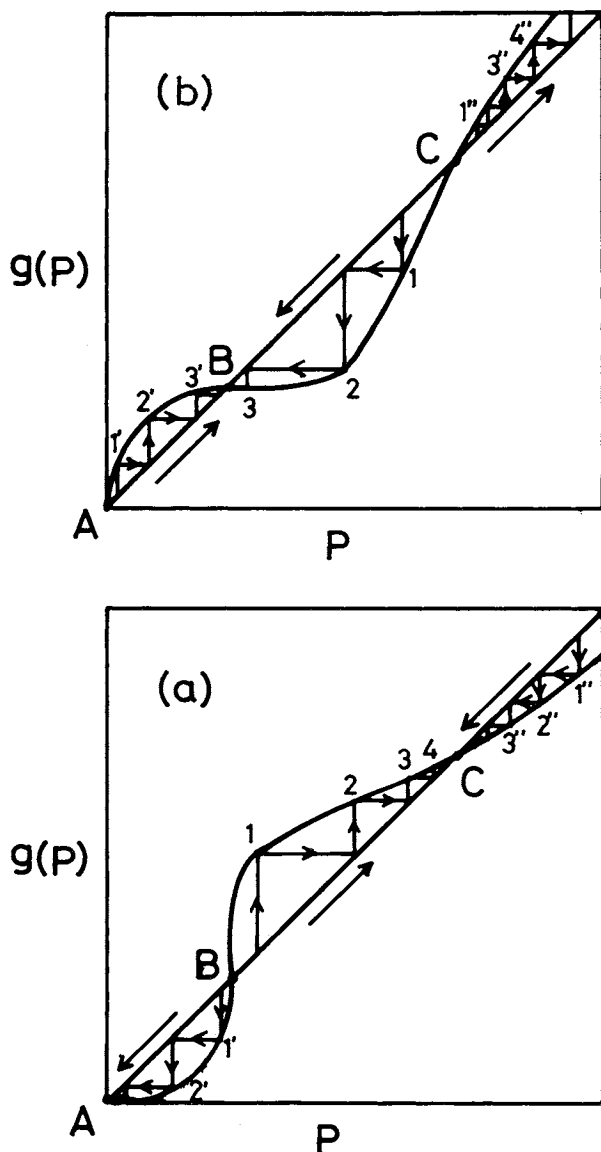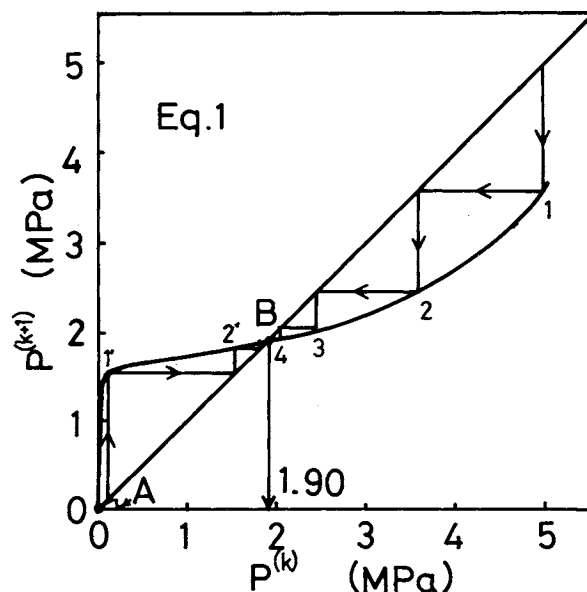Fig. 1. Convergence path of Eq. (6) showing two roots (points B and C) as well as the origin (point A)

Fig. 2. Dew-point calculation for the carbon dioxide-hydrogen sulfide system with an equimolar feed at 273.15 K using Eq. (1) as the pressure iteration formula
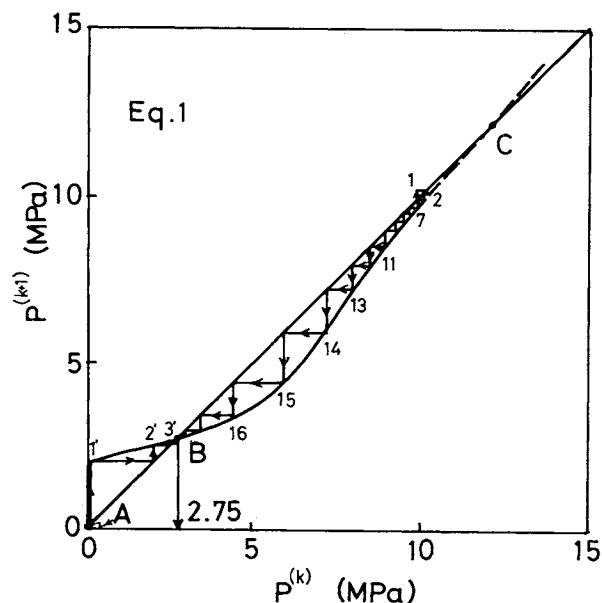

Fig. 3. Lower dew-point pressure calculation for the methane–carbon dioxide–hydrogen sulfide system at 273.15 K, $z_{CH_4}=0.4988$, $z_{CO_2}=0.0987$ using Eq. (1) as the pressure iteration formula

diverge, as suggested by Fig. 1(b), but converges to a "trivial solution" with both phases having the same composition and density and with an arbitrary pressure which each $K_i=1$ in Eq. (10) causes.

The results obtained by Eq. (8) are similar to those by Eq. (1). Using either Eqs. (5) or (7), iterations approach the origin indicated by Fig. 1(a) for a smaller initial pressure P_0 than 1.9 MPa. For $1.9 < P_0 < 40$ MPa, however, they diverge, and for $P_0 \geqq 50$ MPa, they converge to a trivial solution such as already stated. We could not find an upper retrograde dew-point (point C in Fig. 1) for this system. A bubble-point pressure calculation for the same system at 273.15 K gives a similar trend.

The methane–carbon dioxide–hydrogen sulfide system at 273.15 K, $z_{CH4}=0.4988$ and $z_{CO2}=0.0987$, has two dew-points.[4] **Figure 3** shows iterations for a conventional or lower dew-point pressure (point B) of

the above system using 10 and 0.1 MPa as initial pressure and Eq. (1) as the iteration formula. A higher initial pressure than 11 MPa produces a trivial solution having the same composition of both phases and an arbitrary pressure. The results obtained by Eq. (8) are similar to those by Eq. (1).

Figure 4 indicates an upper retrograde dew-point pressure calculation for the above system at 273.15 K using Eq. (10) as the pressure iteration formula. The initial pressure used, 3.0 MPa, is greater than the
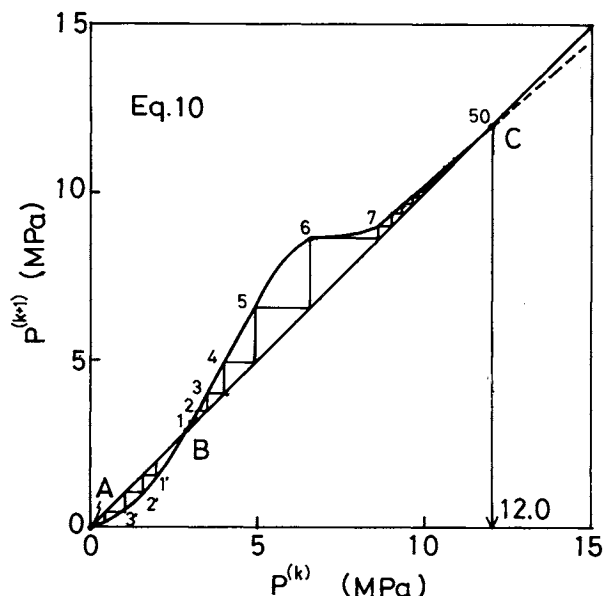
Fig. 4. Upper retrograde dew-point pressure calculation for the methane–carbon dioxide–hydrogen sulfide system at 273.15 K, $z_{CH_4}=0.4988$, $z_{CO_2}=0.0987$ using Eq. (10) as the pressure iteration formula

lower dew-point pressure, 2.75 MPa. The solution gives a retrograde dew-point pressure, 12.0 MPa (point C). The initial pressure of 2.0 MPa, smaller than a lower dew-point pressure, converges to the origin (point A). On the other hand, Eq. (9) for $P_0 \geq 2$ MPa diverges for this system, even though it is anticipated to be applicable for an upper retrograde dew-point calculation. This indicates that Eqs. (9) and (8) may be not symmetric $g(P)$. Eq. (9) is not suitable as an iteration formula of pressure.

In the case of $\theta = 0.7$ as well as $\theta = 1.0$ for the ternary system at 273.15 K, the four iterations give the similar trend.

Figures 2 through 4 reveal that three of four proposed iteration formulae in this work are effective in the pressure determination of vapor–liquid equilibrium, as tabulated in **Table 1**, and that the iteration feature is basically explained by Fig. 1 except at high pressure, where a trivial solution is obtained.

It is applicable to various systems including methane–neo-pentane, methane–decane, ethelyne–butane, ethane–benzene, carbon dioxide–decane, carbon dioxide–cyclohexane, nitrogen–ethane, nitrogen–carbon dioxide and methane–hydrogen sulfide systems. These calculations suggest that the result shown in Table 1 is generally applicable to various systems and that Eqs. (1) and (10) are approximately symmetric with $P=g(P)$ in Eq. (5), even though Eqs. (8) and (9) are not. Equation (9) is not suitable as an iteration formula of pressure.

Conclusion

1. We recommend Eqs. (1) and (8) for con-

ventional or lower pressure, and Eq. (10) for higher pressure, as shown in Table 1, as the initial formula for the pressure determination of vapor–liquid equilibrium using the successive substitution method.

2. To avoid convergence to a trivial solution the following scheme for initial pressure selection is proposed, based on the results elucidated in Fig. 1. First, a lower pressure should be selected as the initial pressure, for example 0.1 MPa. This will lead to a lower pressure (point B in Fig. 1). Second, an initial pressure higher than the converged lower pressure will reach a higher pressure, such as a retrograde dew-point (point C), if it exists.

Nomenclature

g	= function defined by Eq. (5)	[MPa]
K_i	= K-value of a component i	[—]
k	= iteration number	[—]
N	= number of components	[—]
P	= pressure	[MPa]
P_0	= initial pressure	[MPa]
T	= temperature	[K]
x	= mole fraction of a liquid phase	[—]
y	= mole fraction of a vapor phase	[—]
z	= mole fraction of feed	[—]
θ	= mole ratio of a vapor phase to feed	[—]
φ_i	= fugacity coefficient of component i	[—]

⟨Superscript⟩

V	= vapor phase	
L	= liquid phase	

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