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CO₂ Absorption in biphasic solvents with enhanced low temperature solvent regeneration

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Abstract

Reductions of capital cost and energy consumption are the key challenges for the development of amine-based CO₂ capture technology from flue gases. Lipophilic amine solvents exhibit a thermomorphic phase transition upon heating, leading to auto extractive behaviour, which intensifies desorption at temperatures well below the boiling point of the aqueous solutions. Solvent screening experiments in a 100 mL bubble column with CO₂ absorption at a partial pressure of 19.4 kPa and desorption with N₂ gas stripping or magnetic agitation demonstrate that those solvents have a regeneration temperature of less than 80 °C combined with a high net loading capacity of 3.34 mol-CO₂/L. This permits the use of low value and even waste heat for desorption purposes and can thus improves the process economics for CO₂ capture in industrial complexes. The new biphasic solvent system was evaluated in a newly constructed benchmark unit, which is comprised of an absorber column (2.5 cm in diameter and 145 cm in height) filled with high efficiency structured packing and a 500 mL stirred-tank as regenerator. In order to observe the phase transition phenomenon, the absorber and regenerator were made of glass. Three solvent formulations were tested at various regeneration temperatures ranging from 50 to 95 °C. A maximum 100% recovery was attained with certain solvent formulations at a regeneration temperature around 90 °C with total gas flow rate of 300 NL/hr (85% N₂ and 15% CO₂).

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1. Introduction

Anthropogenic CO₂ emissions from fossil fuels combustion are considered to be one of the main causes of global climate change. Amine scrubbing is presently both the preferred option and probably the only commercially mature technology for post-combustion capture of CO₂ [1]. The major challenges for amine-based absorption processes lie in the capture efficiency and unfavourable economics at current and short term forecasted CO₂ market prices, due to the energy requirement for solvent regeneration [2]. Aqueous blends of a primary or secondary amine with a tertiary or sterically hindered alkanolamine seem to be a promising alternative for promoting the absorption rate, but an impact was found on the loading capacity and regenerability[3-5]. Various aqueous solvent systems including...

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Alkanolamines and polyamines have been proposed to reduce the energy requirements with only modest improvements in the net CO$_2$ loading capacity [6,7]. Other proprietary hindered amines seem to be feasible solvents for CO$_2$ capture, but detailed information on their regeneration characteristics and stability is unavailable [8-10]. A phase transitional absorption method has been suggested to increase absorption rate and reduce the process cost, but the solvents and mechanism have not been disclosed and desorption still needs to be carried out at temperatures higher than 110 °C [11].

A novel approach to overcome this problem is to employ aqueous, partially miscible solvents, so called “lipophilic” amines, such as the tertiary amine N,N-dimethylcyclohexylamine (DMCA) and the secondary amine dipropylamine (DPA). Due to the limited aqueous solubility of these species, a thermomorphic (i.e. thermally induced) miscibility gap can be triggered during regeneration [12]. Extensive CO$_2$ desorption is thus achieved at temperatures only slightly in excess of the lower critical phase transition temperatures (LCST), typically 60-70 °C, enabling the utilisation of low temperature or even waste heat for solvent regeneration and potentially cheaper materials of construction. Such lipophilic amines have been studied extensively in previous work with respect to their reactivities, CO$_2$ capacities, regenerabilities, chemical stabilities and so forth [13-15]. However, the slow absorption rate of DMCA and precipitation of protonated DPA ions and bicarbonates represented obvious drawbacks of these solvents. Screening investigations to identify new lipophilic amine solvents were conducted both theoretically and experimentally. A novel alkylamine A1 exhibiting an extremely rapid absorption rate has been selected from a comparison of over thirty lipophilic amines in preliminary screening tests. The improved solvent system so called “a-DMCA”, short for “activated dimethylcyclohexylamine”, comprising alkylamine A1 as activator and DMCA as regeneration promoter, has also been investigated in recent research work. The excellent performance parameters of the new amine solvents make them the most promising candidates for assessing the technical viability in the further evaluation studies.

2. Experiments

2.1 Solvent screening tests

The screening experiments in absorption were carried out in 100 mL glass bubble columns with 40 mL of the aqueous amine solutions at 30 °C. Various amine concentrations from 3 to 5 M and CO$_2$ partial pressure of 19.4 kPa balanced with N$_2$ and saturated with water were employed over contact times of 2-3 hours, to ensure that equilibrium was achieved. Desorption was initially carried out by N$_2$ gas tripping at 75-80 °C and magnetic agitation with PTFE coated round stirring bar (30 mm length and 9 mm diameter) was used in further study. The feed gas flow rate was regulated by mass flow controllers (Bronkhorst EF-FLOW) so as to be constant in the absorption and desorption tests. During the experiments, the outlet gas was monitored online by gas chromatography (GC HP 6890). After the reaction had been completed, the CO$_2$ loading was ascertained by the barium chloride method, total amine concentration was determined by acid-base back-titration and the blended amine compositions were determined by GC analysis.

2.2 Bench-scale tests

As illustrated in Figure 1, the bench-scale unit consists of a glass absorber column, with an internal diameter of 2.8 cm, filled with high efficiency Sulzer structured packing (Ex 316) with a diameter of 2.5 cm. The total packing height is 145 cm. A new regenerator concept, a simple heated stirred tank reactor, is used in the unit, due to the fact that the regeneration temperature is below boiling point and no stripping steam is needed. The stirrer maintained the two-phase solvent in a finely dispersed turbid state and thus avoided extensive phase separation of the biphasic solvent. The two major advantages of using a stirred tank as regenerator are the capital expenditure (CAPEX) saving by dispensing with the packing or trays in regenerator and the energy saving through the absence of stripping steam in the regeneration. For large scale operation of such a process alternative regenerator concepts are being investigated.

The bench scale unit was designed to run continuously and was equipped with an automatic water supply system and a manual amine make-up system to compensate solvent losses and maintain the ratio between amine and water in the solvent. The CO$_2$ and water content in the feed gas, treated gas, and recovered acid gas, are measured by GC.
To measure and monitor the solvent composition in the unit, lean and rich solvent samples were taken and analysed by volumetric Karl Fischer (KF) method. The feed gas composition was set via the mass flow controllers and verified by the GC analysis. The total gas flow can be varied from 100 to 400 NL/hr without giving rise to a significant pressure drop. Both the regenerator wall and the fat solvent line are used to heat the solvent up to the regeneration temperature by using an electric trace heating and oil bath.

3. Results and Discussion

3.1 Performance of biphasic solvents in screening tests

3.1.1. Biphasic solvent A1

A series of screening tests have shown that the novel lipophilic amine A1 can be a very promising alternative solvent for CO₂ absorption, as a result of its excellent performance, and, in particular, the outstanding net loading capacity, which is roughly 150% higher than for the conventional alkanolamine MEA. Table 1 and Figure 2 demonstrate the advantages of using A1 as an activated agent for capturing CO₂. Increasing the concentration of A1 from 1 to 6 M in aqueous solutions promoted the CO₂ loading capacity. But above 5 M there was no significant increase in loading capacity when the concentration was raised to 6M, since water is also an important reactant necessary for achieving high capacity. The absorption rate of A1 is relatively fast, not only at lean loading, but also at rich loading of up to 2.5 mol/L. As a consequence of the conjectured shuttle mechanism, A1 - a moderately soluble amine - has a greater opportunity to come into contact with CO₂ and water. It reacts with both at the gas-liquid interface, at the liquid-liquid interface and in the aqueous phase during absorption via carbamate formation, carbamate conversion and bicarbonate formation, thus ensuring rapid reaction kinetics and high loading capacities.

As shown in Figure 3, A1 shows good regenerability, higher than 85% of solvent recovery in the high concentration (4-6 M) solutions at 80°C, higher than 92% at 90 °C or approaching 100% at 95 °C, due to thermomorphic phase separation and autoextractive behaviour. In the regeneration step, when CO₂ and water were liberated from A1, a separate aqueous phase was subsequently formed at the bottom of the solution due to the
limited miscibility. Since water is a strong self associate component, more and more water and ionic species were accumulated in aqueous phase with CO₂ releasing. Simultaneously the concentration of amine in organic phase was enhanced. After the biphasic system was steadily established, as a result of the similar solubility parameters of amine molecules, the regenerated lipophilic solvent adopted the role of an extractive solvent during regeneration. It withdraws the aqueous dissolved A1 from the aqueous phase, drives water out of organic phase, and is thus a decisive component for intensifying the depth of regeneration. When cooling the solution down to 40 °C, the regenerated biphasic solution was automatically transformed into a homogeneous liquid phase.

Table 1 Performance of 3-6M aqueous lipophilic amine solutions

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Concentration Unit</th>
<th>CO₂ loading mol/L</th>
<th>α_{sw} mol/mol</th>
<th>Regenerability%</th>
<th>Net CO₂ capture mol/L</th>
<th>Phase separation °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>3</td>
<td>2.98</td>
<td>0.99</td>
<td>82.6</td>
<td>2.46</td>
<td>90</td>
</tr>
<tr>
<td>A1</td>
<td>4</td>
<td>3.54</td>
<td>0.88</td>
<td>85.0</td>
<td>3.01</td>
<td>85</td>
</tr>
<tr>
<td>A1</td>
<td>5</td>
<td>3.62</td>
<td>0.73</td>
<td>86.7</td>
<td>3.14</td>
<td>80</td>
</tr>
<tr>
<td>A1</td>
<td>6</td>
<td>3.70</td>
<td>0.61</td>
<td>86.5</td>
<td>3.20</td>
<td>80</td>
</tr>
<tr>
<td>DMCA</td>
<td>3</td>
<td>2.64</td>
<td>0.88</td>
<td>98.4</td>
<td>2.60</td>
<td>70</td>
</tr>
<tr>
<td>DMCA</td>
<td>4</td>
<td>3.23</td>
<td>0.81</td>
<td>98.9</td>
<td>3.19</td>
<td>60</td>
</tr>
<tr>
<td>DMCA</td>
<td>5</td>
<td>3.36</td>
<td>0.67</td>
<td>99.2</td>
<td>3.33</td>
<td>50</td>
</tr>
<tr>
<td>a-DMCA</td>
<td>0.75+2.25</td>
<td>2.66</td>
<td>0.89</td>
<td>98.1</td>
<td>2.61</td>
<td>70</td>
</tr>
<tr>
<td>a-DMCA</td>
<td>1.5+1.5</td>
<td>2.89</td>
<td>0.96</td>
<td>97.2</td>
<td>2.81</td>
<td>75</td>
</tr>
<tr>
<td>a-DMCA</td>
<td>2+2</td>
<td>3.41</td>
<td>0.85</td>
<td>98.0</td>
<td>3.34</td>
<td>70</td>
</tr>
<tr>
<td>MEA</td>
<td>5</td>
<td>2.25</td>
<td>0.45</td>
<td>56.4</td>
<td>1.27</td>
<td>None</td>
</tr>
<tr>
<td>MEA+MDEA</td>
<td>0.75+2.25</td>
<td>2.01</td>
<td>0.67</td>
<td>87.6</td>
<td>1.76</td>
<td>None</td>
</tr>
</tbody>
</table>

* Regeneration by N₂ gas stripping at 80°C.

3.1.2. Biphasic solvent DMCA

Solvent regeneration at high temperature is one of the most significant shortcomings of the alkanolamine-based CO₂ capture process. The novel biphasic solvents presented in this paper were investigated as a means to ameliorate the energy demands and reduce the cost of heat utilities demands by low temperature regeneration through a thermomorphic liquid-liquid phase separation. Compared to A1, using DMCA as absorbent can increase the solvent
regenerability and reduce the operating temperature further. The unloaded aqueous DMCA solution appears as a biphasic solvent at concentrations of 1-5 M. The initially heterogeneous solution becomes homogeneous during absorption and reverts to two phases upon heating after achieving the critical solution temperature in desorption. The thermomorphic phase separation takes place around 60 °C in 4 M aqueous solution of tertiary amine DMCA, which is only slightly miscible in the water. A deep solvent regeneration (>98%) was obtained in 3 M solution at only 80 °C. Increase of concentration intensifies the solvent regenerability but depresses the absorption rate, especially at concentration higher than 4 M.

The regenerated DMCA solution is heterogeneous and its phase transition temperature is rather low. It must be cooled down to 0 °C to achieve homogeneous or 5 °C to obtain an emulsion. The absorption capacity of DMCA is quite high but its absorption rate is very slow, only half of the value for A1 at lean loading of 0.2 mol\(\text{CO}_2\)/mol_amine.

However, the outstanding regenerability makes it one of the most potential candidates for promoting regeneration in the blended solvent system.

3.1.3. Biphasic solvent blend \(\text{a-DMCA}\)

Besides to be regarded as a main absorbent, A1 was also used as an activator in DMCA based blended solvents to accelerate the absorption rate of the tertiary amine, since blending DMCA and A1 in aqueous solution combines the advantages of both. The absorption in lipophilic amine DMCA solutions in the presence of 25 mol% activator takes place 80% more rapidly than that without activator and 50% faster compared to the benchmark amine solution MEA+MDEA (3M, 1:3). The advantage of the lipophilic amine solvent blend lies not only in the high loading capacity but also in the good regenerability in comparison to the benchmark absorbent. Moreover, the net CO₂ capacity of a-DMCA (1:3) solvent is also more than 50% higher than MDEA+MEA. Remarkable phenomenon is its rapid reaction rate in both absorption and desorption, since A1 not only serves as a solubiliser for DMCA but also leads to a vigorous reaction with \(\text{CO}_2\) during the absorption. DMCA acts as an auto extractive agent, forming an organic phase at the top of the solution in regeneration, removing the amine from the aqueous phase and thus favourably displacing the regeneration equilibrium and driving the reaction towards dissociation of the carbamate and bicarbonate species in the loaded aqueous phase according to the Le Chatelier’s principle.

In order to increase the absorption rate further and shift the phase transition temperature of regenerated solvent to room temperature, the blended solution a-DMCA with 1:1 of A1 and DMCA was formulated. In the 3 M and 4 M a-DMCA (1:1), the regenerated biphasic solvents were homogenised in the form of emulsion at 30-40 °C by agitation. The absorption rates were improved to the level being comparable to that for the solution with single amine A1 and the regenerability was very close to DMCA, since DMCA was well performed as regeneration promoter in the blended solvent.

![Figure 4. Intensification of solvent regeneration by agitation in 4 M a-DMCA (1:1) solution](image-url)
Since gas stripping is not feasible in practice, agitation is recommended for intensifying solvent regeneration by
gas disengagement. Figure 4 demonstrates the regenerability of 4 M a-DMCA (1:1) solution for varying agitation
speeds. The regeneration rate by means of agitation is comparable to that for gas tripping and is also positively
influenced by the stirring rate. At high agitation speed such as 1000 rpm the CO₂ release is even faster than that by
gas tripping at 200 mL/min nitrogen flush. With respect to the viability of downstream CO₂ sequestration process,
agitation is superior to gas stripping, since the CO₂ released can directly be compressed without the need for any
other additional separation process.

The regeneration of biphasic solvent can be carried out at a modest temperature of 80°C or lower, which is much
less than the temperature (~120 °C) employed in industrial processes using alkanolamines. Together with the high
cyclic loading capacity of such amines, this offers more opportunity for cost reduction with respect to the amount
and quality of energy requirements. According to the calculation using a thermodynamic evaluation technique [16],
the new solvent a-DMCA can increase the CO₂ capture efficiency by more than 60% and cut down the energy
consumption by more than 40% in comparison to the absorption and regeneration characteristics of the benchmark
aerial absorbent MEA (~4 GJ/t CO₂). The lower operating temperature brings the additional benefits of less
degradation, less corrosion and the potential of using cheaper materials of construction for the regeneration vessel,
for example.

3.2 Performance of biphasic solvents in bench-scale unit

In the first campaign of the bench-scale test, solvent formulations of 4M DMCA, 4M A1, and 2M DMCA + 2M
A1 were studied at various regeneration temperatures ranging from 50 °C to 95 °C. The feed gas flow is 300 NL/hr
with 15% CO₂ and 85% N₂. The solvent flow rate was 0.8 kg/hr. In order to observe the phase change phenomena,
i.e. the formation of a single phase in the absorber (Figure 5) and two phases in the regenerator (Figure 6), both the
absorber and regenerator are constructed from glass.

The phase separation temperature of pre-loaded 4 M MDCA is around 75-80 °C. For 4 M A1, the value rises to
93-94 °C. As shown in Figure 7 that the CO₂ recovery of 4 M DMCA is higher than that of 4 M A1 at temperature
below 85 °C and reaches its plateau (around 50%) at 83 °C. A1 shows lower CO₂ recovery at lower temperature
(<85 °C) but achieves almost 100% recovery even well before the phase separation temperature. This can be
explained by the different characters of the two amines. DMCA has lower phase transition temperature and thus
much easier to be regenerated, but its absorption rate is much lower than for A1. During the bench-scale test, it was
found that the current absorption column is kinetically limited for 4 M DMCA. Therefore the maximum attainable
CO₂ recovery for 4 M DMCA is therefore much lower than that of A1 under the operation conditions of this study.
A1 is relatively difficult to be regenerated and has higher regeneration temperature. However, the absorption rate of
A1 is much higher than that of DMCA, which makes it possible to reach 100% recovery, even below its phase
separation temperature.
In order to exploit the advantages of both DMCA and A1 synergistically, a formulation with 2 M A1 and 2 M DMCA was tested under the same conditions (Figure 7). It can be clearly seen that the recovery in the lower temperature range was improved, which meant the regeneration was promoted by adding DMCA. The maximum CO2 recovery of the blend is increased to around 70% which means that the absorption rate has been accelerated by adding A1. In addition, the regeneration temperature was lowered to the range of 83-86 °C compared to that of A1, which is beneficial for using waste heat with even lower temperature.

4. Conclusions

Biphasic amine solvents such as DMCA, A1 and blended solution a-DMCA have been studied and optimised in this work. Thermomorphic phase transition is a crucial distinguishing characteristic of aqueous lipophilic amine solutions and it intensifies solvent regeneration down to 80-90°C. By varying solvent temperature and agitation, the regenerated heterogeneous solvents were successfully converted to homogeneous solutions or emulsions at 30-40 °C. The excellent performance of these biphasic solvents, such as A1 (5 M), and a-DMCA (4 M, 1:1), in terms of high net loading capacities (up to 3.34 mol/L at 30 °C) and deep regenerability (up to 98.0% at 80°C), is significantly superior to conventional alkanolamines in the screening tests.

In the bench-scale test, three solvent formulations were evaluated. A1 shows a good absorption rate but relatively a high regeneration temperature. In the future, more tests will be carried out to experimentally evaluate the energy consumption of the biphasic solvents, which is expected to be lower than conventional alkanolamine solvents, due to the fact that no stripping steam is needed for the regeneration of biphasic solvent. Other performances parameters, such as corrosion, thermal/oxidative degradation, nitrosamine formation, SO2 compatibility, etc., which are expected to be less serious than for conventional alkanolamine solvents because of the mild regeneration temperature, will be assessed at a later stage of the development work.

References