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Carbon dioxide absorption in biphasic amine solvents with enhanced low temperature solvent regeneration

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Improvement in the CO_2 capture from flue gases and reduction of the energy requirement for solvent regeneration are the most significant challenges facing the post-combustion carbon capture process. Novel absorbents, so-called lipophilic amines, exhibit a thermomorphic phase transition upon heating, giving rise to autoextractive behaviour, which enhances desorption at temperatures well below 80°C. In comparison to conventional alkanolamines, the vapour liquid equilibrium (VLE) data for lipophilic amines indicate their considerable potential for the CO_2 absorption process, in particular the high cyclic loading capacity approaching 0.9 $mol_{-CO2}/mol_{-absorbent}$ and the low regeneration temperature, which enables the use of low value heat utilities for desorption purposes. The absorption enthalpies of selected amine solvents were determined by an indirect method and the solvent degradation with respect to that of alkanolamines was also investigated.

1. Introduction

The amine-based post-combustion CO_2 capture process is the preferred option for achieving rapid cuts in CO_2 emissions from power generation plants using fossil fuels. The key challenge for this technology lies in the process economics, primarily reflected in the energy requirement for solvent regeneration. Some undisclosed solvents, which can allegedly cut the regeneration energy by 20-34% compared to the benchmark system monoethanolamine (MEA) were presented by Mangalapally et al. (2009) and Goto et al. (2009), but the desorption must still be carried out with high quality steam at 120°C. The unnamed absorbents proposed by Puxty et al. (2009) offer good absorption performance at CO_2 partial pressures higher than 20 kPa, but no significant advantage at lower partial pressures. Aqueous ammonia seems to be an alternative solvent for removing CO_2 with its quick reaction rate and high loading capacity, but there is little information concerning the regenerability and economics (Gonzalez-Garza et al., 2009). A novel approach to meet this challenge is to employ aqueous partially miscible solvent comprised of so-called *"lipophilic"* amines. Due to their limited aqueous solubility, a thermomorphic miscibility gap can be induced during regeneration (Agar et al., 2008). Extensive CO_2 desorption is thus achieved at temperatures only slightly in excess of the lower critical phase transition temperatures (typically 60-70°C), permitting the utilisation of low temperature or even waste heat for solvent regeneration.

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Investigations to identify new lipophilic amine solvents were conducted both theoretically and experimentally. Extensive studies on the CO_2 loading capacities, reaction kinetics, regeneration rates, residual loadings and so forth of the promising tertiary amine N,N-dimethylcyclohexylamine (DMCA) and the secondary amine dipropylamine (DPA) were disclosed in previous work (Zhang, 2007 and Tan, 2010). In the meantime, a novel absorbent system comprising the alkylamine B1 as the main absorbent, showing outstanding regeneration characteristics, and the amine A1 as an activator, exhibiting a significantly faster absorption rate, were selected from a comparison of more than thirty lipophilic amines in screening tests.

2. Experiments

2.1 CO_2 absorption and desorption

The experiments were carried out in a 100 mL glass bubble column with 40 mL of the aqueous amine solution. Various amine concentrations from 3 to 5M and CO_2 partial pressures in the range of 3 to 100 kPa were equilibrated for 2-5 hours at 40°C. Desorption was initially carried out by N_2 gas stripping at 70°C and both lower and higher temperatures were also tested, to observe their influence on absorption and regeneration. The feed gas flow rate was regulated by mass flow controllers at a constant value in the absorption and desorption tests. In further investigations, solvent regeneration was also promoted by agitation, since gas stripping is not a technically feasible option in an industrial-scale low temperature desorber. During the experiments, the composition of the gas was monitored on-line by GC (HP6890). Upon completion of the reaction, 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 ascertained by GC analysis.

2.2 Reaction enthalpy measurement

The absorption enthalpy was determined by an indirect method using van’t Hoff’s equation. The system pressure and temperature were measured in a Büchner flask with a ground glass joint connected to a manometer and a thermometer. After adding the loaded amine solution, the flask was evacuated and constituted a closed system containing the liquid solution and CO_2/water/amine gas phase. The pressure measured by the manometer reflected the vapour of aqueous amine solution and desorbed CO_2. The temperature of the solution was varied by submerging the flask in a water bath and the pressure corresponding to the VLE monitored at the prevailing temperature. 3M lipophilic amine solutions in blends or individually were studied at temperatures from 25 to 50°C and pressures from 100 to 800 kPa. The pressure of CO_2 was calculated by subtracting the vapour pressure of water and amine from the total pressure, $\ln(P_{CO2})$ was then plotted against 1/T and the absorption enthalpy of CO_2 in the amine solution was calculated from the slope of this plot according to the Clausius-Clapeyron relation.

2.3 Chemical stability test

The stability tests on the absorbents were carried out at 50°C with 2 mL/min CO_2 and 98 mL/min N_2 or O_2. Prior to analysis, the solutions were treated with 15 mol% CO_2, so that the results could be compared with those from the standard absorption experiments. The amount of residual amine was determined by basicity measurements and the reactivity of the absorbent toward CO_2. In order to minimise the influence of solvent vaporisation, chilled water at 5°C was used in the condenser and a control experiment without O_2 was also carried out for purposes of comparison and to distinguish oxidative degradation from other losses. In further experiments, 0.2 mM iron ions Fe^{2+}/Fe^{3+} were added as a catalyst to promote oxidative degradation.

3. Results and discussion

3.1 Performance of lipophilic amines in absorption and desorption

The aqueous lipophilic amine solution is initially heterogeneous, it becomes homogeneous during absorption and reverts to two phases upon heating after exceeding the critical solution temperature during desorption. The organic phase formed acts as an autoextractive agent, 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 Le Chatelier's principle. The major advantage of using lipophilic amines, with their characteristic thermomorphic transition between single to dual phase systems, is that the regeneration can be carried out at a modest temperature, below 80°C, which is much lower than the temperature employed in industrial processes with alkanolamines, together with an exploitation of the solution entropy effect, offering more degrees of freedom for cost reduction and with respect to the energy requirements.

Lipophilic amines such as B1 and A1, with their remarkable performance, were selected after an extensive series of screening tests. As a consequence of the conjectured shuttle mechanism, A1 - a moderately soluble amine - has a greater opportunity to come into contact with CO_2 and water. It thus reacts with both rapidly at the gas-liquid interface, in the organic phase, at the liquid-liquid interface and in the aqueous phase during absorption. On the other hand, the amine B1, which is only slightly miscible in the aqueous phase, exhibits an outstanding regenerability, because of the thermomorphic phase transition. Blending B1 and A1 in aqueous solution combines the advantages of both. The predominance of the lipophilic amine solvent blend lies not only in the high loading capacity, but also in the good regenerability in comparison with the benchmark absorbent MEA. The cyclic loading capacity of the newly developed 3M B1+A1 solvent blend can be over 75% higher than that for a conventional 5M MEA solution. The blend B1+A1 has superior absorption characteristics to DMCA+DPA (figure 1) and its loading capacity can be higher at extended reaction times, while that of DMCA+DPA is limited due to the precipitation of DPA bicarbonate. Although the absorption rate of B1 is very slow, it can be accelerated significantly by blending with the activator A1, up to a factor of four over the value without activator (table 1). During desorption, B1+A1 exhibits excellent behaviour by virtue of its extremely rapid regeneration kinetics and low residual loadings. In order to improve the release of CO_2 from loaded solution without gas stripping, agitation was applied during solvent regeneration. Figure 2 illustrates that the blended solution B1+A1 shows an extraordinarily fast desorption rate in comparison with other amines and that the agitation velocity also has positive influence on CO_2 desorption, with more CO_2 being desorbed at higher agitation rates. Although the solvent cannot be regenerated by agitation as deeply as with gas stripping - typically 5-20% less CO_2 is released - the regeneration rates are comparable for agitation velocities higher than 500 rpm.

Table 1: Absorption and desorption characteristics of aqueous amine solutions

Absorbent	$\alpha_{abs}{}^{a}$	$\alpha_{des}{}^{b}$	CO_2 Removal	Absorption rate^c x10^5	Rich loading	Lean loading	Cyclic loading
Unit	mol/mol	mol/mol	%	mol/(L·s)	mol/L	mol/L	mol/L
3M MEA	0.67	0.42	37.6	44.2	2.02	1.26	0.76
5M MEA	0.62	0.32	48.1	35.7	3.12	1.62	1.50
3M A1	0.98	0.27	72.5	45.5	2.95	0.81	2.14
5M A1	0.77	0.12	84.8	42.6	3.87	0.59	3.28
3M B1	0.95	0.04	96.1	10.4	2.84	0.11	2.73
3M MDEA+MEA (3:1)	0.67	0.10	84.6	33.4	2.01	0.31	1.70
3M DMCA+DPA (3:1)	0.78	0.08	90.2	42.3	2.34	0.23	2.11
3M B1+A1 (3:1)	0.93	0.05	94.3	40.9	2.80	0.16	2.64
3M B1+A1 (2:1)	0.96	0.10	90.0	43.5	2.89	0.29	2.62
4M B1+A1 (3:1)	0.76	0.05	93.0	32.1	3.02	0.21	2.81

a) absorption at CO_2 partial pressure of 14 kPa at 40°C; b) desorption with 200 mL/min N_2 stripping at 70°C; c) measured at CO_2 loading α=0.2 $mol_{-CO2}/mol_{-absorbent}$

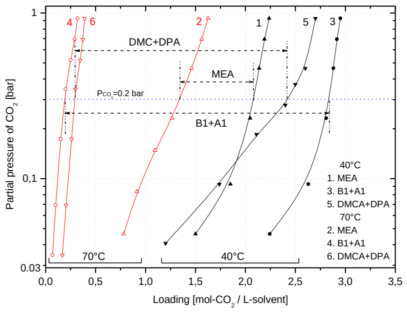

Figure 1: Vapour-Liquid Equilibrium of various 3M amine solutions

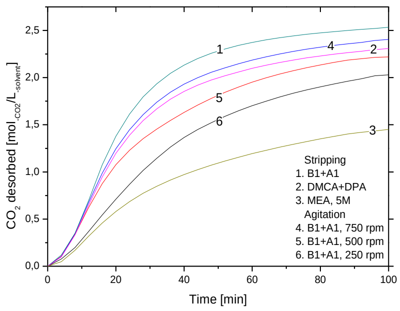

Figure 2: CO_2 desorption by means of gas stripping and agitation

3.2 Optimisation of lipophilic amine blends and reaction conditions

The novel main absorbent B1 was selected because of its high loading capacity and regenerability, but the absorption rate of an aqueous B1 solution is very slow, similar to that of MDEA solutions. An appropriate activator must thus be included to enhance the reaction kinetics. In the lipophilic amine blend, the remarkable acceleration of the absorption reaction rate can be achieved by using A1, which performs much better than MEA, thanks to its rapid absorption rate and high loading capacity. It offers the greatest potential for improving the reaction kinetics of main absorbent without diminishing the loading capacity, which is one of the major weaknesses of MEA. In the regeneration step, CO_2 is first liberated from main absorbent B1; due to its limited aqueous solubility, and a separate organic phase is formed over the solution. As a result of the similar polarity of the two amine molecules, A1 preferentially dissolves in the organic rather than the aqueous phase. B1 thus assumes the role of an extractive solvent during regeneration, withdrawing the activator from the aqueous phase, and is thus the decisive component in enhancing the solvent regeneration rate.

Table 2: Heat of reaction of CO_2 with 3M amine solutions [kJ/mol]

Absorbent	MEA(5M)	MDEA	DMCA	DMCA+DPA	B1	B1+A1
Experimental data	79	48	69	74	56	61
Literature data	82	49	-	-	-	-

The optimisation experiments were carried out at various temperatures (25-90°C) and amine concentrations as well as for different proportions of the main absorbent and activator. The best amine concentrations and ratios were observed at 3M total amine concentration with a 3:1 ratio (mol B1/mol A1). Increasing the amine concentration will generally reduce the solution circulation rate required and hence the plant cost (Kohl and Nielsen, 1997). However, no significant loading capacity increase was found when the concentration was raised, since water is also a reactant in the absorption process. Increasing the proportion of main absorbent to activator slows down the reaction kinetics, but promotes solvent regenerability. The most suitable absorption temperature was found to be 40°C. Although the exothermic reaction means that low temperatures favour high CO_2 loadings, the reaction kinetics are enhanced by higher temperatures. When the temperature exceeds 50°C, the thermomorphic phase transition takes place and the loading capacity is reduced significantly. The optimal regeneration temperature is believed to lie in the range of 70-80°C, since a very high level of regeneration can be achieved and waste heat used as a source of the regeneration energy needed.

3.3 Reaction enthalpies of lipophilic amines

Since the heat of reaction typically contributes roughly half of the energy consumption for regeneration in the CO_2 capture process, it represents an important parameter in assessing the overall heat requirement. Table 2 shows the absorption enthalpy of various amine solutions calculated by means of the van’t Hoff equation. The comparison with literature data measured directly using a calorimeter (Carson et al., 2000) indicates deviations of less than 3%. The values for lipophilic amines lie between those of the conventional alkanolamine solutions MEA and MDEA. However, the economic evaluation of the entire process depends upon not only the heat needed for regeneration, but also on the desorption temperature, which is one of the main advantages of lipophilic amine systems. According to the thermodynamic evaluation technique (Notz et al., 2007), the energy consumption can be cut by more than 35% compared to the benchmark aqueous absorbent MEA (4 GJ/t_{-CO2}).

3.4 Chemical stability of lipophilic amines

Solvent losses were observed to be significant in the biphasic system, primarily due to vaporisation of the organic phase, which represented more than 90% of the total losses. A single water wash equilibrium stage was shown to be able to recover only about 20% of the B1 lost, because of its limited aqueous solubility. However, the losses can be substantially reduced by 70% using a chilled water scrubber. Compared to MEA, the degradation loss was found to be minor. After one week of operation, the amine concentrations remained at a high level, but the CO_2 loadings were reduced significantly, by 70%, 15%, and 4% in solutions of MEA, MDEA and B1 respectively. This implies that up to 70% of the remaining bases in MEA were no longer reactive. The residual inactive bases are the products of CO_2 induced degradation via alkylation, dealkylation or oligomerisation and they are apparently too weak to react with CO_2, since their amino groups have been deactivated by additional alkyl chains or steric hindrance. After one week of oxidation, the solvent basicity reductions in solutions of MEA, MDEA and B1 were only 10%, 2% and 5% respectively, but for the more relevant reactivity, the reduction approaches 75% in MEA but is only 3% for B1, a value comparable to that of MDEA. In further Fe^{2+}/Fe^{3+} ion catalysed experiments, a 20% reduction of reactivity was observed in the B1 solution, while reactivity diminished by 50% and 80% in MDEA and MDA solutions respectively after one week of catalysed oxidative degradation. The lipophilic amine B1 therefore proved to be remarkably chemically resilient during the degradation experiments, primarily by virtue of the lower operating temperatures and the less reactive alkyl groups.

4. Conclusions

The remarkable performance of biphasic amine systems observed is for most intents and purposes superior to that of conventional alkanolamines. The high cyclic loading capacity (115 g_{-CO2}/L_{-B1+A1}), low regeneration temperature (70-80°C), rapid regeneration rates, modest heat of reaction (61 kJ/mol) and good chemical stability of the new lipophilic amine blend offer considerable potential for reducing energy consumption and enhancing the efficiency of CO_2 capture processes in a technically feasible manner.

Acknowledgement

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