Ternary Diffusion Coefficients in Metastable Solutions of Glycine–Valine–H_2O

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The study of diffusion coefficients in supersaturated solutions is of fundamental importance in understanding the mechanisms of crystal nucleation, crystal growth, and the structure and stability of supersaturated solutions. Previous work (Sorell and Myerson, 1982; Chang and Myerson 1985, 1986) has demonstrated that the diffusivity of both electrolytes (sodium chloride and potassium chloride) and nonelectrolytes (urea and glycine) declines dramatically with increasing concentration in the supersaturated region. It has been postulated that this behavior is caused by molecular cluster formation, and will result in a diffusivity of zero at the spinodal concentration [locus of points where $(\partial^2 G)/(\partial x_1^2) = 0$]. This behavior has been observed in liquid-liquid systems near the critical point (Haase and Siry 1968; Claersson and Sundelof, 1957). It is important to note that the critical point is a point on the spinodal curve, and the thermodynamic condition required for prediction of a zero diffusivity (by the Stokes-Enstein or other equations for concentration-dependent diffusivity) requires only the spinodal condition.

In a ternary system made up of a solvent and two solutes, four diffusion coefficients are of importance. Two coefficients, known as the main term coefficients (D_{11}, D_{22}), are usually of the same magnitude as the binary coefficients at the same concentration. The two "cross term" diffusion coefficients (D_{12}, D_{21}) can vary in magnitude depending on the nature of the interactions between solute molecules.

The spinodal in a ternary system is defined by the relation:

$$\begin{vmatrix} \dfrac{\partial^2 G}{\partial x_1^2} & \dfrac{\partial^2 G}{\partial x_1 \partial x_2} \\ \dfrac{\partial^2 G}{\partial x_2 \partial x_1} & \dfrac{\partial^2 G}{\partial x_2^2} \end{vmatrix} = 0 = \frac{\partial^2 G}{\partial x_1} \frac{\partial^2 G}{\partial x_2^2} = \left(\frac{\partial^2 G}{\partial x_1 \partial x_2} \right)^2 \qquad (1)$$

Application of Eq. 1 to the case of ternary diffusion, yields the following predictions for diffusion coefficient behavior at the spinodal:

$$\begin{vmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{vmatrix} = D_{11} D_{22} - D_{12} D_{21} = 0 \qquad (2)$$

Equation 2 yields a relation between the diffusion coefficients at the spinodal, but gives no information about the behavior of the four diffusion coefficients in the metastable region. The purpose of this study is:

- To measure the diffusion coefficients in the system, glycine-valine-water, in the metastable region at 298.15 K
- To predict the location of the spinodal curve at 298.15 K and compare the prediction with the results obtained from extrapolation of $|D_{ij}|$, to a value of zero

Experimental Results

Diffusion coefficients were obtained experimentally, employing a Gouy interferometer and an experimental procedure previously described (Chang and Myerson, 1986a,b; Chang, 1985; Sorrel 1981).

Experimental values of the diffusion coefficients in the glycine-valine-water system at 298.15 K were obtained at glycine concentrations of: 1.5–3.1 kmol/m^3 at a fixed valine concentration of 0.1 kmol/m^3; 0.5–2.9 kmol/m^3 at a fixed valine concentration of 0.3 kmol/m^3; and 2.7–3.2 kmol/m^3 at a fixed valine concentration of 0.05 kmol/m^3. The saturation concentration for glycine at each valine concentration are: 2.68, 2.6, and 2.7, at 0.1, 0.3, and 0.05 kmol/m^3 valine, respectively.

Diffusion coefficient results at each fixed valine concentration are given in Tables 1–3. The results in all cases show that $|D_{ij}|$ declines with increasing glycine concentration, and that the decline becomes very rapid in the metastable region. In addition, the behavior of D_{12} and D_{22} are of interest. D_{12} increases

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Table 1. Diffusion Coefficient in the Glycine–L Valine–Water System

C_1 (kmol/m^3)	$D_{11}\times 10^9$ m^2/s	$D_{12}\times 10^9$ m^2/s	$D_{21}\times 10^9$ m^2/s	$D_{22}\times 10^9$ m^2/s	$\lvert D_{ij}\rvert\times 10^{18}$ m^4/s^2
1.5	0.8674	0.0640	−0.0059	0.6256	0.5430
2.0	0.9458	0.3799	−0.1008	0.5035	0.5146
2.3	0.9779	0.3735	−0.0644	0.5032	0.5162
2.5	0.7404	0.0553	0.0005	0.7377	0.5462
2.7	0.9273	0.3071	−0.1289	0.4824	0.4870
2.8	1.1238	0.8676	−0.2272	0.1971	0.4188
3.0	0.9447	0.9405	−0.1011	0.1875	0.2722
3.1	0.9011	1.1408	−0.0370	0.1335	0.1626

At a fixed L-valine concentration of 0.1 kmol/m^3 and temperature of 298.15 K.

Table 2. Diffusion Coefficient in the Glycine–L Valine–Water System

C_1 (kmol/m^3)	$D_{11}\times 10^9$ m^2/s	$D_{12}\times 10^9$ m^2/s	$D_{21}\times 10^9$ m^2/s	$D_{22}\times 10^9$ m^2/s	$\lvert D_{ij}\rvert\times 10^{18}$ m^4/s^2
0.5	0.9004	0.2378	−0.0514	0.5254	0.4853
1.5	0.6723	0.0142	−0.0028	0.6594	0.4434
1.7	0.7349	0.0647	−0.0216	0.5729	0.4225
2.0	0.8293	0.2385	−0.0316	0.4920	0.4156
2.3	0.8808	0.3667	−0.0952	0.4318	0.4153
2.6	0.7014	0.2087	−0.1043	0.4028	0.3043
2.8	0.8533	0.7604	−0.0964	0.2001	0.2440
2.9	0.7062	0.5925	−0.0997	0.1756	0.1831

At a fixed L-valine concentration of 0.3 kmol/m^3 and temperature of 298.15 K.

Table 3. Diffusion Coefficient in the Glycine–L Valine–Water System

C_1 (kmol/m^3)	$D_{11}\times 10^9$ m^2/s	$D_{12}\times 10^9$ m^2/s	$D_{21}\times 10^9$ m^2/s	$D_{22}\times 10^9$ m^2/s	$\lvert D_{ij}\rvert\times 10^{18}$ m^4/s^2
2.7	1.1615	0.5633	−0.3445	0.2204	0.4501
2.8	0.9891	0.4325	−0.1907	0.3645	0.4431
3.1	1.0920	1.0214	−0.2155	0.0912	0.3197
3.2	0.9364	1.3164	−0.1290	0.0052	0.1748

At a fixed L-valine concentration of 0.05 kmol/m^3 and temperature of 298.15 K.

dramatically with increasing concentration in the supersaturated region, becoming as large as D_{11}. At the same time, D_{22} declines dramatically. This implies that the flux of species 1 (glycine), due to the gradient of species 2 (valine), is of the same magnitude as the flux of species 1, due to its own gradient (Cussler, 1978). The flux of species 2, due to its own gradient, D_{22}, declines rapidly with increasing concentration, while the flux of species 2, due to the gradient of species 1, D_{21}, remains small (and negative). These results show that multicomponent diffusion effects are important in supersaturated solutions and dominate behavior as the spinodal curve is approached.

Calculation of the Spinodal Concentrations

Spinodal concentrations for the glycine-valine-water system at 298.15 K were calculated using the UNIQUAC method for multicomponent systems (Abrams and Prausnitz, 1975). The interaction parameters for the pair, glycine-valine, was assumed to be zero, since they are both solids.

To account for molecular cluster formation in supersaturated solutions, a modification of UNIQUAC (Chang and Myerson, 1986) was used, in which the surface area parameter for glycine was assumed to be a linear function of supersaturation. This function was obtained at several temperatures by Chang and Myerson (1986), by employing experimentally determined spinodal concentrations. Details of the calculation can be found in Lo (1989). Calculated spinodal concentrations at 25°C, with fixed valine mole fractions of 0.001, 0.002, and 0.006, resulted in glycine mole fractions of 0.0775, 0.077, and 0.060, respectively. Glycine mole fractions (at the same fixed valine concentration) obtained from extrapolation of $|D_{ij}|$ data to a value of zero, are 0.069, 0.068, and 0.064. The difference between the calculated mole fractions and those obtained from data extrapolation, are 12, 13, and 6%, respectively. This indicates that the UNIQUAC method for multicomponent systems (including the modification of Chang and Myerson, 1986 to account for clustering), along with binary data on the constituent pairs and binary spinodal concentrations (for the supersaturated species), are sufficient for estimation of activity coefficients and spinodal concentrations in ternary supersaturated solutions.

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