$C_{j,s}$ = concentration of species j at the external surface of the catalyst

D_j = effective diffusivity of species j

E_a = activation energy

m = number of species in the system

n = number of independent reactions

$R_{(i)}$ = intrinsic rate of reaction i, based on catalyst volume

$R_{(i)a}$ = apparent rate of reaction i

$R_{(i)s}$ = rate of reaction i evaluated at the external surface concentration and temperature of the catalyst

R_g = universal gas constant

r = radial coordinate for the catalyst particle

r_o = radius of the catalyst particle

T = temperature

T_s = temperature at the external surface of the catalyst

Greek Letters

α = defined by Eq. 15

α_i = defined by Eq. 12

β = defined by Eq. 16

β_j = defined by Eq. 10

δ = defined by Eq. 11

γ = defined by Eq. 17

ρ = dimensionless radial coordinate, r/r_o

λ_e = effective thermal conductivity

η = effectiveness factor

ν_{ij} = stoichiometric coefficient of jth species in the ith reaction ($+$ for products, $-$ for reactants)

$\Delta H_{(i)}$ = heat of reaction of ith reaction

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Diffusion Coefficients Near the Spinodal Curve

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The study of diffusion coefficients in supersaturated solutions is of fundamental importance in further understanding the mechanism of diffusion and for the rational design of crystallization processes. Sorell and Myerson (1982) measured the diffusivity of urea in supersaturated aqueous solution employing Gouy interferometry. Results of this study show a very rapid decline in the diffusion coefficient with increasing concentration in the supersaturated region. This behavior is similar to behavior noted in liquid-liquid systems near the consolute point. Claersson and Sundelof (1957) and Haase and Siry (1969) reported that the binary diffusion coefficient drops rapidly to zero in the region of the critical solution temperature or consolute point. An explanation of this phenomenon can be made on thermodynamic grounds by employing the thermodynamic criterion for a critical point:

$$\frac{\partial^2 g_1}{\partial x_1^2} = 0 \frac{\partial \mu_1}{\partial x_1} \tag{1}$$

$$\frac{\partial^3 g_1}{\partial x_1^3} = 0 = \frac{\partial^2 \mu_1}{\partial x_1^2} \tag{2}$$

Equations normally used to calculate concentration-dependent diffusion coefficients such as the Gordon equation (1957) or modification of the Stokes Einstein relation (Turner 1975a,b) consist of the product of an infinite dilution diffusivity and a thermodynamic correction term:

$$D = D^0 \left(1 + \frac{\partial ln \gamma_1}{\partial ln x_1}\right) \frac{\mu_1}{\mu_{12}} \quad \text{(Gordon)} \tag{3}$$

$$D = D^0 \left(\frac{\partial ln a_1}{\partial ln x_1}\right) \quad \text{(Stokes-Einstein modified)} \tag{4}$$

The thermodynamic correction terms in Eqs. 3 and 4 are

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equivalent to $\partial \mu_1 / \partial x_1$. At the critical solution temperature the thermodynamic correction term approaches zero while D^0 remains finite. Equations 3 and 4, therefore correctly predict that the diffusion coefficient at the consolute point is zero. It was necessary, however, to only employ one of the thermodynamic criterion for a critical point (Eq. 1) rather than both. A more general state of the observed phenomenon is that the diffusion coefficient is zero at all points where the derivative $\partial \mu_1 / \partial x_1 = 0$. The locus of such points is known as the spinodal curve and represents the boundary between the metastable and unstable region. It is difficult to experimentally approach the spinodal curve in liquid-liquid systems except at the consolute point because of the tendency of the metastable liquid phases to separate. In solid liquid solutions, however, it is quite possible to approach the spinodal curve through careful preparation of supersaturated solutions.

The purpose of this paper is to calculate the location of the spinodal curve in the urea-water system and compare the concentration calculated with that obtained from the extrapolation of supersaturated solution diffusivity data (Sorell and Myerson, 1982) to a diffusivity of zero.

CALCULATION OF THE SPINODAL CURVE IN SOLID-LIQUID SYSTEMS

In order to calculate the locus of points where the derivative $\partial u_1 / \partial x_1 = 0$ it is necessary to employ an equation of state to obtain relations for the fugacity of component 1 (the solute) in solution as a function of concentration. The Patel-Teja (1982) equation of state was employed in our calculations. This equation of state has been found to predict solid-liquid equilibrium in the heptane-methane system with greater accuracy than a number of other commonly used equations of state.

The Patel-Teja equation of state for a pure fluid is:

$$P = \frac{RT}{V - b} - \frac{a[T]}{V(V + b) + c(V - b)} \quad (5)$$

where

$$a[T] = \Omega_a (R^2 T_c^2 / P_c) \alpha[T_R] \quad (6)$$

$$b = \Omega_b (RT_c / P_c) \quad (7)$$

$$c = \Omega_c (RT_c / P_c) \quad (8)$$

In addition, the following definitions are made:

$$\Omega_c = 1 - 3\zeta_c \quad (9)$$

$$\Omega_a = 3\zeta_c^2 + 3(1 - 2\zeta_c)\Omega_b + \Omega_b^2 + 1 - 3\zeta_c \quad (10)$$

and Ω_b is the smallest positive root of the following expression

$$\Omega_b^3 + (2 - 3\zeta_c)\Omega_b^2 + 3\zeta_{cb} - \zeta_c^3 = 0 \quad (11)$$

To complete the generalization for a pure fluid, the following equations are needed:

$$\alpha[T] = \{1 + F(1 - T_R^{1/2})\}^2 \quad (12)$$

$$T_R = T/T_c$$

$$F = 0.452313 + 1.3098w - 0.295937w^2 \quad (13)$$

$$\xi_c = 0.329032 + 0.07699w + 0.0211947w^2 \quad (14)$$

$$w = \text{accentric factor}$$

To expand the equation of state to include mixtures, the following mixing rules have been suggested (Patel and Teja, 1982).

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \quad (15)$$

$$b_m = \sum_i x_i b_i \quad (16)$$
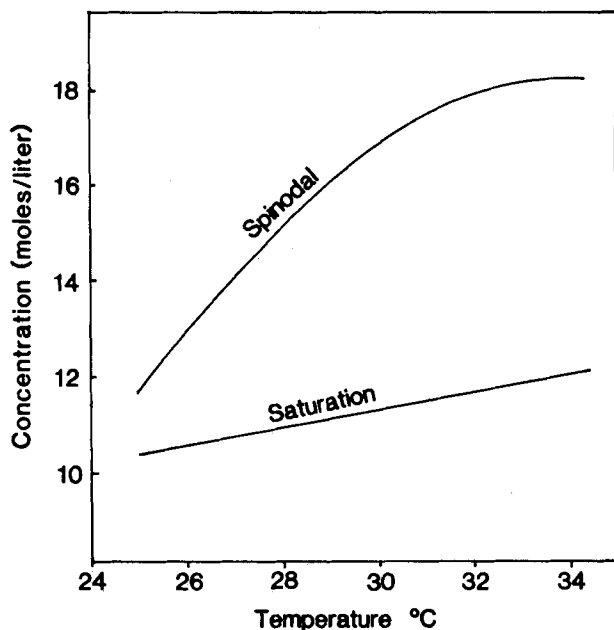
$$c_m = \sum_i x_i c_i \quad (17)$$

Figure 1. Spinodal curve of urea in aqueous solution calculated from the Patel-Teja (1982) equation of state.

where

$$a_{ij} = \epsilon_{ij}(a_{ii}a_{jj})^{1/2} \quad (18)$$

where ϵ_{ij} is a binary interaction coefficient obtained from experimental data.

At equilibrium, the fugacities of all phases of a component are equal. Patel and Teja (1982) derived the fugacity expression

$$RT \ln \frac{f_i}{x_i p} = -RT \ln(z - B) + RT b_i / (v_m - b_m)$$
$$- \frac{\Sigma x_j a_{ij}}{d} \ln\left(\frac{Q + d}{Q - d}\right) + \frac{a_m(b_i + c_i)}{2(Q^2 - d^2)}$$
$$+ \frac{a_m}{8d^3} \{3bmc_i + 3b_i c_m + b_m b_i + c_m c_i\}$$
$$\left[\ln\left(\frac{Q + d}{Q - d}\right) - \left(\frac{2Qd}{Q^2 - d^2}\right)\right] \quad (19)$$
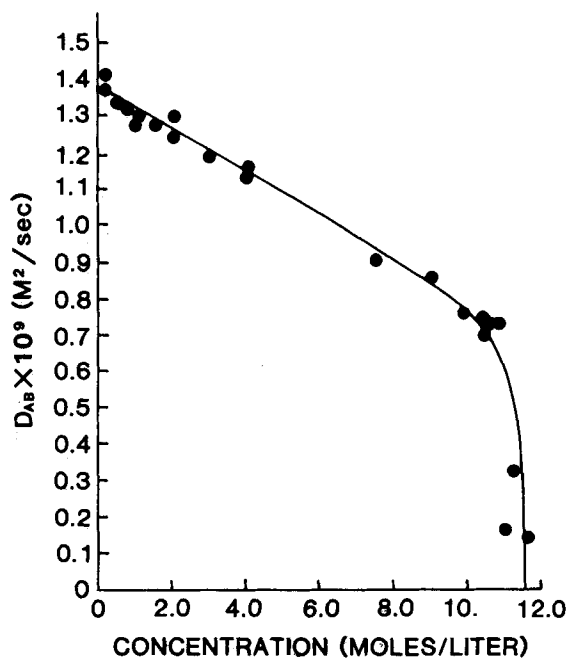

Figure 2. Diffusivity of urea in aqueous solution.

where

$$Q = v_m + \left(\frac{b_m + c_m}{2}\right) \qquad (20)$$

$$d = \left[b_m c_m + \frac{(b_m + c_m)^2}{4}\right]^{1/2} \qquad (21)$$

$$B = b_m P/RT \qquad (22)$$

Equations 5 and 19, and their derivatives were employed in the calculations of the spinodal curve for the urea-water system. Results are presented in Figure 1.

The diffusivity of urea and in aqueous supersaturated solutions is available in the literature (Sorell and Myerson, 1982) and appears in Figure 2. The solid line in the Figure represent extrapolation of this data to a diffusivity of zero.

The concentration at this point should correspond to the spinodal concentration at that temperature. At 25°C the spinodol concentration calculated from the equation of state is 11.89 molar which is within 1.2% of the value of 11.75 obtained from extrapolation of experimental data. While these results support the hypothesis of zero diffusivity at the spinodol curve, additional experimental measurements of diffusion coefficients of a wide variety of materials in supersaturated solutions are needed to further verify the hypothesis.

ACKNOWLEDGMENTS

NOTATION

a_1	= activity
a,b,c	= Constants in Eq. 5
F	= parameter required in Eq. 12
g	= Gibbs free energy
m	= number of components
n	= number of moles
P	= pressure
R	= gas constant
T	= temperature
v	= molar volume
V	= total volume
x	= mole fraction

Greek Letters

α	= temperature function, Eq. 12
γ	= activity coefficient
ζ_c	= parameter required in Eq. 9–11
μ	= chemical potential
ξ	= binary interaction coefficient
$\Omega_a, \Omega_b, \Omega_c$	= constants in Eqs. 6–8

Subscripts

c	= critical value
i,j	= component

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