Diffusivity of Glycine in Concentrated Saturated and Supersaturated Aqueous Solutions

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Introduction

The study of diffusion coefficients in supersaturated solutions is of fundamental importance in understanding the mechanisms of crystal growth, crystal nucleation, and the structure and stability of supersaturated solutions. Previous work (Sorell and Myerson, 1982; Chang and Myerson, 1985) has demonstrated that the diffusivity of both electrolytes (sodium chloride and potassium chloride) and nonelectrolytes (urea) declines dramatically with increasing concentration in the supersaturated region. It has been postulated that this behavior is the result of molecular cluster formation and will result in a diffusivity of zero at the spinodal concentration (Myerson and Senol, 1984). This behavior has also been observed in liquid-liquid systems (Haase and Siry, 1968; Claersson and Sundelof, 1957) near the spinodal curve. The purpose of this study is:

1. To experimentally measure diffusion coefficients in the nonelectrolyte system glycine-water as a function of both temperature and concentration.
2. To correlate the diffusion data through modification of existing relations for concentration-dependent diffusion and activity coefficient calculation techniques for nonelectrolytes.

Experimental Results

Diffusion coefficients were experimentally obtained employing a Gouy interferometer and an experimental procedure that has been previously described in the literature (Chang and Myerson, 1985; Chang, 1984).

Experimental values of the diffusion coefficient for the glycine-water system at 298.15 K were obtained at different mean concentrations $[C = (C_1 + C_2)/2]$ ranging from 0.1–3.4 kmol/m^3. The concentration difference between the solutions $(C_1 - C_2)$ was kept at 0.1 kmol/m^3 for all experiments. Experimental results at concentrations in the undersaturated region were compared to those obtained by Ellerton et al. (1964) and were consistent to within ±3%. The saturation concentration of glycine in water at 298.15 K is 2.9 kmol/m^3 (Stephen and Stephen, 1963)). The results, plotted in Figure 1, show a rapid decline in diffusivity with increasing concentration in the supersaturated region. Crystallization problems prevented measurements above a mean concentration of 3.4 kmol/m^3.

Experiments were also conducted at 308.15 and 318.15 K. The initial concentration difference $(C_1 - C_2)$ was 0.12 kmol/m^3 for all experiments. Experiments were conducted at concentrations ranging from 0.4–4.1 molar at 308.15 K (saturation = 3.5 kmol/m^3) and from 0.15–4.6 kmol/m^3 at 318.15 K (saturation = 4.1 kmol/m^3). Results are given in Figures 2 and 3; they show a rapid decline of the diffusion coefficient with increasing concentration in the supersaturated region.

Extrapolation of the diffusivity data at each temperature to a diffusivity of zero should yield points on the spinodal curve. Results of this extrapolation yield spinodal concentrations of 3.5, 4.15, and 4.7 kmol/m^3 at 298.15, 308.15, and 318.15 K, respectively.

Correlation of Experimental Data

Correlation of experimental diffusivity data requires calculation of a thermodynamic correction term at the concentrations and temperatures of interest.

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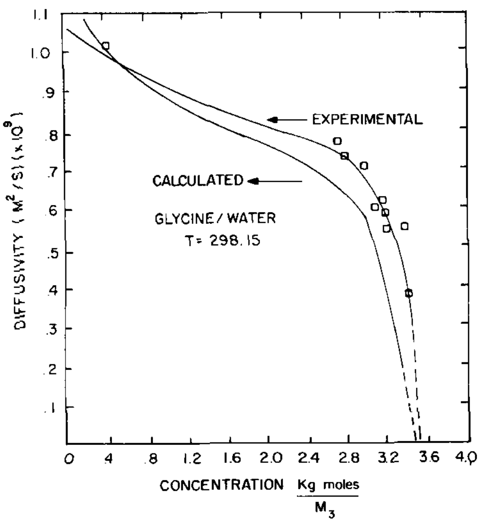

Figure 1. Calculated and experimental diffusion data for glycine-water at 298.15 K.

The activity coefficient of a nonelectrolyte solution may be described by the universal quasi-chemical equation (UNIQUAC) introduced by Abrams and Prausnitz (1975). The equation expresses the activity coefficient of component 1 (solute) of a binary system as

$$\ln \gamma_1 = \ln \phi_1/x_1 + \frac{Z}{2} q_1 \ln \frac{\theta_1}{\phi_1} + \phi_2 \left(l_1 - \frac{r_1}{r_2} l_2 \right)$$

$$\theta_2 q_1 \left(\frac{\tau_{21}}{\theta_1 + \theta_2 \tau_{21}} - \frac{\tau_{12}}{\theta_2 + \theta_1 \tau_{12}} \right) - q_1 \ln (\theta_1 + \theta_2 \tau_{21}) \quad (1)$$

where

$$l_1 = \frac{Z}{2} (r_1 - q_1) - (r_1 - 1) \quad (2)$$

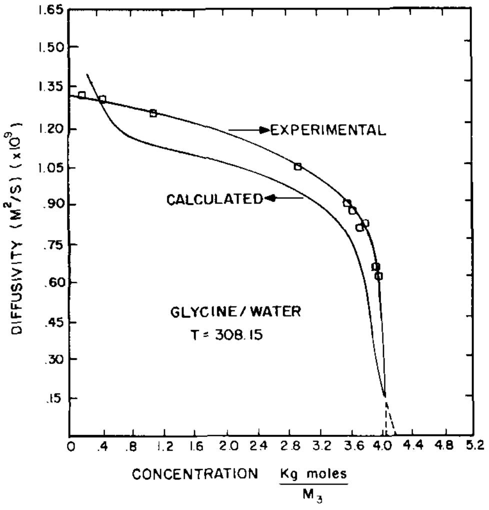

Figure 2. Calculated and experimental diffusion data for glycine-water at 308.15 K.

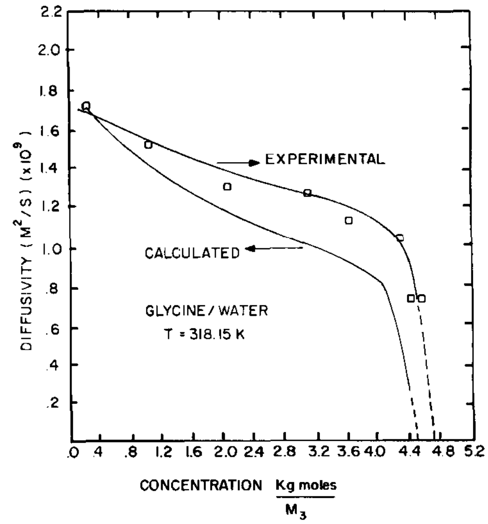

Figure 3. Calculated and experimental diffusion data for glycine-water at 318.15 K.

$$l_2 = \frac{Z}{2} (r_2 - q_2) - (r_2 - 1) \quad (3)$$

$$\phi_1 = x_1 r_1 / (x_1 r_1 + x_2 r_2) \quad (4)$$

$$\phi_2 = 1 - \phi_1 \quad (5)$$

$$\theta_1 = x_1 q_1 / (x_1 q_1 \; x_2 q_2) \quad (6)$$

$$\theta_2 = 1 - \theta_1 \quad (7)$$

where r, q are respectively the volume and surface area parameters of component i, which may be calculated by Bondi's method (1968), and τ_{12}, τ_{21} are the adjustable energetic parameters.

The equation uses only two adjustable parameters, τ_{12} and τ_{21}. The two parameters may be obtained by fitting the UNIQUAC equation with the experimental activity coefficient data in the undersaturated region. These two parameters are considered to be constant over the entire concentration range, including the supersaturated region. The two binary constants, r and q, associated with the solute may vary in the supersaturated region due to the clustering of molecules in supersaturated solutions.

It is assumed that the solute clusters have the structure of crystals, which means the solute molecules incorporate into the microcrystal lattice once they aggregate together. Therefore, it is assumed that the volume parameter does not increase as significantly as the surface area parameter in the solute clustering process. If the surface area parameter increases linearly with increasing supersaturation as shown below:

$$\mathring{q}_1 = q_1 (1 + bS) \quad (8)$$

the activity coefficient becomes

$$\ln \gamma_1 = \ln \phi_1/x_1 + \frac{Z}{2} \mathring{q}_1 \phi \ln \frac{\theta_1}{\phi_1} + \theta_2 \left(l_1 + \frac{r_1}{r_2} l_2 \right)$$

$$- \mathring{q}_1 \ln (\theta_1 + \theta_2 \mathring{q}_1 \left(\frac{\tau_{21}}{\theta_1 + \theta_2 \tau_{21}} - \frac{\tau_{12}}{\theta_2 + \theta_1 \tau_{12}} \right) \quad (9)$$

and $\mathring{q}_1$ replaces q_1 of Eqs. 2, 6, and 7.

The maximum possible value of supersaturation that could be employed with Eq. 8 would be the supersaturation at the spinodal curve. The parameter $\overset{\circ}{q}_1$ will have its maximum value at that concentration, and this $\overset{\circ}{q}_1$ marks the critical surface area of the aggregated solutes.

Equations 1–7 were employed to calculate activity coefficients in the undersaturated region. The interaction parameters τ_{21} and τ_{12} were obtained at 298.15 K by fitting the activity coefficient data of Ellerton et al. (1964). Interaction parameters at other temperatures were calculated from those at 298.15 K employing methods described in the literature (Reid et al., 1977; Abrams and Prausnitz, 1975). Activity coefficients in the supersaturated region were calculated by using the modification of the UNIQUAC model given in Eqs. 8 and 9. The only additional parameter needed for these calculations is b in Eq. 8. This parameter was obtained through a trial and error procedure. A value of b was guessed and activity coefficients calculated over the entire concentration range to a concentration larger than the spinodal. The chemical potential was then calculated along with the derivative $\partial\mu_1/\partial x_1$ at the spinodal concentration. The procedure was repeated until a b was guessed that yielded a value of $\partial\mu/\partial x_1 = 0$ at the spinodal concentration. For the glycine-water systems b was found to be 0.010, 0.013, and 0.012 at 298.15, 308.15, and 318.15 K, respectively.

A predictive diffusion equation that can be used over the entire concentration range for liquid solvent-solid solute systems is that of Hartley and Crank (1949), which appears below:

$$D_{AB} = (x_{H_2O}\, D^{\circ}_{AB} + x_B D^{*}H_2O)\left(\frac{d\ln a_A}{d\ln x_A}\right)\left(\frac{\eta^{\circ}}{\eta}\right) \qquad (10)$$

Equation 10 was employed to calculate the diffusivity of glycine as a function of concentration and temperature. The thermodynamic correction term was calculated employing the UNIQUAC model as previously described. The viscosity data and the self-diffusion coefficient of water were obtained from the literature (Wang et al., 1953; Ellerton et al., 1964). A comparison of the experimental and calculated results at each temperature is given in Figures 1–3. The calculated values are within 12% of the experimental values at 298.15, 17% at 308.15, and 24% at 318.15 K.

The results presented indicate that the UNIQUAC model with an additional parameter (for supersaturated solutions) in conjunction with the Hartley-Crank equation can reasonably estimate concentration-dependent diffusion coefficients of nonelectrolyte solid solute-liquid solvent systems over the entire concentration range from infinite dilution to the spinodal concentration. In order to employ this technique, however, the spinodal concentration at the desired temperature must be predicted or obtained experimentally. The spinodal concentration of commonly crystallized materials can often be estimated from the crystallization literature by assuming that the concentration of the maximum obtainable supersaturation is approximately equal to the spinodal concentration.

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Notation

a = activity
C = concentration
D = mutual diffusion coefficient
G = Gibbs free energy
q = surface area parameter
r = volume parameter
S = supersaturation
T = temperature
x = mole fraction

Greek letters

γ = activity coefficient
η = viscosity
μ = chemical potential
τ = energetic parameter of UNIQUAC

Superscripts

° = infinite dilution
* = self
— = average

Subscripts

A, B = components
AB = solute A in solvent B
BA = solute B in solvent A

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