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Probing the selective salt rejection behavior of thin film composite membranes: A DFT study

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ABSTRACT

We present a density functional theory (DFT) study on the reactivity of piperazine (PIP) and *m*-phenylenediamine (MPDA) with trimesoyl chloride (TMC) to examine the better selective rejection behavior of bivalent salt ions using corresponding thin film composite (TFC) membranes. The conceptual DFT analyses showed that the rejection of bivalent salt ions would be higher with piperazine based TFC membranes compared to *m*-phenylenediamine based TFC membranes. The global and local reactivity descriptors derived from conceptual DFT analysis suggest that the reaction between *m*-phenylenediamine (MPDA) and trimesoyl chloride (TMC) for the preparation of TFC membrane would be much facile compared to the case of piperazine (PIP) with trimesoyl chloride (TMC), which leads to the better selectivity of bivalent salt rejection in the later case. The unreacted acyl moieties in piperazine based TFC membranes are responsible for the development of charges on the surface, which causes the rejection of bivalent counter ions. The positional isomers of MPDA, *o*-phenylenediamine (OPDA) and *p*-phenylenediamine (PPDA) also shows the higher reactivity with TMC compared to piperazine (PIP) with trimesoyl chloride (TMC). This computational approach sheds light on the complex reactivity pattern of these polymeric membranes in an elegant manner, which otherwise requires more intensive computational analysis for such problems.

1. Introduction

The history of the membranes from Reid and Breton's cellulose acetate to Cadotte's polyamide thin film composite has been a long and remarkable one [1–3]. Cellulose acetate is acknowledged as one of the prime materials to prepare the membranes of asymmetric nature. However, some limitations (mechanical, chemical instability, biodegradability) prompted to find out even better polymeric materials. In this regard, the preparation of polyamide thin film composite membrane is a milestone process. There are other examples of membranes where different polymer materials have been used [4]. Researchers' have put their efforts to prepare 'polyamide composite membranes' extensively and their performances for different applications. The applications of these membranes are wide in nature, however, their role in desalination is of prime importance. The preparation of polyamide membranes involves the support of non-woven polyester fabric [5]. The polyamide formation is the result of interfacial polymerization of acyl halide and diamine. Though it is termed as 'interfacial', the polymerization happens to be in organic phase as the high partition co-efficient restricts its availability in aqueous phase. The post-treatment (crosslinking) results the charge property on such membranes.

There is some mumbling in the mechanism of separation of salts through the membranes and growing the Nernst Planck equation which shows the diffusive, convective part as well as electrical part [6]. Considering the variation of electrical charge part, the nature of the membranes is different in terms of desalination.

In this article, we have focused our attention in terms of the variation of diamine (*m*-phenylenediamine vs piperazine) in the interfacial polymerization [4]. *m*-phenylenediamine and piperazine are the most common primary and secondary diamines used in the preparation of high rejection thin film composite membranes. Piperazine (PIP) is a well known monomer for interfacial polymerization which reacted with trimesoyl chloride (TMC) for the formation of poly(piperazineamide) charged nanofiltration membrane and shows the rejection selectivity in bivalent over monovalent ions [4]. On the other hand, *m*-phenylenediamine (MPDA) reacted with trimesoyl chloride to produce composite RO membrane, which shows much less selectivity [4]. The reaction

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occurs at the organic side of the two liquid interface due to the negligible solubility of acid chlorides in water and reasonably good solubility of amines in organic solvents [7]. The polyamide formed contains cross-linked structure with pendant carboxylic acid group. This carboxylic acid groups arise due to the partial hydrolysis of unreacted acyl chloride group during interfacial polymerization [7]. The general accepted proposal towards the selective salt rejection by the membrane is due to the carboxylic acid charge present in the membrane [4,8]. The performance analysis of these membranes shows that piperazine based TFC membranes is more selective in separation of bivalent counter-ion compared to *m*-phenylenediamine based TFC membranes [4,7]. We have examined the difference in the behavior of such diamines employing computational studies. We have explored the difference in the reactivity of these diamines with trimesoyl chloride (TMC) using the conceptual DFT method.

In recent years, density functional theory has been exploited to understand many intricate features in chemistry and biology [9–13]. In particular, the conceptual DFT studies have gained a lot of interest in different areas of research [13–17]. Conceptual DFT has been proven to describe the reactivity between reaction partners. Several different reactivity descriptors such as electronegativity, chemical potential, global hardness, global softness, local hardness, local softness and Fukui functions are used to determine the nature of reactive sites and their consequences in both chemistry and biology [14–17]. The global and local reactivity indexes have been shown to be powerful tools in the study of the polar character of cycloaddition reactions and the regioselectivity in Diels Alder reactions [18]. This theory has been applied for the determination of acidity and basicity of organic molecules [16]. The DFT descriptors also illustrate the kinetics of S_N^2 reactions [16], carbene reactivity [19], enolate formation [20], tautomerizations [21], metal complexes [22], and many other organic reactions [23]. Conceptual DFT can be applied in the study of adsorption behavior of zeolites, using the condensed Fukui function and local softness to estimate and rationalize the interaction energy of several small molecules with a zeolitic framework [15].

In this article, we have reported the reactivity pattern differences between primary and secondary amines with trimesoyl chloride using local reactivity descriptors based on the hard and soft acids and bases (HSAB) principles.

2. Computational methods

Calculations were performed for all these compounds with the density functional theory using Becke's three-parameter hybrid functional with correlation formula of Lee, Yang, and Parr (B3LYP) [24,25]. All geometries were optimized at B3LYP/6-31+G** level of theory in both gas and aqueous phase and harmonic frequency calculations at the same level of theory is used to confirm that the optimized structures were minima, as characterized by positive vibrational frequencies [24–26]. The solvent phase optimization of all the geometries was performed with polarizable continuum solvation model (PCM) using the integral equation formalism variant (IEF-PCM) [27–31]. The default UFF radii were used for the solvent calculation [29]. NBO calculations were carried out at B3LYP/6-31+G** level of theory [32]. According to the NBO method, the total SCF energy (E_{tot}) can be decomposed in two terms. The Lewis energy (E_{Lew}) is associated with the localized B3LYP wave function and is obtained by zeroing all the orbital interactions, that is deleting the off-diagonal elements of the Fock matrix. The delocalization energy (E_{del}) corresponding to all the possible interactions between orbitals, is calculated as: $E_{del} = E_{tot} - E_{Lew}$. E_{Lew} includes all energy contributions apart from delocalization effects. All calculations were performed with Gaussian 09 suite program [33].

Conceptual DFT: the local softness $s(r)$ is achieved as

$$s(r) = f(r)S$$

where, S is the global softness of the species and $f(r)$ is known as Fukui function [34]. This function is defined as the change in electron density at a given atomic site with change in number of electrons at a constant nuclear geometry [18]. It reflects the tendency of the electronic density to distort at a given position to accept or donate electrons. It provides the information about the most reactive sites in a given molecule. The atomic site, having large Fukui function value, is considered as soft center while the site with a small Fukui function is hard [18]. The maximum value Fukui function indicates the most reactive site in a molecule. Three different types of $f(r)$ exist to define for any atom or molecule corresponding to a nucleophilic, electrophilic, or radical attack [16,18].

$$f^-(r) \approx \mathrm{q(N)} - q(N-1) = q(\mathrm{Neutral}) - q(\mathrm{Cation})$$

for electrophilic attack (acts as a nucleophile)

$$f^+(r) \approx q(N+1) - \mathrm{q(N)} = q(\mathrm{Anion}) - \mathrm{q(Neutral)}$$

for nucleophilic attack (acts as an electrophile)

$$f^0(r) \approx (1/2)[q(N+1) - q(N-1)] = (1/2)[q(\mathrm{Anion}) - \mathrm{q(Cation)}] \quad \text{for radical attack}$$

where, q(N), q(N+1), and q(N−1) are the atomic populations for a particular atom in the neutral molecule and its corresponding anion and cation, respectively. For calculating the condensed Fukui function $f(r)$, Natural population charge analysis (NPA) was performed on optimized geometries at B3LYP/6-31+G** level of theory of amines and trimesoyl chloride used in this study [35]. The global softness S is given by the finite difference approximation,

$$S = \frac{1}{I - A}$$

where, I and A represents the ionization energy and the electron affinity, respectively. For calculating global softness, one can apply Koopmans' theorem [36] (assumption of frozen orbitals), approximating I by the energy of the highest occupied molecular orbital ($\in_{\mathrm{HOMO}}$) and A by the energy of the lowest unoccupied molecular orbital ($\in_{\mathrm{LUMO}}$) [23]. So, the global softness S can be written as,

$$S = 1/\in_{\mathrm{LUMO}} - \in_{\mathrm{HOMO}}$$

Further, the local softness for nucleophile and electrophile can be calculated with the following equations:

$$s^-(r) = Sf^-(r)$$

$$s^+(r) = Sf^+(r)$$

In the present study, s^+ indicates the local softness of carbonyl carbon atom of trimesoyl chloride and s^- the local softness of nitrogen atom of diamine systems. The difference in local softness $s(r)$ value (Δs) indicates the preferred reactivity between the reaction partners. For most favorable interactions, the minimum difference in local softness $s(r)$ should be required for the interacting parts (atoms, functional groups) of these reaction partners [37–39].

$$\Delta s(r) = |s^+(r) - s^-(r)|$$

The empirical nucleophilicity index (ω^-) was calculated using the following equation [40,41]:

$$\omega^- = \frac{1}{2}\frac{(\mu_A - \mu_B)^2}{(\eta_A + \eta_B)^2}\eta_A$$

where, μ_A and μ_B are the corresponding chemical potentials, and η_A and η_B are the respective hardnesses. A is the nucleophile and