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Solid Solubility in the Aqueous 2-Amino-2-Methyl-Propanol (AMP) plus Piperazine (PZ) System

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ABSTRACT:

In this work the solid-liquid equilibrium (SLE) of the ternary system 2-amino-2-methyl-propanol (AMP)–piperazine (PZ)–H₂O and the aqueous binary system AMP were determined using a freezing point depression (FPD) setup and differential scanning calorimetry (DSC). A total of 59 new data points are listed in the full concentration range of $0 < w(\text{AMP}) < 100\%$ and $0 < w(\text{PZ}) < 61\%$. The SLE phase boundary of AMP tetrahydrate (AMP·4H₂O) was determined and confirmed by its crystal structure obtained from powder x-ray diffraction (PXRD).

The new data of this work can be used in the creation of thermodynamic model for prevention of AMP and PZ precipitates from solvents used for CO₂ capture. This gives a higher degree of safe

operation. These data will allow for a deeper understanding molecular interaction and bond lengths in the AMP-water system which can be used for molecular simulation.

1. Introduction

Recent CO₂ emission is considered a major contributor to the pollution by greenhouse gases¹. CO₂ capture is a potential technology for reducing industrial emissions and thereby diminishing the effect on global warming. In this process, amine solutions can be used.

Sterically hindered amines are considered promising solvents due to the low energy consumption for regeneration comparable to conventional amines^{2,3}. The well-known sterically hindered amines include methyldiethanol amine (MDEA), triethanol amine (TEA), but also 2-amino-2-methylpropanol (AMP).

Blends of sterically hindered amines and a promoter/or activator have proven to facilitate high CO₂ loadings and absorption kinetics. A well-known promoter is piperazine (PZ). Its potential was discussed by Derks et al.⁴ and Xu et al.⁵. Experimental results showed that PZ was advantageous for the CO₂ loading in MDEA solutions⁵. Furthermore, the kinetics in both PZ and CO₂ were assumed to be first order⁴. The specific case of PZ activated AMP solutions were investigated by Seo et al.³ and Sun et al.⁶. Both conclude that small additions of PZ promote the AMP reaction rate.

The melting point of pure AMP is relevant in the analysis of the solid-liquid equilibrium (SLE) phase boundary. It is not well studied. Gajac et al.⁷ synthesised AMP and stated that the crystalline structure forms at the temperature range 23 to 25 °C.

PZ has several uses. Since 1940's piperazine has been used for treatment of ascariasis in human and animals^{8,9}. AMP solid formation plays an important role in other applications than CO₂ capture. It is well suited as buffers for the determination of alkaline phosphatase activity and for human chymase activity determination^{10,11}. AMP can also be used as ligand to make self-reducible conductive alcohol-solvent based inks¹². Additionally, AMP is used as additives in e.g. acrylic paints¹³.

The objective of this work is to experimentally determine the SLE phase boundaries of the binary and the ternary systems containing AMP-H₂O and AMP-PZ-H₂O for the purpose of thermodynamic modelling of CO₂ capture. The SLE phase boundaries of these systems are still not well described. Freezing points of the aqueous AMP system and the solid-phase behaviour of the AMP-PZ-H₂O system have previously been partially studied by Fosbøl et al.¹⁴.

The data gives a clear picture of which conditions can be used in order to prevent solid formation during use of the AMP-water and AMP-PZ-water CO₂ capture solvents. The crystal analysis in this work gives a deeper understanding of hydrogen bonds between AMP and water molecules, giving the opportunity for more advanced molecular simulation and understanding of interaction in the AMP-water system.

In this work a new hydrate of AMP has been found from SLE measurements and confirmed by the determination of its crystal structure and a related eutectic point was determined. It indicates the existence of two eutectic points in total.

2. Experimental details

2.1 Materials

The chemicals used in this study are listed in Table 1. AMP and PZ were used as received from the chemical suppliers without further purification. Deionised water with a conductivity of 0.2 μS was used to prepare the aqueous sample solutions of AMP and AMP-PZ. The solutions were prepared on an analytical balance with an accuracy of ± 0.1 mg.

Table 1. Samples used in the experiments.

Chemical name	Source	CAS No.	Mass fraction purity	Purification method
2-amino-2-methyl-propanol	Acros	124-68-5	0.99	none
Piperazine	Sigma-Aldrich	110-85-0	0.99	none

2.2 Apparatus

The apparatus used to measure the freezing points of the solutions is described by Fosbøl et al.¹⁵. Determination of the solubility at higher temperatures was performed with the same setup as explained by Fosbøl et al.¹⁴. The experiments were conducted at atmospheric conditions with a CO_2 content of approximately 400 ppm. The eutectic temperature was analysed on a differential scanning calorimetry (DSC) (Setaram $\mu\text{DSC7 EVO}$). Powder x-ray diffraction (PXRD) data were collected on a Huber G670 Guinier camera equipped with an Oxford Cryosystems Cryostream cooler.

2.3 Experimental method

Freezing point measurements were performed as described in details by Fosbøl et al.¹⁵. Precipitates other than ice were determined equivalent to the method outlined by Fosbøl et al.¹⁴.

For freezing point determination, approximately 5 g of aqueous amine solution was added to a sample glass. The sample glass was placed in an ethanol bath. The temperature of the ethanol bath was controlled by a thermostatic bath, which was kept at a temperature 5 °C below the expected freezing point of the aqueous amine samples in the sample glass. Liquid nitrogen was used as cooling agent for samples with very low freezing point. The sample temperature was recorded by a Pt100 temperature probe connected to an Agilent data acquisition unit. The temperature probe was calibrated against freezing point values of aqueous NaCl solutions. The cooling/heating rate was in the range 0.01 to 0.1 °C. When the freezing point was located, the aqueous amine solution in the sample glass was heated by removing it from the ethanol bath and into a beaker containing ethanol. When micro ice crystals were left in the aqueous amine solution the sample glass was placed into the ethanol bath. This procedure was repeated at least three times.

The amine solubility was determined by visually inspecting the melting of the precipitation of the aqueous amine solution. The aqueous amine solution was cooled until precipitation using the FPD setup. The sample glass was taken out from the ethanol bath and the solution was melted at room temperature or by using a beaker containing hot water. The temperature probe used in the FPD setup recorded the temperature of the disappearance of the last crystal in the solution.

For both methods, manual stirring was applied during measurement to ensure a homogeneous sample temperature. Each solution was measured at least three times. Standard deviations of ≤ 0.2 °C and ≤ 0.9 °C were obtained using respectively the FPD and the SLE by FPD methods. Standard deviations close to 1 °C were seen for the highly concentrated samples due to increased viscosity.

Hydrates have a tendency to form in the studied systems and the solid phases were determined by PXRD and basic chemical analysis in the lab after cold filtration of the precipitates. The amount of crystalline water in the solids was quantified by potentiometric titrating of a known amount of precipitate. For each sample, three measurements were obtained to maintain accuracy of the titration method. A reproducibility often better than $w(\text{AMP}) = 0.05$ was obtained. For qualification of the precipitates, PXRD was used.

The eutectic temperature was measured with DSC using a heat-cool-heat cycle approach. Two closed cells, a reference- and a sample cell, were used for the measurements. The sample cell was filled with various concentrations of AMP and put in the DSC. The sample was thermally equilibrated for 10 minutes at 30 °C. The sample was slowly cooled with a ramping of 0.1 °C/min to -40 °C below the anticipated melting point. The temperature was kept at -40 °C for 10 minutes before heating (0.1 °C/min) the sample to 30 °C.

In this study a new hydrate phase of AMP was found in the range of approximately $0.40 < w(\text{AMP}) < 0.60$. For the determination of the AMP hydrate, two samples ($w(\text{AMP}) = 35\%$, called AMP35 and $w(\text{AMP}) = 50\%$, called AMP50) were contained in 0.5 mm glass capillaries spinning during the measurements. Samples were cooled with a heating/cooling rate of 10 °C/min to constant temperature where the powder diffraction patterns were collected. The standard deviation of the temperature is ± 1 °C. The powder diffraction patterns were collected in the 2θ range from 3 to 100° in steps of 0.05° using CuK α 1 radiation ($\lambda = 1.54056$ Å). The data were accumulated for five times 15 min (AMP50) or 1 h (AMP35). Indexing was performed with program ITO¹⁶. The crystal structures were solved with EXPO^{17,18}. The Rietveld refinements utilized a locally modified and Windows adapted version of the LHMP program¹⁹. The parameter set included: 2θ -zero and 16 Chebyshev background parameters; split pseudo-Voigt half-width, peak shape, and preferred

orientation (AMP50); and scale factor, unit cell and fractional coordinates of O, C and N. The coordinates of C2 were fixed due to the polar P1 space group. Thermal parameters were refined initially, but kept fixed during the final cycles. Hydrogen positions were added in calculated positions with distances of 0.95 Å, and were allowed to ride on the corresponding O, C and N, respectively. The powder diffractogram is shown in Figure 1, the data collection and refinement summary is given in the Supporting Information. The crystal structure is illustrated in Figure 2 showing the hydrogen bonding scheme. In Figure 2 is the oxygen atom that belongs to the AMP molecule represented by O1. O2 to O5 are oxygen atoms related to hydrated water. The NH₂ and OH groups are fully engaged by hydrogen bonds and the water oxygen arrangement allows for a complete hydrogen bonding between N and O atoms, both as donors and acceptors. The refined water (ice) contents for the AMP35 and AMP50 samples, $w(\text{H}_2\text{O}) = 39.7 \%$ and $w(\text{H}_2\text{O}) = 11.1 \%$, respectively, are reasonably close to values based on the phase diagram (Figure 2), $w(\text{H}_2\text{O}) = 37 \%$ and $w(\text{H}_2\text{O}) = 10 \%$, respectively. The asymmetric unit of the AMP·H₂O is illustrated in the Supporting Information, which also includes description of the various atoms: oxygen (O), hydrogen (H), carbon (C) and nitrogen (N).

3. Results and discussion

3.1 AMP-H₂O:

The solubility data of aqueous AMP were measured at atmospheric pressure and presented in Figure 3. Solubility data from previous work are also shown. The solubility measurements are listed in Table 2 in conjunction with standard deviations and information of the solid phases. Metastable data measured by FPD are presented in Table 3. They are not included in Figure 3.

Standard deviations better than 0.2 °C are obtained for the FPD analysis. The standard deviation increases expectedly using the SLE by FPD method¹⁴. For some cases, standard deviations up to 0.9 °C were obtained for the highly concentrated samples. This is due to an increased viscosity and intrusion of air bubbles, which makes it difficult to have a uniformly stirring and identification of the solid formation.

Figure 1. Rietveld refinement plot. Black = Observed intensities, Green = Calculated intensities for $\text{AMP} \cdot 4\text{H}_2\text{O}$, Orange = Calculated intensities for ice, RED = Difference curve, BLACK BARS = Bragg peak positions for $\text{AMP} \cdot 4\text{H}_2\text{O}$ (top) and ice (bottom).

Figure 2. The hydrogen bonding of the unit of AMP·4H₂O.

Table 2. Experimental SLE temperatures of the binary AMP-H₂O system. The SLE temperatures are given at Pressure $p = 0.1 \text{ MPa}^a$

$w(\text{AMP})$ $\text{g} \cdot (\text{g total})^{-1}$	t $^{\circ}\text{C}$	σ_t^b $^{\circ}\text{C}$	Solid phase
0.0782	-1.59	0.015	Ice
0.117	-19.70	0.22	Eutectic temperature ^c
0.147	-3.56	0.02	Ice
0.165	-4.45	0.17	Ice
0.170	-4.38	0.025	Ice
0.186	-4.47	0.012	Ice
0.193	-5.29	0.18	Ice
0.228	-6.67	0.019	Ice
0.267	-21.68	0.26	Eutectic temperature ^c
0.273	-9.08	0.039	Ice
0.316	-10.57	0.028	Ice
0.330	-11.16	0.27	Ice
0.340	-12.56	0.43	Ice
0.341	-12.76	0.14	Ice
0.358	-19.83	0.23	Eutectic temperature ^c
0.367	-15.88	0.028	Ice
0.398	-17.44	0.31	Ice
0.401	-17.57	0.45	Ice
0.420	-20.59	0.38	AMP·4H ₂ O ^d
0.453	-18.01	0.30	AMP·4H ₂ O ^d
0.455	-18.16	0.42	AMP·4H ₂ O ^d
0.462	-17.79	0.21	AMP·4H ₂ O ^d
0.467	-17.67	0.27	AMP·4H ₂ O ^d
0.495	-17.19	0.57	AMP·4H ₂ O ^d
0.517	-17.94	0.43	AMP·4H ₂ O ^d
0.539	-19.31	0.86	AMP·4H ₂ O ^d
0.556	-19.47	0.48	AMP·4H ₂ O ^d
0.567	-19.85	0.29	AMP·4H ₂ O ^d
0.600	-21.29	0.055	AMP·4H ₂ O ^e
0.642	-23.21	0.37	AMP·4H ₂ O ^e
0.674	-25.11	1.01	AMP·4H ₂ O ^e
0.769	-33.21	0.82	AMP·4H ₂ O ^e
0.862	-16.32	0.66	AMP·1/3H ₂ O ^f
0.890	-6.41	0.25	AMP·1/3H ₂ O ^f
0.913	2.06	0.24	AMP·1/3H ₂ O ^f
0.936	4.73	0.29	AMP·1/3H ₂ O ^f
0.944	6.25	0.26	AMP·1/3H ₂ O ^f
0.962	10.19	0.35	AMP ^f
0.963	10.36	0.35	AMP ^f
0.976	11.91	0.40	AMP ^f
1.00	22.60	0.92	AMP ^c

^aStandard uncertainties (u) for the temperature, weight fractions, and the pressure are $u(^{\circ}\text{C}) = 0.2^{\circ}\text{C}$, $u(w) = 0.001$, $u(p) = 1 \text{ kPa}$. The temperatures are also reported as the standard deviation of the mean in the table. ^bStandard deviations of two to five consecutive analysis. ^cDetermined by DSC. ^dCrystal structure confirmed by PXRD, ^eMost likely AMP·4H₂O. ^fCrystal structure not confirmed by PXRD.

Table 3. Metastable experimental solubility data of the binary AMP-H₂O system. The SLE temperatures are given at Pressure $p = 0.1 \text{ MPa}$ ^a.

$w(\text{AMP})$	t	σ_t^b	Solid phase	
$\text{g} \cdot (\text{g total})^{-1}$	$^{\circ}\text{C}$	$^{\circ}\text{C}$		Ref.
0.433	-24.17	0.10	Ice	This work
0.432	-25.07	0.65	Ice	This work
0.443	-30.00	0.25	Ice	Fosbøl et al. [15]

^aStandard uncertainties (u) for the temperature, weight fractions, and the pressure are $u(^{\circ}\text{C}) = 0.2^{\circ}\text{C}$, $u(w) = 0.0001$, $u(p) = 1 \text{ kPa}$. The temperatures are also reported as the standard deviation of the mean in the table. ^bStandard deviations of two to five consecutive analysis.

Figure 3. SLE diagram of solid precipitation in the binary AMP-H₂O system as a function of temperature at atmospheric conditions. The line indicates the trend of the experimental data. The dashed lines indicate the formation of a second eutectic point. Dotted lines indicate the eutectic temperature.

A eutectic point, *E* is depicted in Figure 3 at approximately -21 °C. The eutectic temperature was determined by DSC. A second eutectic point may lie in the range $0.77 < w(\text{AMP}) < 0.86$ but in this study it was impossible to determine the temperature due to cooling limitations in the used equipment. In general ice is formed at $w(\text{AMP}) < 0.40$, this was also confirmed by PXRD. A

hydrate, H is formed in the AMP-H₂O system. Titration of the transparent solids in the range $0.40 < w(\text{AMP}) < 0.60$ gave further information. The hydrate seems to contain between 3 to 6 moles of water with a local maximum in the region $0.49 < w(\text{AMP}) < 0.60$ with a melting point of approximately -17 °C.

PXRD was used to analyse the crystal structure of solids in the range $0.30 < w(\text{AMP}) < 1$. The PXRD analysis revealed that the AMP hydrate is AMP·4H₂O, built from AMP molecules surrounded by water molecules (Figure 1). The water content of AMP·4H₂O is $w(\text{AMP}) = 55.3 \%$, which is indicated by Figure 3 also.

In the interval $0.86 < w(\text{AMP}) < 0.95$ the solid AMP·1/3H₂O is a possible precipitate. The crystal structure could not be solved from the powder PXRD data. Pure anhydrous AMP precipitates at $0.96 < w(\text{AMP}) < 1$. This precipitate could be metastable even though, this was not confirmed by the PXRD experiment.

Solubility data in the region $0.40 < w(\text{AMP}) < 0.90$ are generally difficult to measure. In this region, a significant amount of sub-cooling needs to be applied in order to form the first crystal. In these cases, liquid nitrogen was used for cooling. The aqueous AMP solutions are difficult to stir due to an increased viscosity at the low temperature. The consistency of the solution is similar to rubber. The precipitates of AMP·4H₂O are white to transparent crystals. For concentrations below $w(\text{AMP}) = 0.40$ the solutions are completely solid at -21 °C indicated by the dotted eutectic temperature line in Figure 1. The melting point of pure AMP was observed to be ~23 °C. The melting point was analysed on DSC, which has an accuracy of ± 0.5 °C. The melting point is equivalent to the melting point reported by Gajac et al.⁷.

The measured data presented in Figure 1 are in agreement with data obtained from the previous work in the concentration range $0.025 < w(\text{AMP}) < 0.4$ ¹⁴. Data points below the eutectic

temperature in the region $0.40 < w(\text{AMP}) < 0.44$ (Table 3) are most likely metastable point and this is also true for the measurement of Fosbøl et al.¹⁴ at $w(\text{AMP}) = 0.443$.

In this work it was intended to formulate solutions in the range $0.60 < w(\text{AMP}) < 0.86$ but the driving force for solid precipitates was not great enough for crystals to occur in the analysis performed. Further investigation in this region is required.

3.2 AMP-PZ-H₂O:

The solid-phase boundary of the ternary AMP-PZ-H₂O system is depicted in Figure 4 and listed in Table 4. Former work¹⁴ of the ternary AMP-PZ-H₂O as well as the binary PZ-H₂O systems is also plotted in the figure. The table presents the corresponding solubility measurements determined from FPD and SLE by FPD¹⁴. Additional standard deviations and solid phase information are given. Concentrations $w(\text{PZ}, \text{AMP free}) > 0.47$ result in a lower accuracy of the SLE by FPD analysis up to 0.2 °C. The effect of the addition of AMP in aqueous PZ was in this work determined for $b(\text{AMP}) = 4.0 \text{ mol AMP} \cdot \text{kg}^{-1} \text{ H}_2\text{O}$.

The data obtained in this work are in line with measurements from previous work¹⁴. The solid formation for the ternary system is equivalent to the PZ-H₂O system. The figure shows that adding $b(\text{AMP}) = 4.0 \text{ mol AMP} \cdot \text{kg}^{-1} \text{ H}_2\text{O}$ to the samples depress the solid phase boundary by approximately 5 to 7 °C. Aqueous PZ freezes completely to solid below the eutectic temperature at -10 °C compared to -1 °C for the binary PZ-H₂O system. At 25 °C precipitation may form at $w(\text{PZ}) = 0.22$. The melting point for the local maximum of the PZ·6H₂O is observed to decrease from 45 to 38 °C. Solutions of $w(\text{PZ}, \text{AMP free}) > 0.48$ become solid below -29 °C, which is indicated by the dotted line below the eutectic point, E₂ in Figure 4. Precipitates at the vicinity of E₂ had a tendency to creep up the sample container surfaces.

Figure 4. SLE diagram of solid precipitation in the ternary AMP-PZ-H₂O system as a function of temperature at atmospheric conditions. Lines indicate the trend of the experimental data.

Table 4. Solubility data of the ternary AMP-PZ-H₂O system. The SLE temperatures are given at Pressure $p = 0.1 \text{ MPa}^a$.

$w(\text{AMP})$	$w(\text{PZ})$	t	σ_t^b	Solid phase
$\text{g} \cdot (\text{g total})^{-1}$	$\text{g} \cdot (\text{g total})^{-1}$	$^{\circ}\text{C}$	$^{\circ}\text{C}$	
0.260	0.0102	-8.85	0.018	Ice
0.253	0.0353	-9.68	0.054	Ice
0.250	0.0493	2.92	0.17	PZ·6H ₂ O
0.234	0.111	16.75	0.17	PZ·6H ₂ O
0.217	0.173	25.14	0.081	PZ·6H ₂ O
0.203	0.226	30.69	0.22	PZ·6H ₂ O
0.131	0.500	31.58	0.2	PZ·6H ₂ O
0.135	0.486	32.8	0.19	PZ·6H ₂ O
0.185	0.297	35.74	0.18	PZ·6H ₂ O
0.173	0.342	37.78	0.2	PZ·6H ₂ O
0.157	0.401	38.12	0.022	PZ·6H ₂ O
0.106	0.597	43.06	0.27	PZ·1/2H ₂ O
0.101	0.616	45.5	0.25	PZ·1/2H ₂ O

^aStandard uncertainties (u) for the temperature, weight fractions, and the pressure are $u(^{\circ}\text{C}) = 0.08 \text{ }^{\circ}\text{C}$, $u(w) = 0.001$, $u(p) = 1 \text{ kPa}$. The temperatures are also reported as the standard deviation of the mean in the table. ^bStandard deviations of four to five consecutive analysis.

4. Conclusion

The solubility of the binary AMP-H₂O and the ternary AMP-PZ-H₂O systems were determined in this work by FPD, SLE by FPD, DSC and PXRD. A total of 59 new data points were determined in the temperature range -33 to 46 $^{\circ}\text{C}$. The SLE curve decreases on addition of $b(\text{AMP}) = 4.0 \text{ mol AMP} \cdot \text{kg}^{-1} \text{ H}_2\text{O}$ in PZ, which is in accordance with previous work. New data points of the aqueous

AMP system revealed the existence of a tetrahydrate, which melts at -17 °C. The existence of the AMP tetrahydrate phase was confirmed by powder PXRD at 35 and 50 wt% AMP. Additionally, the system has a eutectic point at -21 °C between the intersection of ice and tetrahydrate. Further analyses of the SLE boundary in the range $0.40 < w(\text{AMP}) < 0.90$ is required. The data will contribute to the quality of thermodynamic modelling of the CO₂ absorption relevant for the reduction of greenhouse gases.

The PXRD analysis performed in this work creates a basis for further molecular simulation in order to understand the atomic interactions in the AMP molecule in combination with water. This data supplies a deeper understanding of the molecular and hydrogen bonds in the AMP molecule.

ASSOCIATED CONTENT

Supporting Information.

Powder diffraction data is included in the Supporting Information file.

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Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

AMP, 2-amino-2-methyl-propanol; DSC, differential scanning calorimetry; FPD, freezing point depression; MDEA, methyl diethanol amine; PZ, piperazine; PXRD, powder x-ray diffraction; SLE, solid-liquid equilibrium; TEA, triethanol amine.

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SYNOPSIS

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