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Substituent Effect in Amine-CO_2 Interaction Investigated by NMR and IR Spectroscopies

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The donor property changes of amines by methyl or hydroxyl substituents were studied by NMR and FT-IR spectroscopies. This fundamental investigation can contribute for identifying CO_2 absorption capacity of amine solution mainly due to electron releasing and withdrawing effects of substituents.

The prospect of global climate change is a matter of genuine public concern. The concentration of man-made CO_2 in the atmosphere has been increasing by fossil fuel combustion generated from power generation and chemical industry. Among acid gas treating technologies, absorption process using alkanolamine solution has been widely used and in general identified as the most efficient and feasible one.

In CO_2–alkanolamine reaction, two different paths of carbamate [Eq. (1)] and bicarbonate formation [Eq. (2)], are possible to occur.[1] When carbamate formation is dominant, 2 mol of amine are needed to react with 1 mol of CO_2, while 1 mol of amine react with 1 mol CO_2 for bicarbonate formation. This simple stoichiometric comparison indicates that alkanolamine in reaction (2) has twice higher CO_2 absorption capacity than reaction (1).

$$2RNH_2 + CO_2 \leftrightarrow RNHCOO^- + RNH_3^+ \qquad (1)$$

$$RNH_2 + CO_2 + H_2O \leftrightarrow HCO_3^- + RNH_3^+ \qquad (2)$$

The relative amount of carbamate and bicarbonate which results from carbamate instability largely depends on structual types of amines.[2] This carbamate instability means that the bonding strength between the nitrogen atom in amine and CO_2 is very weak and therefore the electron density in nonbonding nitrogen lone-pair orbital becomes lean and reaction (2) is more favorable. Accordingly, the accurate determination of electron density in nitrogen enables to estimate the CO_2 loading capacity in amine solutions. Some researchers attempted to calculate the non-bonding orbital properties on the nitrogen atom of amine molecules,[3] but failed to explain the unusual high loading capacity of primary and particularly, sterically hindered amines. However, in the present work, we will examine the amine-CO_2 interaction strength by using NMR as well as IR.

A primary amine of monoethanolamine (MEA) and three different sterically hindered primary amines of 2-amino-2-methyl-1-propanol (AMP), 2-amino-2-methyl-1,3-propanediol (AMPD), and 2-amino-2-ethyl-1,3-propanediol (AEPD) have been investigated to compare their substituent effects. Structurally, AMP has two methyl substituents at the α-carbon atom compared to MEA. In addition, AMPD has one more hydroxyl group than AMP and one less methyl substituent than AEPD at the β-carbon atom. The amount of CO_2 absorbed in amine solution was determined by bubble blowing apparatus described elsewhere.[4] Using this gas blowing apparatus, CO_2 absorption capacities in various amine solutions of 20 wt% were measured at 298 K. The moles of CO_2 solubilized in MEA, AMP, AMPD, and AEPD solutions (mol CO_2/mol amine) were determined to be 0.723, 1.020, 0.966, and 0.947, respectively. The previous work reported that the increase of structural bulkiness of the substituents bonded to nitrogen atom makes general carbamate stability decrease and therefore loading capacity increase.[2] However, in the present investigation, we confirmed that MEA and AMP followed the above trend for their loading capacities, but sterically hindered amines of AMP, AMPD, and AEPD failed to follow this pattern.

To clarify these contradictory results the electron densities on nitrogen lone-pair orbital in amine were carefully examined by using the Bruker DMX600, 600 MHz NMR spectrometer. In condensed matter nuclei are surrounded by atomic or molecular electron clouds that interact with nuclear spin angular momentum. The principal influence of the surrounding electrons is the magnetic shielding which results when electronic orbitals are perturbed by the applied magnetic field.[5] Therefore, the chemical shifts of NMR spectra might reflect the electronic environment around atom. The ^{15}N NMR spectra of four amines were determined and ammonia was used as an external standard at 298 K. The resulting chemical shifts and CO_2 loading capacities of four amines are depicted in Figure 1. This figure shows a proportional relationship between the solubilities of CO_2 in amine solutions and ^{15}N chemical shifts. This relation is not linear because of the influence of steric hindrance. Thus, the steric hindrance shows a smaller effect on the amine–CO_2 interaction than the electron density on nitrogen. A close comparison of MEA and AMP clearly informs that methyl substitutions at the α-carbon atom affect the lone-pair orbital in nitrogen and make the amine–CO_2 bonding weak. Similar methyl substitution effects can be found from Chakraborty et al.[6] The interaction between two π orbitals of methyl group and nitrogen is expected to influence the donor property of nitrogen resulting in redistribution of electron density. In the present NMR study the hydroxyl

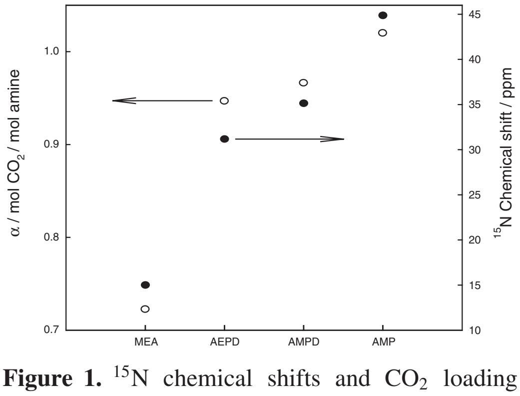

Figure 1. ^{15}N chemical shifts and CO_2 loading capacities of four amines at 20 wt% and 298 K.

substituent attached to the β-carbon atom was found to make a ^{15}N chemical shift more downfield shifted than methyl substituent attached to the β-carbon atom. In particular, a hydroxyl substituent gives more electrons to the nitrogen than a methyl substituent because of electron releasing inductive effect that the oxygen atom in the hydroxyl group has many free electrons to release but the carbon atom in the methyl group does not. The similar tendency for ^{15}N chemical shift relation can be found in the literature.[7]

To clarify the ^{15}N NMR results, the ^{13}C NMR spectra of CO_2 absorbed amine solutions were obtained and the resulting equilibrium percents of carbamate and bicarbonate existing in 20 wt% amine solutions at 298 K were summarized in Table 1. The MEA solution that was confirmed to have the lowest ^{15}N chemical shift produced the largest amount of carbamate anion and the other amines were followed as AEPE ≈ AMPD > AMP. It must be again noted that both qualitative and quantitative results were consistent with the ^{15}N chemical shift results that depicted the electron density on the nitrogen atom.

To examine more closely and confirm the amine substituent effects on carbon dioxide absorption, the infrared spectra were determined using a Bomem-MB 100, FT-IR spectrometer with 25–40 scans at 4 cm^{-1} resolution. It was established that the bonding strength of the adduct can be linearly related to the frequency shift of the OH band in phenolic acid complex with nitrogen donor.[8] Because of strong hydrogen bond between nitrogen donor and phenolic acid, the OH bond in phenolic acid weakened. Consequently, this complexation leads to broadening and downfield shift of the OH stretching band in phenolic acid. By comparing the OH band frequency shifts of complexes, we can determine the relative hardness and softness of donors. The IR experiments of amine–phenolic acid complex diluted with carbon tetrachloride were performed at 298 K. Figures 2 and 3 show the spectra of OH bands for phenol–amine and *p*-chlorophenol–amine complexes, respectively. In these figures, other bands for phenolic acid and amine were eliminated. Phenols have an absorption band at 3620–3590 cm^{-1} for the free OH band. In Figure 2, the bonded OH band of phenol–AMP complex is most shifted to lower wavenumber and has wide breadth with subsequent order of AMPD, AEPD and MEA. It means that the phenol, which has the softer acid site than *p*-chlorophenol, forms strong bond with bases, as following the softness order of AMP, AMPD, AEPD, and MEA. In contrast, the bonded OH band of *p*-chlorophenol with MEA is most shifted to lower wavenumber and has greatest width with the subsequent order of AEPD, AMPD and AMP (Figure 3). The *p*-chlorophenol, which has the harder acid site than phenol, forms strong bond with amines, as following the hardeness order of MEA, AEPD, AMPD, and AMP.

Table 1. Percent amount of carbamate and bicarbonate in CO_2 absorbed amine solutions determined by ^{13}C NMR spectra

	COO^-	HCO_3^-
MEA	38.01	61.99
AMP	2.63	97.37
AMPD	4.98	95.02
AEPD	4.61	95.39

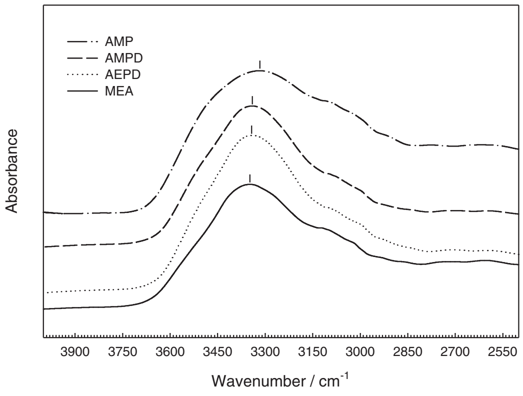

Figure 2. Infrared spectra of the bonded OH bands for amines with phenol at 298 K.

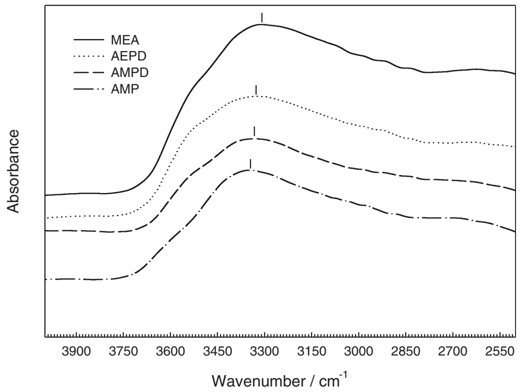

Figure 3. Infrared spectra of the bonded OH bands for amines with *p*-chlorophenol at 298 K.

Using NMR and FT-IR spectra, we could draw conclusion that the methyl substituent at α-carbon atom exerts electron withdrawing effect, while the methyl or hydroxyl substituents at β-carbon atom exerts electron releasing effect. Moreover, the hydroxyl group exerted higher releasing effect than methyl group.

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