Cluster Diffusion in Metastable Solutions

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The existence of molecular clusters in supersaturated solutions has long been postulated. Direct evidence of the existence of these clusters has recently appeared in the literature (Hussmann et al., 1984; McMahon et al., 1984). Khamskii (1969) reported that light transmission through supersaturated solutions increased continuously prior to the onset of crystallization, however, no change in solution properties such as viscosity, density, refractive index, or electrical conductivity were noted. Larson and Garside (1986) reported the formation of concentration gradients in vertical columns of supersaturated solutions, which they attributed to cluster formation. They estimated the typical cluster size to be approximately 10^3 molecules.

The diffusivity of a number of electrolytes and nonelectrolytes (urea, glycine, KCL, NaCl) in aqueous supersaturated solutions have been reported (Sorell and Myerson, 1982; Chang and Myerson, 1985; Chang, 1984). In all systems the diffusion coefficient was found to decrease rapidly toward zero with increasing concentration in the supersaturated region. Equations for the prediction of concentration-dependent diffusion coefficients all result in a diffusion coefficient of zero at the spinodal curve (the boundary of the metastable region). Thermodynamic arguments, while predicting a diffusion of zero at the spinodal give little information on the metastable supersaturated region. It is postulated that the rapid drop in diffusion coefficients observed in the supersaturated region is the result of molecular clusters. The formation of these clusters might result in time-dependent diffusion coefficients. It is the purpose of this work to examine the diffusion coefficients of supersaturated solutions of glycine as a function of solution age to determine whether diffusivity varies with time in supersaturated solutions.

Cluster Formation

If a cluster containing g molecules is called a g-mer, the change in the number of g-mers of a given size will result from the following:

1. The formation of g-mers from other clusters smaller or larger than the g-mer
2. The consumption of the g-mer to form larger or smaller clusters

This can be represented by the relation

$$\frac{dn_g}{dt} = \frac{1}{2}\sum_{g'=1}^{g-1} K_{g-g'} n_{g-g'} n_{g'} - \sum_{g=1}^{\infty} K_{g-g'} n_g n_{g'} + \sum_{g'=1}^{\infty} S_{g-g'} n_{g-g'} - \frac{1}{2}\sum_{g'=1}^{g-1} S_{g-g'} n_g \quad (1)$$

Since $n_{g-g'}$ and $n_{g'}$ are counted twice, ½ is used to correct the over-counting. Using Binder and Mirold's (1973) estimation for rate constants

$$K_{g-g'} = c\left[\left(\frac{g}{g'}\right)^{0.333} + \left(\frac{g'}{g}\right)^{1.333}\right] \quad (2)$$

Eq. 2 states that the reaction rate constant K is a function of the sizes of the reaction clusters only. Other degrees of freedom of the cluster (such as interactions between clusters) do not enter explicitly. The rate of dissociation can be derived from equilibrium conditions at which microscopic reaction rates are equal.

$$K_{g-g'} n_g n_{g'} = S_{g-g'} \cdot n_{g-g'} \quad (3)$$

The dissociation reactions become negligible when the cluster size is greater than the critical cluster size. The critical size ρ_C

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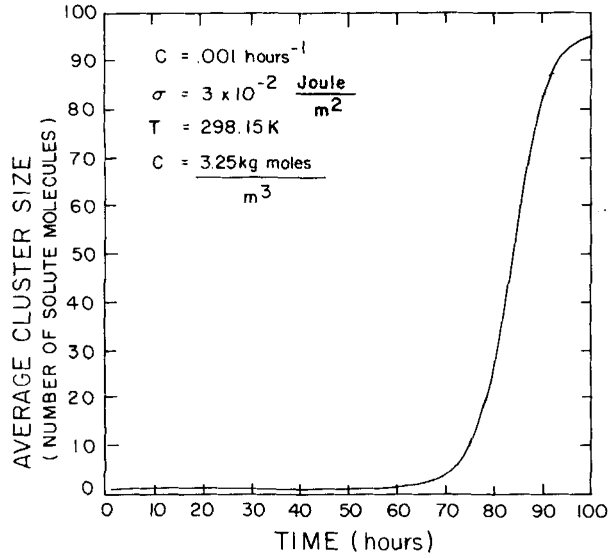

Figure 1. Average cluster size as a function of time.

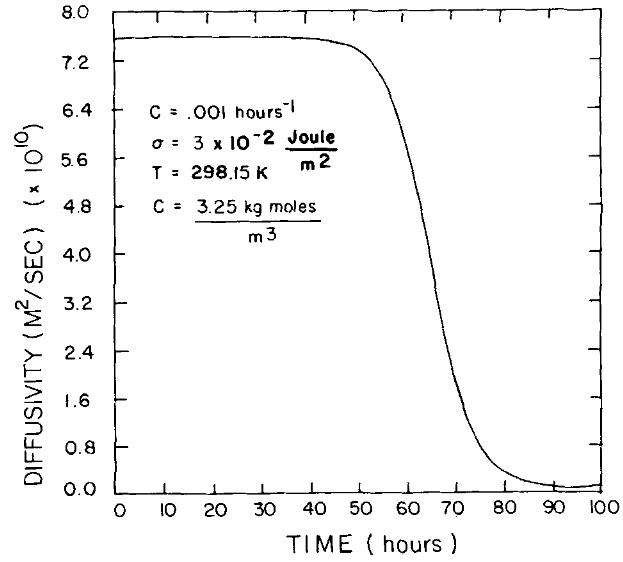

Figure 2. Predicted diffusion coefficient in a supersaturated solution as a function of time.

can be described by the relation:

$$\rho_c = \sigma V_m / kT \ln (1 + S) \tag{4}$$

Therefore, the dissociation constants are subject to the additional constraint:

$$S_g = 0 \text{ if } g\text{-mer' radius} > \rho_c \tag{5}$$

Employing Eqs. 1–5, Eq. 1 may be solved completely to give the time evolution of the cluster size distribution. The average cluster size, in terms of the number of molecules in the cluster, at any instant in time is defined as:

$$\bar{g} = \sum_{g=1}^{\infty} g n_g \Big/ \sum_{g=1}^{\infty} n_g \tag{6}$$

Cussler (1980) derived a relation for the diffusivity in concentrated solutions containing molecular clusters:

$$D = \frac{kT}{2\pi\eta\epsilon} \tag{7}$$

where ϵ is approximately equal to the average cluster size. If it is assumed that no clustering occurs in the solution at saturation then the diffusivity at saturation can be written as:

$$D_s = \frac{kT}{2\pi\eta} r_o \tag{8}$$

and the diffusivity in the supersaturated solution is simply

$$D = \frac{D_s}{\bar{g}} \tag{9}$$

Equation 9 indicates that the diffusion coefficient in a supersaturated solution will be time-dependent since $\bar{g}$ is a function of time. Equations 1–6 provide the means for calculation of the average cluster size as a function of time. Unfortunately, the parameters c, a constant related to the aggregation rate, and σ, the surface energy density, are not available. Assuming arbitrary values of these parameters and employing physical property data of the glycine-water system at 3.25 kmol/m^3 and 298.15 K, Eqs. 1–6 and 9 were employed to calculate the average cluster size and diffusivity as a function of time. The results, shown in Figures 1 and 2, indicate that there is an induction period during which little clustering occurs. This is followed by a period when the average size increases rapidly with time. The average cluster size then increases slowly toward a maximum value, the critical cluster size. When this size is reached, nucleation should occur. In practice the period required to reach the maximum size, and hence for nucleation to occur, can be

Table 1. Diffusion Coefficients as a Function of Time

Concentration kmol/m^3	Post-cooling Sitting Time h	Diffusivity m^2/s x 10^{10}
	Glycine-Water, T = 298.15 K	
3.3	0	7.6
3.3	8	6.8
3.3	18	5.6
3.3	24	5.2
3.5	2	6.4
3.5	11	6.0
3.5	18	5.1
3.5	20	3.6
	Valine-Water, T = 298.15 K	
0.7	0	6.7
0.7	9	6.5
0.7	22	5.85
0.7	24	5.8
0.74	2	6.4
0.74	12	6.3
0.74	18	5.4

extremely long as indicated by the fact that stable supersaturated solutions can often be stored for very long periods.

Results and Discussion

Theories of cluster evolution in supersaturated solutions indicate that the cluster size distribution is a function of time. The rapid decline in diffusion coefficient with increasing concentration observed in supersaturated solutions has been postulated to be the result of cluster formation. A time-dependent cluster size distribution therefore would result in a time-dependent diffusivity. Experiments to examine the diffusivity of supersaturated solutions of glycine as a function of time were conducted employing Gouy interferometry.

The experiments employed the Gouy interferometer apparatus previously described (Chang and Myerson, 1985). The procedure employed was identical to those used in previous studies of diffusion in supersaturated solution except in the cooling method used. In all previous studies (Chang and Myerson, 1985; Chang, 1985; Sorell and Myerson, 1982), the solutions were prepared at 333.15 K, allowed to cool naturally to 298.15 K, and kept standing at 298.15 K for 24 h prior to their use in an experiment. In these experiments the solutions were cooled from 332.15 to 298.15 K in 4 h, employing a temperature programmer. The solutions were then allowed to sit for various time intervals from 0 to 24, h after which diffusivity measurements were made. Experiments employing the glycine-water system were conducted at 3.3 and 3.5 kmol/m^3 (saturation = 2.86 kmol/m^3). The results, given in Table 1, show a decline in the diffusivity with increasing time. To further verify the phenomenon, experiments were also conducted with the valine-water system. Experiments were conducted at 0.7 and 0.74 kmol/m^3 (saturation = 0.62 kmol/m^3). These results are also given in Table 1 and they too a decline in diffusivity with time. Attempts to perform experiments for significantly longer time intervals (at the supersaturations reported above) were unsuccessful because of crystallization problems.

The results presented in this work indicate that diffusion coefficients in supersaturated solutions vary with the age of the solution. It is likely that the method of solution preparation and/or the method of cooling will also affect the diffusion coefficient. Further studies of the formation and evolution of molecular clusters in supersaturated solutions will be required to understand this phenomenon.

Acknowledgment

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Notation

G = Gibbs free energy
$\bar{g}$ = average number of solute molecules in clusters
k = Boltzman constant
$Kg\text{-}g^1$ = reaction rate constant for cluster formation
n_g = number of clusters containing a solute molecule
r_o = molecular radius of diffusing species
S = supersaturation
$Sg\text{-}g^1$ = cluster dissociation constant
t = time
T = temperature
V_m = molecular volume
x = mole fraction
ρ_c = critical cluster size
σ = surface energy density
η = viscosity

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