Diffusional Separation in Ternary Systems

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Introduction

The diffusivity of a number of binary solid-solute/liquid-solvent systems has been measured in aqueous supersaturated solutions (Sorell and Myerson, 1982; Chang and Myerson, 1985, Chang, 1984). In all cases a rapid decline in diffusivity toward zero with increasing concentration in the supersaturated region was observed. This behavior and similar behavior noted in liquid-liquid systems near the consolute point (Claersson and Sundelof, 1957; Haase and Siry, 1968) has been attributed to the fact that diffusion coefficients should equal zero at all points on the spinodal curve (locus of points when $\partial^2 G_1/\partial x_1^2 = 0$). The spinodal curve is the limit of the metastable region and can be approached in solid-solute/liquid-solvent systems where metastable supersaturated solutions can often be prepared. The rapid decline of diffusivity in the supersaturated region and the resulting large difference in diffusivity between a dilute and a supersaturated solution of a given species suggests the possibility of using diffusivity differences as the basis for a separation process. In a ternary system made up of a solvent and two solutes (in which one solute is concentrated, and one is dilute), four diffusion coefficients are of importance. The behavior of these coefficients when one solute is supersaturated will determine whether significant separations can be achieved, based on differences in the coefficient. It is the purpose of this work first to experimentally determine the diffusion coefficients in two ternary systems (KCl-NaCl-water and glycine-KCl-water) when one species is undersaturated and one species is supersaturated, and second to examine experimentally the use of diffusion coefficient differences as a possible separations technique.

Experimental

A schematic diagram of the Gouy interferometer apparatus employed in the diffusion studies appears in Figure 1. A detailed description of the apparatus can be found in Chang (1985). Illumination of the system was provided by a Spectra Physics model 146 randomly polarized helium neon laser. The diffusion cell employed is a modification of the cell described by Sorell (1981). Temperature was regulated by a model RTE 9D refrigerated circulation bath with an MTP-5 controller manufactured by Neslab. The control of temperature was ±0.01 K.

The systems NaCl-KCl-water and glycine-KCl-water were chosen for study since binary diffusivity data in the undersaturated and supersatured regions were available (Chang and Myerson, 1985; Chang, 1985) for each solute in aqueous solution.

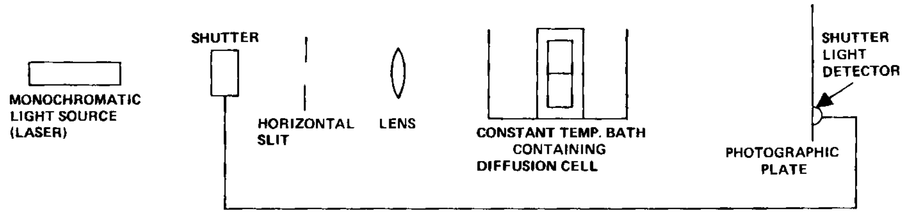

Figure 1. Diagram of Gouy interferometer.

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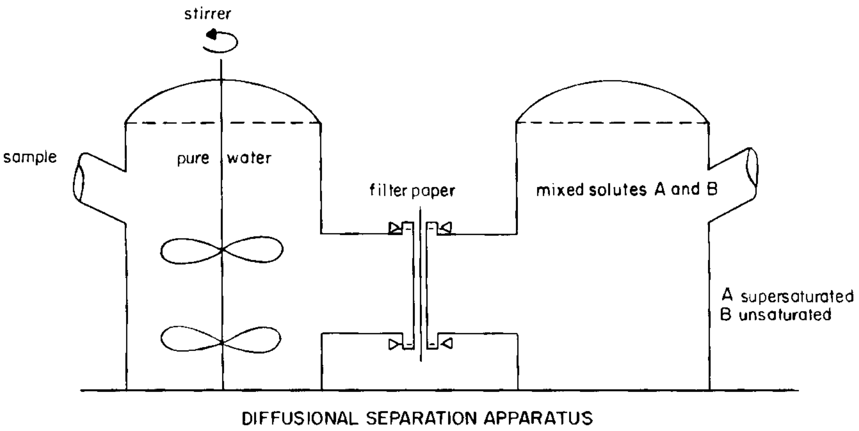

Figure 2. Diagram of diaphragm cell apparatus.

The measurement of ternary diffusion coefficients by Gouy interferometry at a given mean concentration requires that four experiments be performed. In each experiment the mean concentration must be the same but the concentration difference must vary. Photographic exposures for each experiment are analyzed to yield experimental fringe distances between the undeviated slit image and each of the bottom eleven fringes in the photograph. This fringe deviation data for each of the four experiments is then employed in a rather complex calculation procedure to yield the four diffusion coefficients at the mean concentration of the experiments. Details of the procedure can be found in Chang (1985).

Separation experiments were conducted in a diaphragm cell apparatus shown in Figure 2. The apparatus consists of two chambers separated by a filter with a pore size of 20–50 μm. Both chambers are well stirred to insure that concentration gradients do not form within the cell. The experimental procedure involves preparing a ternary solution of the desired concentration and temperature and adding it to one of the compartments of the apparatus. Water at the same temperature is added to the other side. Samples are withdrawn regularly from the solvent side and analyzed for the solute concentration, employing atomic absorption (KCl, NaCl) or ninhydrin reaction (glycine).

Table 1. Diffusion Coefficients for NaCL-KCl-Water and Glycine-KCl-Water Systems at 298.15 K

Concentration, C kmol/m^3	Coefficients, D, (m^2/s) × 10^{-9}					
	Binary		Ternary			
	$D_{KCl\text{-}H_2O}$	$D_{NaCl\text{-}H_2O}$	D_{11}	D_{12}	D_{21}	D_{22}
[Subscript 1 = KCl, 2 = NaCL]						
$C_1 = 3.0$	2.1	—	0.8122	0.5749	0.1680	1.565
$C_2 = 1.0$	—	1.48				
$C_1 = 3.4$	2.16	—	1.2933	1.1306	−0.0367	2.8765
$C_2 = 1.333$	—	1.49				
	$D_{Gly\text{-}H_2O}$	$D_{KCl\text{-}H_2O}$				
[Subscript 1 = Glycine, 2 = KCl]						
$C_1 = 3.25$	0.51	—	0.6896	0.1279	0.088	2.29
$C_2 = 0.325$	—	1.84				
$C_1 = 2.0$	0.78	—	0.7288	0.1524	−0.1680	2.2765
$C_2 = 0.2$	—	1.83				

Results and Discussion

The experimentally determined main and cross-term diffusion coefficients of the KCl-NaCl-water and glycine-KCl-water systems are presented in Table 1. For comparison the binary diffusion coefficients of each species at the appropriate concentration are also given. The results show that the KCl-NaCl-water system is highly interactive, with the cross-term diffusion coefficient D_{12} nearly as large as D_{11}, the main-term KCl coefficient. The glycine-KCl-water system is not as strongly interacting, with the main-term diffusion coefficient close to the binary coef-

Table 2. Diaphragm Cell Separation Results

Time	Concentration, (kmol/m^3) × 10^3				
	Compartment A (Initial Conc.)		Compartment B		Ratio in Comp. B
s	C_1	C_2	C_1	C_2	C_1/C_2
[Subscript 1 = KCl, 2 = NaCl]					
0	3,000	1,000	0	0	0
200	—	—	18.33	7.77	2.36
400	—	—	32.00	13.00	2.46
700	—	—	65.38	26.43	2.47
800	—	—	79.20	30.52	2.60
0	3,400	1,330	0	0	0
200	—	—	15.38	12.26	1.25
400	—	—	25.80	17.52	1.47
700	—	—	49.48	25.76	1.92
900	—	—	97.62	72.80	1.34
[Subscript 1 = Glycine, 2 = KCl]					
0	2,000	200	0	0	0
200	—	—	3.65	0.55	6.64
500	—	—	9.58	1.402	6.83
3,000	—	—	44.55	6.226	7.15
8,700	—	—	88.92	13.4	6.63
0	3,200	320	0	0	0
700	—	—	6.5	1.43	4.54
1,200	—	—	10.55	3.25	3.25
1,500	—	—	14.00	4.03	3.47
3,000	—	—	28.85	7.09	3.81

ficients of the individual components and the cross-term coefficients significantly smaller than the main-term coefficients.

Diaphragm cell experiments were conducted for the KCl-NaCl-water and glycine-KCl-water systems at two different initial concentrations. In the first experiment with the KCl-NaCl-water system both KCl and NaCl were undersaturated. In the second experiment KCl was supersaturated while NaCl was undersaturated. This procedure was also employed in the glycine-KCl-water system so that glycine and KCl were undersaturated in the first experiment, and glycine was supersaturated but KCl undersaturated in the second experiment. The conditions employed in the experiments and the results are summarized in Table 2. The results show that an initial molar ratio of K/Na of 3/1 in compartment *A* produced a ratio of K/Na of 2.6/1 in compartment *B* (after 800 s) when both solutes were undersaturated, compared to a ratio of K/Na of 1.34/1 when KCl was initially supersaturated (after 900 s). Similar results were obtained in the glycine-KCl-water system. An initial glycine/KCl ratio of 10/1 in compartment *A* resulted in a glycine/KCl ratio of 6.64/1 in compartment *B* (after 8,700 s) when both species were undersaturated, compared to a ratio of 3.81/1 when glycine was initially supersaturated (after 3,000 s).

The results show an improvement in separation when one species was initially supersaturated. As the concentration of the supersaturated species declines, the diffusion coefficient increases, causing a decrease in the separation efficiency. This could be prevented by programmed cooling of the solution. This would keep the solute supersaturated and thus prevent the diffusion coefficient from increasing during the separations process. The separation achieved in this process is the result of the interaction of the four diffusion coefficients. Further work is required to determine how each of these diffusion coefficients varies with concentration in a solution supersaturated with respect to one solute. This would allow determination of the initial concentration necessary to achieve maximum separation for a particular system.

Acknowledgment

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