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Inhibition of aqueous chemical reactions by strong liquid structure makers: experimental demonstration with amides and acid-base reactions.

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KEYWORDS acid-base reactions, amides, hydrogen bond, acid gas, aqueous amine, liquid structure maker, reaction inhibitor

ABSTRACT: The chemical absorption of CO₂ and H₂S in aqueous tertiary amines are well-known acid-base reactions. Kinetic and vapor-liquid equilibrium experiments show that the addition of an amide such as HMPA, that is known to be a strong liquid structure maker, significantly inhibits the acid-base reactions. The impact is more pronounced for CO₂ than for H₂S absorption. Despite the presence of water in the solvent, the absorption becomes almost physical. Due to hydrogen bonding and the hydrophobic effect, each amide molecule is involved in a cluster containing several water molecules thus rendering the water molecules less available to participate in the reaction and to solvate HS⁻ and HCO₃⁻ ions. This effect is absent when ethylene glycol, a weak structure maker, is added, even in large quantities. This study clearly demonstrates the importance of solvent structure in the study of chemical reactions. State-of-the-art molecular dynamics simulations of the water-HMPA system could not reproduce the strongly negative excess volume of the mixture. This illustrates the need for more accurate force fields to simulate the structuring effect and their impact on chemical reactions.

Introduction

The effect of the solvent on reaction rates and chemical equilibrium has been studied for a long time [1]. The intrinsic properties of the solvent, namely, dipole moment, polarizability, dielectric constant, nucleophilic and electrophilic properties, among others, are not always sufficient to describe the solvent effects, rather, one needs to look at the complex physicochemical interactions of solvents, reactants, transition states, and products. Therefore, there are many ways solvents can influence the kinetic and thermodynamic properties of a reaction [2]. In aqueous solutions, hydrogen bonding as well as the hydrophobic effect, play a crucial role [3], [4]. They can result in the formation of clusters or complexes between water and co-solvent molecules [5]. Their impact on chemical reactions has not been studied extensively and is not sufficiently understood. In this paper we report a case for which the addition of a strong liquid structure maker to an aqueous solvent significantly inhibits acid-base chemical reactions, even in the presence of excess water.

System and Experimental Methods:

In this study, the chemical absorption of CO₂, a Lewis acid, and H₂S, a Brønsted and Lewis acid, in an aqueous tertiary amine (Am) were chosen because they are well-known acid-

base reactions in which, according to the literature, the role of water is different between CO₂ and H₂S absorption [6]. In the chemical absorption reaction of CO₂, water participates via the reactions $\text{OH}^- + \text{CO}_2 \leftrightarrow \text{HCO}_3^-$, $\text{Am} + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{AmH}^+ + \text{HCO}_3^-$, and, as a solvation medium for the ions. In the chemical absorption reaction of H₂S, water mainly solvates the ions, and does not directly participate in the direct and very fast proton transfer via $\text{Am} + \text{H}_2\text{S} \leftrightarrow \text{AmH}^+ + \text{HS}^-$, but via $\text{OH}^- + \text{H}_2\text{S} \leftrightarrow \text{H}_2\text{O} + \text{HS}^-$. Following solvents have been studied (see SI for suppliers and purity): aqueous MDEA (MethylDiEthanolAmine), aqueous MDEA with physical co-solvent EG (Ethylene Glycol) and, aqueous MDEA with physical co-solvent HMPA (HexaMethylPhosphorTriAmide). Aqueous DEAE-EO (2-(2-Diethylaminoethoxy)ethanol), pure, or with EG or HMPA, has also been investigated (results presented in SI). Pure HMPA is a polar aprotic solvent with a very strong dipole moment $\mu = 5.54\text{D}$, a dielectric constant $\epsilon=30$ and a relatively low acceptor number (AN=10.6), making it a Lewis base, selectively solvating cations and Lewis acids [7]. Pure EG is a polar protic solvent with a low dipole moment $\mu = 2.28\text{D}$, a high dielectric constant $\epsilon=41.4$ and a relatively high acceptor number (AN=44.9).

Vapor-Liquid Equilibria (VLE) were measured using the static-analytical method as described in ref. [8]. CO₂ and H₂S

absorption rate were measured in a Lewis cell, according to the method described in ref. [9]. For all tests, CO₂ and H₂S absorption were measured simultaneously. In all experiments the amine concentration is 13 mol%. Viscosity measurements were carried out using an Anton Paar Lovis 2000 ME visco/densitometer based on the falling sphere principle. According to the manufacturer, the accuracy is 0.5% of the measured value.

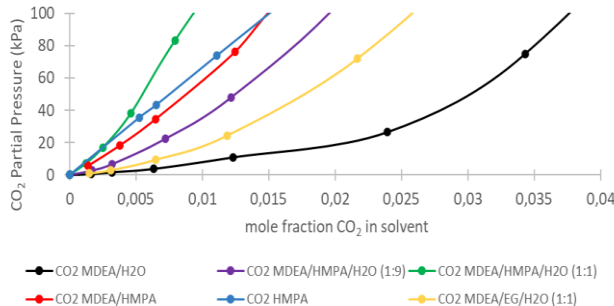


Figure 1. Experimental vapor-liquid equilibrium of CO₂ absorption at 323 K. (a:b) is the rounded molar ratio a/b of the last two components. The amine concentration is always 13 mol%. The solid lines are a guide to the eye.

Figure 1 shows the VLE data for the absorption of CO₂ in aqueous MDEA. In the absence of HMPA there is a strong absorption of CO₂ because the CO₂ partial pressure in the gas phase is relatively low. When 9 mol% HMPA is added to the solvent (HMPA/water (1:9) molar ratio), there is a significant shift of the absorption isotherm to the left, in comparison to the aqueous MDEA isotherm, indicating a much weaker absorption of CO₂, even if for every HMPA molecule there are still 9 H₂O molecules in the solvent. Replacing half of the water molecules by HMPA (HMPA/water (1:1) molar ratio) further shifts the isotherm to the left, but the shift is smaller. Replacing all the water by HMPA (MDEA/HMPA isotherm), results in an isotherm that is almost identical to the isotherm of the physical CO₂ absorption in pure HMPA. The MDEA/HMPA and pure HMPA isotherms are close to and in between the isotherms for 9 mol% HMPA (MDEA/HMPA/water (1:9)) and 43.5 mol% HMPA (MDEA/HMPA/water (1:1)). This indicates that even with a large excess of water (9 water molecules per HMPA molecule), the CO₂ absorption is close to physical absorption in non-aqueous MDEA/HMPA. The complete absence of water even favors the physical absorption of CO₂ (water is a bad physical solvent for CO₂). This explains why the 43.5 mol% HMPA isotherm (MDEA/HMPA/water (1:1)) is left of the two nonaqueous solvents. Interestingly, when half of the water molecules is replaced by ethylene glycol (EG), the shift of the isotherm to the left is less pronounced than when only 1 out of 9 molecules is replaced by a HMPA molecule.

In Figure 2 the results are given for H₂S absorption.

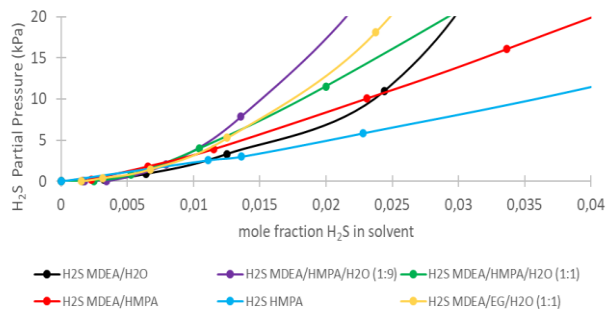


Figure 2. Experimental vapor-liquid equilibrium data points for H₂S absorption at 323 K. (a:b) is the molar ratio a/b of the last two components. The amine concentration is always 13 mol%. The solid lines are a guide to the eye.

Likewise for CO₂, the impact of replacing one out of nine water molecules by HMPA results in a stronger shift to the left of the isotherm than when half of the water molecules are replaced by ethylene glycol. The isotherms for 43.5 mol% HMPA, and the nonaqueous isotherms are all linear, indicating a physical absorption of the H₂S. HMPA is reported to be an excellent solvent for physical H₂S absorption [10]. This is confirmed here by the low partial pressures of H₂S at higher H₂S mole fractions. At lower H₂S mole fractions the chemical solvents absorb more H₂S (see Figures at very low partial pressures in SI). Note that experimental measurements at very low H₂S partial pressures are challenging.

In the SI the same figures are given, with the loading of the solvent expressed in mol of acid gas per mol of amine. The observations are unchanged.

In Figure 3 the absorption of CO₂ is shown as a function of time. Replacing half of the water molecules by ethylene glycol has barely any impact on the overall absorption rate of CO₂. However, the CO₂ absorption rate slows down significantly when only 1 out of 9 water molecules is replaced by a HMPA molecule.

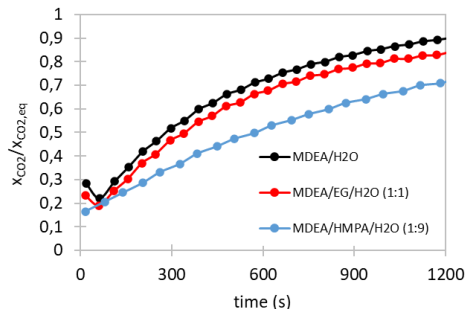


Figure 3. Time-evolution of the fraction of CO₂ in the solvent relative to its fraction at equilibrium. (a:b) is the molar ratio a/b of the last two components. The amine concentration is always 13 mol%. T=323,15 K. The solid lines are a guide to the eye.

In Figure 4 shows the results for H₂S, for which the observation is very similar to CO₂. Note that, as expected, H₂S absorbs much faster than CO₂, because it is a rapid proton transfer.

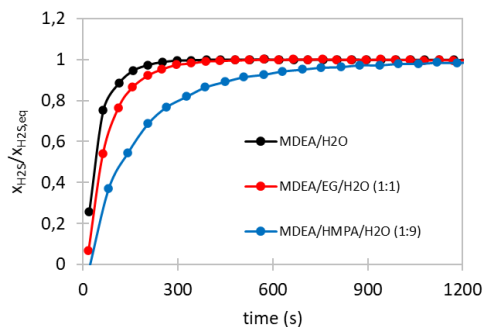


Figure 4. Time-evolution of the fraction of H_2S in the solvent relative to its fraction at equilibrium. (a:b) is the molar ratio a/b of the last two components. The amine concentration is always 13 mol%. $T=323,15$ K. The solid lines are a guide to the eye.

The kinematic viscosities of the three solvents are shown in Figure 5.

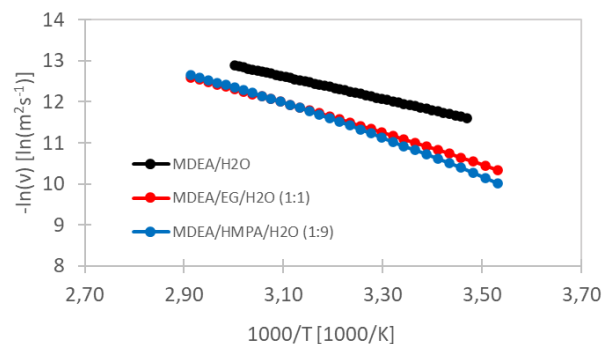


Figure 5. Kinematic viscosity as a function of temperature. (a:b) is the molar ratio a/b of the last two components. The amine concentration is always 13 mol%.

The kinematic viscosities of both the EG and HMPA containing solvents are very similar and thus don't explain their different impact on the CO_2 absorption rate. The results for DEAE-EO ($pK_a=10,15$) are given in the SI and are similar to MDEA ($pK_a= 8,65$), indicating that they don't depend on the reactivity of the tertiary amine. The pH of the solvents has also been measured at ~ 323 K and is 11,7 for aqueous MDEA (13 mol%), 10,0 for aqueous MDEA (13 mol%) with 9 mol% HMPA and 10,6 for aqueous MDEA (13 mol%) with ethylene glycol (42,5 mol%). The addition of HMPA thus lowers the basicity of the solvent more than the addition of ethylene glycol. The change in basicity impacts the acid gas absorption properties.

Discussion

To explain the significant difference in impact between HMPA and ethylene glycol one needs to include their interactions with water in the analysis. In Figure 6 the reduced excess molar volumes [11] for the binary mixtures HMPA-water [12] and EG-water [13] are compared. The addition of HMPA molecules to water quickly results in a strongly non-ideal behavior (strongly negative reduced excess volume), indicating a strong structuring effect of HMPA due to the formation of HMPA-water clusters [11], [12], [14]. Note that this corre-

sponds to a destruction of the water structure. Similar observations have been made for other aprotic polar solvents like NMP, DMI, and so on [15], [16]. It has been reported that such molecules form stronger hydrogen bond clusters with several water molecules and are therefore structure makers. The water-amide hydrogen bonds are stronger than those between water molecules and their strength increases with increasing donor number (lower acceptor number) of amides [12], [17], [18]. Despite steric effects, the water-HMPA hydrogen bonds should thus be much stronger than the water-water hydrogen bonds. A Prigogine-Flory-Patterson analysis of the HMPA-water mixture (see SI) confirms that the overall negative excess volume originates mainly from the intermolecular interactions, and to some extent from the free volume. The internal pressure contribution is positive. Moreover, HMPA shows a pronounced hydrophobicity and the hydrophobic effect will also significantly contribute to non-ideal behavior. Interestingly, the acceptor number of the HMPA-water mixture decreases almost linearly from 54.8 (pure water) to 10.6 (pure HMPA) as a function of HMPA content [19]. The non-ideality of the mixture in terms of excess volume, excess heat capacity and acid gas absorption, thus doesn't seem to be captured by the acceptor number (Lewis basicity). The non-ideality of the EG-water mixture is much less pronounced: EG is only a weak structure maker [13]. Similarly, for the MDEA-water system the excess volumes are only slightly negative [20].

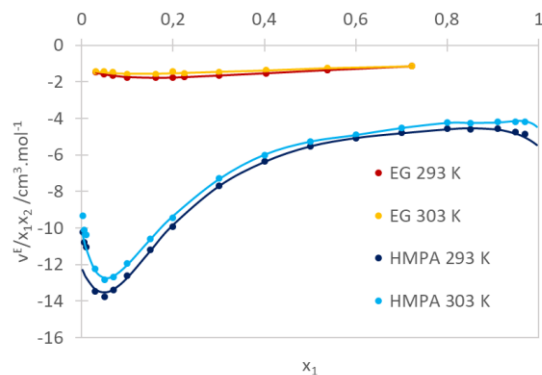


Figure 6. Reduced excess molar volume of EG-water [13] and HMPA-water [12] mixtures as function of the EG or HMPA molar fraction x_1 , at 293,15 K and at 303,15 K. Circles are experimental datapoints, the full lines are the Redlich-Kister equations [14].

The acceptor number of the HMPA-water mixture decreases from 54.8 (pure water) to 10.6 (pure HMPA) as a function of HMPA content [19] indicating the mixture becomes gradually more basic with the addition of HMPA and thus that the activation energy for acid-base reactions with amines should change [7]. However, in the presence of a tertiary alkanolamine like MDEA, a Lewis base, measurements of the pH show a decrease by $\sim 1,7$ units after the addition of 9 mol% HMPA (Lewis base), indicating a lower overall basicity. Water, which plays the role of the acid, thus seems to have a lower activity, probably due to its strong hydrogen bonds with HMPA. Indeed, because of the preferential H-bonding between water and HMPA, a significant part of the water is only present passively, thus not participating in any acid-base reaction. In thermodynamics this non-ideality is modelled by an activity that represents the active concentration of each solvent

component available to participate in the chemical reaction, as a reactant or as a product, or as a solvation medium [21]. The activity coefficient of water in the aqueous HMPA-amine solvent is thus lower than one (the activity of water is lower than expected from its concentration). The equilibrium of the dissociation reaction of water into H^+ and OH^- is thus shifted towards less dissociation, resulting in a lower basicity of the solvent. In a previous analysis using Hansen solubility parameters Wanderly et al. didn't include the hydrophobic effect in his analysis and suggested that the solvent hydrogen-bonding might not play an important role in CO_2 absorption [22]

This effect is almost absent in the presence of ethylene glycol. The gradual replacement of water by ethylene glycol results in a linear reduction of CO_2 absorption. Moreover, due to its hydroxyl groups, EG can even stabilize the reaction products, although weaker than water.

To better understand and visualize the structuring effect of HMPA, state-of-the-art molecular dynamics simulations were performed of the aqueous HMPA mixture (see SI). The simulated temperature dependency of pure water and pure HMPA agree well with experimental results. The non-ideal experimental behavior of the density of the mixture of water and HMPA could not be reproduced by the molecular dynamics simulations. The strong experimental increase in density (negative excess volume) when a small amount of HMPA is added to water (structuring effect), for example, is not captured by the atomistic model, which can thus not be used to gain more insight in the molecular mechanisms. This demonstrates the need for more accurate force fields to simulate the structuring effect of solvent molecules and their impact on chemical reactions.

Conclusion: The lower thermodynamic absorption capacity as well as the slower absorption rate of CO_2 , and, to a lesser extent H_2S , in an aqueous tertiary amine solution in the presence of excess water and limited amount of a strong structure maker such as HMPA can be explained by the strong non-ideality between water and HMPA. The formation of clusters of HMPA molecules and several water molecules due to strong hydrogen bonding results in water, although present in the solvent, being unavailable to participate in the chemical reaction (specifically for CO_2 absorption) and to stabilize the products of the absorption reactions, mainly HCO_3^- and HS^- . This effect dominates the other intrinsic properties of the system. The impact of EG is much weaker.

ASSOCIATED CONTENT

Supporting Information. The supporting information section includes information on the chemicals used, experimental VLE data for aqueous MDEA and aqueous DEAE-EO with and without co-solvents, kinetic data for DEAE-EO, viscosity of DEAE-EO and the molecular simulations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author 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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Notes

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ABBREVIATIONS

MDEA MethylDiEthanolAmine; DEAE-EO 2-[2-(Diethylamino)ethoxy] - ethanol; HMPA HexaMethylPhosphorAmide; EG Ethylene Glycol; NMP N-MethylPyrrolidone; DMI 1,3-Dimethyl-2-imidazolidinone; AG Acid Gas; AN Acceptor Number; DN Donor Number; Am Amine.

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TOC graphical abstract:

Strong impact of co-solvent
on molecular solvent structure



Strong impact on acid gas
absorption properties

