Review

POSSIBLE APPLICATIONS OF DIETHYLENETRIAMINE (DETA) IN CO_2 CAPTURING- A MINI - REVIEW

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Abstract

In the past decades, reduction of carbon dioxide (CO_2) emissions into the atmosphere has become a challenging goal. Capturing the CO_2 directly before storage is becoming a thriving alternative approach. Septavaux et al. (1) have proposed a CO_2 fixation method using diethylenetriamine (DETA) to produce a range of carbamation species that can be used for metal separation and recovery. They could show that lanthanum and nickel can be separated from the exhaust gases of vehicle engines by successive CO_2-induced selective precipitations. Individual metal components of La_2Ni_9Co alloys used to manufacture batteries for electric vehicles can also be separated. Here we suggest to use DETA as a mediator for an attractive interaction between like-charged macroions.

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1. Introduction

Carbon dioxide (CO_2) emission into the atmosphere has increased at an alarming rate. In order to reduce CO_2 emissions, adequate measures for CO_2 capture and storage (CCS) or utilization (CCU) need to be taken (2). Since CCS is expensive therefore more attention is directed towards CCU because it has other economic advantages. CCU would significantly reduce the cost of storage due to recycling of CO_2 for further usage. In this context, Septavaux et al. (1) recently showed that the cost of CO_2 capturing with the industrial polyamine DETA can be reduced even further with another environmentally beneficial process (3). The authors proposed to selectively remove metal contaminants from water by adding DETA to aqueous solutions before bubbling CO_2 through the mixture. In this process, a series of ligand exchange reactions results in the formation of insoluble carbonates of the contaminating metals (4).

This contribution is a mini-review of DETA induced metal purification and recovery from waste streams using CO_2 fixation as proposed by Septavaux et al. (1). In addition, the possible application of DETA for mediating attractions in a solution of macroions is presented. Based on theoretical modelling, simulations and experiments with the chemically related molecule spermidine (5,6), we propose that DETA can induce attraction between like-charged macroions. Mobile DETA ions with spatially separated individual charges (**Figure 1**) can interact with like-charged macroins, as predicted by models using the mean-field level PB theory (5) and MC simulations (6). For instance, Gimsa et al. (6) studied the effect of spermidine, which is structurally similar to DETA (**Figure 1**), to induce attraction between borosilicate beads attached to AFM cantilevers and mica surfaces (both surfaces are negatively charged).

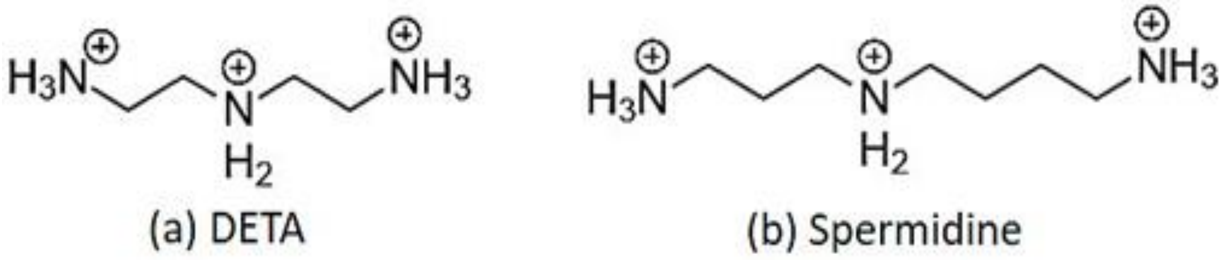

Figure 1. Structural representation of triprotonated (a) diethylenetriamine (DETA) and (b) spermidine molecule.

2. Cleaning of metal contaminants from waste streams using CO_2 capture and DETA

Septavaux et al. (1) demonstrated the efficiency of their technique by removing lanthanum as $La_2(CO_3)_3$ from a La–Ni mixture and separating the metal components of a La_2CoNi_9 alloy, as used in the electrodes of batteries, into the individual components with a purity of 97% or higher.

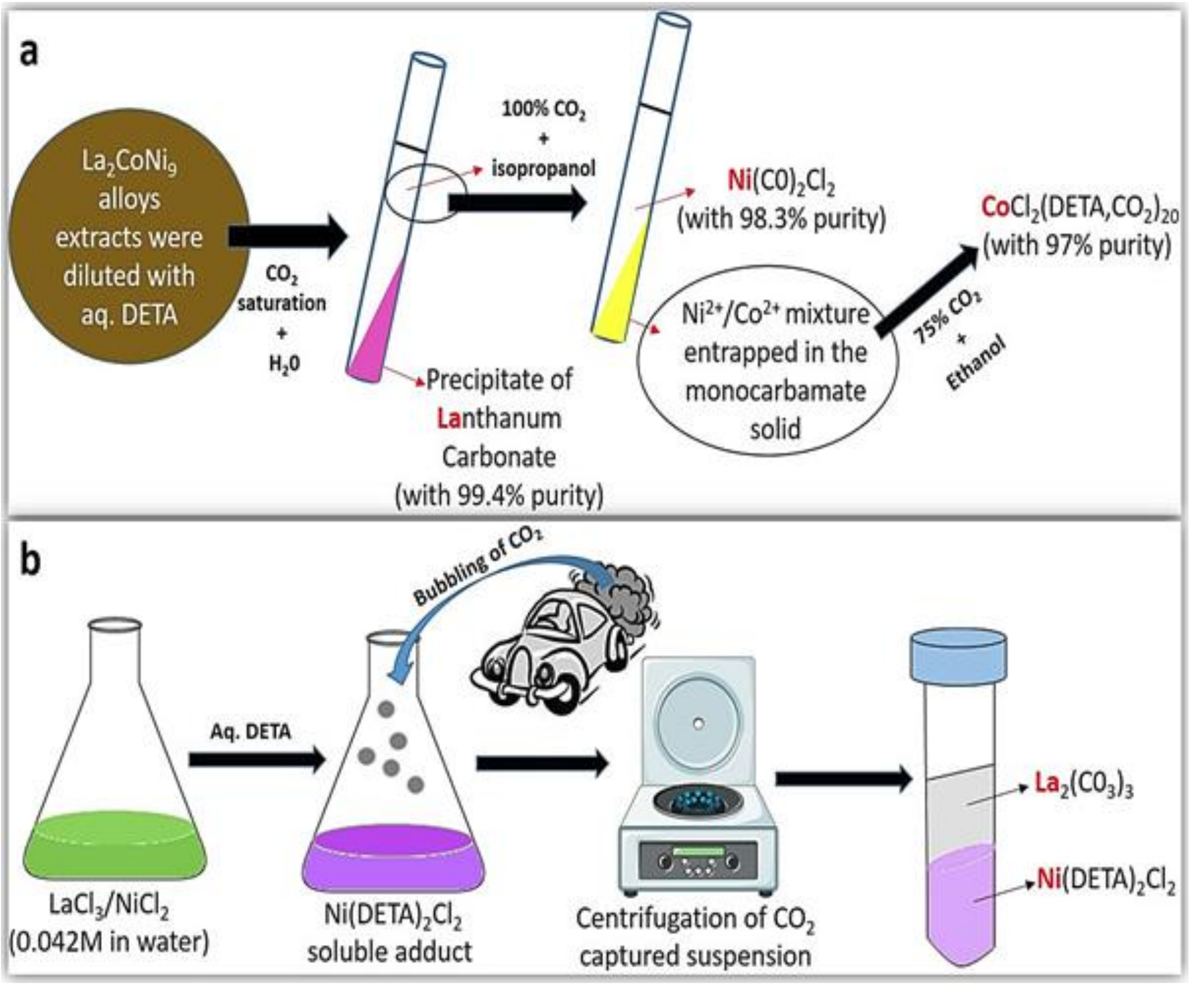

Figure 2. (a). Schematic of individual metal separation from La_2CoNi_9 alloys **(b)**. Schematic of bimetallic separation of LaNi liquid extract using gas from an internal combustion engine. Both mechanisms are suggested and described in details in (1).

In the *first case* (**Figure 2a**), the tri-metallic extract of the La_2CoNi_9 alloy was diluted with aqueous DETA after acid dissolution and saturated with CO_2. This yielded 99.4% of La, which was initially used in the form of carbonate. After dissolution of CO_2 and dilution with ethanol precipitates of two solids were sequentially obtained from the resultant solution. In the first step, a solid precipitate was generated by loading DETA with CO_2 up to 100% and adding isopropanol.

Isopropanol decreased the polarity of the medium, in order to fully precipitate Co and to increase the Ni purity in the remaining solution (solution; $Ni(C0)_2Cl_2$). In the second step, precipitate was obtained by thermal stripping of CO_2 resulting in the release of Ni^{2+}/Co^{2+} mixture entrapped in the monocarbamate solid, followed by capture at CO_2 loading used for precipitation of Co in the first step (precipitate; $CoCl_2(DETA,CO_2)_{20}$).

In the *second case* (**Figure 2b**), Septavaux et al. (1) studied the possibility of direct metal separation from $LaCl_3$–$NiCl_2$, by capturing CO_2 from the exhaust pipe of internal combustion engine of vehicle using aqueous DETA. Lanthanum carbonate tetra hydrate was precipitated within minutes and was isolated from a $Ni(DETA)_2Cl_2$ complex (purple solution). After separation, both metals were recovered with 99% yield and 99% purity.

For a better understanding of the combinatorial chemistry (4) behind the conducted experiments, more insight into the mediating mechanisms is needed. DETA was chosen as a precursor for this system which acts as a complexing agent for metals because of the presence of three amine groups. These basic sites provide a backbone for mono-, di- and tri-carbamates (**Figure 3**), increasing the number of different complexes that can be obtained at the next level.

The first bond that DETA forms is a N–CO2 carbamate bond (Figure 3, highlighted), which generates a dynamic system of ligands based on carbamation process (dC) (7,8). Difference in the degree of protonation and carbamation provides a set of carbamation states from C0-C2 (where C denotes that species are generated in the carabamation system and the number indicates the number of carbamated sites on DETA). 13C NMR study of DETA, H2O and CO2 solution were conducted by Hartono et al (9). Their study revealed that at low CO2 loading carbamate species are produced, whereas dicarbamate species dominate at higher CO2 loading. Experiments revealed that bimolecular carbamation of C0 with intramolecular abstraction of a proton produced an assymetric monocarbamate (C1a) as the dominant species at low CO2 loading. X-ray analysis of C1aH indicated that it is a zwitterionic specie. On the other hand, intramolecular fixation of CO2 at the secondary nitrogen of DETA yielded C1sH. At high CO2 loading, fixation of second CO2 molecule on the triamine backbone can follow a termolecular pathway. That is, it can involve intermolecular abstraction of a proton from zwitterionic monocarbamate C1aH (11,12,1).

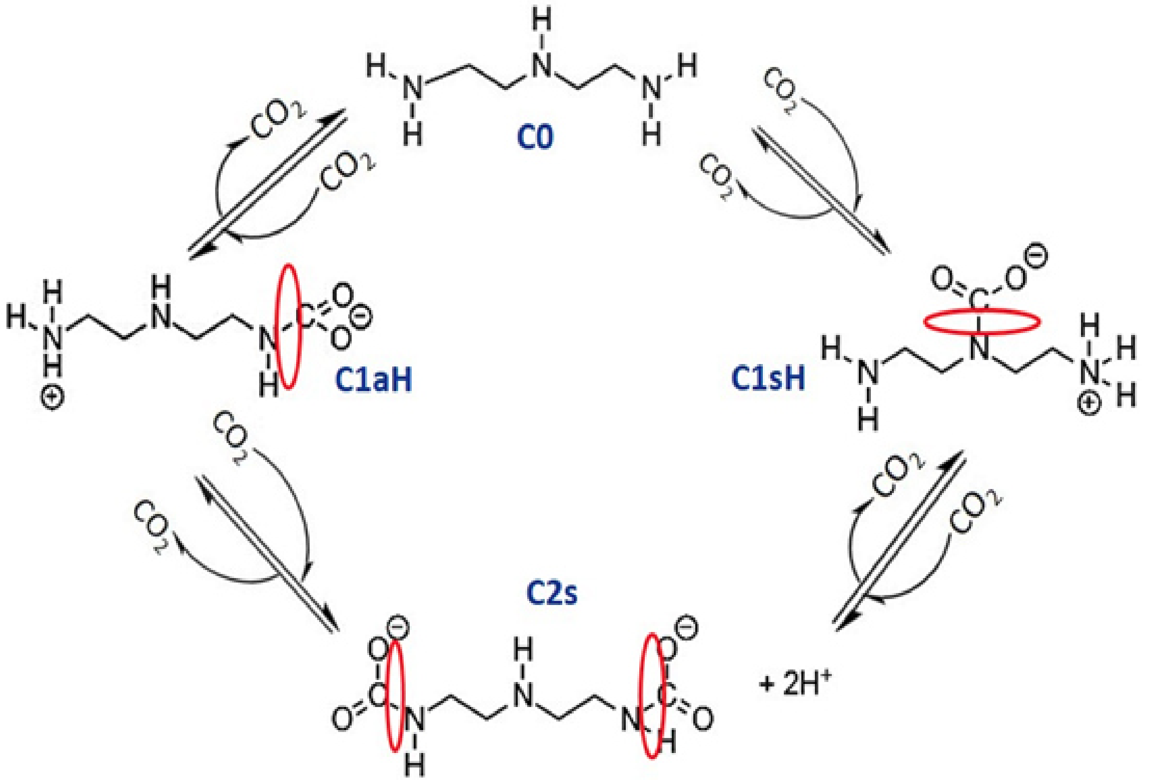

Figure 3. Network of carbamation species formed when DETA reacts with CO_2 ($N\text{-}CO_2$ bonds are marked with red circles), where C0 denotes carbamation, C1aH denotes asymmetric monocarbamate, C1sH denotes symmetric monocarbamate and C2s denotes symmetric bicarbamate species (described in more details in (1)).

Figure 3 illustrates how C0, C1a or C1s act as a base to generate $C0H_2$-C2s, $C1aH_2$-C2sH and $C1sH_2$-C2sH ion pairs, respectively. Products and reactants from the carbamation system combine with metal halides to form a second level library of complexes denoted by **dL** (Ligation process)(12). These metal chlorides (note that chlorides are strong cation binders) act as counter ions for cationic metal template forming a salt bridge with organic or organometallic cations. Members involved in first (dC) and second (dL) level systems usually contain hydrogen bonding sites (charged species) for further bonding. These charged species proceed to form ion pairing that encompasses the third level association denoted by **dIP** (ion pairing process). Finally, a combinatorial 3-level system is formed, denoted as **dCLIP** (4). In the dCLIP system, cationic metal complexes produced in dL system interact with carbamate oxyanions produced at the dC level through ion pairing. This leads to DETA induced complexation of metal particles (**Figure 4**). This process may later be used to balance protonated or metallated DETA-assisted amplification of complexes in solution.

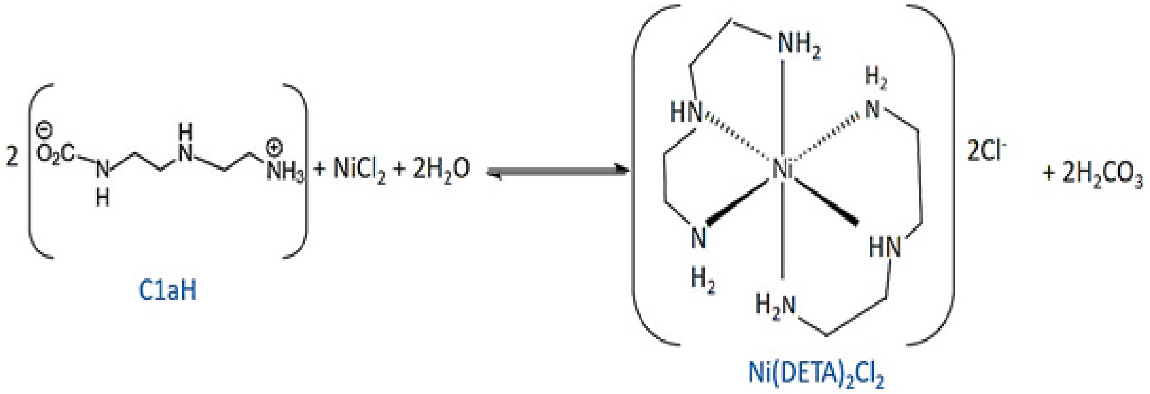

Figure 4. Reaction scheme of asymmetric monocarbamate (C1a) reacting with nickel chloride to yield $Ni(DETA)_2Cl_2$ complex.

Discussion

Electrostatic interaction between charged bodies is of fundamental importance in material science and biology (13). In the presence of multivalent ions, electrostatic interactions/ correlations render the nature of this interaction nontrivial (14). Superposition of electrostatic and van der Waals forces is explained forthrightly by the DLVO theory (13,15). Electrostatic double layer repulsion dominating at long distances may be overcome by van der Waals attraction at short distances (16). Meanwhile, some refinement by ion correlation and ion condensation have been introduced into the DLVO theory. Before employing Monte-Carlo simulations, Kirkwood and Shumaker experimentally studied ion correlation with polyvalent macroions (17). After studying charge fluctuations in the counterion cloud of polyions, Oosawa predicted the condensation of large ions (18) based on charge fluctuations, which develop attractive forces between induced dipoles of ion clouds of adjacent electric double layers (16). Also in the presence of multivalent counterions (CIs), like-charged surfaces can be mutually attracted (13,6,19-23).

Gimsa et al. (6) experimentally and theoretically (using Monte Carlo simulations) investigated the effects of spermidine (**Figure 1**) on the attractive forces between negatively like-charged surfaces. Experimentally, the effect of spermidine protonation on the attractive forces between borosilicate and mica surfaces was studied using AFM. For this borosilicate beads were attached to AFM cantilever tips. At pH 9.0 when spermidine is diprotonated, repulsion was detected above spermidine concentration of 0.02 mg/mL. This is mainly due to the fact that some spermidine molecules adhere parallel to the surface (see also **Figure 5**) and reduce the effective surface charge. And secondary factor is the energy barrier, which is generated by the repulsion of perpendicularly oriented positively charged headgroups of spermidine molecules, forming “brushes” at the surfaces. However, once the repulsive barrier forces are overcome, a “bridging force mechanism” comes into effect generating maximum displacement forces. At pH 7.8, independent of spermidine concentration, no repulsion was observed due to the higher effective charges of the di- and triprotonated spermidine species. These species reduce the effective surface charge and reduce the free energy of the surfaces thus decreasing electrostatic repulsion (16). Monte Carlo simulations of the spatial distribution and orientational ordering of spermidine molecules showed that some of the rod-like spermidine molecules attach to the mica and

borosilicate surfaces in perpendicular orientation, while others are oriented parallel to the surface (16,6) (see also **Figure 5**). For small gap widths between the surfaces, this polyvalent cationic molecule mediates the so-called “bridging force mechanism” (6) that forms an electrostatic bridge-pull effect between the like-charged surfaces (20,21). This mechanism becomes more efficient at higher surface charges due to a quantitative increase in perpendicularly oriented molecules. Simulations also showed that the spermidine molecules condensed at the surface in parallel orientation. For large gaps, these molecules subside the effective surface charge densities reducing electrostatic repulsion (6,22). For narrow gaps, osmotic surface repulsion and counterion concentration is reduced due to lower effective surface charge densities (6).

In general, it was shown that that orientational ordering of quadrupolar counterions can induce attractive interactions between like-charged surfaces or macroions if the distances between the individual charges within the quadrupolar counterions are large enough (5,20,23). It was also shown that within Poisson-Boltzmann mean-field theory monovalent counterions cannot mediate attractive interaction between like-charged objects or surfaces (5,23).
However, if direct interactions are taken into account, also monovalent counterions can mediate attractive interaction between like-charged surfaces, but this transcends the mean-field approach (25). Spermidine-like biological molecules (24) (i.e. charged rod-like molecules) are an example of quadrupolar counterions, which have point-like charges located at well-defined finite distances (6).
Therefore, for finite separation distance between point-like charges within the individual molecules, intraionic positional correlations and orientational ordering are decisive for predicting short-range attractive bridging forces in the mean-field electrostatic models (5,6,21,22), as also confirmed by Monte Carlo simulations (6,23). From the theoretical studies (5,6), it can therefore be concluded that DETA-based polyvalent ions can function as mediators for attractive bridging forces between like-charged macroions (see **Figure 5**).
Monte Carlo simulations (6,23) and theoretical models (5,21,23) are both successful in explaining the suggested bridging mechanism (5,6,20-23) for DETA-mediated attraction between like-charged macroions (**Figure 5**).

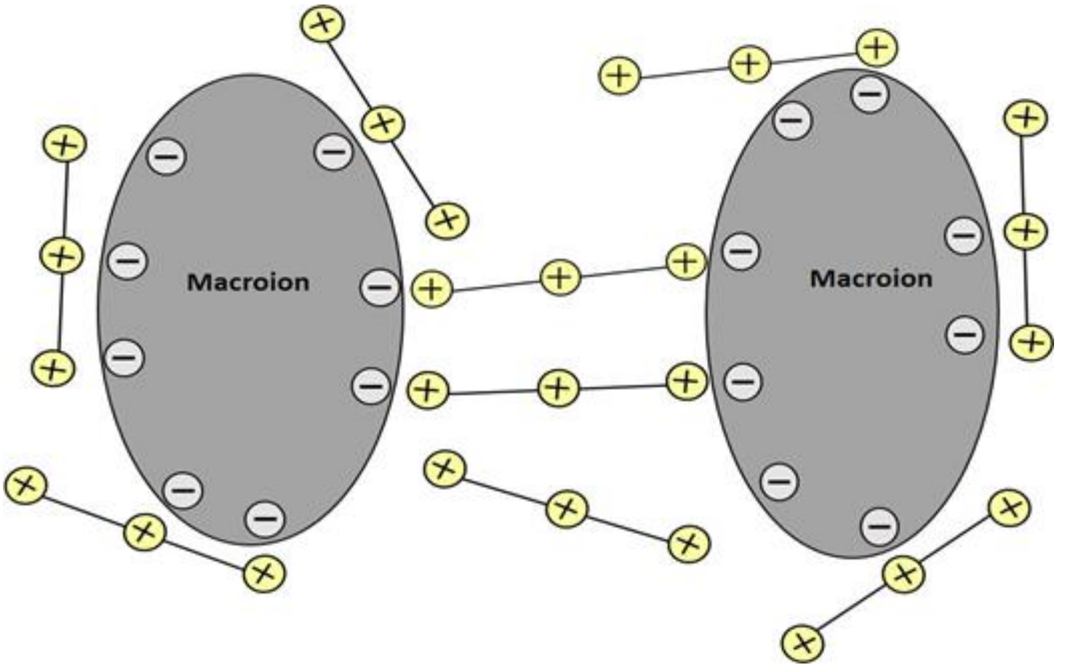

Figure 5. Schematic illustration of the proposed DETA-mediated attraction between like-charged macroions, assuming a triprotonated DETA state.

The DETA molecule, which is structurally similar to spermidine is a polycation with two primary and one secondary amine functionalities in the carbon chain (**Figure 1**). DETA can be in a tri-, di- or monoprotonated state. These properties increase the capacity of DETA to capture CO_2 at a high absorption rate (**Figure 3**). The kinetic rate constant for the primary amine group is higher than that of the secondary amine group or of water, i.e. the primary amine group is more reactive than the secondary amine group (10). Differences in the degrees of protonation, carbamation and CO_2 loading provide different carbamation sets for metal complexation. While some of the DETA molecules in a solution are free, others attach to the surface of macroions. At smaller distances the cationic DETA molecule would generate an electrostatic bridge-pull effect between like-charged macroions as shown in **Figure 5**.
To conclude, theoretical and experimental studies (5,6,20-23) have shown that orientational ordering and protonation of multivalent rod-like polyions like DETA, and the effective surface charge of macroions are important factors that determine the attraction between like-charged macroions mediated by rod-like polyions (**Figure 5**).
We hypothesise that spatially separated individual charges of DETA molecule cangenerate bridging forces that induce attraction between like-charged macroions. Our model helps in explaining the chemical interactions behind the DETA-induced metal complexation for the selective removal of metal contaminants from water.

Acknowledgement

This research work was supported by the Slovenian Research Agency (ARRS) grants P2-0232.

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