CARBON DIOXIDE CAPTURE BY AMINES: INCREASING THE EFFICIENCY BY AMINE STRUCTURE MODIFICATION

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Introduction

Carbon dioxide is the largest contributor to the greenhouse effect, being produced in the combustion of fossil fuels as oil, natural gas or coal, for energy production or heating, and in industrial processes.

Carbon dioxide can be recovered by using several technologies such as the absorption into an appropriate solution or the membrane separation. The former is used in several industrial applications such as CO2 separation from power plants flue gases, natural gas treatment and landfill gas upgrading. The capacity of the amine to uptake/bind CO2 is of fundamental importance for sizing the separation tower.

In this paper we consider the advantage of using new amines for capturing carbon dioxide from gas mixtures. The kinetics of CO2 uptake using four new different amines is compared with that of absorption by MEA.

Experimental

All data were recorded under the same conditions: 1 atm of CO2 and 298 K. The kinetics was followed in tetrahydrofuran (THF) as solvent. 8 mL of THF were saturated with CO2 in the absorption flask, then the amine (0.90 mmol) was added. The uptake of CO2 was followed using a gas burette. Neat amines have been also used.

Results and Discussion

Aliphatic amines are known to react promptly with CO2 [Eq 1] to afford an ammonium carbamate.3

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2 \text{RNH}_2 + \text{CO}_2 \rightarrow \text{RNH}_3^+\text{O}_2\text{CNHR}
\] (1)

We have investigated the behaviour of mono- (A, B, C) and di-aminines (D, E)3 towards CO2 at various temperatures. Mono-amines A, B and MEA (C) react rapidly with CO2 at 298 K in THF. Figure 1a-b-c show that the reaction is almost complete in 15 minutes and the amount of CO2 taken up by the amine (ca. 0.55 mol/mol amine) says that one mol of CO2 reacts with two moles of amine, as required by the stoichiometry of reaction 1, to afford ammonium carbamates.

Amines A and B are as performing as MEA. In all cases, the solution at the end of the reaction is cloudy due to a fine suspension of a white solid. Interestingly, if the reaction is carried out at 273 K, the amount of CO2 fixed by amines A and B, after a fast initial uptake, of ca. 0.50 mol/mol, increases slowly to 1 mol/mol within three hours. This feature can be explained assuming that at low temperature any of the ammonium carbamates RNHCOO^+HNR slowly converts into the dimeric form of the relevant carbamic (RNHCOOH)2 acid. We have already shown that, in the same conditions, the carbamate/carbamic acid conversion takes place with benzylamine and other N-compounds. (Eq.2) In the case of R-benzyl, the dimeric carbamic acid has been isolated and characterized by X-ray.

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\text{RNHCOO}^+\text{H}_2\text{NR} + \text{CO}_2 \rightarrow (\text{RNHCOOH})_2 \quad \text{R = Benzyl}
\] (2)

Carbamates of amines (A and B) do not release CO2 easily upon heating. Therefore, they are not good candidates for the separation of carbon dioxide from other gases (e.g., from flue gases) as they can not advantageously operate in a cyclic system implying the uptake and release of carbon dioxide.

When diamine D or E is used, the CO2 uptake curve (Fig. 2) at 298 K has a different shape with respect to that of monoamines.

![Figure 2. Kinetics of reactions of di-aminines with carbon dioxide](image)

We are now working at some improvement of the amine molecular structure in order to further increase the separation efficiency.

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References

(2) RUCADI Project, BRRT-CT98-5089.
The structure of the amines A, B, C, D will be discussed at the symposium.