

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231371519>

Sodium Carbonate Extractive Crystallization with Poly(ethylene glycol) Equilibrium Data and Conceptual Process Design

ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · JANUARY 2004

Impact Factor: 2.59 · DOI: 10.1021/ie030692a

CITATIONS

11

READS

53

3 AUTHORS:



María E. Taboada

University of Antofagasta

47 PUBLICATIONS 435 CITATIONS

SEE PROFILE



Teófilo A. Graber

Universidad de Antofagasta, Chile

60 PUBLICATIONS 479 CITATIONS

SEE PROFILE



Luis A. Cisternas

University of Antofagasta

96 PUBLICATIONS 608 CITATIONS

SEE PROFILE

RESEARCH NOTES

Sodium Carbonate Extractive Crystallization with Poly(ethylene glycol) Equilibrium Data and Conceptual Process Design**Maria E. Taboada,* Teófilo A. Graber, and Luis A. Cisternas***Departamento de Ingeniería Química, Universidad de Antofagasta, Casilla 170, Antofagasta, Chile*

Experimental data are given for the sodium carbonate–poly(ethylene glycol)–water system at 313.15 K. Two interesting results are that at 313.15 K sodium carbonate crystallizes as an anhydrous molecule and the system forms two aqueous phases: one free of sodium carbonate and the other free of poly(ethylene glycol). These two characteristics allow the exclusion of steps for the extractive crystallization of anhydrous sodium carbonate from Trona or other raw materials.

Introduction

Sodium carbonate is one of the products of greatest importance in terms of chemical production. About 50% of the output of this reagent is used in the glass industry and about 22% is directed to the chemical industry. Sales of sodium carbonate are generally as the anhydrous form (soda ash), at above 99% purity. Small quantities of sodium carbonate are sold for special applications as monohydrate or decahydrate. In general, production of the anhydrous form is carried out starting with Trona ore, a mineral that contains up to 95% of sesquicarbonate ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$). A common method to produce dense soda ash (a commercial grade of soda ash) from Trona is known as the “monohydrate process”, which requires large quantities of water (a scarce and valuable resource in some soda ash plants) and energy.¹ In that process, crushed Trona ore is calcined at a temperature between 400 and 523 K to convert sodium bicarbonate into sodium carbonate and form crude soda ash. This crude soda ash is dissolved in water and filtered. The filtered solution of sodium carbonate is fed to an evaporative crystallizer, where sodium carbonate forms into sodium carbonate monohydrate crystals. Then the monohydrate crystals are removed from the mother liquor and calcined (420–470 K) to form anhydrous sodium carbonate. This yields a product with a typical bulk density of 550 kg/m³. Also, soda ash can be produced synthetically using the Solvay process² or its modifications. In this process, sodium bicarbonate is produced, which is then calcined to sodium carbonate (a product known as light soda ash). Most of the light soda ash is converted into dense soda ash because dense soda ash is preferred over light soda ash. Light soda ash is typically converted to dense soda ash by adding water to allow the production of sodium carbonate monohydrate. Then the monohydrate crystals are calcined to form soda ash. Because of the energy that these processes require, there is interest to develop a new process.^{3–6}

Anhydrous sodium carbonate is only stable at temperatures above 382 K, which is higher than the boiling

point of a saturated soda ash solution (378 K). Although it is possible to produce soda ash by increasing the crystallization pressure, the monohydrate process is preferred because crystallization in pressurized vessels is expensive.

There is continuing interest in the development of alternative methods for the separation of salts. The use of an external agent such as an organic solvent has drawn attention because the solubility of electrolytes in water may be very different from that of water containing an external agent.^{7–10} The effect of the addition of poly(ethylene glycol) (PEG) to aqueous solutions of electrolytes has been reported in the literature.^{11–13} In these studies, it was observed that these systems tended to form liquid–liquid and liquid–liquid–solid equilibrium zones. Also, the hydration number of the solid phase tends to decrease in the presence of PEG.

Oosterhof et al.¹⁴ studied the behavior of phase equilibrium in 10 aqueous sodium carbonate systems with different alkanediols at temperatures from 313.15 to 363.15 K. The study included PEG 200, PEG 400, and tri(ethylene glycol), which showed liquid–liquid equilibrium. The differences in miscibility of these increased with an increase in the molecular weight and decreased with an increase in the temperature. Unfortunately, studies of the solid phase present were not included. The cited study also included other antisolvents, among which di(ethylene glycol) was the best antisolvent, giving 99% recovery of sodium carbonate. It has been possible to obtain soda ash with bulk densities of up to 950 kg/m³ at temperatures as low as 353 K using ethylene glycol.⁶ Ethylene glycol did not give liquid–liquid equilibrium zones and thus required a step such as distillation for recovery of the solvents. On the basis of the preceding statements, Taboada et al.¹⁵ carried out tests with PEG of molecular weight of 4000 at 298.15 K in order to obtain a difference in miscibility sufficient to recuperate the PEG by liquid–liquid separation in the $\text{Na}_2\text{CO}_3 + \text{PEG 4000} + \text{H}_2\text{O}$ system. Although a liquid–liquid equilibrium zone was observed, the solid

Table 1. Tie Lines for Na₂CO₃ (1) + H₂O (2) + PEG (3) System at 313.15 K (Weight Percentage)

initial composition		top phase			bottom phase			partition coefficient (K)
Na ₂ CO ₃	PEG	Na ₂ CO ₃	PEG	ρ (g mL ⁻¹)	Na ₂ CO ₃	PEG	ρ (g mL ⁻¹)	
8.0312	10.0105	1.2742	33.8013	1.0634	10.9883	0.0000	1.1027	8.62
10.9967	21.0098	0.5295	48.7294	1.0797	18.2889	0.0000	1.1875	34.54
12.9769	28.0113	0.2053	58.3322	1.0901	24.4050	0.0000	1.2544	117.72
16.9818	34.9912	0.2020	74.4493	1.1068	31.9776	0.0000	1.3519	158.34

phase was monohydrate sodium carbonate, and therefore soda ash was not a feasible product at these conditions.

The objective of the present study was to determine the feasibility of producing anhydrous sodium carbonate from an aqueous sodium carbonate solution using PEG as an antisolvent. Following this objective, an experimental study was made of the behavior of the liquid–liquid–solid equilibrium of the Na₂CO₃ + PEG 4000 + H₂O system at 313.15 K, and then a conceptual process was proposed to produce soda ash from crude soda ash.

Na₂CO₃ + PEG 4000 + H₂O System at 313.15 K. Because the product of major interest was carbonate anhydrous, experimental tests were carried out at temperatures of 303.15, 308.15, and 313.15 K; our goal was to find a temperature where the solid phase was anhydrous sodium carbonate. The temperature found was 313.15 K, and therefore the phase diagram was determined at that temperature.

Reagents utilized included sodium carbonate p.a. (Merck) and synthesis-grade PEG (Merck), with nominal molecular weights of 4000 (medium molecular weights of 3819 and a polydispersity of 1.02). The sodium carbonate was dried at 393 K for 48 h to eliminate moisture. The PEG was dried for a week at 323 K, after which the percentage humidity was determined to be 0.46%. Milli-Q quality distilled water was used throughout the experimentation. Details of the experimental procedure were previously described by Taboada et al.¹⁵ The binodal curve was plotted by addition of small amounts of PEG (0.01 g) to an aqueous solution of Na₂CO₃ until turbidity appeared; this characteristic indicated the formation of two liquid phases. The composition for each point on the binodal curve was calculated in accordance with the masses added until the moment turbidity was observed. The binodal curve was completed using the same procedures as those used for aqueous solutions of PEG and adding 0.02 g amounts of Na₂CO₃. This procedure, previously employed by Taboada et al.,¹⁵ was uncomplicated and gave accurate results. All points of the binodal curve were determined at 313.15 ± 0.1 K. The tie lines were determined in triplicate from a mixture of known overall composition above the binodal curve (typically 40 g in capped graduated flasks), which were agitated for 48 h in a rotatory bath with the temperature controlled at 313.15 ± 0.1 K. Biphasic solutions obtained were separated by isothermic sedimentation over 24 h. Longer stirring at settling periods did not result in any observable changes in the phase compositions. Once the solutions in equilibrium were separated, samples were taken in triplicate to determine the composition of each phase (reproducibility was ±1.8%). The density and refractive index were also measured for each solution in equilibrium. The refractive index was measured using a Mettler Toledo model RE50 refractometer having a precision of ±0.0001, and the density was measured in a Mettler Toledo model DE50 densimeter with a precision of ±0.000 05 g/mL. Both physical properties were

measured under isothermic operating conditions at 313.15 ± 0.1 K. The concentration of PEG in the samples was determined by measurement of the refractive index and density.¹⁵ Calibration curves were obtained by the preparation of standard solutions of Na₂CO₃ between 0 and 24% and of PEG from 0 to 40%. Carbonate was determined by standard volumetric acid–base methods, and sodium was determined by atomic absorption at 589 nm using a Varian model SpectraAA 220 flame spectrophotometer. No influence of the initial concentration of PEG was observed. The solid-phase anhydrous sodium carbonate was identified by means of X-ray diffraction analysis.

The liquid–liquid equilibrium data are listed in Table 1. The density of the top phases was between 1.06 and 1.11 g/mL, and the bottom phase was between 1.10 and 1.35 g/mL in this system. The difference in densities between the phases increased with the tie-line length. A column has been included with the partition coefficient of the K salt, defined as the mass fraction of salt retained in the lower phase over the salt in the upper phase. The high values of *K* suggest that there is a good separation of the salt. For the tie line most distant from the water vertex, the percentage of sodium carbonate recovered in the lower phase is 99.37%.

The binodal curve was fitted using the following nonlinear expression:¹⁶

$$\ln X_{\text{PEG}} = a + bX_{\text{Na}_2\text{CO}_3}^{0.5} + cX_{\text{Na}_2\text{CO}_3}^3 \quad (1)$$

where X_{PEG} and $X_{\text{Na}_2\text{CO}_3}$ are the mass percents of PEG and Na₂CO₃, respectively. The fit parameters were $a = 4.689$, $b = -0.971$, and $c = 0.006$ for $X_{\text{Na}_2\text{CO}_3}$ between 0 and 2% and $a = 5.573$, $b = -1.453$, and $c = -0.002$ for $X_{\text{Na}_2\text{CO}_3}$ between 2 and 14%. The parameters were obtained using MINOS 5 (GAMS) from 1000 random starting points for the search of a global optimum. The average differences between the experimental values and those calculated from eq 1 were 0.57 and 0.83 for the first and second sets of data. Masses according to the density and refractive index calibration equations were compared with those obtained according to the mass balances obtained by measurement of the volume and density of each phase, obtaining a mean error of 3.2%.

Empirical equations are used to model the equilibrium results of the traditional liquid–liquid extraction, which correspond to the Othmer–Tobias correlations (eq 2) and the Bancroft potential equation (eq 3),¹⁵

$$\frac{1 - w_{\text{PEG,t}}}{w_{\text{PEG,t}}} = k \left(\frac{1 - w_{\text{Na}_2\text{CO}_3,\text{b}}}{w_{\text{Na}_2\text{CO}_3,\text{b}}} \right)^n \quad (2)$$

$$\frac{w_{\text{water,b}}}{w_{\text{Na}_2\text{CO}_3,\text{b}}} = k_1 \left(\frac{w_{\text{water,t}}}{w_{\text{PEG,t}}} \right)^r \quad (3)$$

where $w_{\text{PEG,t}}$ indicates the mass fraction of PEG in the

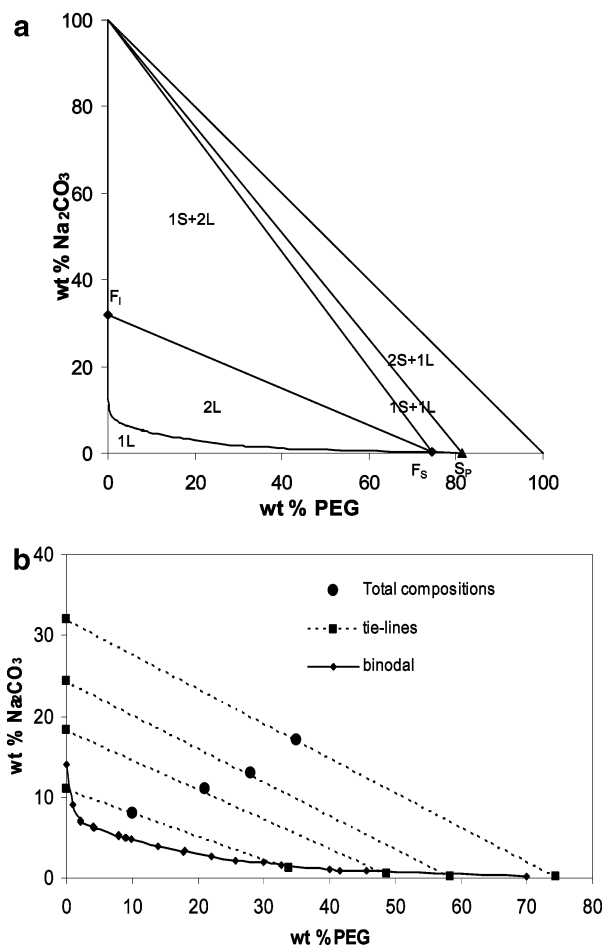


Figure 1. (a) Phase diagram for the Na_2CO_3 -PEG- H_2O system at 313.15 K. (b) Binodal curve and tie line for the Na_2CO_3 -PEG- H_2O system at 313.15 K.

top phase, $w_{\text{Na}_2\text{CO}_3,b}$ the mass fraction of Na_2CO_3 in the bottom phase, $w_{\text{water},b}$ the mass fraction of water in the top phase, and $w_{\text{water},t}$ the mass fraction of water in the bottom phase and k , n , k_1 , and r are parameters to be determined. The following values were obtained: $k = 0.150$, $n = 1.263$, $k_1 = 4.523$, and $r = 0.775$. The regression coefficients were 0.974 for eq 2 and 0.972 for eq 3.

In the phase diagram of the system at 313.15 K as shown in Figure 1, there is observed a zone of liquid-liquid immiscibility of size similar to the one observed at 298 K but where the stable solid phase consists of anhydrous sodium carbonate. This latter datum represents the major difference between the diagrams at both temperatures and indicates that PEG 4000 may be an adequate antisolvent for the production of anhydrous sodium carbonate when working at 313.15 K. Figure 1a shows the existence of various zones. Region 1L represents unsaturated aqueous solutions. It should be noted here that PEG 4000 is a solid in its pure state. The biphasic zone is termed 2L. The 1S + 2L region represents a zone of stability of the anhydrous sodium carbonate with two liquid phases, F_1 with a negligible quantity of PEG but high in sodium carbonate (31.99%) and F_S with a negligible quantity of sodium carbonate (0.21%) but high in PEG (72.29%). The 2S + 1L zone includes anhydrous salt, solid PEG, and a saturated solution such as that at point S_P . Figure 1b shows the binodal curve and the tie lines for the system.

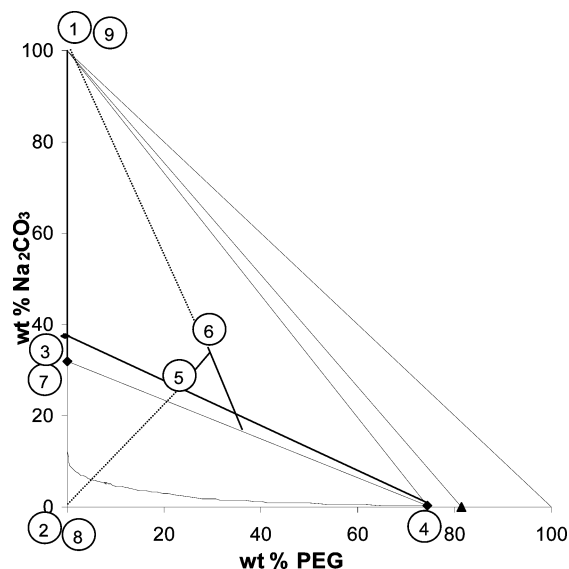


Figure 2. Conceptual process design for the production of soda ash.

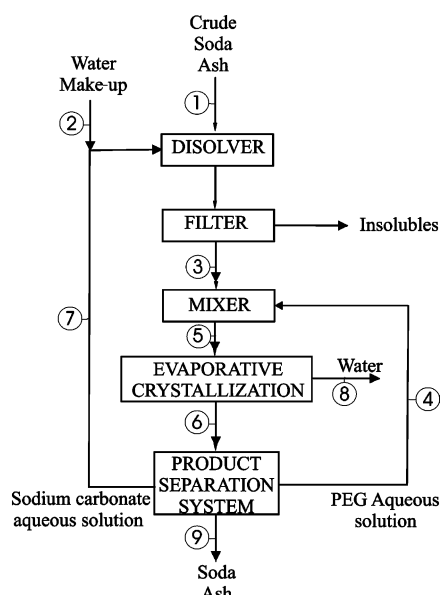


Figure 3. Conceptual process flow path on the phase diagram.

Conceptual Process Design. On the basis of the phase diagram at 313 K, our goal was develop a conceptual process to produce anhydrous sodium carbonate directly, allowing the calciner to be omitted from the flowsheet and resulting in a considerable savings in energy. In Figure 2, an alternative process is presented based on the use of PEG for the production of anhydrous sodium carbonate at atmospheric pressure and 313 K.

As shown in Figure 2, crude soda ash (1), containing impurities, is continuously charged to a dissolver along with a recycled aqueous sodium carbonate solution (7) from the product separation system. The product is sent to a filter to eliminate the insoluble impurities. The solution (3) is mixed with a rich PEG aqueous solution (4); this mixing can produce some supersaturation in soda ash. This solution is crystallized in one or more continuous evaporative crystallizers where water (8) is removed at the optimal time in an optimal amount to produce the desired soda ash product. The resulting slurry (6) is separated into three phases; a liquid PEG aqueous phase containing almost all PEG (4), a liquid

aqueous phase containing almost all sodium carbonate not crystallized (7), and a solid product containing anhydrous sodium carbonate (9). The product separation system can be a tricanter centrifugate or a filter-decanter system, where the filter removes the solid product and the decanter allows the separation of the two-phase liquid stream. This recovery is facilitated when the continuous phase is the aqueous phase rich in sodium carbonate; the time observed in the laboratory was about 2 min. Figure 3 shows the process on the phase diagram; the same numbers of the flowsheet of Figure 2 were used. The quality of the product is expected to be very good because high density should be obtained if soda ash is crystallized directly and average particle sizes should be possible to control in evaporative crystallization.

Conclusions

The phase diagram for the *sodium carbonate*–*PEG*–*water* system at 313.15 K was determined. A triphasic system was observed where the solid phase is anhydrous sodium carbonate and one of the liquid phases is almost free of sodium carbonate and the other liquid phase is almost free of PEG. This behavior allows the development of a conceptual process to produce soda ash, without the calciner step, at a temperature as low as 313 K and vacuum pressure. It is concluded that PEG 4000 is an alternative for the separation of anhydrous sodium carbonate by extractive crystallization.

Acknowledgment

The authors thank CONICYT for financing of this study (FONDECYT Project 1020892).

Literature Cited

- (1) Delling, D. M.; Green, K. L.; Phillip, J. D.; Robertson, D. M. Process for production of dense soda ash from soda ash fines. U.S. Patent 5,759,507, 1998.
- (2) Francis, R. Sodium Carbonate. *Kirk–Othmer Encyclopedia of Chemical Technology*, 4th ed.; John Wiley & Sons: New York, 1991; Vol. 1, p 1025.
- (3) Copenhafer, W. C.; Newman, T. H. Bicarbonate conversion in a carbonate monohydrate process. U.S. Patent 6,576,206, 2003.

- (4) Smith, D. E.; Copenhafer, W. C.; Chastain, R. W. Production of feed liquor for sodium carbonate crystallization processes. U.S. Patent 6,428,759, 2002.
- (5) Weingaertner, D. A.; Lynn, S.; Hanson, D. N. Extractive crystallization of salts from concentrated aqueous solution. *Ind. Eng. Chem. Res.* **1991**, *30*, 490.
- (6) Oosterhof, H.; Witkamp, G. J.; Van Rosmalen, G. M. Antisolvent crystallization of anhydrous sodium carbonate at atmospheric conditions. *AIChE J.* **2001**, *47*, 602.
- (7) Ata, L.; Alfassi, Z. B. Precipitation of Nitrates and Nitrites by Solventing Out from Aqueous Solutions. *Sep. Sci. Technol.* **1985**, *21* (6 & 7), 655.
- (8) Gomis, V.; Ruiz, F.; Asensi, J. C.; Cayuela, P. Liquid–liquid–solid equilibria for the ternary system water–lithium chloride–1-propanol or 2-propanol at 25 °C. *Fluid Phase Equilib.* **1996**, *119*, 191.
- (9) Gomis, V.; Ruiz, F.; Asensi, J. C.; Saquete, M. D. Liquid–liquid–solid equilibria for the ternary system butanols + water + sodium chloride or + potassium chloride. *J. Chem. Eng. Data* **1996**, *41*, 188.
- (10) Fontenot, K. J. Extractive solution crystallization of chemical compounds. U.S. Patent 6,500,973, 2002.
- (11) Ho-Gutierrez, I. V.; Cheluget, E. L.; Vera, J. H.; Weber, M. E. Liquid–Liquid Equilibrium of Aqueous Mixtures of Poly(ethylene glycol) with Na₂SO₄ or NaCl. *J. Chem. Eng. Data* **1994**, *39* (2), 245.
- (12) Graber, T. A.; Taboada, M. A.; Asenjo, J. A.; Andrews, B. A. Influence of Molecular Weight of the Polymer on the liquid–liquid Equilibrium of the Poly(ethylene glycol) + NaNO₃ + H₂O System at 298.15 K. *J. Chem. Eng. Data* **2001**, *46*, 765.
- (13) Hammer, S.; Pfenning, A.; Stumpf, M. Liquid–liquid and Vapor–Liquid Equilibria in Water + Poly(ethylene glycol) + Sodium Sulfate. *J. Chem. Eng. Data* **1994**, *39* (3), 409.
- (14) Oosterhof, H.; Witkamp, G. J.; van Rosmalen, G. M. Some Antisolvents for Crystallisation of Sodium Carbonate. *Fluid Phase Equilib.* **1999**, *155*, 219.
- (15) Taboada, M. E.; Asenjo, J. A.; Andrews, B. A. Liquid–liquid and liquid–liquid–solid equilibrium in Na₂CO₃–PEG–H₂O. *Fluid Phase Equilib.* **2001**, *180*, 273.
- (16) Mistry, S. L.; Kaul, A.; Merchuk, J. C.; Asenjo, J. A. Mathematical modeling and computer simulation of aqueous two phase continuous protein extraction. *J. Chromatogr. A* **1996**, *741*, 151.

Received for review August 26, 2003

Revised manuscript received December 9, 2003

Accepted December 18, 2003

IE030692A