

The effect of hydrocarbon condensate and anti-foaming agents on the performance of CO₂ absorption with activated MDEA

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ABSTRACT

The use of aqueous solutions of methyldiethanolamine (MDEA) activated with primary or secondary amines for removal of CO₂ is finding increasing use in gas processing plants. In industrial use, the amine solution is frequently exposed to hydrocarbon condensate and additives such as anti-foaming agents. This paper investigates the effects of the presence of these contaminants in activated MDEA solutions with respect to CO₂ absorption.

The robustness to contamination of activated MDEA-solutions has been studied using the process conditions at the Sleipner Vest CO₂ removal plant in the North Sea as a base case. Solutions of 39 % MDEA containing 6 % butylethanolamine (BEA) or 6 % aminoethylethanolamine (AEEA), in addition to amine samples taken from the Sleipner plant have been investigated with respect to CO₂ absorption rate and heat of reaction.

These performance data have been achieved with a specially designed solvent characterisation reactor operated at a CO₂ pressure of 1.5 bar (22 psia) and temperatures between 20 and 50°C (68 and 122 °F). The reactor is designed to mimic typical operating conditions in the absorption tower and to allow the contaminant to be introduced as a homogeneously dispersed liquid.

Using AEEA as an activator, the absorption rate decreases approximately linearly with increasing CO₂-loading of the amine, while the BEA-activated solution is less sensitive to the CO₂-loading. The heat of reaction for activated amine and CO₂ is somewhat higher with AEEA than with BEA, and drops slightly with increasing CO₂-loading.

Typically, the measured CO₂ absorption rate is reduced by 40-55 % when hydrocarbon condensate or anti-foaming agent are added to the MDEA/BEA mixture, whereas less than 20 % reduction in absorption rate is measured for the MDEA/AEEA solvent.

Introduction

CO₂ removal by means of absorption in aqueous amine solutions is an important industrial process within processing of natural gas. The tertiary amine methyldiethanolamine (MDEA) is becoming increasingly more popular due to its chemical stability, the low stripping steam requirement and the potential for partial regeneration by pressure reduction (*Kohl and Nielsen, 1997*). In order to increase the reaction rate between CO₂ and the solvent, the MDEA-solution is activated by adding primary or secondary amines with higher reactivity than MDEA.

The Statoil operated Sleipner Vest field in the North Sea produces natural gas containing typically 9.3 % CO₂. The Sleipner amine plant installed at the Sleipner T platform is designed for purifying a total gas flow of 21 million Sm³/d (740 mmscfd). A simplified flow sheet is shown in Fig. 1. Typically the plant is operated continuously at 103 bar (1513 psi), and the liquid feed temperature to the two parallel absorbers is 68 °C (154°F). The applied amine is MDEA activated with butylethanolamine (BEA). The entire recirculation flow is partially regenerated by pressure reduction to form a semi-lean amine, and a 10 % slip-stream of this semi-lean solution is further treated in a stripping tower to form a lean amine. The amine plant was designed to reduce the CO₂-concentration below the sales specification of 2.5 mol%. However, since the start-up in 1996 the molar concentration of CO₂ in the purified gas has been significantly above this; typically 3.6 ± 0.4 %. Whereas the absorbers were designed for a minimum of 4 theoretical stages, the typical performance experienced corresponds to 1.8 theoretical stages.

A possible explanation for the limited CO₂-removal has been the entrainment of hydrocarbon liquid into the gas absorbers, resulting in either reduced performance of the amine solution and/or improper flow conditions in the absorbers.

In order to identify potential effects from the entrained hydrocarbons and anti-foaming additives, in 1998 Statoil initiated an experimental study of the absorption rate characteristics of amine solvents. The work focused on the effect of entrained hydrocarbons into the absorption towers, and also the effect of using anti-foaming agents.

It is well known from the literature that the presence of liquid hydrocarbons in the absorption tower may cause foaming. However, very little research or plant data indicate how the absorption properties of the amine are affected by the presence of hydrocarbon liquids. Similarly, stable operation of amine plants often requires injection of small amounts of anti-foaming agents, but very limited knowledge is available describing the effect of these compounds on the absorption properties.

The effect of hydrocarbon liquid on the CO₂ absorption rate in amine solutions has been investigated by *Peytavy et al. (1998)* in a pilot absorption tower and a laboratory wetted wall column. They concluded that the hydrocarbon decreased the interfacial area between the amine solution and the gas, leading to a significant drop in the absorption rate.

Peytavy et al. (2001) have reported the testing of different activators for MDEA in an absorption tower where liquid hydrocarbons were sprayed into the gas feed. They concluded that AEEA provided a higher degree of CO₂ removal than other activators tested at these conditions, including BEA.

The objective of this study has been to determine the CO₂ absorption rate of MDEA-based solvents in the presence of condensate and anti-foaming agents. The MDEA-based solvent has been tested both with the activator presently being used at Sleipner, BEA, and an alternative activator; AEEA. For comparison the solvent without any activator as well as solvent samples from the Sleipner plant have been tested.

Experimental method

In order to investigate the absorption rate of CO₂ in solvents, a characterisation reactor, essentially a bubble flow column, was built. The interfacial area between the gas and liquid is not known, but remains the same for liquids with similar viscosity. Also, the flow pattern as generated by the recirculated gas and solvent, allows the existence of a dissolved and a homogeneously dispersed hydrocarbon phase in the solvent phase. This could not be easily achieved in e.g. a stirred cell absorber. Also, the relatively large gas/liquid interfacial area generated allows the gas/liquid phase equilibrium between solvent and CO₂ to be reached within a reasonable time. The flow pattern is expected to be similar to that obtained in an absorber tray.

A schematic sketch of the experimental set-up is shown in Figure 2. The set-up consists of two vessels: the insulated gas-solvent reactor (0.045 m³/12 USgal) and the gas reservoir (0.235 m³/62 USgal). The vessels are connected via a pipe in which a pressure reduction valve is located. Gas and liquid can be circulated by means of a compressor and a pump respectively.

The solvent is exposed to pure CO₂ -gas via bubble flow injected from two identical sintered weld nozzles in the reactor bottom. As the absorption of CO₂ proceeds, the pressure in the gas reservoir decreases, while the pressure in the reactor is kept constant by the pressure reduction valve. In order to avoid any solvent non-homogeneity in terms of solvent loading, the liquid is recirculated counter-currently to the gas flow. Temperature and pressure in the gas reservoir and the reactor are recorded during the experiment.

Initially, the reactor is flushed with CO₂ in order to remove all air in the system. The liquid (20 l/5.3 US gal) is filled smoothly through the reactor bottom to minimise CO₂ absorption prior to the data acquisition. The valve between the reservoir and the reactor is opened, and the reactor pressure is stabilised at 1.5 bar (22 psig), as set by the pressure reduction valve. The data acquisition is then started. The gas circulation and liquid pump are started simultaneously, and the absorption of CO₂ begins. The instrument data are recorded until the reservoir pressure has reached a constant value. Liquid samples (20 ml) are taken from the reactor bottom before gas circulation is started, after 10 minutes of circulation and after the reservoir pressure has stabilised. The samples are analysed for CO₂ content by titration.

The solvent samples from the Sleipner process have been taken from two locations; just downstream of the stripper (denoted lean amine) and from the high-pressure pumps feeding the absorbers (denoted semi-lean amine). The lean amine is virtually

free of CO₂, whereas the semi-lean amine from Sleipner has a CO₂ -loading of 0.30 mol/mol. Only 10 % of the semi-lean amine has been thermally regenerated in the stripper, whereas the remaining 90% has been regenerated by pressure reduction only.

The solvent systems tested are listed in Table 1 in terms of volume percent of the different amines (MDEA, BEA, AEEA, Sleipner lean amine and Sleipner semi-lean amine) and additives (condensate and anti-foaming agents).

Table 1: Volumetric composition of solvent systems tested

Comb.	Sleipner [%]		Fresh amines [%]			Condensate [%]	Anti-foam [%]	
	Lean amine	Semi-lean amine	MDEA	BEA	AEEA		Drew 210	Pluronic
1			39					
2			39	6				
3			39	6		3		
4			39	6			0.4	
5			39	6		3	0.4	
6			39		6	3		
7			39		6	3		
8			39		6		0.4	
9			39		6			0.4
10			39		6	3	0.4	
11	100							
12		100						

The amine concentration at Sleipner was reported to be 39 % MDEA with 6 % BEA at the time of this study, hence this concentration has been used as base case when preparing fresh solutions in the laboratory.

The abbreviation, chemical formula, density and molecular mass for the pure amine substances are listed in Table 2. The densities apply at 20 °C (68 °F).

Two kinds of anti-foaming agents were used in this work. One is denoted Drew 210, produced by Ashland Chemical Company and supplied by Dyno Oilfield Chemicals. The other, denoted Pluronic, is supplied by BASF. The stabilised condensate was taken from the Sleipner process.

Table 2: Amines and additives tested

Short name	Chemical name	Density [kg/m ³]	Molar mass [g/mole]
MDEA	2,2-methyldiethanolamin	1046	119.2
BEA	2-butylaminoethanol	896	117.2
AEEA	aminoethylethanolamine	1036	104.1
Condensate		742	
Drew 210		1020	
Pluronic		Not reported	

Determination of absorption properties

The CO₂-absorption rate and the heat of reaction are determined from the relevant conservation equations.

Absorption rate

The CO₂ -absorption rate dn/dt (moles of CO₂ absorbed per second) for the solvent mixture is determined from the mass (mole) balance of the CO₂ –gas for the total system of the reservoir and the reactor:

$$\frac{dn}{dt} = \frac{d}{dt} \left(\frac{p \cdot V}{z \cdot R \cdot T} \right)_{reservoir} - \frac{d}{dt} \left(\frac{p \cdot V}{z \cdot R \cdot T} \right)_{reactor} \quad (1)$$

where

dn/dt - solvent absorption rate CO₂ [mole CO₂/s]

p - absolute pressure

V - volume

T - absolute temperature

R - gas constant

z - compressibility factor

The first term on the RHS of Eq. (1) represents the molar flux from the reservoir (pure CO₂-gas), and the second term represents the change in number of moles CO₂ in the gas phase in the reactor and its associated tubes and compressor volume. Notice that as the reactor pressure is nearly constant (1.5 bar, nominally) the second term is negligible compared to the first term on the RHS.

Heat of reaction

The heat of reaction h (J/mole CO₂ absorbed) for the solvent system is calculated from the energy balance for the reactor:

$$\frac{dn}{dt} \cdot h = (c_{pL} \cdot \rho_L \cdot V_L + c_{pFe} \cdot \rho_{Fe} \cdot V_{Fe}) \cdot \frac{dT}{dt} + U \cdot A \cdot (T - T_{amb}) \quad (2)$$

where

- h - heat of reaction
- c_p - specific heat capacity
- ρ - density
- V - volume
- A - surface of the reactor,
- U - overall heat transfer coefficient
- T - reactor temperature
- T_{amb} - ambient temperature

The indices L and Fe represent the liquid and the solid material respectively, and amb represent the ambient conditions.

The LHS of Eq. (2) represents the power (J/s) generated in the reactor due to the CO₂–solvent reactions. The first term on the RHS represents the power consumed by heating of the solvent and the reactor material (the power requirement to heat the gas is negligible). The second term on the RHS represents the heat loss to ambient. The value of the product $U \cdot A$ is determined experimentally at relevant conditions, with compressor and pump running.

Results and discussion

The absorption experiments are presented as CO₂ absorption rate vs. the CO₂ loading of the amine solution. At the end of each experiment, vapour-liquid equilibrium is obtained at the system temperature, and the absorption rate has decreased to zero.

Figure 3 shows the measured absorption rates of the main systems without additives plotted against the CO₂-loading. It is readily shown that the systems MDEA/BEA and MDEA/AEEA as prepared “fresh” from the barrels yield the highest absorption rates. As the solvent becomes loaded, the absorption rate drops steadily for these two systems. Initially the absorption rates of MDEA/AEEA and MDEA/BEA are quite similar, but the AEEA-activated solution is somewhat more affected by the CO₂-loading. Thus, in the loading range 0.3-0.6 mol/mol, which is the operational range of the Sleipner absorption columns, MDEA/BEA has the highest absorption rate. This observation may indicate that BEA has a higher degree of steric hindrance than AEEA and thus maintains a higher free activator concentration at higher CO₂ - loadings.

The Sleipner lean amine has a somewhat lower absorption rate than the fresh solutions at corresponding loadings. This may be due to the non-filtered impurities in the amine. The semi-lean Sleipner amine starts at a CO₂ loading of 0.3 mol/mol, and has an even lower absorption rate than the lean amine at the same loading values. However, the apparent difference between the lean and the semi-lean amine may be caused by the somewhat lower temperature in the latter experiment. Clearly, the MDEA solution without any activator yields the slowest absorption rate.

The measured absorption rates in aqueous solutions of 39 % MDEA and 6% BEA with various additives are shown in as a function of CO₂ loading. The presence of both the antifoaming agent Drew 210 and hydrocarbon condensate reduces the absorption rate of CO₂ significantly. The effects of hydrocarbon condensate and anti-

foaming agent are similar, and it is observed that the absorption rate decreases by 40-50 % when one of these impurities is present. However, the largest reduction in absorption rate is observed when both the hydrocarbon condensate and the anti-foaming agent are present.

Figure 5 shows the absorption rates for solutions of 39 % MDEA and 6 % AEEA. As for the BEA-activated solutions, the presence of the anti-foaming agent Drew 210 and hydrocarbon condensate have a similar effect on the absorption rate. However, the reduction in absorption rate is much less for this solvent, some 15-20 %. Also, the addition of the antifoaming agent Pluronic does not seem to have a significant effect on the CO₂ absorption rate in the MDEA/AEEA solution.

The condensate and the anti-foaming agent both yield low solubility in amine solutions. Hence, the main volumetric part of these compounds form a thin separate liquid layer at the gas-liquid interface in the reactor. The rest of the additives are either dissolved in the amine solution or exist as dispersed droplets in the liquid bulk, as the solution is mixed vigorously when the additives are introduced. Almost all contact between gas and liquid is found on the interface of the rising bubbles. The absorption rate measurements without gas and liquid circulation showed that the absorption at the liquid surface was negligible. Hence, it must be the presence of dispersed droplets, and/or dissolved components in the amine solution, which are responsible for the observed rate drop. It may be speculated whether the fact that AEEA is a di-amine can explain the higher robustness towards impurities and the related surface phenomena.

In order to preserve the absorption rate properties of the amine solution, precautions should be taken to avoid liquid hydrocarbons in the absorber. Proper separation and dew-point control of the feed gas are essential in order to prevent entrainment of hydrocarbon droplets or hydrocarbon condensation in the absorption plant. The use of anti-foaming agent may be required in amine plants in order to control foaming and thus improve the flow conditions and the operation of the absorption towers. However, as shown in this work, the anti-foaming agent may have a negative effect on the absorption rate of the amine solution.

Figure 6 shows the averaged absorption rates for the CO₂ loading range 0.0-0.4 mol/mol for all experiments performed in this work. Similarly, Figure 7 shows the averaged rates for the CO₂ loading range of 0.3 - 0.6 mol/mol. The latter loading range is representative for the solvent loading found in the Sleipner absorption columns. In both figures the absorption rates are scaled with the maximum absorption rates obtained for the two loading intervals. For both intervals it is clearly seen that the BEA-activator is much more sensitive to hydrocarbon condensate and anti-foam agent than is the AEEA-activator. The difference between the two activators concerning robustness against hydrocarbon condensate, as observed in this work, coincide with the findings reported by *Peytavy et al.* (2001).

The heat of reaction as calculated from the absorption rate and the temperature recordings, ref. Eq. (2), is presented in Figure 8. The oscillations in the heat of reaction as observed at high loadings are unphysical and due to numerical effects from signal noise. As can be seen, the AEEA activated solution has a significantly higher heat of reaction than when using BEA as an activator, especially at low CO₂

loadings. MDEA with no activator has the lowest heat of reaction, as expected. For all solutions, the reaction heat drops with CO₂ loading, which is consistent with other studies on heat of reaction of amines with CO₂ (Kohl and Nielsen, 1997). It is expected that the heat of reaction contributes significantly to the stripping energy necessary to regenerate the amine solution. Furthermore, the heat of reaction is also important for the temperature profile in the absorbers and hence also the absorption rate and loading capacity.

Conclusions

When condensate, the anti-foam agents Drew-210 or Pluronic, or combinations of these additives are added to MDEA solutions activated by BEA, the activator used in the Sleipner plant, the CO₂ absorption rate is recorded to drop between 40 and 55 %.

When AEEA is used as the activator in the above solutions instead of BEA, the reduction in the absorption rate is much less, with a 20 % reduction being recorded as maximum.

Although the anti-foaming agent serves to improve the hydrodynamic performance of the absorption tower, the presence of this additive in the amine solution may deteriorate the absorption performance of the amine solution itself. Proper scrubber design and dew-point control of the gas upstream of the absorber is vital in order to prevent the presence of hydrocarbon condensate in the amine solution. Accordingly this is also of key importance for alleviating a reduction in the CO₂ absorption caused by the presence of hydrocarbon liquid.

When the CO₂ loading of the liquid increases, the absorption rate is reduced for all solutions due to the lower free amine concentration. However for systems without anti-foaming agent or hydrocarbon liquid, the MDEA/BEA solvent maintains a higher absorption rate at high CO₂ loadings as compared to MDEA/AEEA. Thus for such “clean” systems, MDEA/BEA yields the better absorption rate performance in the intermediate CO₂ loading range 0.3-0.6 mol/mol, the operational range for the Sleipner absorbers.

Especially for low solvent loadings the heat of reaction is higher when using AEEA rather than BEA, which indicates that more stripping energy is required for the regeneration of MDEA solutions activated with AEEA as compared to BEA.

References

Kohl, A. and Nielsen, R., 1997, "*Gas Purification*", 5th. ed., Gulf Publishing Company, Houston, Texas

Peytavy J.-L., Elgue J. and Hoang-Dinh V. (1998) “Amine treatment of Natural Gas on Structured Packing: Harmful Influence of the Presence of Liquid Hydrocarbons”, presented at the *IGRC 98*, San Diego, California.

Peytavy J.-L., Capdeville S. and Lacamoire H. (2001) ”Regenerative Process for the deacidification of a gas containing CO₂ and liquid hydrocarbons using an absorbent liquid based on activated methyldiethanolamine”, *US Patent 6,920,754*

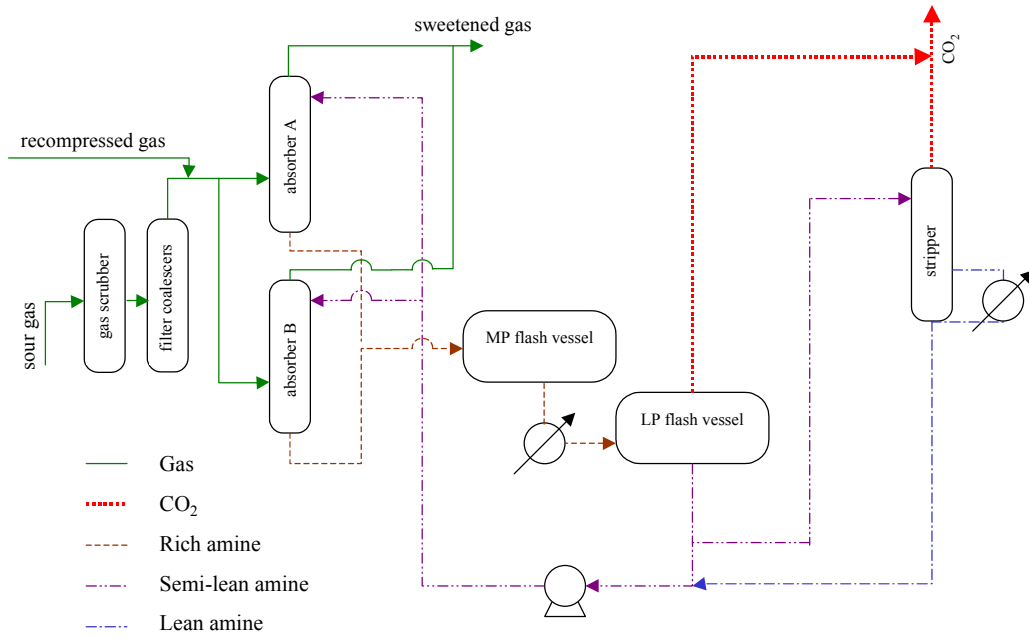


Figure 1: Simplified flowsheet of the Sleipner CO₂ removal plant

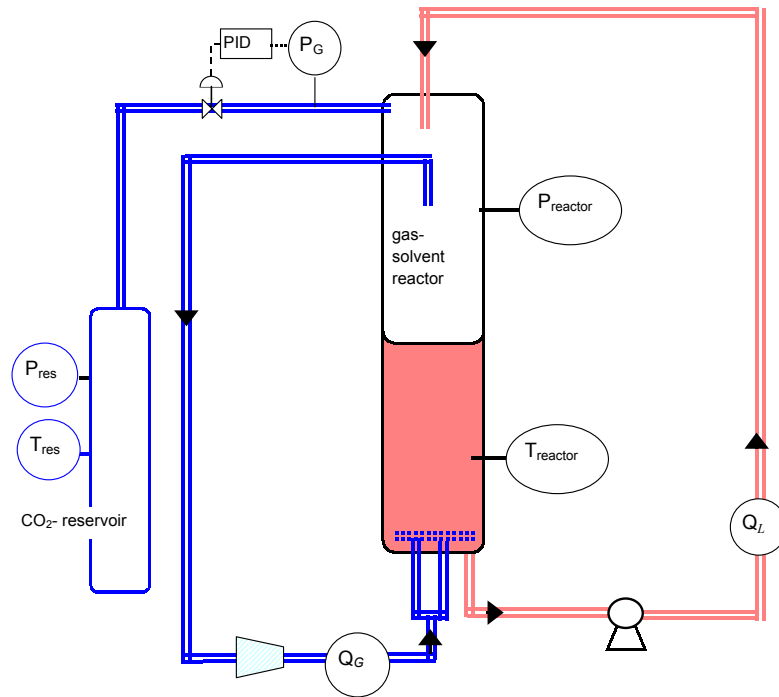


Figure 2: Schematic of the characterisation reactor

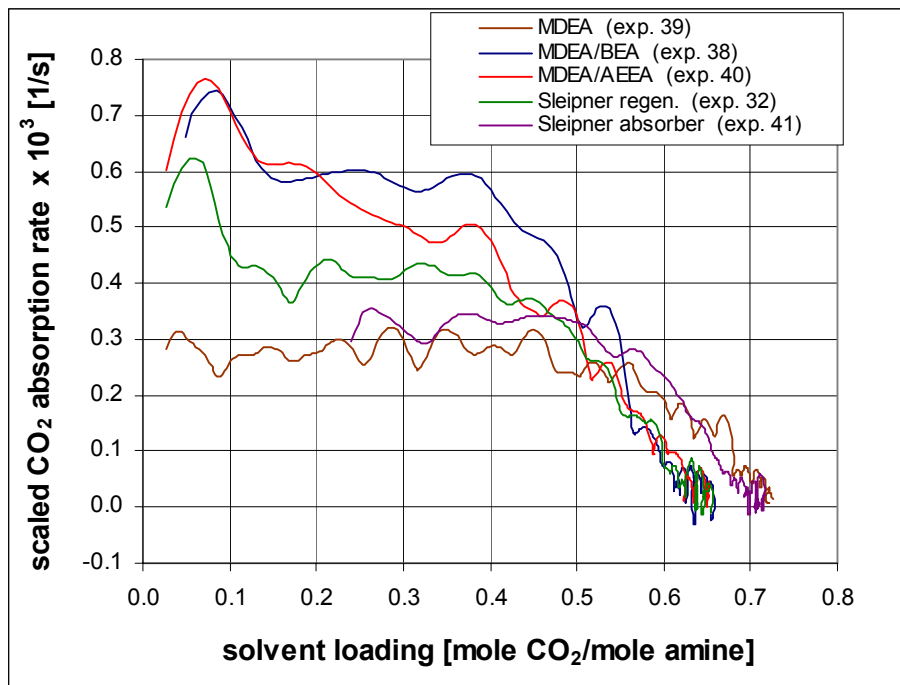


Figure 3: The absorption rates of main systems

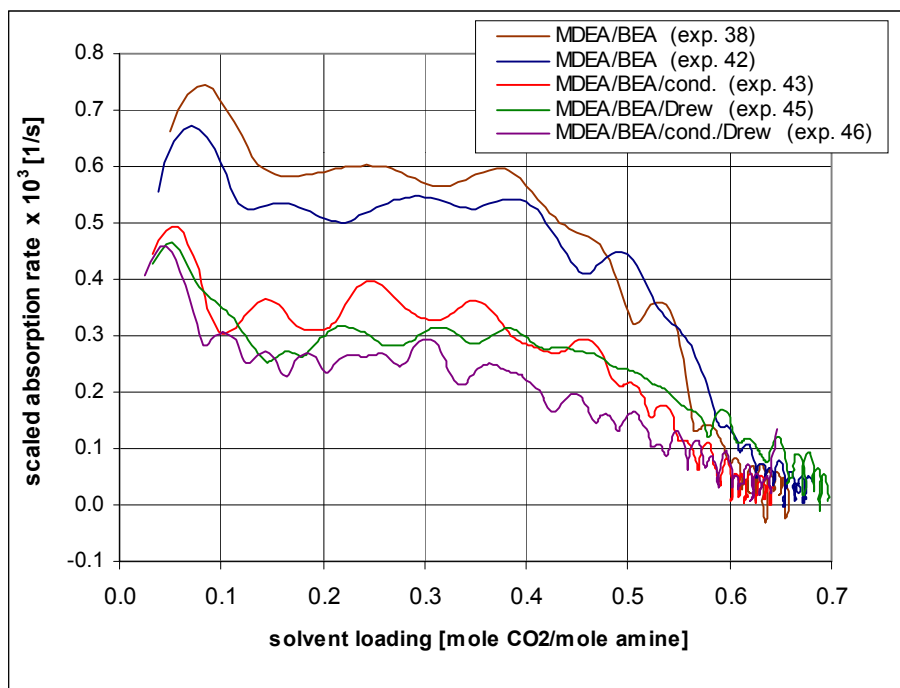


Figure 4: The absorption rates of 39 % MEA + 6 % BEA with additives

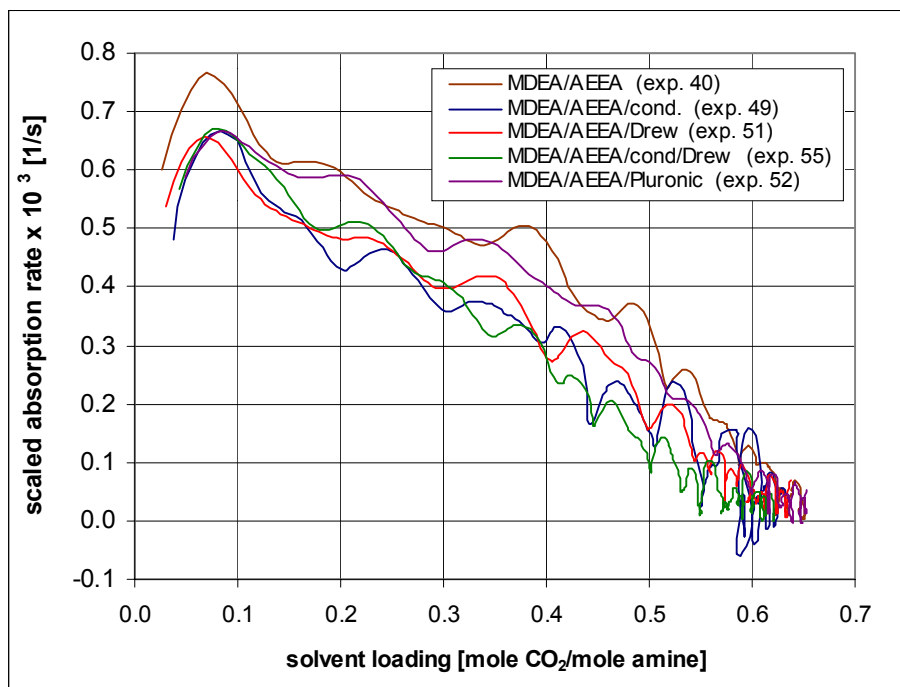


Figure 5: The absorption rates of 39 % MEA + 6 % AEEA with additives

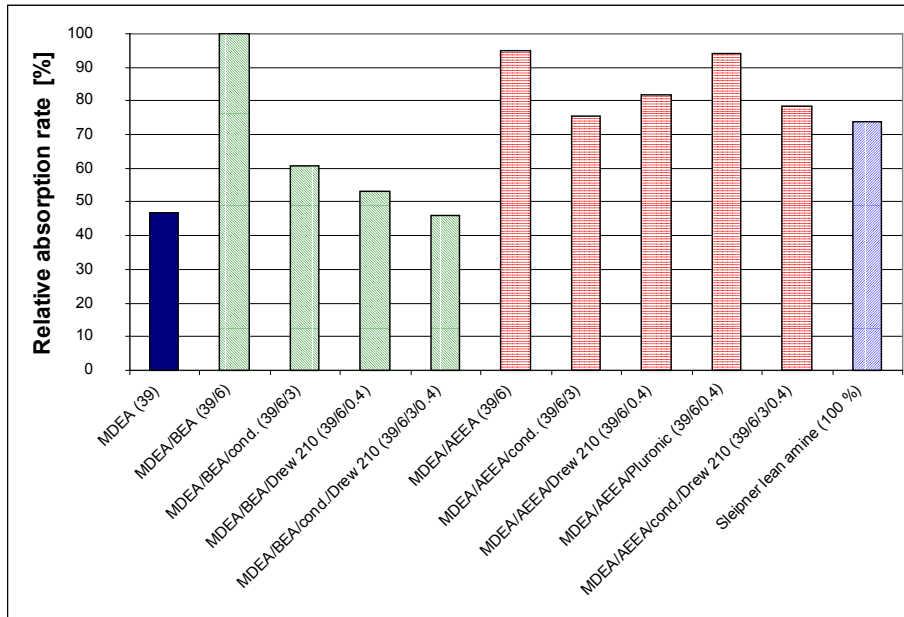


Figure 6: The average absorption rates for the loading range 0-0.4 mol/mol

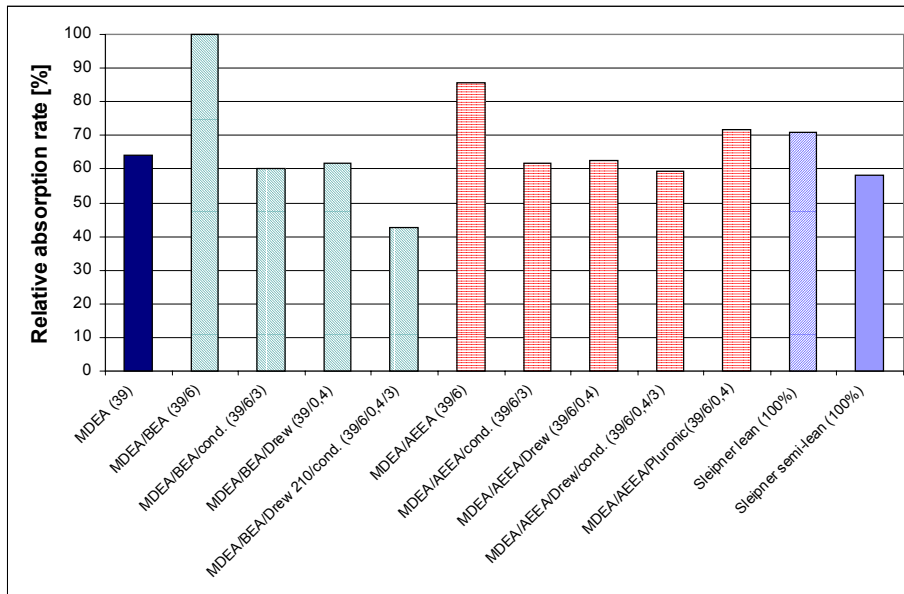


Figure 7: Average absorption rates for the loading range 0.3 – 0.6 mol/mol

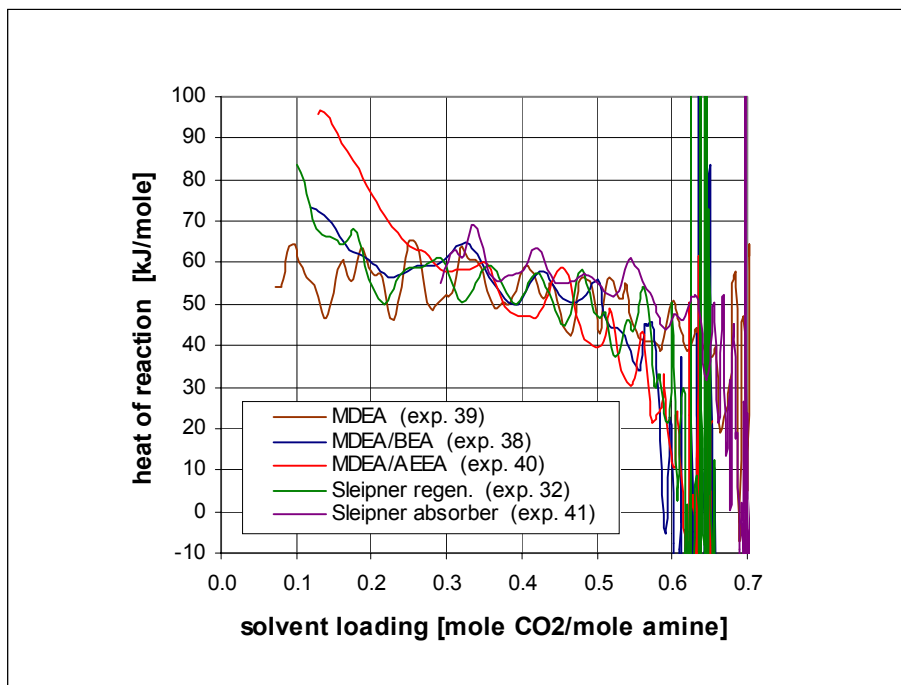


Figure 8: Heat of reaction for amine solutions investigated