Effect of competing amines on the removal of tetramethylammonium hydroxide from solution using ion exchange

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ABSTRACT

Tetramethylammonium hydroxide (TMAH, TMA$^+$) has been widely used as the photoresist developer in semiconductor and thin film transistor liquid crystal display manufacturing. In this study, TMAH-containing wastewater was treated by ion exchange method. Strong acid cation exchange resin was used. A kinetics study revealed that the ion exchange reaction reached equilibrium within 20 min and it could be described by a pseudo-second-order model. To assess the effects of competing ions, wastewater was spiked with three different amines, namely ethylamine (EA$^+$), diethylamine (DEA$^+$), and triethylamine (TEA$^+$). TMAH uptake decreased when in the presence of amines, and it decreased in the order EA$^+$ < DEA$^+$ < TEA$^+$. It could be attributed to different proton affinity (PA) and the strength of affinity between amine molecules and resin matrix, as found from the ab initio calculation values and Langmuir isotherm parameters. However, the interaction energy between sulphonic acid groups and interfering amines in solution using density functional theory (DFT) calculation resulted in a different trend compared with that of PA. The difference might be caused by stabilization of amines by resin matrix and different molecular structures.

Key words | amine, ion exchange, selectivity coefficient, tetramethylammonium hydroxide (TMAH), wastewater

INTRODUCTION

The rapid developments of the electronics industry, such as semiconductor and thin film transistor liquid crystal display (TFT-LCD) manufacturing, have been phenomenal. The manufacturing processes involve significant amounts of ultrapure water, energy, and various types of chemicals. The sustainable utilization of resources and the environmental impacts associated with the electronics industry have become an important issue. Take tetramethylammonium hydroxide (TMAH) as an example; it is an essential chemical used as cleaning solution, alkaline etchant, and photoresist developer. It is a very strong corrosive alkaline, and is highly toxic to the human body and has caused fatal occupational accidents (Wu et al. 2008). The toxicity of TMAH to aquatic organisms and the synergistic action with potassium iodide has been reported (Mori et al. 2015).

The presence of TMAH in wastewater is also a challenging issue that needs to be solved. Various treatment technologies have been examined for TMAH-containing wastewater. Adsorption using activated carbon with micro-pores was effective, and it could be enhanced via pretreatment of nitric acid oxidation (Prahas et al. 2012; 2014). Graphene oxide showed a high affinity toward TMAH owing to the oxygen-containing surface functional groups (Chang et al. 2014). A full-scale methanogenic up-flow anaerobic sludge blanket followed by an aerobic bioreactor could treat TMAH-containing wastewater well (Hu et al. 2012). It can be recycled using electrodialysis process (Wang et al. 2013). Compared with other technologies, ion exchange has been employed widely in wastewater treatment and has proven to be versatile. In our previous work, we demonstrated that ion exchange process was a feasible way to remove TMAH from solution (Citraningrum et al. 2013). Both strong acid cation (SAC) and weak acid cation (WAC) exchange resin showed excellent uptake of TMAH, while Mg$^{2+}$ exerted the most notable interference compared with Na$^+$, K$^+$, and NH$_4^+$. doi: 10.2166/wst.2016.167
Since the occurrence of interfering ions in TFT-LCD manufacturing wastewater is unavoidable, the effect of interfering ions needs to be assessed. It is estimated that over 30% of total TFT-LCD manufacturing wastewater is organic solvents, containing dimethyl sulphoxide and monoethanolamine as stripper, also TMAH as developer (Hu et al. 2012). Studies on how competing ions affected ion exchange have been performed, in which the presence of interfering ions retarded the uptake of target ions (Inglezakis et al. 2005; Chen et al. 2010). In this study, amines, chemicals having similar structure to TMAH and often present in TFT-LCD and semiconductor manufacturing wastewater, was chosen. It is aimed to explore the effect of different competing amines, namely primary, secondary, and tertiary amine, to the uptake of TMAH using SAC exchange resin. Experimental results will be compared with those from \textit{ab initio} calculation of proton affinity (PA) and interaction energy.

**MATERIALS AND METHODS**

**Resin used**

Dowex™ Monosphere™ 650C in H\(^+\) form, a SAC exchange resin, was used in ion exchange. The matrix is styrene-divinylbenzene (DVB) in gel form, with bead size of 650 ± 50 \(\mu\)m. The properties of SAC per manufacturer datasheet are listed in Table 1.

**Kinetics study**

All TMAH concentrations in this study are expressed in mg of tetramethylammonium ion (TMA\(^+\))/L. Stock solution of 255.52 g/L was used to prepare the working solution. In the kinetic study, TMAH solution of initial concentration of 400 mg/L was allowed to react with 2 g/L of SAC in total volume of 500 mL and the pH was adjusted by 1 N HCl so that equilibrium pH (\(pH_e\)) of 3 ± 0.2 was obtained. The flasks were placed on a thermostat shaker set at 25 °C and stirred at 100 rpm. Samples were taken at different time intervals. The concentrations of TMA\(^+\) before and after ion exchange were determined using an ion chromatograph (IC, Dionex ICS-1000), equipped with polyether ether ketone (PEEK) IonPac® CS 12A cation exchange column, IonPac® CG 12A guard, and Dionex CSRS® 500 4 mm suppressor. The eluent used was 20 mM methanesulfonic acid. The amount of TMAH removed from the solution was calculated from the initial and final concentrations of TMAH in the aqueous phase.

To represent ion exchange process, pseudo-second-order kinetic model was chosen. This model was developed under the occurrence of valence forces through sharing or electron exchange, such as what occurs in ion exchange. The equation for pseudo-second-order kinetics is shown below:

\[
q_t = q_e \left( \frac{q_e k_2 t}{1 + q_e k_2 t} \right)
\]

where \(q_t\) denotes uptake capacity at any given time (mg/g), \(t\) represents time (min), \(q_e\) and \(k_2\) were pseudo-second-order parameters, representing the equilibrium adsorption capacity (mg/g) and the rate constant (g/mg/min).

**Effect of competing amines on TMAH removal**

In this study, three different amines were spiked to the TMAH solution. Ethylamine (expressed as its protonated form, EA\(^+\)) was chosen to represent primary amine, diethylamine (DEA\(^+\)) to represent secondary amine, and triethylamine (TEA\(^+\)) to represent tertiary amine. Working solutions of the amines were prepared from 568 g/L ethylamine (Acros), 694.83 g/L diethylamine (Sigma-Aldrich), and 718.45 g/L triethylamine (Sigma-Aldrich). Measured amounts of these amines were added to the solution containing 400 mg/L of TMAH in total volume of 50 mL containing 0.1 g/L SAC resin. The ion exchange reactions were performed in a thermostat shaker set at 25 °C and 100 rpm. Hydrochloric acid (1 N) solution was added to maintain the final pH (\(pH_e\)) at 3.0 ± 0.2. TMA\(^+\) concentration before and after ion exchange reactions was then measured by using IC.

**Ab initio calculation on PA and interaction energy**

To obtain optimized structure, electronic energy and the zero point vibrational energy (ZPVE) of the base molecule
and its protonated form, Gaussian® 09 package program was employed in this study (Frisch et al. 2009). The geometries of all species were fully optimized at B3LYP computational level, which was also used for frequency determination. The 6-311+G(d) basis set was used in all calculations. Bulk solvent effect was included via the polarizable continuum model (PCM) in the integral equation formalism (IEFPCM). Molecular structure of DVB matrix of SAC was assumed as a sulphonic acid group attached to one benzene ring, as illustrated in Figure 1. Molecular structure of ions used in this study was drawn using CPK coloring notation: white represents hydrogen, grey for carbon, sulphur is yellow, oxygen uses red, and nitrogen is colored in blue.

PA is defined as the negative enthalpy change at 298 K for the reaction (Lias et al. 1964):

\[ A + H^+ \rightarrow AH^+ \]  

and is calculated according to the following expression:

\[ PA = \Delta E_{el} + 2.5RT \]  

where \( \Delta E_{el} \) and \( \Delta ZPVE \) are the differences between the total electronic energy and the ZPVE of the base molecule and its protonated form at 25°C, respectively.

The interaction energy (\( \Delta E_I \)) is defined as the energy difference between the resin-amines complex (\( E_{\text{resin-amine}} \)) and the sum of the separated resin molecule and the free protonated amine (\( E_{\text{resin}} + E_{\text{amine}} \)), according to the following equation:

\[ \Delta E_I = (E_{\text{resin}} + E_{\text{amine}}) - E_{\text{resin-amine}} \]  

RESULTS AND DISCUSSION

Kinetic study

Kinetic study revealed that equilibrium time needed for TMA\(^+\) exchange using SAC was 20 min (Figure 2). Ion exchange is considered a fast reaction since hydrogen ions from resin matrix are readily dissociated in solution. Similar study using Amberlite resin for TMAH removal showed that 5 min contact time was sufficient (Shibata et al. 2006). Ion exchange for other ions, such as dimethylamine, also revealed short contact time (Hu et al. 2011). Earlier studies on ammonium removal using several different ion exchange materials showed that ion exchange process was fast, with equilibrium time varying from 10 to 60 min (Du et al. 2005; Thornton et al. 2007). Equilibrium time varies as it is affected by different operating conditions, including target ions, concentration, pH, and type of ion exchangers.

Calculated parameter values for pseudo-second-order kinetic model are shown in Table 2. Experimental variables affect the variation in \( k_2 \) value. It has been reported that \( k_2 \) value for adsorption of TMAH using activated carbon was 0.0027–0.0496 g/mg/min (Prahas et al. 2012) under different experimental conditions. Pseudo-second-order kinetic model parameter implies that the exchange rate between TMA\(^+\) ion and H\(^+\) on SAC is slightly faster compared to

![Figure 2](https://iwaponline.com/wst/article-pdf/74/2/466/460546/wst074020466.pdf)

![Figure 1](https://iwaponline.com/wst/article-pdf/74/2/466/460546/wst074020466.pdf)

<table>
<thead>
<tr>
<th>Samples</th>
<th>( q_e ) (mg/g)</th>
<th>( k_2 ) (g/mg/min)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAC</td>
<td>177.55</td>
<td>0.0036</td>
<td>0.9751</td>
</tr>
</tbody>
</table>

Figure 2 | Pseudo-second-order kinetic model of TMA\(^+\) uptake using SAC \((C_0 = 400 \pm 40 \text{ mg/L, } \text{pH} = 3 \pm 0.2, \text{ resin dose: } 2 \text{ g/L})\).
WAC exchange resin as performed in previous study (Citraningrum et al. 2013). It is reasonable since SAC matrix contains sulphonic acid groups which are readily dissociated in solution; hence, exchange between ions occurs rapidly.

**Effect of competing amines on TMAH removal**

Since ion exchange process involves the replacement of existing ions in resin matrix by ions from a solution with similar charge, the presence of competing ions in the solution will affect the uptake of target ions, either enhance or hinder target ions’ uptake. A study found that the presence of competing ions enhanced the uptake of specific ions (Jorgensen & Weatherley 2003). However, the competition frequently hampered target ion uptake to a certain extent (Inglezakis et al. 2003; Chen et al. 2003). The interference of simple cations, such as Na\(^{+}\), K\(^{+}\), Mg\(^{2+}\), and NH\(_{4}\)\(^{+}\) on TMA\(^{+}\) uptake has been studied previously, and Mg\(^{2+}\) was to be the most significant one (Citraningrum et al. 2013). The decrease was attributed to both valence and ionic radii.

In the present study, three different amines were spiked into TMAH solution to see how their presence affects TMA\(^{+}\) uptake. Amines behave like a weak base, and will be protonated in water to form positively charged ions, in this case, EA\(^{+}\), DEA\(^{+}\), and TEA\(^{+}\). Results are presented in Figure 3. When in the presence of amines, TMA\(^{+}\) uptake decreased significantly. The uptake decrease was as high as 36% in the presence of TEA\(^{+}\). High molecular weight of TEA\(^{+}\) is a possible reason; a similar trend has been observed for different molecular weights of amines in which the larger the molecular weight, the higher the maximum adsorption capacity on resin (Pirogov et al. 2003). In water, those amines accept hydrogen ions and become protonated. Due to their positive charge, EA\(^{+}\), DEA\(^{+}\), and TEA\(^{+}\) will compete with TMA\(^{+}\). The decrease is more prominent compared to single ions’ interference, of which TMA\(^{+}\) uptake decreased to ca. 80% (a 20% decrease) when Mg\(^{2+}\) was present (Citraningrum et al. 2013). This might be attributed to a similarity in structure of those amines and TMA\(^{+}\), as depicted in Figure 4. A previous study also suggested that amines were retained more strongly in sorbent’s matrix compared to monovalent cations (Pirogov et al. 2003). Interestingly, with the increasing concentration of amines, the decrease in TMA\(^{+}\) uptake for individual amines did not vary much. This phenomenon might be attributed to the low equivalent concentration of amines present in the solution due to their high molecular weights.

**Ab initio calculation of PA and interaction energy**

Interaction between SAC resin and amine can also be described as acid-base interaction or neutralization reaction. SAC resin possesses strong acid property and is thus assumed to have a stronger interaction with a stronger base. The basicity of amines was then described using PA and the higher the PA, the stronger the base. *Ab initio* PA calculation was then performed using DFT calculation in Gaussian®09 program to predict how strong an amine is
attracted to fixed group in resin matrix. The results are presented in Table 3. Alkyl groups in amines provide electrons to the nitrogen, thus the negative charge increases, as well as the basicity. That is to say, the more alkyl groups attached to nitrogen, the more pronounced the effect (Miessler & Tarr 2004). Since TEA\(^+\) possesses three ethyl groups, the value of PA, and in extension, basicity, is higher compared to EA\(^+\) and DEA\(^+\), making it the one with stronger interaction with sulphonlic acid group of SAC resin matrix.

To further assess the adsorption energy, Langmuir adsorption isotherm was employed to describe the interaction between TMA\(^+\), amines and SAC. The results were presented in Figure 5. The calculated Langmuir parameters are shown in Table 4. Langmuir parameter \(b\) is related to the affinity between adsorbent and adsorbate, thus the higher the value, the stronger the interaction between adsorbent and adsorbate. Interaction between SAC and three interfering amines is lower compared to that of SAC and TMA\(^+\). Langmuir model yielded a \(b\) value of 0.0747, indicating high interaction between resin matrix and TMA\(^+\). It is probably due to strong electrostatic interaction between acid groups in SAC and TMA\(^+\) ion from solution. When other amines were present in the solution, competition occurred due to similar positive charge possessed by those amines and TMA\(^+\). The competition resulted in TMA\(^+\) uptake decrease. Compared to other two amines, TEA\(^+\) has the highest \(b\) value. This value and the affinity obtained from \textit{ab initio} PA calculation could explain why TEA\(^+\) showed the most significant effect on TMA\(^+\) uptake.

Other than the Langmuir isotherm, an established technique to investigate interaction energy between two molecules, or in another term, adsorption energy is microcalorimetry (Bordawekar & Davis 2000; Savitz et al. 2000). Another method is infrared (IR) spectroscopy, which is commonly used to estimate adsorption strength of ions with ion exchangers such as zeolites (Rudakova et al. 2003). The difficulty in employing measurement method is finding suitable probe molecules. Theoretical calculations (\textit{ab initio}) are thus helpful in determining electrostatic interactions between molecules.

To carry out theoretical calculation of interaction energy between sulphonic acid groups and interfering amines in solution using DFT calculation, in which resin matrix is assumed as a benzene ring attached to a SO\(_3^-\)/C\(_0\) group. This molecule was then brought to interact with each protonated amine, and the interaction energy was calculated according to Equation (3). The value of interaction energy is presented in Table 5. DFT calculation resulted in different trend compared to that of PA, with increasing \(\Delta E_I\) in the order of EA\(^+\) > DEA\(^+\) > TEA\(^+\). The difference might be caused by stabilization of amines by resin matrix and different molecular structures (Jiang et al. 2004). However, the difference is less than 10 kJ/mol. The value of interaction energy calculated in this study is also significantly smaller compared to experimentally derived adsorption energy of methylamine,
dimethylamine, and trimethylamine on zeolite, which ranged from 200 to 225 kJ/mol (Parrillo et al. 1993; Gorte & White 1997). The underestimation of interaction energy might be caused by the simplification in interaction simulation, since the DVB matrix of resin was assumed as one benzene ring with one sulphonic acid group. It also might be due to the choice of model used, for example, B3LYP functional does not take dispersion forces as adsorption mechanism into account (Seponer et al. 1996; Vos et al. 2001; Clark et al. 2003). The value of interaction energy indicates strong hydrogen bonds interaction between amines molecule and resin matrix rather than chemical bonding (Desiraju & Steiner 2001). Further work is needed to better correlate our results from experiments and calculation.

## CONCLUSIONS

This study investigates the effect of interfering amines on TMAH removal using strong acid ion exchange resin. The conclusions of this study are listed as follows:

1. From the kinetic study, it is revealed that the rate of exchange between TMA⁺ and H⁺ ion is fast and equilibrium time was reached in 20 min.
2. The presence of amines in TMAH solution significantly affected TMA⁺ uptake, and TEA⁺ had the most significant effect.
3. The effect can be explained using ab initio PA calculation, which showed the value of PA in the order of EA⁺ < DEA⁺ < TEA⁺.
4. Langmuir isotherm also showed that SAC and tertiary amine had the strongest interaction energy.
5. Ab initio calculation of interaction energy resulted in a different trend compared to PA and Langmuir interaction energy calculations. It might be attributed to simplification in interaction simulation and the model used.

## REFERENCES

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