Effect of CO_2 on Expansion and Supersaturation of Saturated Solutions

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Crystallization from solution is usually performed by cooling or evaporating a saturated solution. An alternative is by the addition of a liquid or solid precipitant, which decreases the solubility of solution. Such a process, called salting-out, has several advantages: it allows low operation temperatures, eases high solute recovery, and produces crystals of high purity (Mullin, 1972). In spite of these merits, the salting-out process requires a separation unit to recover the precipitant; thus, it might become economically inefficient.

Recently, gases at elevated pressure are found to be soluble in many organic solvents, and then to expand the solvents and reduce the solvent power of dissolving solids. Due to this finding, a revised salting-out process known as gas antisolvent crystallization (GAS) has been proposed using a compressed gas as the precipitant. The GAS process removes the obstacle of economic inefficiency for recovering the precipitant, because the dissolved gas can be recovered easily by the release of simple pressure. It also takes advantage of the fact that pressure can be readily programmed to make high-quality crystals (Gallagher et al., 1989, 1991b; Berends et al., 1994) and to accomplish fractional crystallization (Dixon and Johnston, 1991).

Although the GAS processes have been investigated, including the measurement and modeling of solubility (Chang and Randolph, 1990; Dixon and Johnston, 1991; Kordikowski et al., 1994), the applicability of separating mixtures (Chang et al., 1991; Gallagher et al., 1991a; Shishikura et al., 1991; Liou and Chang, 1992), and the control of crystal-size distribution (Gallagher et al., 1991b; Berends et al., 1994), fundamental work on the saturation behavior of solute during the expansion of solution is lacking.

In a GAS process an increase in pressure to expand the solution is usually accompanied by a rise in temperature. Thus, the cause of solubility change is difficult to distinguish between the pressure and temperature. The purposes of this study are to find the expansion profile of solutions and to investigate the saturation behavior of solutes of various systems operated at constant temperature. Carbon dioxide was used to expand a number of solutions with a technique of low expansion rates, that is, CO_2 was introduced above the liquid and diffused into the saturated solution, while the solution temperature remained constant. Higher rates of expansion, either by stirring the liquid or by bubbling CO_2 through the solution, which caused a rapid rise in temperature, are excluded here. The solution expansion profiles were recorded and modeled with a derived equation. The distinct types of solute saturation behavior caused by solution expansion are described.

Experimental Studies

In this experiment, over 30 solutions were expanded with carbon dioxide at room temperature and under a pressure between 30 and 60 bar. Various solutes and solvents were selected to prepare the solutions, including organic, metal-organic, and inorganic compounds for solutes, and acetone, ethanol, and ethanol-water mixtures for solvent. The use of a methanol-water mixture allows the investigation of many solids that are only sparingly soluble in pure organic solvents. The apparatus used in this experiment was designed for observing the solution expansion and solute saturation behaviors, and for measuring the expansion level during the expansion courses. The key component is a crystallization cell where solutions can be expanded. The cell is a modified liquid level gage of 160 mL in volume (Jerguson, Model 18-T-30, 3.2 cm $\times$ 1.6 cm $\times$ 30 cm) equipped with a jacket and a thermistor-type thermometer (Marlin, Model 410A) for controlling and indicating temperatures in the cell. It is also equipped with a needle for mounting seed crystals and with a camera-microscope system (Nikon, Model SMZ-10) for detecting crystallization from the solution expanded in the cell.

The procedure of conducting an experimental run began by loading the cell with a saturated solution of 120 mL or 100 mL, depending on the expansion ratio, and inserting a seed crystal into it. The saturated solution was prepared at room temperature and atmospheric pressure, with the solubilities determined by the gravimetric method. The seed, either a single crystal of 0.5 to 1.0 mm or a compressed powder, came directly from the purchased chemicals without recrystallization. After loading the solution and inserting the seed, carbon dioxide (99%) was introduced into the cells above the top of the saturated solution to elevate the system pressure to a desired level, while the crystallization cell was kept at room temperature. Then, the solution was allowed to expand gradually by absorbing carbon dioxide. This way, the solution temperature would be able to remain constant and the saturation behavior of solution due to expansion alone can be identified. During the expansion course, the volume of the solution was recorded with time to study the expansion profile and the seed was photographed to examine its change when it became immersed in the expanded solution. An experimental run was normally stopped after the expansion process reached equilibrium, or the seed crystal dissolved entirely, depending on the solubility behavior of the system. The chemicals used in this study were purchased from various sources with all of them being reagent grade.

Results and Discussion

Expansion profiles of solutions

Most of the solutions selected in this study were expandable, and their expansion profiles fitted the following equation as exemplified in Figure 1

$$\Delta V/V_o = (\Delta V/V_o)_e[1-\exp(-t/\tau)] \qquad (1)$$

The equation was derived by assuming that the expansion rate of a solution is proportional to the difference between the saturated expansion level and the instant level in question

$$d(\Delta V/V_o)/dt = [(\Delta V/V_o)_e - (\Delta V/V_o)]/\tau \qquad (2)$$

where $\Delta V/V_o$ is the instant expansion level, $(\Delta V/V_o)_e$ the equilibrium expansion level, and τ a time constant.

The obtained equilibrium expansion levels and expansion time constants are summarized in Table 1. The equilibrium expansion levels of ethanol solutions were between 13% and 36%. They were lower than the equilibrium expansion level of acetone solution and generally higher than the equilibrium expansion levels of methanol-water solutions. This finding is consistent with the "like dissolves like" rule. Alcohols are polar protic and acetone is polar aprotic. The latter is less polar than the former. Carbon dioxide has a similar carbonyl group as acetone. Therefore, carbon dioxide is expected to dissolve highly in acetone, moderately in ethanol, and scarcely in a very polar methanol-water mixture. Expansion data are limited in the literature, especially at low-pressure levels. However, our data of acetone solution can be compared with that reported by Gallagher et al. (1991a). Under the comparable operating conditions, a difference of 16% is noted. The difference is expected because acetone is saturated with different solute in each case. Solute has an effect on the expansion as can be seen from Table 1 for the ethanol solutions.

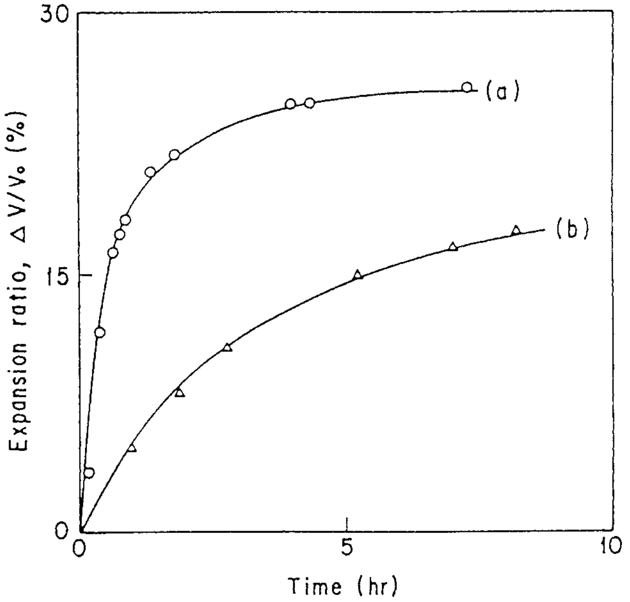

Figure 1. Transient expansion ratios of: (a) NH_4ClO_4/ethanol solution; (b) NsSCN/ethanol solution under pressurized carbon dioxide.

Table 1. Expansion Parameters of Eq. 1 for Various Solutions

Solvent	Solute	T, °C	Co, g/100g	P, bar	$(\Delta V/V_o)_e$ %	τ, h	§ %
		Systems with Moderate Expansion					
Acetone	LiCl	26	2.0	30.9	43	0.41	8
Ethanol	Acetaminophen	26	21	48.4	29	1.8	12
	Tartaric acid	26	30 ‡	54.5	22	2.7	3
	Urea	26	6.3††	51.5	36	1.2	6
	$NaCH_3COO$	27	2.2	54.8	17	8.2	1
	$NaClO_3$	29	1.0††	34.9	13	1.3	5
	NaSCN	26	20	54.4	18	3.1	3
	NH_4Cl	29	1.0	43.5	23	1.1	7
	NH_4ClO_4	27	1.9†	38.7	25	0.74	12
Meth 80*	Sucrose	30	8.5	51.4	23	3.4	2
	NaCl	26	3.3	34.1	16	4.9	3
70*	Monosodium glutamate	26	3.8	51.4	16	1.5	1
	$MgSO_4 \cdot 7H_2O$	26	1.4	43.2	6.2	0.92	7
60	Pentaerythritol	26	3.2	61.2	11	3.5	5
	$NH_4H_2PO_4$	26	1.1	60.2	16	5.2	16
		Systems Difficult to Expand					
Meth 44	K_2SO_4	28	—	61.1	1	—	—
Etha 44**	NaCl	29	—	61.1	2	—	—
Etha 95	Citric acid monohydrate	29	52 ‡	53.1	0	—	—

*Meth X means methanol-water mixture of X wt. % methanol.
**Etha X means ethanol-water mixture of X wt. % ethanol.
†Seidell (1940).
‡Seidell (1941).
††Windholz et al. (1983).
§Is the standard error in fitting Eq. 1.

The expansion time constants varied randomly from 0.4 to 8.2 h and correlated neither with the solute solubilities (Co), nor with the equilibrium expansion levels. The randomness may be due to the different diffusion rates of carbon dioxide in the miscellaneous solutions since carbon dioxide must diffuse through the solution which is about 20 cm in height. It is understood that the expansion time constant, which is a kinetic quantity, is not related to solubility or expansion level, which are of thermodynamic nature. Therefore, the time constants may be used to estimate the relative diffusion rates of carbon dioxide in the solutions.

In contrast to the expandable systems, a few of the solutions in this study were found difficult to expand, which are also listed in Table 1. The almost zero expansion of the potassium sulfate and sodium chloride solutions may be caused by the high water content of the solutions, since carbon dioxide can hardly dissolve in water at moderate pressures. This reason, however, cannot be used to explain the difficult expansion of the citric acid solution, which contains no more than 10% water. The difficulty is probably due to the unusually high solubility of citric acid in ethanol. The high solubility implies strong cohesive force between citric acid and ethanol molecules, making few free ethanol molecules available to interact with carbon dioxide molecules.

Saturation behaviors of expanded solution

Various saturation behaviors were observed in this experiment. Accordingly, the expandable solutions were divided into three groups: the nucleation system, the growth system, and the undersaturation system, as summarized in Table 2 (see Table 1 for the information on the expansion parameters). The nucleation systems were characterized by the catastrophic nucleation in some stage of their expansion course. For example, numerous crystals of sodium acetate about 10 μm were nucleated from the bulk of ethanol solution after it was expanded. As is suggested by the catastrophic nucleation, the nucleation systems encountered high supersaturation in their expansion course. The growth systems were identified by the nucleation and noticeable growth of individual crystals on the cell walls, however, with no detectable nucleation from the bulk solution. For example, many polyhedral crystals about 0.3 mm were found on the cell walls and grew at a rate of 3×10^{-9} m/s in the expansion course of the methanol-water-sucrose solution with no bulk-nucleation being observed. As is implied by the heterogeneous nucleation, the growth systems experienced moderate supersaturation when they were expanded. Unlike the nucleation and growth systems, the undersaturation systems exhibited no nucleated crystal, and the seeds dissolved in the expanded solutions such as the naphthalene-toluene system. As is indicated by the seed dissolution, the systems became undersaturated in their expansion courses.

Table 2. Classification of Solutions Expanded with Carbon Dioxide

System	Solute	Solvent	*T*, °C	Co, g/100 g	*P*, bar
Nucleation	$NaCH_3COO$	ethanol	27	2.2	54 ± 8
	LiCl	acetone	26	2.0	30 ± 9
Growth	Acetaminophen	ethanol	26	21	48 ± 4
	Anthracene	ethanol	26	1.9**	52 ± 9
	Fructose	ethanol	27	8.4**	49 ± 1
	Pentaerythritol	meth60*	26	3.2	61 ± 2
	Sucrose	meth80	30	8.5	51 ± 4
	Urea	ethanol	26	6.3**	51 ± 5
	Monosodium glutamate	meth70	26	3.8	51 ± 4
	NH_4Cl	ethanol	29	1.0	32 ± 3
	NH_4ClO_4	ethanol	27	1.9†	38 ± 7
	$NH_4H_2PO_4$	meth60	26	1.1	60 ± 2
	$NH_2OH \cdot HCl$	ethanol	29	6.7**	50 ± 6
	NaCl	meth80	26	3.3	34 ± 1
	$NaClO_3$	ethanol	29	1.0**	34 ± 9
	NaSCN	ethanol	26	20	54 ± 4
	KNO_3	ethanol	25	2.1	57 ± 7
	$MgSO_4 \cdot 7H_2O$	meth70	26	1.4	43 ± 2
Under-saturation	Adipic acid	ethanol	26	22	59 ± 1
	Benzoic acid	ethanol	25	10‡	46 ± 3
	Diphenyl	ethanol	26	10‡	36 ± 4
	Methenamine	ethanol	26	10**	55 ± 2
	Naphthalene	toluene	25	58	49 ± 1
	Phenanthrene	toluene	25	46	35 ± 5
	L-Leucine	meth60	26	0.7	51 ± 1
	L-Phenylalanine	meth60	25	1.3	39 ± 3
	Phenolphthalein	meth60	25	1.0	42 ± 6

*Meth X means methanol-water mixtures of X wt. % methanol.

**Windholz et al. (1983).

†Seidell (1940).

‡Seidell (1941).

Some distinct features are revealed from the solution-expansion experiments. First, showers of miniature crystals appeared in the nucleation systems consisting of metal-organic and inorganic solutes, in spite of the low expansion rates and the low expansion levels. The sodium acetate-ethanol solution, for example, belong to a nucleation system with a large expansion time constant of 8.2 h and a low equilibrium expansion level of 17%. Clearly, atomspherically saturated solutions may become highly supersaturated even though they are expanded to low levels at low rates. A second feature is that the majority of the solutions belong to growth systems and they contained a variety of solutes, including organic(sucrose), metal-organic (monosodium glutamate), and inorganic compounds (sodium chloride). This suggests that atmospherically saturated solutions will very likely become moderately supersaturated if they are expanded to low levels and at a low rate. This conclusion is consistent with the theoretical analysis of Gallagher et al. (1989) who showed that the supersaturation of solutions lay below the critical supersaturation of bulk-nucleation when solutions were expanded at low rates and to low levels. Another feature, which is far more interesting, is that there exist undersaturation systems at the low operating pressures and all of them were found to be organic solutes. This result is consistent with those published in the literature. In our experiments, no crystal of naphthalene and phenanthrene was nucleated from toluene solutions expanded with carbon dioxide at 49 bar and 35 bar, respectively. Similar results have recently been reported that carbon dioxide below 42 bar cannot precipitate phenanthrene from toluene solutions (Berends et al., 1994). These results are checked by the solubility data of Dixon and Johnston (1991). Their data were recalculated on a CO_2-free basis, that is, the mole ratio of solute/toluene, and are presented in Figure 2 in which the data points are connected by freehand. It is clearly seen that the solute/toluene mole ratio for naphthalene and phenanthrene below 55 and 45 bar, respectively, is larger than that at atmospheric pressure. The reason to use the carbon-free basis is as follows: the operation of a batch GAS process starts with a CO_2-free solution, which is saturated at atmospheric pressure, and the solute/toluene mole ratio remains constant during the expansion course. Thus, it is more convenient to judge the saturation behavior by the solute/toluene mole ratio. For example, when a saturated solution of naphthalene in toluene at atmospheric pressure is pressurized with CO_2, the solution will become unsaturated before the system reaches 55 bar, as shown in Figure 2.

In summary, atmospherically saturated solutions may become highly, moderately, or negatively supersaturated when they are expanded to low levels at a low rate. As a result, solutes may precipitate by catastrophic nucleation from bulk solutions or by heterogeneous nucleation on container walls, or they may not even precipitate at all. Generally, most inorganic solutes precipitate by the heterogeneous nucleation and

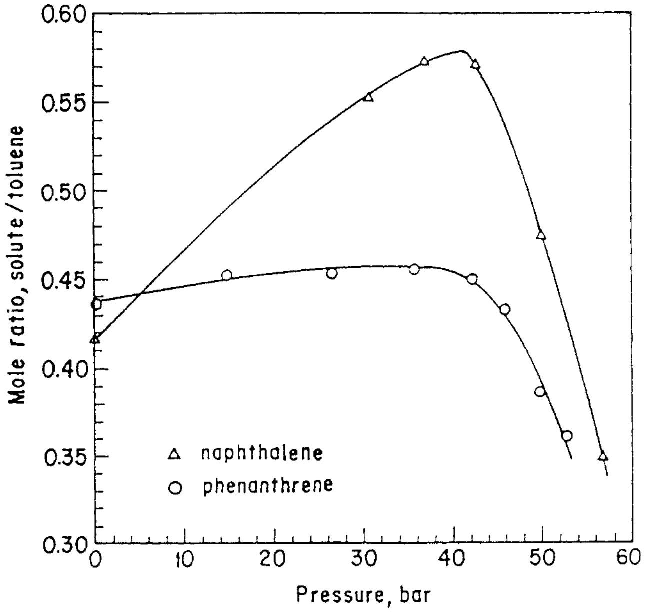

Figure 2. Mole ratio of solute/toluene in a saturated solution pressurized with carbon dioxide.

From Dixon and Johnston (1991).

a few by the catastrophic nucleation, metal-organic solutes may precipitate either by the heterogeneous nucleation or by the catastrophic nucleation and organic solutes may precipitate by the heterogeneous nucleation or may not precipitate at all.

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