Solubility in the NH$_4$HCO$_3$ + NaHCO$_3$ + H$_2$O System

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Mutual solubility of NH$_4$HCO$_3$ and NaHCO$_3$ in aqueous solutions over a temperature range 293 K to 323 K has been measured. On the basis of these results, a polytherm section for the NH$_4$HCO$_3$ + NaHCO$_3$ + H$_2$O system has been drawn. In addition, a correlation between the solution densities and both salt concentrations has been found.

Introduction

For plotting the equilibrium diagram of the reciprocal salt pairs system NaVO$_3$ + NH$_4$HCO$_3$ + H$_2$O in the oblique projection according to Jänecke's (Wiktorow, 1975), a precise knowledge of the mutual solubility for the specific three-component systems is required. These are NaVO$_3$ + NaHCO$_3$ + H$_2$O, NH$_4$HCO$_3$ + NH$_4$VO$_3$ + H$_2$O, NaVO$_3$ + NH$_4$VO$_3$ + H$_2$O, and NH$_4$HCO$_3$ + NaHCO$_3$ + H$_2$O. The monovariant lines separating each plane of the salt co-crystallization and the triple points located inside the equilibrium diagram square are also necessary for constructing the solubility isotherms. The above mentioned three-component systems in the oblique projection on the NaVO$_3$ + NH$_4$HCO$_3$ + H$_2$O plane are represented by the adequate sides of the diagram square. Equilibrium studies for NaVO$_3$ + NaHCO$_3$ + H$_2$O and NH$_4$HCO$_3$ + NH$_4$VO$_3$ + H$_2$O systems, respectively, have been recently published by Trypuć and Kiełkowska (1995, 1996), whereas the NaVO$_3$ + NH$_4$VO$_3$ + H$_2$O system has been partly reported by Andrejew (1959) and subsequently by Trypuć and Kiełkowska (1997). The literature data concerning the title system were reported within the period of 1904–1947 by a number of investigators: Fedotieff (1904, 1910–1911, 1914), Fedotieff and Kolosow (1923), Toporescu (1922), Nishizawa (1920), Neuman and Domke (1928), Bielopolski and Szpunt (1931, 1940), Reinders and Nicolai (1947), and Utida (1942). However, the data base is very limited and does not allow one to construct the solubility isotherms over the temperature range 293 K to 323 K. Since the cited authors include very few experimental data over a different range of temperatures, for example, 0 °C, 7 °C, 15 °C, 35 °C, not reporting the solution densities, the solid-phase compositon, or the measurement technique, especially for temperatures above 30 °C, it was hard to make a comprehensive and reliable evaluation of that system. Experimental solubilities for NH$_4$HCO$_3$ + H$_2$O and NaHCO$_3$ + H$_2$O systems, respectively, being a component of the NH$_4$-HCO$_3$ + NaHCO$_3$ + H$_2$O system, have been described over the desired temperature range 293 K to 323 K, without providing the solution densities (Pelsh, 1961).

The investigated range of temperatures has been chosen on the basis of the operating parameters used in the Solvay method of producing sodium carbonate (Niederliński et al., 1978) and repeated as in the other papers by Trypuć and Kiełkowska (1995, 1996, 1997). Both salts existing in the investigated system are chemically unstable, especially
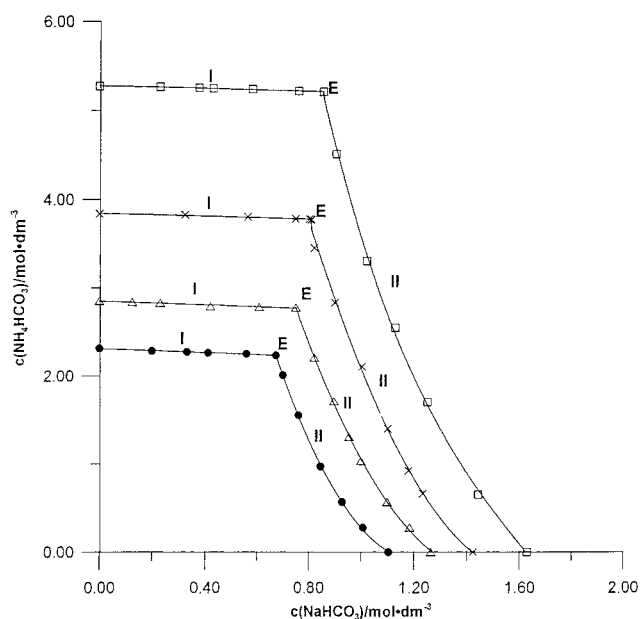
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Figure 1. Solubility of NH$_4$HCO$_3$ and NaHCO$_3$ in the NH$_4$HCO$_3$ + NaHCO$_3$ + H$_2$O system: (●) T = 293 K; (△) T = 303 K; (×) T = 313 K; (□) T = 323 K (in mol·dm^{-3}).

Table 1. Comparison of Solubility Data Presented in This Work with the Literature Data for the Binary System NH$_4$HCO$_3$ + H$_2$O

references	293 K	303 K	313 K	323 K
		c/(mass %)		
this work	17.08	20.62	27.19	36.66
Fedotieff (1904, 1914)		21.26		
Jänecke (1929)	17.80	22.10	26.80	31.60
Nishizawa (1920)		20.72	24.95	
Toporescu (1920)				30.9
		c/(g·dm^{-3})		
this work	183.2	225.6	303.5	417.1
Neumann and Domke (1928)	183.2	241.4		
Utida (1942)				307.5

NH$_4$HCO$_3$, and decompose at higher temperatures under atmospheric pressure. For example, at T = 331 K NH$_4$-HCO$_3$ undergoes a total decomposition to generate NH$_3$, CO$_2$, and H$_2$O. Considering that fact, all investigations have been carried out under known pressure conditions preventing the decomposition process. In the measurement flask the CO$_2$ pressure was set up both to prevent the NH$_4$-HCO$_3$ decomposition and to ensure the presence of HCO$_3^-$

Table 2. Comparison of Solubility Data Presented in This Work with the Literature Data for the Binary System NaHCO$_3$ + H$_2$O

references	293 K	303 K	313 K	323 K
		c/(mass %)		
this work	8.78	9.99	11.16	12.64
Fedotieff (1904, 1914)	8.80	9.93	11.30	12.60
Nishizawa (1920)		9.92	11.15	
Freeth (1922)	8.70	9.90		
Toporescu (1922)				12.65
Makarow and Waksberg (1930, 1933)	8.73	9.99		
Hill and Bacon (1927)		9.80		12.4
Oglesby (1929)		9.95		
Luznaja and Kosiaczkowa (1956)				12.64
		c/(g·dm^{-3})		
this work	92.83	106.3	119.7	136.9
Neumann and Domke (1928)	90.80	104.2		
Utida (1942)				123.5

ions in the solution (confirmed by the carbonization degree determinations (R)). That fixed value was mainly limited to temperature and location of the chosen measurement points lying on the particular isotherms.

Experimental Section

Mutual solubility for the NH$_4$HCO$_3$ + NaHCO$_3$ + H$_2$O system has been investigated within temperature range 293 K to 323 K. Branches I (Figure 1) of the solubility isotherms have been plotted on the basis of the equilibrium solution analysis, where NH$_4$HCO$_3$ precipitated with the increasing NaHCO$_3$ concentration toward the eutonic points (E). Branches II (Figure 1) of the solubility isotherms correspond to the NaHCO$_3$ saturated solutions with the increasing NH$_4$HCO$_3$ concentration toward the eutonic points.

Chemicals. NH$_4$HCO$_3$ and NaHCO$_3$ p.a. were supplied by POCh S.A Poland. As NH$_4$HCO$_3$ contains up to 15% of (NH$_4$)$_2$CO$_3$, a method of recarbonizaton of the solutions with gaseous CO$_2$ was used and provided a carbonization degree (R) of the given solutions that was approximately above 98% for the temperature range studied. To achieve the highest possible carbonization degree equal to 100%, particularly for temperatures 313 K and 323 K, a CO$_2$ partial pressure of approximately 10 bar was required. However, running the measurements under such a pressure using a glass apparatus both is dangerous and does not allow the determination of solution densities. It has been reported that HCO$_3^-$ concentration changes only a little above $R > 95\%$ (Koneczny, 1967). For two specific temperatures, 293 K and 303 K, the measurements were done employing a glass pressure apparatus described in

detail previously (Trypuć and Kiełkowska, 1996). At $T = 313$ K and $T = 323$ K, respectively, the measurements were carried out in a specially constructed pressure apparatus, which both provided safe working conditions and enabled achievement of equilibrium for the fixed conditions. The upper and lower parts of this apparatus were made of stainless steel, and the middle was made of organic glass "Plexi". The inner volume of the equilibrium cell was 466 cm^3. At the top of the lid, pressure valves were installed to maintain vacuum and add both distilled water and CO$_2$. A glass tube combined with the lid was used for direct liquid sampling. The apparatus was also equipped with a diaphragm pressure gauge to keep the desired pressure conditions. The pressure was controlled to an accuracy of ±0.1 bar. At $T = 293$ K and $T = 303$ K the sampling was done under CO$_2$ pressure P_{CO_2} of approximately 1.5 bar and 2.5 bar, respectively, whereas for $T = 313$ K and $T = 323$ K P_{CO_2} was 3.5 bar and 6.0 bar, respectively. Then the apparatus was placed in a thermostated water bath (maintained constant to ±0.1 K) and stirred using the magnetic stirrers. The thermostating time was 12 h. Details of the measuring technique are reported by Trypuć and Kiełkowska (1997). Each equilibrium solution was sampled and density measured with a calibrated Ostwald pycnometer in such a way as to prevent gaseous phase bubbles to appear. Each sample was in the compressed liquid state. The solution sample was taken to the pycnometer at 313 K and then at 323 K and cooled, and a solid-phase precipitation was observed. Therefore, the quantitative sampling of the pycnometer content to the graduated flask was done under a low partial underpressure to ensure the sampling accuracy (i.e., crystallization in the pycnometer). The pycnometer content was then used for determining the solution densities, the total gaseous CO$_2$ concentration, and the ion concentration outcome, i.e., HCO$_3^-$, NH$_4^+$, Na$^+$, after their accurate dilution.

The concentration of sodium ions was determined using the Kolthoff and Barbera balance method in the form of sodium zinc uranyl acetate (Furman, 1962). Accuracy of the measurement was better than ±1%.

The concentration of NH$_4^+$ ions was measured by the distillation method (Struszyński,1954), with an accuracy of approximately ±1%. NH$_3$ being removed in the isolated system (using a strong base solution) was absorbed into the adjusted volume of test acid solution. The residual excess of an acid was then potentiometrically titrated with test NaOH solution.

The HCO$_3^-$ concentration was determined using the potentiometric titration with 0.1 M HCl employing the

Table 3. Analysis of Solubility Data Presented in This Work with the Cited Literature Data for the Three-Component System NH$_4$HCO$_3$ + NaHCO$_3$ + H$_2$O

				c/(mass %)				
	this work		Fedotieff (1904, 1914)		Nishizawa (1920)		Toporescu (1922)	
T/K	NH$_4$HCO$_3$	NaHCO$_3$	NH$_4$HCO$_3$	NaHCO$_3$	NH$_4$HCO$_3$	NaHCO$_3$	NH$_4$HCO$_3$	NaHCO$_3$
293	16.20	5.18						
303	19.85	5.69	19.26	5.43	13.61	4.72		
313	26.50	6.05			22.45	5.34		
323	36.14	6.32					27.65	5.89

		c/(g·dm^{-3})					
	this work		Neumann and Domke (1928)		Utida (1942)		
T/K	NH$_4$HCO$_3$	NaHCO$_3$	NH$_4$HCO$_3$	NaHCO$_3$	NH$_4$HCO$_3$	NaHCO$_3$	
293	176.9	56.6	171.0	55.4			
303	219.9	63.1	228.6	60.7			
313	298.4	68.1			234.8	56.29	
323	412.0	72.0			287.8	61.33	

Table 4. Solubility in the System NH₄HCO₃ + NaHCO₃ + H₂O

ρ/g·cm⁻³	c/mol·dm⁻³		xᵃ		solid phase
	NH₄HCO₃	NaHCO₃	NH₄HCO₃	NaHCO₃	
			T/K = 293 K		
1.072	2.317	0.000	1.000	0.000	NH₄HCO₃
1.075	2.285	0.200	0.920	0.080	NH₄HCO₃
1.077	2.277	0.331	0.873	0.127	NH₄HCO₃
1.080	2.265	0.412	0.846	0.154	NH₄HCO₃
1.085	2.255	0.560	0.801	0.199	NH₄HCO₃
1.092	2.238	0.674	0.769	0.231	NH₄HCO₃, NaHCO₃
1.090	2.011	0.701	0.742	0.258	NaHCO₃
1.085	1.554	0.762	0.671	0.329	NaHCO₃
1.078	0.972	0.846	0.535	0.465	NaHCO₃
1.070	0.569	0.928	0.380	0.620	NaHCO₃
1.063	0.277	1.008	0.216	0.784	NaHCO₃
1.057	0.000	1.105	0.000	1.000	NaHCO₃
			T = 303 K		
1.094	2.854	0.000	1.000	0.000	NH₄HCO₃
1.095	2.842	0.125	0.958	0.042	NH₄HCO₃
1.097	2.831	0.232	0.924	0.076	NH₄HCO₃
1.100	2.792	0.421	0.869	0.131	NH₄HCO₃
1.104	2.785	0.609	0.821	0.179	NH₄HCO₃
1.108	2.782	0.751	0.787	0.213	NH₄HCO₃, NaHCO₃
1.102	2.210	0.823	0.729	0.271	NaHCO₃
1.095	1.712	0.898	0.656	0.344	NaHCO₃
1.088	1.310	0.955	0.578	0.422	NaHCO₃
1.083	1.035	1.001	0.508	0.492	NaHCO₃
1.075	0.569	1.101	0.341	0.659	NaHCO₃
1.068	0.278	1.185	0.190	0.810	NaHCO₃
1.063	0.000	1.265	0.000	1.000	NaHCO₃
			T = 313 K		
1.116	3.839	0.000	1.000	0.000	NH₄HCO₃
1.119	3.825	0.324	0.922	0.078	NH₄HCO₃
1.122	3.807	0.566	0.871	0.129	NH₄HCO₃
1.124	3.785	0.750	0.835	0.165	NH₄HCO₃
1.125	3.780	0.804	0.825	0.175	NH₄HCO₃
1.126	3.775	0.811	0.823	0.277	NH₄HCO₃, NaHCO₃
1.124	3.454	0.823	0.808	0.292	NaHCO₃
1.119	2.834	0.901	0.759	0.241	NaHCO₃
1.111	2.106	1.005	0.677	0.323	NaHCO₃
1.100	1.401	1.103	0.560	0.440	NaHCO₃
1.092	0.925	1.182	0.439	0.561	NaHCO₃
1.086	0.665	1.234	0.350	0.650	NaHCO₃
1.073	0.000	1.425	0.000	1.000	NaHCO₃
			T = 323 K		
1.138	5.277	0.000	1.000	0.000	NH₄HCO₃
1.138	5.264	0.231	0.958	0.042	NH₄HCO₃
1.138	5.256	0.377	0.933	0.067	NH₄HCO₃
1.138	5.247	0.432	0.924	0.076	NH₄HCO₃
1.139	5.241	0.584	0.900	0.100	NH₄HCO₃
1.139	5.219	0.762	0.873	0.127	NH₄HCO₃
1.140	5.212	0.857	0.859	0.141	NH₄HCO₃, NaHCO₃
1.137	4.511	0.906	0.833	0.167	NaHCO₃
1.129	3.302	1.024	0.763	0.237	NaHCO₃
1.121	2.549	1.131	0.693	0.307	NaHCO₃
1.111	1.701	1.253	0.576	0.424	NaHCO₃
1.092	0.653	1.445	0.311	0.689	NaHCO₃
1.083	0.000	1.630	0.000	1.000	NaHCO₃

ᵃ x is mole fraction.

automatic titrator 716 DMS with a glass electrode supplied by Metrohm Switzerland. Accuracy of the measurements was better than ±1%.

The carbonization degree (R) of the given solution was evaluated using the originally constructed apparatus described earlier by Koneczny et al. (1964). Quantitatively generated CO₂ was absorbed by a NaOH solution, and then a diluted BaCl₂ solution was added to give a BaCO₃ precipitate. Excess of NaOH solution was titrated with an acid in the presence of mixed acid–base indicators (thymol blue + cresol red). Finally, methyl orange was added and CO₂ determined by titrating the BaCO₃ precipitate with diluted HCl solution. The identification of the solid phases was performed using an X-ray diffractometer HZG 4/A-2 (Germany) with continuous registration.

Results and Discussion

The comparison of available literature data with the present work for the binary systems NH₄HCO₃ + H₂O and NaHCO₃ + H₂O and for the three-component system NH₄HCO₃ + NaHCO₃ + H₂O in the temperature range 293 K to 323 K is summarized in Tables 1–3.

It is well-recognized that the NaHCO₃ concentration values correlate consistently with the cited literature data, as NaHCO₃ salt is chemically stable over the desired temperature range. In fact, the difference between the experimental and the cited results given in Tables 1 and 3 can be associated with NH₄HCO₃ salt. Most authors do not discuss the measurement conditions (solution densities, solid-phase composition, etc.). Obviously, the observed data discrepancies depend upon the CO₂ pressure conditions not being maintained at a fixed level (what ensures the total existence of HCO₃⁻ ions in the solution).

The reciprocal solubility data for NH₄HCO₃ and NaHCO₃, respectively, in water are shown in Table 4. On the basis of the collected results, a polytherm section for the title system is presented (Figure 1). The course of branches I of the respective isotherm shows that with increasing NaHCO₃ concentration the values of NH₄HCO₃ concentration slightly decrease toward the eutonic points (E). This concentration difference is evaluated to be at T = 293 K, 0.079 mol·dm⁻³; T = 303 K, 0.072 mol·dm⁻³; T = 313 K, 0.064 mol·dm⁻³; T = 323 K, 0.065 mol·dm⁻³. This small NH₄HCO₃ concentration decrease can be associated with the presence of the common ion HCO₃⁻. It is reasonable to conclude that for the given temperature the NH₄HCO₃ concentration difference for both NH₄HCO₃ + H₂O and NaHCO₃ + H₂O systems (in the eutonic point, E) is constant.

The course of branches II of the solubility isotherms shows that the NaHCO₃ concentration decreases at first slowly with increasing NH₄HCO₃ concentration and then more rapidly tending toward the eutonic points. It is also significantly dependent upon the common ion effect because of the lower NaHCO₃ solubility in the binary system as compared to that of NH₄HCO₃. The solubility differences are determined to be at T = 293 K, 0.431 mol·dm⁻³; T = 303 K, 0.514 mol·dm⁻³; T = 313 K, 0.614 mol·dm⁻³; T = 323 K, 0.773 mol·dm⁻³.

To identify the binary salts or any additive combination created in the system, equilibrium diagrams of property–composition type are required (Sułajmankułov, 1971). When a new solid phase is generated, some inflections or dashed lines at points corresponding to this new combination are visible on curves presenting the solution density dependence on the component's concentration, given in mole fraction. From the results collected in Table 1, a close relationship between the solution densities and both salt concentrations, given in mole fraction, has been found (Figure 2).

The solution densities increase with increase in the NH₄HCO₃ concentration (for NaHCO₃ saturated solutions) reaching the maximum values at the eutonic points (E). After these points are crossed, the density decreases slowly to attain the values corresponding to the NH₄HCO₃ saturated solutions. The course of the respective curves indicates that a new chemical combination is not observed. X-ray analysis of the precipitate and the course of the solubility isotherms (Figure 2) show that in the investigated temperature range 293 K to 323 K in the solid phase only the following, NH₄HCO₃ (branch I), NaHCO₃ (branch II), and both salts mixture in the eutonic points (E), can be detected. Both the shape and the course of the solubility
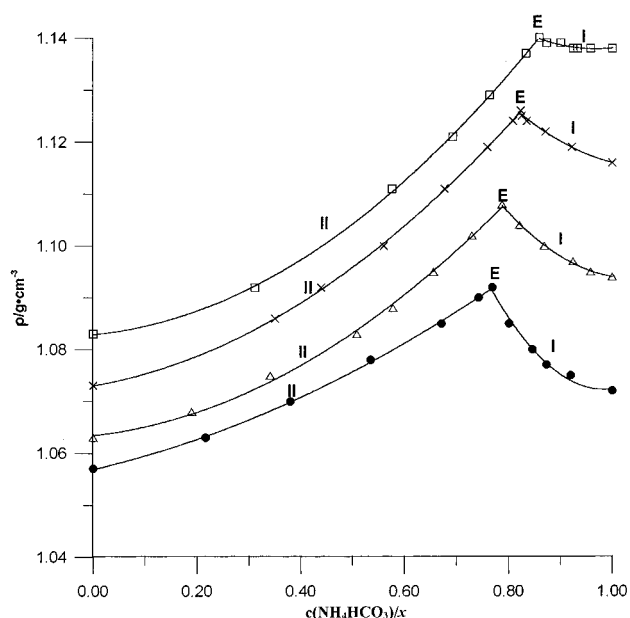
Figure 2. Density–mole fraction relationships of NH_4HCO_3 in the NH_4HCO_3 + $NaHCO_3$ + H_2O system: (●) T = 293 K; (△) T = 303 K; (×) T = 313 K; (□) T = 323 K.
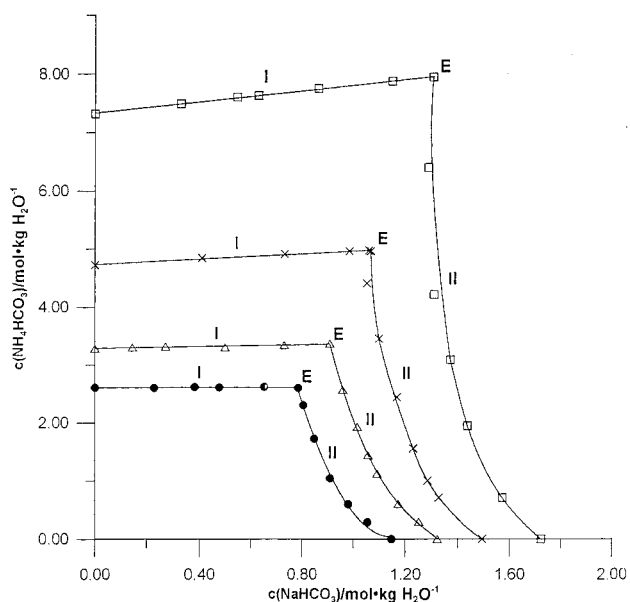
Figure 3. Solubility of NH_4HCO_3 and $NaHCO_3$ in the NH_4HCO_3 + $NaHCO_3$ + H_2O system: (●) T = 293 K; (△) T = 303 K; (×) T = 313 K; (□) T = 323 K (in mol·kg of H_2O^{-1}).

isotherms are dependent upon the component's concentration. Calculating the salt concentration in mol·kg of H_2O^{-1} enables one to observe the ongoing changes of the mutual salts solubility and to compare them with the other systems. On the basis of the results compiled in Table 1, a solubility units conversion was done to express all the concentration values in mol·kg of H_2O^{-1} and plot a solubility polytherm section (Figure 3). The course of branches I of the respective isotherm shows that, with the coexisting

increase of $NaHCO_3$ concentration, the concentration of NH_4HCO_3 systematically increases toward the eutonic points. This rise becomes still more visible for the higher temperature values. The observed correlation is reverse in the case of defining the salt concentration in mol·dm^{-3}. For branches II of the solubility isotherms, the relationship is similar to that presented in Figure 1, but their location is shifted toward the higher values of the $NaHCO_3$ concentration given on the X-axis.

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