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Solvents for CO_2 capture. Structure-activity relationships combined with Vapour-Liquid-Equilibrium measurements

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Abstract

In this study a systematic approach was chosen to test and characterize amine systems for CO_2 capture. Vapour-Liquid-Equilibrium measurements were performed on a homologue series of amines, with ethylene amine as base structure. Various functional groups were used that ranged in chemical and physical properties. The effect of the addition of the following functional groups was investigated: $-NH_2$ (ethylene diamine), -COOH (β-alanine), -SH (cysteamine), SO_3H (taurine) and –OH (monoethanolamine). Of these amine systems, MEA and taurine showed comparable behaviour in CO_2 absorption and desorption. β-alanine formed relatively more (bi)carbonate. As expected, no direct correlation in absorption behaviour with pKa was found, whereas there was a linear correlation between desorption behaviour at a fixed partial pressure with pKa.

Keywords: CO_2 capture, amino acid, amino alcohol, ethylene amine, ethylene diamine, taurine, cysteamine, β-alanine, monoethanolamine (MEA), VLE

1. Introduction

Carbon dioxide removal is currently a hot topic to reduce the possibility of global warming. Most commercial processes to remove CO_2 from gaseous streams are based on amino alcohols. Monoethanolamine (MEA) is the industrial standard today, but has a major drawback that the volatility is rather high [1].

A common technique to test the performance of amines, amino alcohols or amino acids for CO_2 capture is measuring vapour-liquid equilibria (VLE) at a range of temperatures. A range of amines was tested which vary in structure by changing the functional groups at the tail of the chain. The base structure is ethylene amine and the effect of the addition of the following functional groups was investigated: $-NH_2$ (ethylene diamine), -COOH (β-

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alanine), -SH (cysteamine), SO_3H (taurine) and –OH (monoethanolamine). The amino acids among this series form an interesting class of possible solvents for CO_2 capture because of their non-volatility.

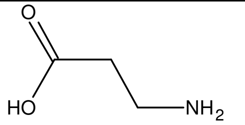
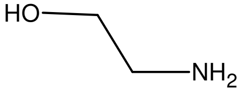
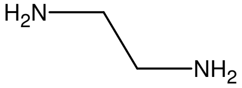
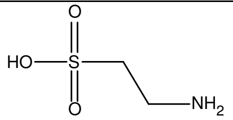
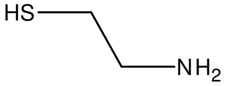
By choosing a homologous series in which one tail molecule is varied, the behaviour of these molecules in CO_2 capture can be studied systematically. The VLE behaviour of the range of amine systems chosen, is compared in relation to their structure and their pKa value. The results reported here are an onset to a larger study [2] in which molecular modeling is used to get insight in and to predict better performing molecules for CO_2 absorption and desorption.

2. Experimental

2.1. Amines

In this series ethylamine (pKa = 10.8) is taken as a base structure. The influence of five different functional groups on CO_2 capture was investigated. Table 1 shows some characteristics.

Table 1. Amino acids/ amines / amino alcohol

Amine system	Structure	Molarity (M)	pKa (-)	Supplier
β-alanine		2	10.24	Aldrich
Monoethanolamine (MEA)		2	9.5	Acros
Ethylenediamine (EDA)		2	9.8	Sigma
Taurine		2	9.06	SAFC
Cysteamine[$]		2	10.5	Fluka

[$] cysteamine decomposes above 353K

KOH is used to deprotonate the amine dissolved in water.

2.2. Vapour-liquid equilibrium

Vapour-liquid equilibrium measurements (VLE) are measured in a 1 liter vessel, equipped with a turbine stirrer with gassing stirrer shaft for effective gas dispersion, pH sensor and a pressure gauche. Typically, 0.5 liter of solvent is used. The solvent in the vessel can be heated up and equilibria can be determined at a constant temperature of the solvent. The vapour-liquid equilibrium is determined at several partial CO_2 pressures at a temperature of 40°C and 120°C for all solvents, except for cysteamine which was only measured at 40°C.

A 100% CO_2 gas flow is used (Air Liquide). The absolute volume of the CO_2 pulse is dependent on the molarity of the solvent. Generally, 0.05 mol CO_2 per pulse is dosed into the vessel at low molarities and 0.1 mol CO_2 per pulse at high molarities. The CO_2 pulses are controlled by software.

The stirring speed was set to 750 rpm for all measurements. Before starting the experiments, the solvent was evacuated to a pressure of about 10 to 50 mbar, while stirring vigorously. A typical measurement takes between 16 to 20 hours.

2.3. Attenuated Total Reflection - Fourier Transform Infrared Spectroscopy

Attenuated Total Reflection Fourier Transform Infrared Spectroscopy, abbreviated to ATR – FTIR was performed with a Nicolet 6700 of Thermo with an ATR unit. With an ATR crystal the chemical composition at the interface of liquid and crystal can be determined. An average of 32 spectra were taken in a range from 500 to 4000 cm^{-1}. The resolution was 0.482 cm^{-1}. A DTGS KBr detector was used with a KBr beam splitter.

Two amines, MEA and β-alanine, were chosen to follow the reaction with CO_2 in time at room temperature. Therefore, a reaction vessel was connected with a flow chamber which was mounted on top of the ATR crystal. The change of the FTIR spectra was followed in time. A 100% CO_2 gas flow was used, supplied by Air Liquide. The CO_2 gas flow rate was set to 11.2 l/h (The flow rate was chosen as such that saturation can be reached within 2 hours of testing).

With an increasing reaction time solvents become increasingly more acidic, which can lead to changes in peak position and peak intensity as function of reaction time or pH. Therefore, experiments were performed in which 2M β-alanine was titrated with HCl. As a reference, spectra of 1M $KHCO_3$ and 1M K_2CO_3 were also measured.

3. Results

3.1. Vapour-liquid-equilibrium

In Figure 1 the measured VLE curves are displayed. Cysteamine was only measured at 40°C due to decomposition of the molecule above temperatures of about 80°C. For the ease of comparison, the loading values of 2M ethylenediamine are displayed in mol CO_2 per $–NH_2$ group in Figure 1. Table 2 shows the loading values in mol CO_2 per mol amine for taurine, β-alanine, monoethanolamine, cysteamine and in mol CO_2 per $–NH_2$ group for ethylenediamine.

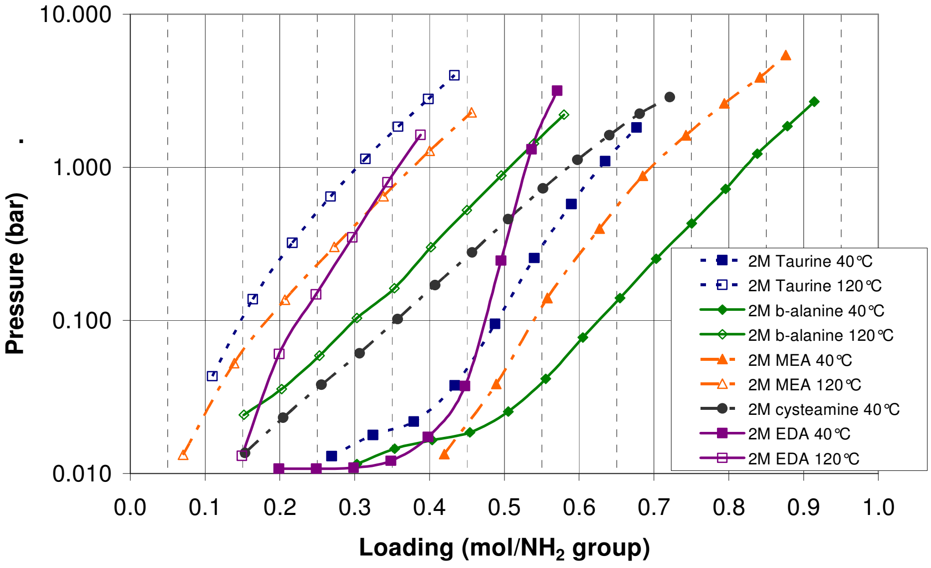


Figure 1. VLE curves of 2M taurine, β-alanine, MEA, ethylene diamine and cysteamine at 40 and 120°C. Cysteamine was only measured at 40°C. Mind: the loading values are all displayed in mol CO_2/NH_2 group.

Regarding the VLE data, taurine and MEA shows the best absorption and desorption behaviour. However, when the CO_2 capacity is calculated by subtracting the loading at 40°C and 120°C at a pressure of 0.1 or 1 bar, it is seen that the differences are rather small with the exception of ethylene diamine. The second amine group of the EDA molecule is more difficult to address after absorbing CO_2 than the first amine group, leading to less CO_2 uptake than expected on the basis of the number of amine groups present. The VLE data show that in case of MEA and taurine, predominantly carbamate is formed. The absolute CO_2 uptake is larger for β-alanine, which means that also (bi)carbonates are formed.

Table 2. Loading values of amino acids, alcohols and amines at a partial CO_2 pressure of 0.1 and 1 bar as determined from VLE measurements for 2M taurine, 2M β-alanine, 2M MEA and 2M cysteamine at 40 and 120°C.

Amine system	**Temperature (°C)**		**Difference**
P_{CO2} = 0.1 bar	**40**	**120**	**(mol/mol)**
Taurine	0.49	0.12	0.37
β-alanine 2M	0.63	0.30	0.33
MEA	0.53	0.18	0.35
Cysteamine *	0.36		
Ethylene diamine **	0.48	0.25	0.23
P_{CO2} = 1 bar			
Taurine	0.63	0.30	0.33
β-alanine	0.82	0.51	0.31
MEA	0.70	0.37	0.33
Cysteamine *	0.58		
Ethylene diamine **	0.53	0.36	0.17

* only measured at 40°C

** in mol CO_2 per $–NH_2$ group

3.2. ATR-FTIR

As reference spectra, a 1M solution of $KHCO_3$ and 1M K_2CO_3 solutions were measured. The spectrum of $KHCO_3$ shows a peak at 1360 with a shoulder at 1310 cm^{-1}, while for K_2CO_3 a peak at 1390 cm^{-1} is found [3]. Both peaks are assigned to the symmetric stretch of the –C=O bond. The results show that there is a small but distinguishable difference between bicarbonate and carbonate.

Peak assignment is difficult in the range between 1800 and 1000 cm^{-1} as peak overlap can occur. Characteristic peaks of β-alanine in the 1800 to 1000 cm^{-1} range are: 1630 cm^{-1} , 1550 cm^{-1}, and 1410 cm^{-1}. For β-alanine (Figure 2), the peak at 1550 cm^{-1} is assigned to the asymmetric stretch of the carboxylate anion [4, 5,]. The peak found at 1550 cm^{-1} shifts towards higher wavenumbers as the pH decreases from 11.77 to a pH of 9.27 (not shown here). Conjugation of the acidic group lengthens and weakens the –C=O bond, which results in a reduction of the frequency [4, 6]. Inductive effects, on the other hand, shortens and strengthens the –C=O bond, resulting in a frequency increase [4]. With a decrease of the pH an increasing concentration of the zwitterionic form of β-alanine is found. Upon decreasing the pH even further, the zwitterion is protonated and the –C=O bonds becomes shorter and stronger, resulting in a shift of the –C=O bond towards higher wavenumbers. The intensity of the peak changes from strong to medium. This implies that the dipole moment decreases upon acidification [4]. The peak at 1410 cm^{-1} for β-alanine is assigned to the symmetric stretch of the carboxylate anion [4, 5,].

In Figure 2 the spectra of β-alanine as function of the reaction time with CO_2 are given. When 2M β-alanine is loaded with CO_2, new peaks appear at 1305 cm^{-1} (weak), 1340 cm^{-1} (medium), 1490 cm^{-1} (weak) and a shoulder at 1390 cm^{-1}, as can be seen in Figure 2. Furthermore, the peak at 1550-1570 cm^{-1} broadened and remained strong in intensity. The peak found at 1390 cm^{-1} in Figure 2 can be assigned to carbonate as CO_3^{2-} shows a stretching vibration at around 1390 cm^{-1}.

The peak at 1340 cm^{-1} can be ascribed to carbamate [7]. Due to lone pair electron donation from the nitrogen atom into the carbonyl, the wavenumber of the carbonyl will shift towards lower values. The peak at 1340 cm^{-1} is ascribed to the symmetric stretch of carbamate and the peak at 1490 cm^{-1} to the asymmetric stretch of carbamate in analogy to the carboxylate anion. Furthermore, a broadening of the peak at 1550 cm^{-1} was found, which retained its strong absorption, in contrast to the diminishing intensity of the peak at around 1550 cm^{-1} found with a decreasing pH (not shown here). This broadened peak seems to consists of two peaks. The shift towards higher wavenumbers is due to induction with increasing acidity, thus protonation of the carboxylate. The remaining peak at 1550 cm^{-1} can be ascribed to the zwitterionic form of β-alanine which is formed during the reaction.

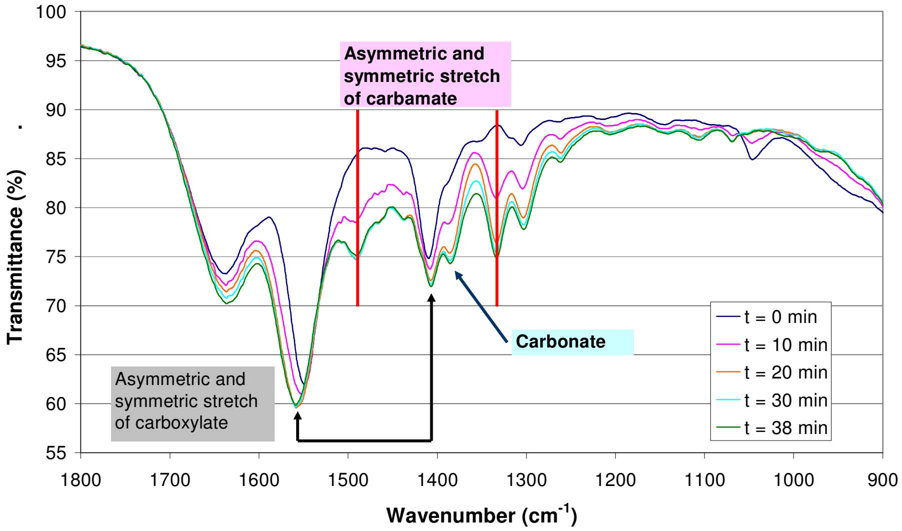


Figure 2. ATR-FTIR spectra of 2M β-alanine as function of CO_2 loading time.

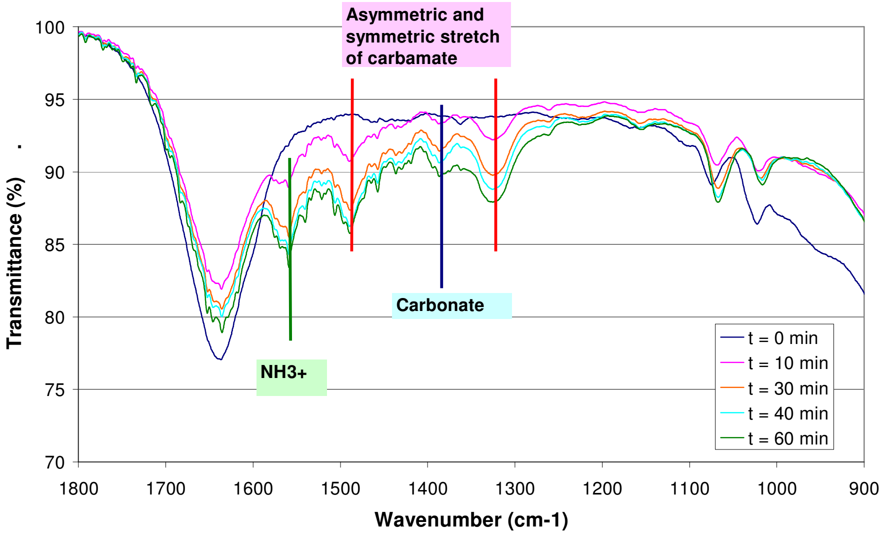


Figure 3. ATR-FTIR spectra of 2M MEA as function of the CO2 loading time.

For some samples, the CO_2 loading was determined. After 30 minutes loading of CO_2 at room temperature, a value of 0.37 mol/mol was found. That means that at this low loading values, carbonate is already formed in significant concentrations as can be seen in Figure 2. VLE measurements (Figure 1) showed that β-alanine absorbs more CO_2 than a loading value of 0.5 mol/mol, indicative of the occurrence of direct hydrolysis of CO_2 to (bi)carbonate or to the hydrolysis of carbamate. At a loading of 0.5 mol/mol, the pH was about 9.4.

2M MEA (Figure 3) shows the peak of primary amine at 1640 cm^{-1}, together with peaks of the –C-O stretch at 1070 cm^{-1} and the –C-N stretch at 1025 cm^{-1} [7]. When MEA reacts with CO_2 peaks arise and grow at wavenumbers 1330, 1490 and 1560 cm^{-1}. Also a small peak can be distinguished at 1390 cm^{-1}. The asymmetric and symmetric stretch of carbamate at 1330 and 1490 cm^{-1} are distinguished and a small contribution of carbonate (1390 cm^{-1}). The peak at 1560 cm^{-1} can be ascribed to N^+H_3 bending [8].

3.3. Structure-activity relationships

When the effect of molecule structure on the strength of acids and bases are considered, two effects are most pronounced: field and resonance effects. Field effects operate through space, by solvent molecules or by sigma bonds while resonance effects operate through π-electrons of a system. Functional groups that withdraw electrons by the field effect decrease basicity. These effects are felt along 2-3 carbon atoms. Furthermore it is known that charge dispersal leads to greater stability and thus acidity. In case of amines: electron withdrawing groups withdraw electron density from the central nitrogen atom of amines and so decrease their basic properties. Alkyl groups for example, donate electronic charge, increasing the electron density at the nitrogen atom, thus producing stronger bases. Electron withdrawing groups also alter the orientation patterns of solvent molecules around the molecule and its functional groups due to changes in the electron density distribution. In solution, especially aqueous solution, pK values do largely correlate with resonance and field effects [9]. Calculations of the electrostatic potential at the molecular isosurface show that there is a fair relationship between the level of negative electrostatic charge on amine molecules and their pKa values [10].

Ammonia is the simplest nitrogen base and has a pKa of 9.24. Any substituent that increases the electron density on the nitrogen atom raises the energy of the lone pair. This makes the lone pair more available for protonation and will increase the basicity of the amine [4]. Alkyl groups are electron releasing groups and will therefore increase the basicity of the amine, which is shown in case of ethyl amine, which has a pKa value 10.8. Introducing an alcohol group to ethyl amine, as in MEA, will result in a reduction of the basicity due to the electron withdrawing action of the –OH group. In going from methanol to acetic acid to methylsulfonate negative charge is first located on one oxygen atom, delocalised on two oxygen atoms in acetic acid and on three oxygen atoms in the sulfonate group. Due to this negative charge delocalisation these molecules becomes increasingly more acidic as their conjugated bases becomes more stable [4].

When the basicity of the amines and amino acids is compared with ethylamine as starting point, one can see that the introduction of electron withdrawing groups leads to a decrease in basicity. Oxygen atoms are more electronegative than nitrogen atoms and sulphur atoms. The pKa decrease is therefore expected in the order of: ethylamine (10.8) > cysteamine (10.5)> ethylenediamine (9.8) > ethanolamine (9.5) > taurine (9.06). β-alanine, with a pKa value of 10.24, has a decreased basicity compared to propylamine (pKa = 10.54) due to the presence of two electronegative oxygen atoms. pKa values in our homologue series can be explained by actions of electron withdrawing or releasing groups.

In literature, correlations between kinetic constants for the acid-base reaction and the pKa value of amines are found, the so-called Brønsted relations. [11-13]. Some authors investigated if correlations between pKa and CO_2 absorption exists [14]. Puxty et.al. [14] studied the absorption of CO_2 at 40°C for 76 different amines. The absorption capacity of all amines were plotted as function of the pKa [14]. Two areas were indicated: one were carbamate is preferably formed and one were the hydrolysis reaction prevails. Some amines showed a higher loading than expected. Possible explanations were sought in destabilizing the carbamate formation by the formation of intramolecular hydrogen bonds or by assuming that the pKa of the amine carbamic acid has such a low value that the carbamate formed is a weak acid and does not deprotonate [14].

Da Silva [15] uses computational models to calculate carbamate stabilities and correlate them with molecular structures. Da Silva shows that there is a substantial variation in carbamate stability of a range of amine systems, while the variation in bicarbonate formation energy (and thus base strength) shows less variation [15]. Electron withdrawing properties of groups of the molecule and the accessibility of the nitrogen atom are important factors [15]. It is to be expected that for the homologue series described in this paper that the accessibility of the N-atoms are comparable. However, the electron withdrawing groups are different. This leads to a strong variation in the interaction with CO_2. From the results presented, it can also be concluded that more knowledge related to the carbamate stability is needed for better understanding of reactive absorption of CO_2.

As expected, no correlation is found between pKa and CO_2 absorption as measured with VLE of our homologue series of amines. The results show that not only pKa, which is a reflection of several physical properties as well, but most likely also other properties such as charge, size, charge dispersal, solvation by water molecules [9], intramolecular hydrogen bonds [15] can play a role in CO_2 absorption. However, when the loading values at a fixed pressure at the 120°C VLE measurements are considered, a linear relation between pKa and loading is found (Figure 4) which suggests that at high temperatures hydrolysis of carbamate or direct hydrolysis of CO_2 prevails. Preliminary high temperature (up to a temperature of 75°C) NMR results of 2M β-alanine point toward preferential formation of (bi)carbanate as well [16]. In Figure 4 the following amine systems, with their pKa values between brackets, are also included: sarcosine (pKa=10.1), MMEA (pKa=9.8), proline (pKa=10.64), α-alanine (pKa=9.87), glycine (pKa=9.8), aspartic acid (pKa=9.66), 6-amino hexanoic acid (pKa=10.95), threonine (pKa=8.96), 2-(2-aminoethoxy)-ethanol (pKa=9.42), 1-amino-2-propanol (pKa=9.46).

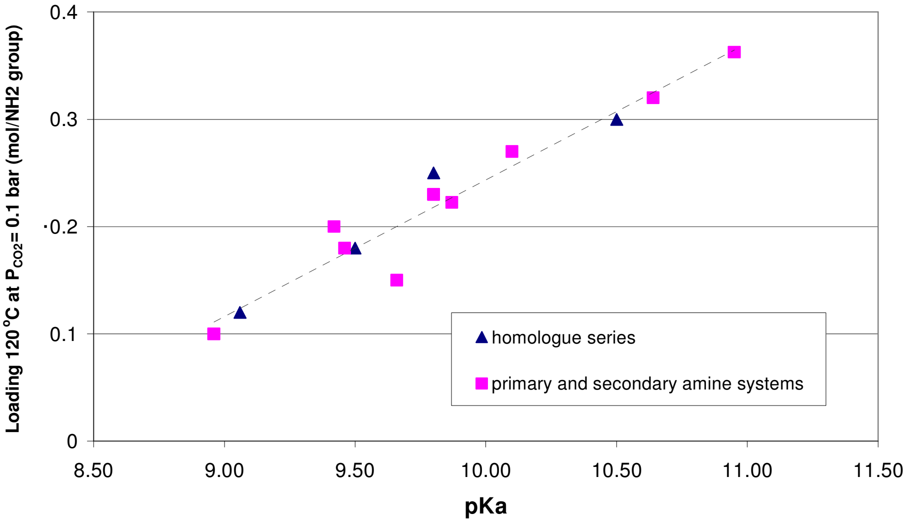


Figure 4. Loading at 0.1 bar in mol CO_2 per NH_2 group taken from VLE measurements at 120°C as function of pKa value. Cysteamine was left out. Blue triangles: homologue series as described in this paper. Pink squares: other VLE data (see text for more information). The dotted line is a guide to the eye.

In Figure 4, pKa values at 25°C are used. It is known that pKa values decrease with an increasing temperature. Calculations and measurements, in a temperature interval from 25 to 80°C, showed that for the amines measured here, the decrease with increasing temperature is linear and comparable for all four amines within measuring error [2].

4. Conclusions

A range of amines was tested which differ only in one functional group at the tail. Ethylamine was chosen as base molecule and $–NH_2$, -SH, -COOH, -OH and SO_3H were chosen as the functional groups. The pKa value of these amines can be explained by the influence of the functional groups on the electron withdrawing properties of those groups. Based on VLE measurements it can be concluded that there is no direct relation between the absorption at 40°C and the pKa values. Other (physical) properties must play a role as well. However, desorption measurements showed a linear relation with pKa values, indicating that at high temperatures hydrolysis reactions prevail. These results are confirmed by preliminary high temperature NMR measurements.

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