Solid Phases and Their Solubilities in the System Na_2CO_3 + $NaHCO_3$ + Ethylene Glycol + Water from (50 to 90) °C

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Solubilities in the system sodium carbonate + sodium bicarbonate were measured over a range of temperatures from (50 to 90) °C in mixed aqueous solvents containing (50 to 100) mass % (salt-free solvent) ethylene glycol. Mixtures of solid sodium carbonate anhydrate ($Na_2CO_3(s)$) and solid sodium bicarbonate ($NaHCO_3(s)$) in different ratios and also trona ($Na_2CO_3{\cdot}NaHCO_3{\cdot}2H_2O(s)$) were allowed to recrystallize and equilibrate with the mixed solvents at the given temperatures. The solubility of CO_3^{2-} was generally found to decrease with increasing ethylene glycol content irrespective of the occurring solid phase, while HCO_3^- solubility displayed a minimum at (80 to 90) mass % (salt-free solvent) ethylene glycol and then increased sharply. For pure carbonate phases, CO_3^{2-} solubility displayed little temperature dependence. In equilibrium with mixed carbonate−bicarbonate phases, the CO_3^{2-} solubility usually decreased with temperature, most likely because it was linked to the HCO_3^- concentration via the solid's solubility product. The solubility of HCO_3^- increased significantly with temperature for all sodium bicarbonate containing solid phases. For the temperature range from (30 to 90) °C and an ethylene glycol concentration range of (50 to 100) mass % (of salt-free solvent), the CO_3^{2-} solubility varied between (0.058 and 1.023) mol/kg solution, and the HCO_3^- solubility concentration ranged between 0.000 (i.e. the lower detection limit of the analytical method) and 1.153 mol/kg solution. The occurring solid phases were the same as those formed in the aqueous system. They were identified in the recrystallization experiments as sodium carbonate anhydrate ($Na_2CO_3(s)$), sodium carbonate monohydrate ($Na_2CO_3{\cdot}H_2O(s)$), trona ($Na_2CO_3{\cdot}NaHCO_3{\cdot}2H_2O(s)$), wegscheiderite ($Na_2CO_3{\cdot}3NaHCO_3(s)$), and sodium bicarbonate ($NaHCO_3(s)$). No solvate phases with ethylene glycol were observed.

Introduction

Dealing with any kind of electrolyte system in academic research or industrial application requires detailed knowledge of the species occurring in the system, both in the solution as well as in the solid phases. Aqueous systems are reasonably well documented and understood. A variety of electrolyte models, like Chen/Electro-NRTL,[1−3] Pitzer[4−6] or Helgeson,[7,8] can be used to describe speciation, phase stability, and solubility. Organic or even mixed solvent systems are much less well understood, partly because detailed solubility and solid-phase stability data are lacking in most cases. But given extensive mixed solvent solubility and phase stability data, the cited aqueous electrolyte models can already be extended to include mixed solvent systems.

For example, Koo et al.[9,10] were able to parametrize and model the solubility of the compound L-ornithine + L-aspartate (LOLA) in water + methanol mixed solvents with the Chen model, which is based on the NRTL model and simple Debye−Hückel interactions, based on their detailed solubility and phase data.

Work by Pitzer[4] shows that the ionic interactions in a concentrated aqueous solution of Na_2CO_3 + $NaHCO_3$ are far more complex than those predicted by the Debye−Hückel theory, and only limited mixed solvent solubility and solid-phase stability data of this important salt system are available in the current literature.[11,12]

The aim of this work is to provide solubility and phase stability data of the system Na_2CO_3 + $NaHCO_3$ + H_2O + ethylene glycol.

The System Na_2CO_3 + $NaHCO_3$ + H_2O

The actual solubility concentration of a solute depends not only on the ability of the solvent to solvate the solute but also on the solid phase of the solute. Most substances can form more than one solid phase, either as polymorphs, pseudopolymorphs (e.g. hydrates), mixed solid phases, solid solutions, or amorphous solids. The stable solid phase, that is, the one with the minimal solubility, determines the solubility concentration.

Four solid phases are known for the aqueous system of sodium carbonate:

The anhydrate ($Na_2CO_3(s)$, natrite) and three hydrate phases: monohydrate ($Na_2CO_3{\cdot}H_2O(s)$, thermonatrite), heptahydrate ($Na_2CO_3{\cdot}7H_2O(s)$), and decahydrate ($Na_2CO_3{\cdot}10H_2O(s)$, natron). Each of these hydrate phases is stable in a specific range of temperature, carbonate (CO_3^{2-}) concentration, and bicarbonate (HCO_3^-) concentration.[13−16] The anhydrate does not form from its pure aqueous solution at atmospheric pressure, since it is only stable above 109 °C, which is above the normal boiling point of the pure saturated sodium carbonate solution of 104.9 °C.[13−15]

In the system Na + CO_3 + HCO_3, three additional phases are found:

The pure sodium bicarbonate ($NaHCO_3(s)$, nahcolite), and two mixed phases, sodium sesquicarbonate ($Na_2CO_3{\cdot}NaHCO_3{\cdot}2H_2O$, trona) and sodium carbonate tri-bicarbon-

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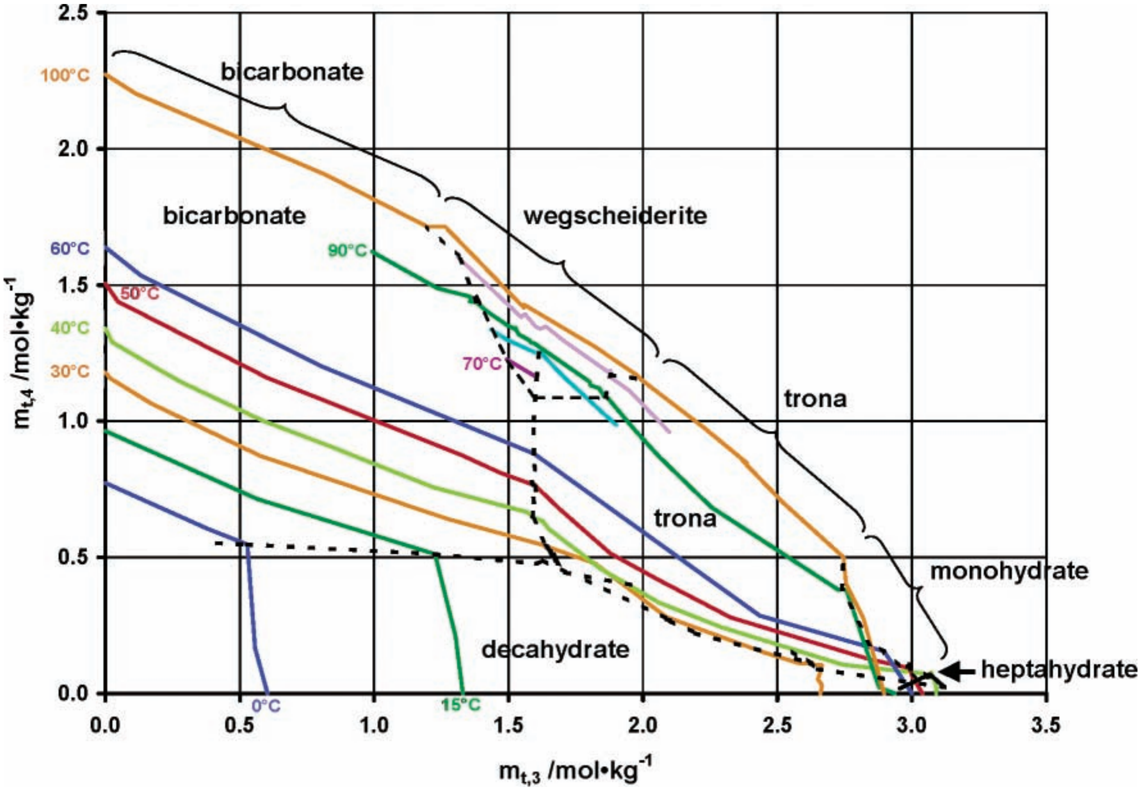

Figure 1. Phase stability and solubility chart for the system Na_2CO_3 (3) + $NaHCO_3$ (4) + H_2O (2) from (0 to 100) °C, derived from literature solubility data.[13−20] Two-phase lines are depicted as broken black curves, and solubility isotherms are represented by the colored lines.

ate (Na_2CO_3·$3NaHCO_3$(s), wegscheiderite or decimite). Again, each of these phases is stable in a specific temperature, carbonate concentration, and bicarbonate concentration range. The stability ranges of these solid phases were first documented by Wegscheider et al.[17] and extended by Hill et al.[18,19] Extensive phase stability and solubility charts of the system are given by Garret.[20]

The phase stability chart of Figure 1 was constructed from solubility data from the listed sources.[13−20] Solubility is given as m_t, that is, moles per kilogram of solution (i.e. solvents + solutes), in all figures and tables throughout this article. The unbroken, colored lines represent solubilities of the system at a given temperature, that is, the solubility isotherms. The dotted, black lines indicate conditions of temperature and composition, where the solution is in equilibrium with two solid phases, that is, the two-phase lines. The areas between the two-phase lines outline the ranges of composition and temperature in which a specific solid phase is stable in contact with the solution, that is, the stability range of a solid phase. The phase stability ranges of monohydrate and anhydrate could not be outlined as clearly as those of the other phases, since they overlap with the ranges of other phases at lower temperatures. Generally, the almost vertical part of each solubility isotherm in Figure 1 is the solubility line of either monohydrate or anhydrate. They can be distinguished by the fact that monohydrate is only stable up to 109 °C. Therefore, all isotherms of higher temperature represent the solubility of the anhydrate.

Limited data on the solubilities and phase stabilities of sodium carbonate in mixed solvents of ethanol + water, propan-1-ol + water, 2-propanol + water, isobutanol + water, allyl alcohol + water, glycerol + water, pyridine + water, and 2-picoline + water and of aliphatic amines in water can be found in ref 12.

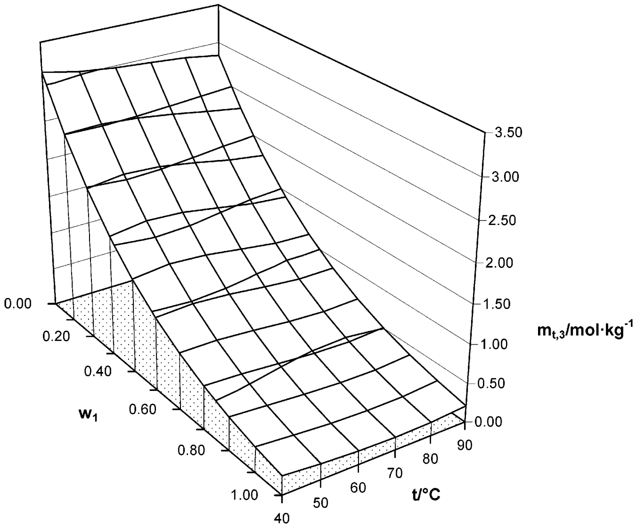

Figure 2. Na_2CO_3 (3) solubility of sodium carbonate anhydrate (Na_2CO_3(s)) and monohydrate (Na_2CO_3·H_2O(s)) in ethylene glycol (1) + water (2), derived from solubility data by Oosterhof et al.;[11] see Table 2. w_1 is the mass fraction of ethylene glycol in the salt-free solvent.

The solubilities and stabilities of sodium carbonate anhydrate and monohydrate in (0 to 100) mass % (salt-free) mixed solvents of ethylene glycol, di-ethylene glycol, glycerol, and 1,2-propanediol in a temperature range from (40 to 90) °C were measured by Oosterhof et al.[11] These solubilities and phase stabilities in ethylene glycol are reproduced in Figure 2 and Table 2.

The mixed solvent ethylene glycol + water has special technical relevance for the salt system Na_2CO_3 + $NaHCO_3$, because ethylene glycol has been shown by Oosterhof et al.[11,21] to be a particularly suitable antisolvent for the

Table 1. Solubility Concentrations of Nahcolite ($NaHCO_3(s)$) in Ethylene Glycol (1) + Water (2) in Moles per Kilogram of Solution (m_t) (Temperature Averaged), Solution Densities ($\rho_{solution}$), and Their Standard Deviations (s_m and s_ρ)[a]

	solubility concentration of sodium bicarbonate ($NaHCO_3$ (4)), $m_{t,4}$/mol·kg^{-1}					
t/°C	$w_1 = 0.50$	$w_1 = 0.60$	$w_1 = 0.70$	$w_1 = 0.80$	$w_1 = 0.90$	$w_1 = 1.00$
15	0.5450	0.4651	0.3971	0.4042	0.4883	1.1315
s_m/mol·kg^{-1}:	± 0.0875	± 0.0126	± 0.0024	± 0.0288	± 0.0130	± 0.1305
20	*0.5590*	*0.4597*	*0.4040*	*0.3956*	*0.4701*	*0.8998*
30	*0.5944*	*0.4706*	*0.4238*	*0.3956*	*0.4484*	*0.7896*
40	*0.6414*	*0.5072*	*0.4526*	*0.4153*	*0.4452*	*0.7358*
50	0.7002	0.5657	0.4904	0.4487	0.4640	0.7483
s_m/mol·kg^{-1}:	± 0.0036	± 0.0016	± 0.0020	± 0.0003	± 0.0016	± 0.0044
60	0.7863	0.6425	0.5452	0.5040	0.4808	0.7383
s_m/mol·kg^{-1}:	± 0.0026	± 0.0004	±0.0009	±0.0125	±0.0070	±0.0328
70	0.8812	0.7254	0.6043	0.5560	0.5378	0.9061
s_m/mol·kg^{-1}:	±0.0010	±0.0072	±0.0030	±0.0068	±0.0016	±0.0350
80	1.0004	0.8221	0.6903	0.6137	0.5939	1.0207
s_m/mol·kg^{-1}:	± 0.0062	±0.0075	±0.0006	±0.0051	±0.0065	±0.0072
90	1.1527	0.9219	0.7820	0.6829	0.6621	1.1361
s_m/mol·kg^{-1}:	±0.0070	±0.0182	±0.0023	±0.0045	±0.0137	±0.0247
$\rho_{solution}$/g·cm^{-3}	1.074	1.075	1.098	1.096	1.106	1.131
s_ρ/g·cm^{-3}:	±0.044	±0.026	±0.025	±0.023	±0.005	±0.017

[a] w_1 is the mass fraction of ethylene glycol in the salt-free solvent. Values in *italics* were obtained by interpolation of the measured data points.

Table 2. Solubility of Na_2CO_3 Anhydrate (A) and Monohydrate (M) in Ethylene Glycol (1) + Water (2) in Moles Per kg Solution (mt), Calculated from Solubility Functions Given by Oosterhof et al.[11] [a]

	solubility concentration of sodium carbonate (Na_2CO_3 (3)), $m_{t,3}$/mol·kg^{-1}										
t/°C	$w_1 = 0.00$	$w_1 = 0.10$	$w_1 = 0.20$	$w_1 = 0.30$	$w_1 = 0.40$	$w_1 = 0.50$	$w_1 = 0.60$	$w_1 = 0.70$	$w_1 = 0.80$	$w_1 = 0.90$	$w_1 = 1.00$
40	3.12^{M}	2.50^{M}	1.99^{M}	1.57^{M}	1.23^{M}	0.96^{M}	0.74^{M}	0.57^{M}	0.43^{M}	0.32	0.24^{A}
50	*3.03^{M}*	*2.52^{M}*	*2.05^{M}*	*1.64^{M}*	*1.28^{M}*	*0.98^{M}*	*0.74^{M}*	*0.55^{M}*	*0.40^{M}*	*0.29*	*0.20^{A}*
60	*2.98^{M}*	*2.48^{M}*	*2.02^{M}*	*1.61^{M}*	*1.26^{M}*	*0.95^{M}*	*0.71^{M}*	*0.52^{M}*	*0.37^{M}*	*0.26^{A}*	*0.17^{A}*
70	2.94^{M}	2.42^{M}	1.95^{M}	1.54^{M}	1.19^{M}	0.90^{M}	0.67^{M}	0.49^{M}	0.35^{A}	0.24^{A}	0.16^{A}
80	2.90^{M}	2.34^{M}	1.87^{M}	1.46^{M}	1.13^{M}	0.86^{M}	0.64^{M}	0.48^{A}	0.35^{A}	0.25^{A}	0.18^{A}
90	2.83^{M}	2.27^{M}	1.81^{M}	1.42^{M}	1.11^{M}	0.86^{M}	0.66^{A}	0.50^{A}	0.38^{A}	0.28^{A}	0.21^{A}

[a] w_1 is the mass fraction of ethylene glycol in the salt-free solvent. Values in italics were obtained by interpolation of the measured data points.

crystallization of soda (sodium carbonate anhydrate). Its impact on the crystal growth of soda is small compared to those of other organic solvents, and the hydroscopic nature of ethylene glycol[22] makes it an effective antisolvent, because of its tendency to bind the water in solution.

Experimental Section

The phase stabilities and corresponding solubilities at a range of temperatures and mixed solvent compositions were determined with the following experimental procedure: Approximately 15 g of solid and 40 g of mixed solvent were shaken in 50 mL Nalgene PTFE bottles in a thermostated shaking bath. Mixed solvents with ethylene glycol contents of (50, 60, 70, 80, 90, and 100) mass % (salt-free), prepared by mass from technical grade ethylene glycol and ultrapure water, were used. The solids added to the mixed solvent mixture were (1) $NaHCO_3(s)$ of technical grade (purity > 99.5 mass %, obtained from Boom, The Netherlands), (2) a mixture of $Na_2CO_3(s)$ (Brunnermond, The Netherlands) and $NaHCO_3(s)$ (Boom, The Netherlands), both of technical grade (purity > 99.5 mass %), in a molar ratio of 1:3, (3) a mixture of $Na_2CO_3(s)$ and $NaHCO_3(s)$, both of technical grade (purity > 99.5 wt %, see above), in a molar ratio of 3:1, and (4) trona, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O(s)$ (purity > 99.8 mass %, obtained from Solvay, France). The bottles were shaken at a constant temperature of 50 °C for at least 24 h. Previous recrystallization experiments[23] had shown that this period of time was sufficient to reach the equilibrium state of the system. The temperature was increased every 24 h after sampling by 10 K to 90 °C. In some of the experiments, the system was then cooled for 1 day to room temperature (~15 °C) or 30 °C. All samples were prepared in duplicate to test for reproducibility.

It had been found in previous work[24] that solid bicarbonate recrystallized at temperatures > 90 °C in the mixed solvent due to thermal decomposition of the dissolved bicarbonate. Since this thermal decomposition significantly impaired the determination of the solubilities of the bicarbonate containing solid phases, temperatures above 90 °C were not investigated.

Solution samples were taken after each shaking period of 24 h and titrated with 0.1 M HCl (Merck Titriplex) in a Radiometer VIT 90 Video Titrator. The concentrations of CO_3^{2-} and HCO_3^- were determined from the titration curves. The experimental error of the method and the titration equipment was checked every 24 h period prior to the titrations of the solubility samples by titration of calibration samples of known carbonate and bicarbonate content. The uncertainty of the titration was found to be generally in the range (0.5 to 2.5)% of the measured concentration. All titrations were performed in triplicate, and the amount of sample was chosen for a required titrant volume > 5 mL (0.1 M HCl) to achieve good resolution of the titration curve. The solubility data points given in Tables 1 and 3−5 are the mean values of the results of the triplicate titrations of the duplicate samples (i.e. from six measured values). The given standard deviations s_m were calculated from these six measured values and reflect the reliability of each solubility data point.

These standard deviations reflect not only the uncertainty of the titration method but also the experimental reproducibility of the respective data point. For example, for pure ethylene glycol, the reproducibility of the HCO_3^- concentrations is below average: The measured values deviate by 10% or more. The HCO_3^- solubility concentration increases rapidly from its minimum at (80 to 90) mass

% ethylene glycol (salt-free) to its high level in 100 mass % (salt-free) ethylene glycol; see Figure 5. Small amounts of condensing water vapor from the shaking bath might have entered the sample bottles with the pure ethylene glycol solvent, adding water to the solvent. The resulting decrease in HCO_3^- solubility concentration then resulted in these larger standard deviations.

The solid phases were identified from (polarized) light microscopy and SEM images. In cases of doubt, samples were also analyzed by powder XRD. Additionally, the mass loss upon heating (at 200 °C) of the solid was determined after completion of the experimental series. No significant decomposition of either dissolved or solid bicarbonate was found below 90 °C in the mass balances of the dissolved and solid bicarbonate contents in the samples measured at the end of the experimental procedure.

The solution densities given in the tables were obtained by pipetting a known volume of solution and weighing it. No significant temperature dependence of the density was found: The error of the analytical method was estimated to be up to 5% of the measured value, which was in most cases larger than the noted standard deviation s_ρ of the temperature averaged mean density ρ_{solution} given in the tables.

Table 2 lists data points calculated from solubility functions published by Oosterhof et al.[11] for sodium carbonate in ethylene glycol + water. These functions were derived as second order polynomial fits to their solubility data with correlation coefficients (R^2) of at least 99.2%. The data points for (50 and 60) °C were extrapolated by fourth-order polynomial fits to the derived data points, because Oosterhof et al.[11] did not measure solubilities at these temperatures. An overview of the solubility results by Oosterhof et al.[11] is given in Figure 2.

In addition to the measured solubilities, solubility points were interpolated between 50 °C and room temperature. To distinguish these estimated points from the measured data, these points are rendered in *italics* and no error range is given for them; see Tables 1−3. They were obtained from polynomial fits of at least fourth order with a correlation coefficient (R^2) of at least 99.9% to the measured data points in the range from (15 to 90) °C. They are only intended to give an impression of the development of the presented data sets. The polynomial fits were checked visually, to ensure that they would properly reproduce the developments of the solubilities found in the measured data points. Although the developments of the so extrapolated solubility lines were steady in these regions, these points might not represent the actual solubilities.

Results

Measured Solubilities in the Mixed Solvent. The measured solubilities and the corresponding solid phases are listed in Tables 1 and 3−5. The solubilities of the pure $NaHCO_3$ system and of the pure Na_2CO_3 system in the mixed solvent are listed in Tables 1 and 2 and displayed graphically in Figures 3 and 4.

The concentration of dissolved Na_2CO_3, that is, in equilibrium with either anhydrate or monohydrate as solid (see Figure 3 or Table 2), decreased strongly with increasing ethylene glycol concentration but showed little dependence on temperature.

The solubility of sodium bicarbonate ($NaHCO_3$(s), nahcolite) showed a comparatively slower decline with increasing ethylene glycol content, reached a minimum around (80 to 90) mass % ethylene glycol, and then sharply increased again toward pure ethylene glycol; see Figure 4.

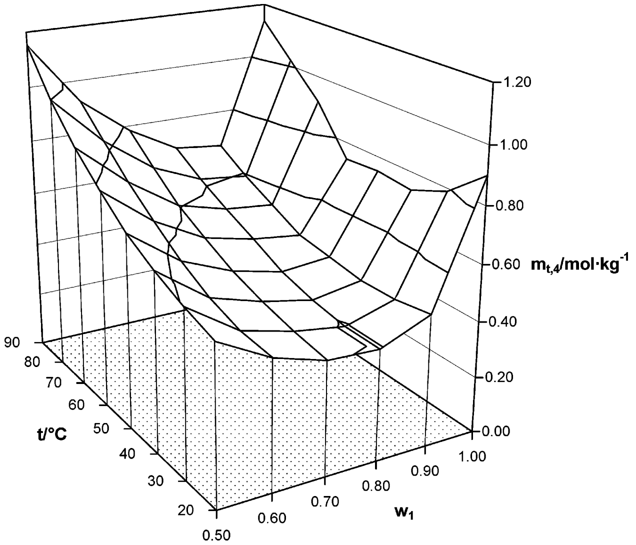

Figure 3. $NaHCO_3$ (4) solubility of sodium bicarbonate ($NaHCO_3$-(s), nahcolite) in ethylene glycol (1) + water (2). w_1 is the mass fraction of ethylene glycol in the salt-free solvent.

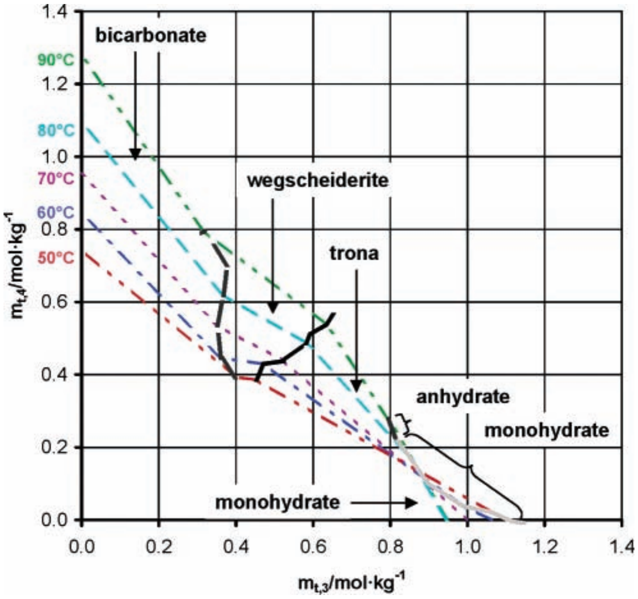

Figure 4. Phase stability and solubility chart for Na_2CO_3 (3) + $NaHCO_3$ (4) in 50 mass % (salt-free) ethylene glycol mixed solvent. Two-phase lines are indicated by black and gray curves, and solubility isotherms for (50 to 90) °C are represented by the colored, broken lines.

Unlike the solubility concentration of Na_2CO_3 in Figure 4, the solubility of sodium bicarbonate showed strong temperature dependency and increased with increasing temperature for most bicarbonate containing solid phases; see Tables 3−5. In mixed solvents of (50 to 90) mass % ethylene glycol content, the solubility concentration more than doubled from (20 to 90) °C. For (90 and 100) mass % ethylene glycol, there was a solubility minimum around (40 to 50) °C.

The high solubility of sodium bicarbonate in pure ethylene glycol can probably be explained by the presence of soluble complexes of ethylene glycol with the HCO_3^- ion or with neutral, dissolved but undissociated $NaHCO_3$. Small amounts of water apparently break up these complexes and act as an antisolvent in this case. Most likely, the water, with its higher capability for hydrogen bonding, replaces the HCO_3^- at the complex-forming bonding sites of the ethylene glycol. The uncomplexed HCO_3^- ion and

Table 3. Solubility Concentrations of Na_2CO_3 and $NaHCO_3$ Anhydrate (A), Monohydrate (M), Trona (T), and Wegscheiderite (W), Forming from a Starting Solid Composition Ratio of $Na_2CO_3(s)/NaHCO_3(s)$ of 3:1 (mol), in Ethylene Glycol (1) + Water (2) in Moles per Kilogram of Solution (m_t) (Temperature Averaged), Solution Densities (ρ_{solution}), and Their Standard Deviations (s_m and s_ρ)[a]

	solubility concentration of sodium carbonate (Na_2CO_3 (3)), $m_{t,3}$/mol·kg^{-1}					
t/°C	$w_1 = 0.50$	$w_1 = 0.60$	$w_1 = 0.70$	$w_1 = 0.80$	$w_1 = 0.90$	$w_1 = 1.00$
30	1.0230	0.7296	0.5395	0.4950	0.3792	0.2308
s_m/mol·kg^{-1}:	±0.0017	±0.0322	±0.0237	±0.0411	±0.0072	±0.0225
40	*0.9971*	*0.7117*	*0.5231*	$0.4335^{\mathrm{A,T}}$	$0.3393^{\mathrm{A,T}}$	0.3120^{A}
s_m/mol·kg^{-1}:				±0.0021	±0.0018	±0.0100
50	$0.9535^{\mathrm{M,T}}$	$0.6710^{\mathrm{M,T}}$	$0.4905^{\mathrm{M,T}}$	$0.3821^{\mathrm{A,T}}$	$0.2615^{\mathrm{A,W}}$	$0.2387^{\mathrm{A,W}}$
s_m/mol·kg^{-1}:	±0.0087	±0.0005	±0.0088	±0.0060	±0.0012	±0.0379
60	$0.8951^{\mathrm{M,T}}$	$0.6195^{\mathrm{M,T}}$	$0.4451^{\mathrm{A,T}}$	$0.3235^{\mathrm{A,T}}$	$0.2119^{\mathrm{A,W}}$	$0.1464^{\mathrm{A,W}}$
s_m/mol·kg^{-1}:	±0.0038	±0.0031	±0.0081	±0.0099	±0.0006	±0.0179
70	$0.8187^{\mathrm{M,T}}$	$0.5653^{\mathrm{M,T}}$	$0.3901^{\mathrm{A,T}}$	$0.2568^{\mathrm{A,T}}$	$0.1692^{\mathrm{A,W}}$	0.1074^{A}
s_m/mol·kg^{-1}:	±0.0300	±0.0094	±0.0015	±0.0025	±0.0027	± 0.0196
80	$0.7735^{\mathrm{M,T}}$	$0.5159^{\mathrm{A,T}}$	0.3578^{A}	$0.2224^{\mathrm{A,W}}$	$0.1366^{\mathrm{A,W}}$	$0.0726^{\mathrm{A,W}}$
s_m/mol·kg^{-1}:	±0.0100	±0.0018	±0.0135	±0.0037	±0.0053	±0.0049
89.8	$0.7336^{\mathrm{A,T}}$	$0.5314^{\mathrm{A,T}}$	$0.3099^{\mathrm{A,W}}$	$0.2084^{\mathrm{A,W}}$	$0.1120^{\mathrm{A,W}}$	$0.0672^{\mathrm{A,W}}$
s_m/mol·kg^{-1}:	±0.0125	±0.0713	±0.0119	±0.0074	±0.0005	±0.0077

	solubility concentration of sodium bicarbonate ($NaHCO_3$ (4)), $m_{t,4}$/mol·kg^{-1}					
t/°C	0.50		0.70		0.90	$w_1 = 1.00$
30	0.0000	0.0000	0.0000	0.0000	0.0696	0.3884
s_m/mol·kg^{-1}:	±0.0070	±0.0143	±0.0106	±0.0211	±0.0027	±0.0729
40	*0.0000*	*0.0146*	*0.0199*	$0.0134^{\mathrm{A,T}}$	$0.0895^{\mathrm{A,T}}$	0.0886^{A}
s_m/mol·kg^{-1}:				±0.0050	±0.0091	±0.0411
50	$0.0215^{\mathrm{M,T}}$	$0.0327^{\mathrm{M,T}}$	$0.0391^{\mathrm{M,T}}$	$0.0491^{\mathrm{A,T}}$	$0.1611^{\mathrm{A,W}}$	$0.1732^{\mathrm{A,W}}$
s_m/mol·kg^{-1}:	±0.0155	±0.0029	±0.0010	±0.0069	±0.0045	±0.0407
60	$0.0374^{\mathrm{M,T}}$	$0.0578^{\mathrm{M,T}}$	$0.0714^{\mathrm{A,T}}$	$0.1187^{\mathrm{A,T}}$	$0.2001^{\mathrm{A,W}}$	$0.3626^{\mathrm{A,W}}$
s_m/mol·kg^{-1}:	±0.0082	±0.0076	±0.0088	±0.0084	±0.0033	±0.0201
70	$0.1005^{\mathrm{M,T}}$	$0.1161^{\mathrm{M,T}}$	$0.1308^{\mathrm{A,T}}$	$0.2026^{\mathrm{A,T}}$	$0.2493^{\mathrm{A,W}}$	0.4233^{A}
s_m/mol·kg^{-1}:	±0.0038	±0.0094	±0.0057	±0.0030	±0.0031	±0.0181
80	$0.1817^{\mathrm{M,T}}$	$0.1790^{\mathrm{A,T}}$	0.1908^{A}	$0.2745^{\mathrm{A,W}}$	$0.3024^{\mathrm{A,W}}$	$0.4820^{\mathrm{A,W}}$
s_m/mol·kg^{-1}:	±0.0121	±0.0079	±0.0234	±0.0248	±0.0227	±0.0050
89.8	$0.2712^{\mathrm{A,T}}$	$0.3072^{\mathrm{A,T}}$	$0.3385^{\mathrm{A,W}}$	$0.3330^{\mathrm{A,W}}$	$0.3522^{\mathrm{A,W}}$	$0.5379^{\mathrm{A,W}}$
s_m/mol·kg^{-1}:	±0.0003	±0.0628	±0.0175	±0.0074	±0.0128	±0.0097
ρ_{solution}/g·cm^{-3}	1.108	1.133	1.134	1.113	1.116	1.134
s_ρ/g·cm^{-3}	±0.044	±0.041	±0.022	±0.017	±0.027	±0.028

[a] w_1 is the mass fraction of ethylene glycol in the salt-free solvent. Values in italics were obtained by interpolation of the measured data points.

$NaHCO_3$(sol) are less soluble in the comparatively unpolar ethylene glycol, because both are rather polar species. The less polar glycol is rather attracted to other glycol molecules or water molecules.

A steady increase of HCO_3^- solubility concentration at water contents from (70 to 0) mass % (salt-free solvent) ethylene glycol was observed. This could be explained by the formation of hydration hulls, which distribute the ion's charge over the molecules participating in them, reducing long-range ion interactions.

Phase Stabilities in the Mixed Solvent System. As can be seen from Tables 1−5, the different starting solid compositions resulted in the formation of different solid phases after equilibration. The following solid phases were identified by microscopy, heating weight loss analysis, and powder XRD: trona (T), wegscheiderite (W), sodium bicarbonate (B), sodium carbonate anhydrate (A), and sodium carbonate monohydrate (M). The solid phase analysis gave no indication for any further solid phases, and the measured solubilities can be adequately explained by the occurrence of the given phases. No solid solvate phases with ethylene glycol were formed in the investigated temperature and concentration range.

Solubility and phase stability diagrams for (50, 70, and 90) mass % (salt-free) ethylene glycol mixed solvent are given in Figures 4, 6, and 7. Generally, the solid phases occurred in the same sequence as in the aqueous system: From HCO_3^--rich solutions, sodium bicarbonate (nahcolite) was formed. With increasing CO_3^{2-} concentration, first wegscheiderite, then trona, and finally sodium carbonate monohydrate or anhydrate became the stable phase of the system. The broken, colored lines indicate the solubility isotherms, while the unbroken, black and gray lines mark two-phase lines over the investigated temperature range.

Most measured data points correspond to such two-phase lines, as a sufficient amount of solid Na_2CO_3 as well as solid $NaHCO_3$ was present in most experiments to form more than one solid phase. The depicted solubility isotherms are lines between the measured data points. Therefore, they are only approximations of the actual solubilities. It is likely that the actual solubility isotherms have a more hyperbolic shape, due to their dependency on the thermodynamic solubility products of the occurring solid phases:

$$K_{\mathrm{sp},xyz} = a_{\mathrm{Na_2CO_3}}{}^{x} a_{\mathrm{NaHCO_3}}{}^{y} a_{\mathrm{H_2O}}{}^{z} = \gamma_{\mathrm{Na_2CO_3}}{}^{x} m_{\mathrm{Na_2CO_3}}{}^{x} \gamma_{\mathrm{NaHCO_3}}{}^{y} m_{\mathrm{NaHCO_3}}{}^{y} a_{\mathrm{H_2O}}{}^{z} \quad (1)$$

$$m_{\mathrm{NaHCO_3}} = \sqrt[y]{\frac{K_{\mathrm{sp},xyz}}{\gamma_{\mathrm{NaHCO_3}}{}^{y} \gamma_{\mathrm{Na_2CO_3}}{}^{x} m_{\mathrm{Na_2CO_3}}{}^{x} m_{\mathrm{H_2O}}{}^{z}}} \quad (2)$$

$$m_{\mathrm{NaHCO_3}} \propto \left(\frac{1}{m_{\mathrm{Na_2CO_3}}}\right)^{x/y} \quad (3)$$

In eqs 1−3, x, y, and z represent the stoichiometric coefficients of Na_2CO_3, $NaHCO_3$, and water in the given

Table 4. Solubility Concentrations of Na_2CO_3 and $NaHCO_3$ Anhydrate (A), Wegscheiderite (W), Trona (T), and Nahcolite ($NaHCO_3(s)$, B), Forming from a Starting Solid Composition Ratio of $Na_2CO_3(s)/NaHCO_3(s)$ of 1:3 (mole), in Ethylene Glycol (1) + Water (2) in Moles per Kilogram of Solution (m_t) (Temperature Averaged), Solution Densities ($\rho_{solution}$), and Their Standard Deviations (s_m and s_ρ)[a]

	solubility concentration of sodium carbonate (Na_2CO_3 (3)), $m_{t,3}$/mol·kg^{-1}					
t/°C	$w_1 = 0.50$	$w_1 = 0.60$	$w_1 = 0.70$	$w_1 = 0.80$	$w_1 = 0.90$	1.00
30	$0.3833^{W,B}$	$0.2272^{W,T}$	0.1623	$0.0676^{W,B}$	0.0575^{W}	$0.1369^{A,B}$
s_m/mol·kg^{-1}:	±0.0198	±0.0031	±0.0230	±0.0015	±0.0062	±0.0003
50	$0.3482^{W,B}$	$0.2431^{W,B}$	$0.1714^{W,B}$	$0.1476^{W,B}$	$0.2097^{W,T}$	$0.1682^{A,B}$
s_m/mol·kg^{-1}:	±0.0043	±0.0024	±0.0061	±0.0022	±0.0017	±0.0044
60	$0.3392^{W,B}$	$0.2348^{W,B}$	$0.1857^{W,B}$	$0.1361^{W,B}$	0.1107	$0.0998^{A,B}$
s_m/mol·kg^{-1}:	±0.0035	±0.0005	±0.0078	±0.0011	±0.0004	±0.0151
70	$0.3540^{W,B}$	$0.2363^{W,B}$	$0.1873^{W,T}$	0.1414^{W}	0.0706^{W}	$0.0886^{A,B}$
s_m/mol·kg^{-1}:	±0.0036	±0.0017	±0.0014	±0.0072	±0.0060	±0.0108
80	$0.3636^{W,B}$	0.2361^{W}	0.1959^{W}	0.1015^{W}	0.0894^{W}	$0.0731^{A,B}$
s_m/mol·kg^{-1}:	±0.0013	±0.0123	±0.0143	±0.0132	±0.0024	±0.0002
84.8	$0.3077^{W,B}$	$0.2260^{W,B}$	0.1800^{W}	0.0761^{W}	0.0766^{W}	$0.0696^{A,B}$
s_m/mol·kg^{-1}:	±0.0106	±0.0016	±0.0033	±0.0021	±0.0268	±0.0025
89.8	$0.3017^{W,B}$	$0.2002^{W,B}$	$0.1695^{W,B}$	$0.0703^{W,B}$	0.0773^{W}	$0.0673^{A,B}$
s_m/mol·kg^{-1}:	±0.0092	±0.0173	±0.0336	±0.0013	±0.0037	±0.0046

	solubility concentration of sodium bicarbonate ($NaHCO_3$ (4)), $m_{t,4}$/mol·kg^{-1}					
t/°C	$w_1 = 0.50$	$w_1 = 0.60$	$w_1 = 0.70$	$w_1 = 0.80$	$w_1 = 0.90$	$w_1 = 1.00$
30	$0.3802^{W,B}$	$0.3688^{W,T}$	0.3317	$0.4040^{W,B}$	0.4226^{W}	$0.8621^{A,B}$
s_m/mol·kg^{-1}:	±0.0453	±0.0095	±0.0482	±0.0040	±0.0063	±0.0718
50	$0.4299^{W,B}$	$0.3850^{W,B}$	$0.3607^{W,B}$	$0.3320^{W,B}$	$0.1830^{W,T}$	$0.5595^{A,B}$
s_m/mol·kg^{-1}:	±0.0126	±0.0027	±0.0136	±0.0002	±0.0005	±0.0460
60	$0.5125^{W,B}$	$0.4591^{W,B}$	$0.3756^{W,B}$	$0.3384^{W,B}$	0.3287^{W}	$0.7638^{A,B}$
s_m/mol·kg^{-1}:	±0.0130	±0.0042	±0.0207	±0.0029	±0.0259	±0.0273
70	$0.5883^{W,B}$	$0.5329^{W,B}$	$0.4096^{W,T}$	0.3530^{W}	0.3948^{W}	$0.8477^{A,B}$
s_m/mol·kg^{-1}:	±0.0059	±0.0033	±0.0367	±0.0091	±0.0050	±0.0373
80	$0.6627^{W,B}$	0.5577^{W}	0.4102^{W}	0.4301^{W}	0.4148^{W}	$0.8555^{A,B}$
s_m/mol·kg^{-1}:	±0.0239	±0.0164	±0.0172	±0.0005	±0.0176	±0.0134
84.8	$0.7447^{W,B}$	$0.6175^{W,B}$	0.4655^{W}	0.4310^{W}	0.4429^{W}	$0.9946^{A,B}$
s_m/mol·kg^{-1}:	±0.0105	±0.0058	±0.0022	±0.0014	±0.0370	±0.0494
89.8	$0.7403^{W,B}$	$0.5151^{W,B}$	$0.4935^{W,B}$	$0.3626^{W,B}$	0.4257^{W}	$0.9443^{A,B}$
s_m/mol·kg^{-1}:	±0.0157	±0.0248	±0.0490	±0.0263	±0.0022	±0.0190
$\rho_{solution}$/g·cm^{-3}	1.087	1.074	1.105	1.122	1.127	1.137
s_ρ/g·cm^{-3}	±0.024	±0.034	±0.019	±0.028	±0.032	±0.014

[a] w_1 is the mass fraction of ethylene glycol in the salt-free solvent.

solid phase, for example, $x = 1$, $y = 1$, and $z = 2$ for trona: $Na_2CO_3·NaHCO_3·2H_2O$.

In Figure 4, the solubilities of the occurring phases in 50 mass % (salt-free) ethylene glycol from (50 to 90) °C are given. The solubilities of nahcolite, wegscheiderite, and trona increased steadily with temperature, while the solubility of monohydrate decreased with temperature. This resulted in a crossing of solubility isotherms in the trona−monohydrate region. While some anhydrate was formed at 90 °C as second solid in equilibrium with trona, from solutions containing no HCO_3 (i.e. along the x-axis of Figure 4) only the monohydrate is formed; see also Table 2.

In Figure 5, the solubilities of the occurring phases in 70 mass % (salt-free) ethylene glycol from (50 to 90) °C are displayed. Again, the solubilities of bicarbonate (nahcolite), wegscheiderite, and trona increased steadily with temperature, while the solubility of monohydrate decreased with temperature and the solubility of anhydrate increased slightly with temperature. This resulted in a crossing of solubility isotherms in the trona−monohydrate/anhydrate region. In solutions containing no HCO_3 (i.e. along the x-axis of Figure 5), monohydrate is stable till approximately 70 °C, while anhydrate was found at (80 and 90) °C; see also Table 2. The two-phase lines for bicarbonate + wegscheiderite and wegscheiderite + anhydrate are given till 95 °C. For this reason, these lines exceed the 90 °C solubility isotherm.

In Figure 6, the solubilities and stabilities of the occurring phases in 90 mass % (salt-free) ethylene glycol from (50 to 90) °C are plotted. The solubilities of bicarbonate (nahcolite), wegscheiderite, and trona were noticeably less temperature dependent than those at the lower ethylene glycol contents; see Figures 4 and 5. Only anhydrate formed from (50 to 90) °C from solutions containing no HCO_3 (i.e. along the x-axis of Figure 6). The solubility isotherms cross in the region of wegscheiderite, because the solubility of anhydrate decreased from (50 to 70) °C and then increased again from (70 to 90) °C; see Table 2.

Two solubility plots are given in Figure 6, since a significant difference in phase stability between the trona formed during the experiments in mixed solvent solution and the trona obtained from Solvay, France (i.e. formed from aqueous solution), was found. The Solvay trona was stable up to 70 °C, while the mixed solvent formed trona was only stable till 40 °C.

The phase stabilities in 100 mass % ethylene glycol differed significantly from the phase stabilities in the water containing mixed solvents; see Figure 7. The only stable phases observed were sodium bicarbonate (nahcolite), sodium carbonate anhydrate, and wegscheiderite.

Which phases would form depended apparently on the composition of the starting solid of the experiment. Wegscheiderite only formed in the experiments with a starting solid CO_3/HCO_3 ratio of 3:1; see Table 3. In all other cases only bicarbonate and anhydrate would occur. As can be seen in Figure 7, also the two-phase line of bicarbonate + anhydrate differed significantly between experiments. Most probably due to the special mechanism of HCO_3^- solvation in ethylene glycol, the solubility concentrations of CO_3^{2-}

Table 5. Solubility Concentrations of Na_2CO_3 and $NaHCO_3$ Anhydrate (A), Wegscheiderite (W), Trona (T), and Nahcolite ($NaHCO_3$(s), B), Forming from Trona (Solvay, France) as Starting Solid, in Ethylene Glycol (1) + Water (2) in Moles per Kilogram of Solution (m_t) (Temperature Averaged), Solution Densities ($\rho_{solution}$), and Their Standard Deviations (s_m and s_ρ)[a]

	solubility concentration of sodium carbonate (Na_2CO_3 (3)), $m_{t,3}$/mol·kg^{-1}					
t/°C	$w_1 = 0.50$	$w_1 = 0.60$	$w_1 = 0.70$	$w_1 = 0.80$	$w_1 = 0.90$	$w_1 = 1.00$
50	0.4315^{T}	0.3347^{T}	0.1985^{T}	0.1884^{T}	0.1778^{T}	$0.1916^{A, B}$
s_m/mol·kg^{-1}:	±0.0105	±0.0014	±0.0145	±0.0011	±0.0182	±0.0217
60	0.4500^{T}	0.3582^{T}	0.2385^{T}	0.2125^{T}	0.1882^{T}	$0.1415^{A, B}$
s_m/mol·kg^{-1}:	±0.0020	±0.0065	±0.0105	±0.0006	±0.0200	±0.0049
70	0.4961^{T}	0.3934^{T}	0.3125^{T}	0.2687^{T}	$0.1994^{A,W}$	$0.0927^{A, B}$
s_m/mol·kg^{-1}:	±0.0081	±0.0078	±0.0007	±0.0006	±0.0024	±0.0066
80	0.5470^{T}	0.4209^{T}	0.3342^{T}	0.2455^{T}	$0.1629^{A,W}$	$0.0656^{A, B}$
s_m/mol·kg^{-1}:	±0.0169	±0.0032	±0.0027	±0.0013	±0.0090	±0.0124
84.8	0.5581^{T}	0.4506^{T}	0.2950^{T}	$0.2203^{A,W}$	$0.1445^{A,W}$	$0.0714^{A, B}$
s_m/mol·kg^{-1}:	±0.0086	±0.0127	±0.0019	±0.0066	±0.0034	±0.0160
89.8	0.5927^{T}	0.4683^{T}	0.3457^{T}	$0.2208^{A,W}$	$0.1364^{A,W}$	$0.0537^{A, B}$
s_m/mol·kg^{-1}:	±0.0052	±0.0012	±0.0070	±0.0110	±0.0054	±0.0339
93.5	0.6109^{T}	0.4697^{T}	$0.3320^{A,W}$	$0.2134^{A,W}$	$0.1290^{A,W}$	$0.0754^{A, B}$
s_m/mol·kg^{-1}:	±0.0045	±0.0028	±0.0156	±0.0132	±0.0080	±0.0084

	solubility concentration of sodium bicarbonate ($NaHCO_3$ (4)), $m_{t,4}$/mol·kg^{-1}					
t/°C	$w_1 = 0.50$	$w_1 = 0.60$	$w_1 = 0.70$	$w_1 = 0.80$	$w_1 = 0.90$	$w_1 = 1.00$
50	0.3740^{T}	0.2868^{T}	0.1741^{T}	0.1632^{T}	0.1489^{T}	$0.4470^{A, B}$
s_m/mol·kg^{-1}:	±0.0114	±0.0002	±0.0183	±0.0095	±0.0158	±0.0550
60	0.4141^{T}	0.3175^{T}	0.2017^{T}	0.1919^{T}	0.2348^{T}	$0.5382^{A, B}$
s_m/mol·kg^{-1}:	±0.0101	±0.0117	±0.0038	±0.0043	±0.0110	±0.0219
70	0.4224^{T}	0.3247^{T}	0.2544^{T}	0.2145^{T}	$0.2576^{A,W}$	$0.5972^{A, B}$
s_m/mol·kg^{-1}:	±0.0035	±0.0131	±0.0001	±0.0011	±0.0119	±0.0320
80	0.4683^{T}	0.3652^{T}	0.2784^{T}	0.2812^{T}	$0.2918^{A,W}$	$0.7009^{A, B}$
s_m/mol·kg^{-1}:	±0.0054	±0.0047	±0.0068	±0.0020	±0.0099	±0.1029
84.8	0.4885^{T}	0.3582^{T}	0.2648^{T}	$0.2935^{A,W}$	$0.3258^{A,W}$	$0.6069^{A, B}$
s_m/mol·kg^{-1}:	±0.0089	±0.0042	±0.0098	±0.0006	±0.0027	±0.1868
89.8	0.5156^{T}	0.3797^{T}	0.3304^{T}	$0.3336^{A,W}$	$0.3377^{A,W}$	$0.7792^{A, B}$
s_m/mol·kg^{-1}:	±0.0072	±0.0007	±0.0065	±0.0033	±0.0006	±0.2342
93.5	0.5380^{T}	0.3964^{T}	$0.3820^{A,W}$	$0.3502^{A,W}$	$0.3593^{A,W}$	$0.8612^{A, B}$
s_m/mol·kg^{-1}:	±0.0284	±0.0106	±0.0128	±0.0081	±0.0010	±0.0198
$\rho_{solution}$/g·cm^{-3}	1.036	1.058	1.083	1.081	1.094	1.128
s_ρ/g·cm^{-3}	±0.049	±0.057	±0.040	±0.023	±0.018	±0.027

[a] w_1 is the mass fraction of ethylene glycol in the salt-free solvent.

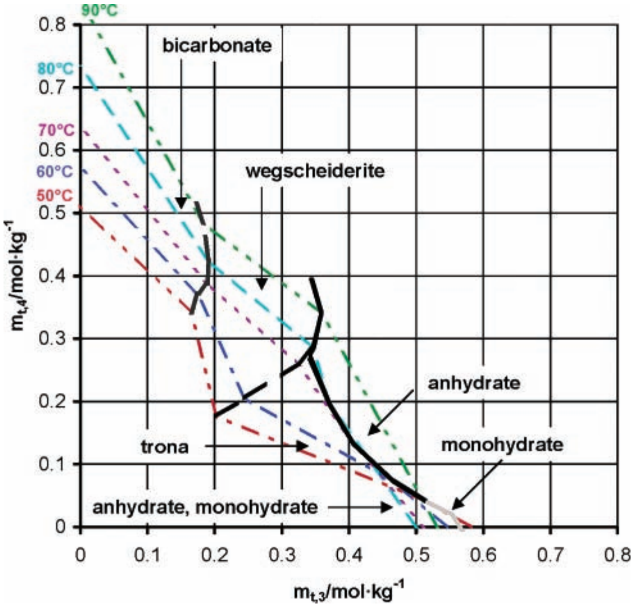

Figure 5. Phase stability and solubility chart for Na_2CO_3 (3) + $NaHCO_3$ (4) in 70 mass % (salt-free) ethylene glycol mixed solvent. Two-phase lines are indicated by black and gray curves, and solubility isotherms for (50 to 90) °C are represented by the colored, broken lines.

and HCO_3^- were not very stable and were apparently easily shifted by outside influences. The three-phase point of wegscheiderite, anhydrate, and bicarbonate at 50 °C is rather surprising, not only due to the occurrence of all three phases outside the observed stability range of wegscheiderite but also due to the high solubility concentrations of CO_3^{2-} and HCO_3^-. It is possible that this point reflects a metastable state, with the system still in the process of recrystallization from bicarbonate to wegscheiderite.

The crystals of wegscheiderite and anhydrate formed in pure ethylene glycol were small (<10 μm), while bicarbonate could form crystals of significantly larger size (up to 50 μm). Due to the low solubility of anhydrate and wegscheiderite, these phases would grow only slowly and the recrystallization was dominated by nucleation.

For the development of the solubilities and phase stabilities with increasing ethylene glycol content, the following effects were observed:

While wegscheiderite only occurred at temperatures above 70 °C in the aqueous system (see Figure 1), it was already found at 50 °C in 50 mass % (salt-free solvent) ethylene glycol. It appears that, for higher ethylene glycol concentrations, wegscheiderite might occur at even lower temperatures.

Also of significance was the fact that, while anhydrate was not a stable phase in aqueous solution, it was a stable phase in 50 mass % (salt-free solvent) ethylene glycol at 80 °C or higher; see Figure 4.

At higher ethylene glycol concentrations, anhydrate formed at even lower temperatures, effectively replacing monohydrate, trona, and even wegscheiderite. In 70 mass

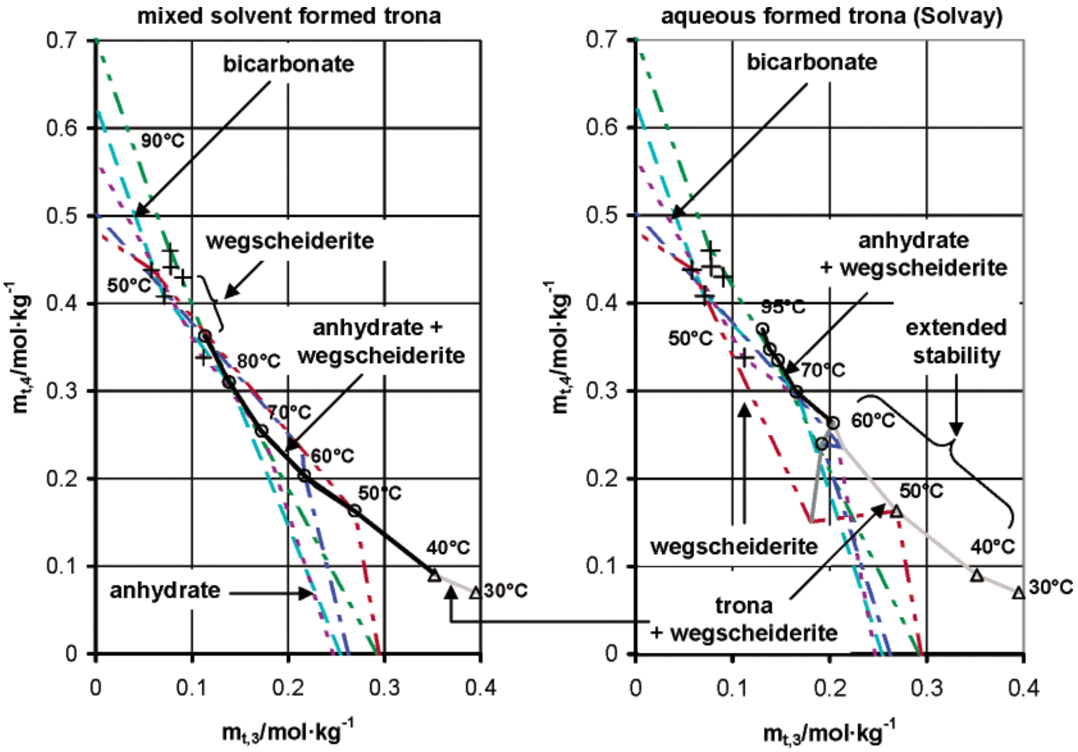

Figure 6. Phase stability and solubility chart for Na_2CO_3 (3) + $NaHCO_3$ (4) in 90 mass % (salt-free) ethylene glycol mixed solvent. Solubility isotherms for (50 to 90) °C are represented by the broken, colored curves, and two-phase lines are indicated by the gray and black curves: △, trona + anhydrate; ○, wegscheiderite + anhydrate; +, bicarbonate + wegscheiderite.

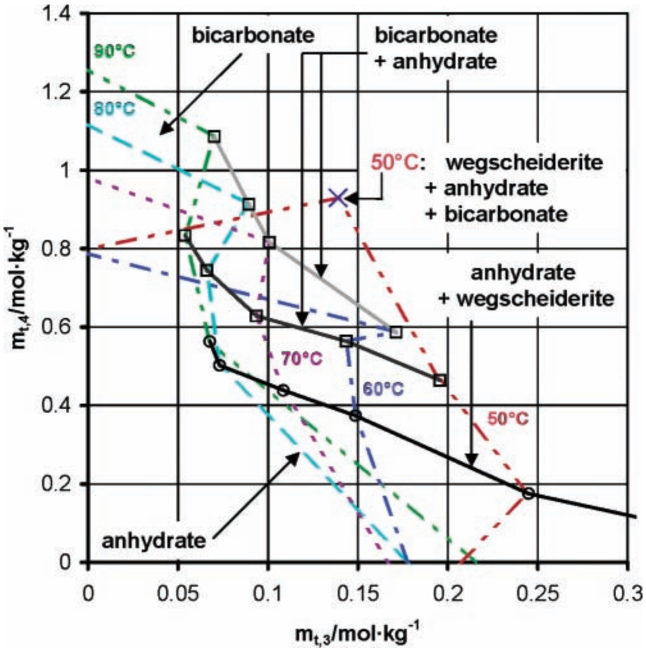

Figure 7. Phase stability and solubility chart for Na_2CO_3 (3) + $NaHCO_3$ (4) in 100 mass % (salt-free) ethylene glycol mixed solvent. Solubility isotherms for (50 to 90) °C are represented by the broken, colored curves, and two-phase lines are indicated by the gray and black curves: □, bicarbonate + wegscheiderite; ○, wegscheiderite + anhydrate.

% (salt-free solvent) ethylene glycol, anhydrate occurred already at (60 to 70) °C, and it occurred in 90 mass % (salt-free solvent) ethylene glycol at a temperature as low as 50 °C. These results were not surprising, since monohydrate and trona are hydrates, whose stabilities decrease with increasing antisolvent content.

As can be seen from Figure 4−7, the mixed solvent's ability to solubilize CO_3^{2-} decreased more strongly with increasing ethylene glycol content than its ability to solubilize HCO_3^-; for example, the maximal solubility concentration of $NaHCO_3$ (i.e. along the y-axis) became higher than the maximal Na_2CO_3 solubility concentration (i.e. along the x-axis).

Due to the decreasing solubility concentration of CO_3^{2-}, the anhydrate was stable at increasing ratios of bicarbonate (HCO_3^-) to carbonate (CO_3^{2-}) concentration with increasing ethylene glycol content. This effect went so far that, in 90 mass % (salt-free solvent) ethylene glycol, wegscheiderite was replaced by anhydrate at increased temperature and no wegscheiderite was found in pure ethylene glycol from (50 to 90) °C in two series of experiments (see Figure 7).

The phase behavior at high contents of ethylene glycol displayed some similarity with the aqueous system at increased temperatures (see ref 20), for example, the reduced hydrate stability, or the increasing ratio of the bicarbonate (HCO_3^-) solubility concentration in the $NaHCO_3$ system (see y-axis in Figures 1 and 4−7) to the carbonate (CO_3^{2-}) solubility concentration in the Na_2CO_3 system (see x-axis in same figures).

For 25 °C and aqueous solution, this ratio is 0.52, while, in aqueous solution at 200 °C and in 90 mass % (salt-free solvent) ethylene glycol at 90 °C, the ratio is 2.3.

Unfortunately, the measured phase stability behavior was not completely conclusive:

The stability and solubility of trona (sodium sesquicarbonate) recrystallized from the mixed solvent were lower than the stability and solubility of trona obtained from Solvay, France, that is, trona crystallized from aqueous solution; see Figure 7. For this phenomenon, it did not matter whether the trona was recrystallized in the mixed solvent from sodium carbonate anhydrate (soda) and sodium bicarbonate (nahcolite) or from a mixture of weg-

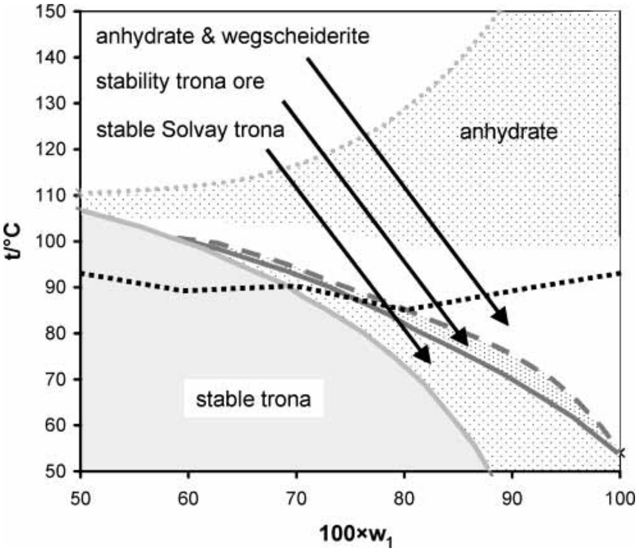

Figure 8. Stability of trona of different origin in ethylene glycol (1) + water (2): light gray line, transition line of mixed solvent formed trona; darker gray line, transition line of Solvay trona; gray dashed line, transition line of trona ore; black dashed line, transition line nahcolite ($NaHCO_3(s)$); gray dotted line, boiling point line of the mixed solvents. The stability ranges are indicated with the word labels and with the arrows.

scheiderite and anhydrate, which had been formed previously by recrystallization of Solvay trona. Therefore, it is unlikely that this difference in stability was a result of impurities in one of the trona types.

The stability of both types of trona in dependence on temperature and in dependence on ethylene glycol content is outlined in Figure 8, which is derived from data of Gärtner et al.[24] The difference in solubility and stability increased with increasing ethylene glycol content.

Up to 50 mass % (salt-free) ethylene glycol, both types of trona recrystallized at the same *transition temperature*, but the Solvay trona recrystallized at 60 mass % at a slightly higher temperature than the mixed solvent formed one. With increasing ethylene glycol content this difference increased to the extent that Solvay trona appeared stable in pure ethylene glycol, from which no trona could possibly form by recrystallization, due to the lack of sufficient water.

This difference in stability and solubility could not be detected in Figures 5 and 6, although a significant difference in trona transition temperature can be observed in the 70 mass % (salt-free solvent) ethylene glycol mixed solvent from Figure 8.

As HCO_3^- undergoes significant thermal decomposition to CO_3^{2-} and CO_2 at $t > 90$ °C, only anhydrate was found beyond ~110 °C as the thermodynamically stable phase under atmospheric conditions.[25]

Powder XRD showed a slight broadening of the diffraction peak of the mixed solvent trona compared to the Solvay trona. This indicated a possible slight difference of crystallinity in the crystal lattice of the two types of trona. This difference in crystal structure might well explain the difference in stability, but why this difference was only found in mixed solvents of more than 60% by mass ethylene glycol could not be explained on the basis of the presented data.

It was found in a related study[23] that thermodynamic data derived from measurements of the aqueous systems predict the phase transition line of the mixed solvent formed trona and not the aqueous-crystallized Solvay trona.

Trona ore, supplied by IMC Chemicals, CA, displayed behavior similar to that of the trona obtained from Solvay; see Figure 8. The increased stability was therefore not only a property of the Solvay trona but rather appeared to generally apply to trona formed from aqueous solution.

Conclusion

The solubilities in the system $Na_2CO_3 + NaHCO_3$ were measured in mixed solvents of ethylene glycol + water over a range of temperatures and mixed solvent compositions. Sodium carbonate anhydrate (natrite, $Na_2CO_3(s)$), sodium carbonate monohydrate (thermonatrite, $Na_2CO_3 \cdot H_2O(s)$), sodium bicarbonate (nahcolite, $NaHCO_3(s)$), sodium sesquicarbonate (trona, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O(s)$), and sodium carbonate tri-bicarbonate (wegscheiderite or decimite, $Na_2CO_3 \cdot 3NaHCO_3(s)$) were identified as the occurring solid phases. No solvate phases with ethylene glycol were formed.

For all observed solid phases, the solubility concentration of CO_3^{2-} decreased with increasing ethylene glycol content, while for HCO_3^- it reached a minimum at 80 to 90 mass % (salt-free solvent) ethylene glycol and then sharply increased again. While the CO_3^{2-} solubility concentration showed little temperature dependence, the HCO_3^- solubility concentration was very temperature dependent for all $NaHCO_3$ containing solid phases. The solubility concentration of HCO_3^- approximately doubled in the temperature range from (50 to 90) °C.

The solubility of nahcolite, wegscheiderite, and trona increased steadily with temperature, the solubility of sodium carbonate monohydrate decreased with increase in temperature, and the solubility of sodium carbonate anhydrate showed a slight increase with temperature for all mixed solvent compositions in the investigated temperature range.

Increasing ethylene glycol content decreased the stability of hydrates, like monohydrate and trona, and increased those of anhydrous phases such as anhydrate and wegscheiderite. These anhydrous phases occurred therefore in the mixed solvents at significantly lower *transition temperatures* in aqueous solution.

The stability of the trona that was crystallized from mixed solvents with ethylene glycol contents higher than 60 mass % in the salt-free solvent was lower than that of the trona formed from aqueous solution. This discrepancy in stability could not be explained within the framework of this work, but there was some indication that the crystal lattice of the mixed solvent formed trona differed slightly from the one obtained from aqueous crystallization.

These results offer some interesting possibilities for technical applications of the system of $Na_2CO_3 + NaHCO_3$ + ethylene glycol + water:

The stability range of the industrially relevant sodium carbonate anhydrate (soda) is significantly extended compared to the case of the aqueous system. This allows, for example, the crystallization of sodium carbonate anhydrate from a broader range of sodium carbonate−bicarbonate compositions.

Also the stability range of wegscheiderite ($Na_2CO_3 \cdot 3NaHCO_3(s)$) is increased compared to the case of the aqueous system, which can facilitate the preparation of this salt for, for example, analytical purposes.

Literature Cited

(1) Chen, C. C.; Evans, L. B. Local Composition Model for Excess Gibbs Energy of Aqueous Electrolyte Systems. *AIChE J.* **1982**, *28*, 588−596.

(2) Chen, C. C.; Evans, L. B.; Mock, B. Thermodynamic Representation of Phase Equilibria of Mixed Solvent Electrolyte Systems. *AIChE J.* **1986**, *32*, 1655−1664.

(3) Chen, C. C.; Mathias, P. M.; Orbey, H. Use of Hydration and Dissociation Chemistries with the Electrolyte-NRTL Model. *AIChE J.* **1999**, *45*, 1576−1586.

(4) Pitzer, K. S. *Activity Coefficients in Electrolyte Solutions*, 2nd ed.; CRC Press: Boca Raton, FL, 1991.

(5) Pitzer, K. S.; Kim, J. J. Thermodynamics of Electrolytes. IV. Activity Coefficients for Mixed Electrolytes. *J. Am. Chem. Soc.* **1974**, *96*, 5701−5707.

(6) Marion, G. M. Carbonate Mineral Solubility at Low Temperatures in the Na−K−Mg−Ca−H−Cl−SO_4−OH−HCO_3−CO_3−CO_2−H_2O System. *Geochim. Cosmochim. Acta* **2001**, *65*, 1883−1896.

(7) Johnson, J. W.; Oelkers, E. H.; Helgeson, H. C. SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000 °C. *Comput. Geosci.* **1992**, *18*, 899−947.

(8) Oelkers, E. C.; Helgeson, H. C.; Shock, E. L.; Sverjensky, D. A.; Johnson, J. W.; Pokrovskii, V. A. Summary of the Apparent Molal Gibbs Free Energies of Formation of Aqueous Species, Minerals, and Gases at Pressures 1 to 5000 Bars and Temperatures 25 to 100 °C. *J. Phys. Chem. Ref. Data* **1995**, *24*, 1401−1560.

(9) Kim, Y.; Haam, S.; Koo, K. K.; Shul, Y. G.; Son, J. H.; Jung, J. K. Representation of Solid−Liquid-Equilibrium of L-Ornithine-L-Aspartate + Water + Methanol System Using the Chen Model for Mixed Solvent Electrolyte Solution. *J. Chem. Eng. Data* **2001**, *46*, 1387−1391.

(10) Kim, Y.; Haam, S.; Koo, K. K.; Shul, Y. G.; Kim, W. S.; Jung, J. K.; Eun, H. C. Pseudopolymorphic Crystallization of L-Ornithine-L-Aspartate by Drowning Out. *Ind. Eng. Chem. Res.* **2003**, *42*, 883−889.

(11) Oosterhof, H.; Witkamp, G. J.; van Rosmalen, G. M. Some antisolvents for crystallisation of sodium carbonate. *Fluid Phase Equilib.* **1999**, *155*, 219−227.

(12) Seidell, A. *Solubilities of Inorganic and Metal Organic Compounds*; Van Nostrand: New York, 1958; Vol. II, pp 940−946.

(13) Taylor, C. E. Thermodynamics of Sodium Carbonate in Solution. *J. Phys. Chem.* **1955**, *59*, 653−657.

(14) Kobe, K. A.; Sheehy, T. M. Thermochemistry of Sodium Carbonate and Its Solution. *Ind. Eng. Chem.* **1948**, *40*, 99−102.

(15) Waldeck, W. F.; Lynn, G.; Hill, A. E. Aqueous Solubility of Salts at High Temperatures. I. Solubility of Sodium Carbonate from 50 to 348 °C. *J. Am. Chem. Soc.* **1932**, *54*, 928−936.

(16) Seidell, A. *Solubilities of Inorganic and Metal Organic Compounds*; Van Nostrand: New York, 1940; Vol. I, pp 1193−1200.

(17) Wegscheider, R.; Mehl, J. Über Systeme Na_2CO_3−$NaHCO_3$−H_2O und das Existenzgebiet der Trona. *Monatsh. Chem., Sitzungsberichte Akademie der Wissenschaften in Wien* **1928**, *49*, 283−315.

(18) Hill, A. E.; Bacon, L. R. Ternary Systems. VI. Sodium Carbonate, Sodium Bicarbonate and Water. *J. Am. Chem. Soc.* **1927**, *59*, 2487−2495.

(19) Waldeck, W. F.; Lynn, G.; Hill, A. E. Aqueous Solubility of Salts at High Temperatures. II. The Ternary System Na_2CO_3−$NaHCO_3$−H_2O from 100 to 200 °C. *J. Am. Chem. Soc.* **1934**, *56*, 43−48.

(20) Garret, D. E. *Natural Soda Ash—Occurrences, Processing and Use*; Van Nostrand Reinhold: New York, 1992; p 565.

(21) Oosterhof, H.; de Graauw, J.; Witkamp, G. J.; van Rosmalen, G. M. Continuous Double Recrystallization of Light Soda Ash into Super Dense Soda Ash. *Cryst. Growth Des.* **2002**, *2*, 151−157.

(22) Zavitsas, A. A. Properties of Water Solutions of Electrolytes and Nonelectrolytes. *J. Phys. Chem. B* **2001**, *105*, 7805−7817.

(23) Gärtner, R. S.; Seckler, M. M.; Witkamp, G. J. Recrystallization of Trona (Sodium Sesquicarbonate) into Soda (Sodium Carbonate Anhydrate) in a Mixed Solvent. Part I: Fundamental Conversion Steps. In preparation for publication.

(24) Gärtner, R. S.; Witkamp, G. J. Wet Calcining of Trona (Sodium Sesquicarbonate) and Bicarbonate in a Mixed Solvent. *J. Cryst. Growth* **2002**, *237−239*, 2199−2205.

(25) Gärtner, R. S.; Seckler, M. M.; Witkamp, G. J. Reactive Recrystallization of Sodium Bicarbonate. In preparation for publication.

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