Interactions among trioctylamine–sulfuric acid–water: experiments and molecular dynamics simulations

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Abstract. Trioctylamine (TOA) has been widely regarded as a cost effective extractant and received extensive applications in the metallurgical industry. However, TOA is prone to aggregate and form something like viscoelastic material when it meets the sulfuric acid. However, there is no unified understanding of the mechanism of aggregation. Based on the possible molecular interaction model proposed in our previous work, we are going to probe the interaction of TOA and the sulfuric acid as well as to obtain a chemical structure corresponding to various molar ratios through molecular dynamics calculations together with a specific distance distribution function. The results show that the hydrogen bonding of the whole system strengthens with the increase of the molar ratio of sulfuric acid and water to TOA. When the molar ratio of sulfuric acid and water to TOA is comparatively low, the hydrogen bonds interactions between TOA and water was predominated. When the ratio is high, TOA will react with sulfuric acid through protonation. The results of the simulation is consistent with our previous studies.

1.Introduction
Trioctylamine (TOA) has been received extensive applications in the metallurgical industry. However, TOA–sulfuric acids complex are prone to aggregate, which may be something like viscoelastic scum. This phenomenon greatly diminished the potential usage of TOA[1]. The aggregation phenomenon of amine extractant with sulfuric acid was first reported by Allen[2,3]. After that, many research groups proposed their explanations.

In the system of quaternary ammonium surfactant[4] reacting with acid, the one-dimensional vermicular micelles grew in the form of spheres and rod micelles[5]. Along with the changes of concentration or environmental conditions, worm-like micelles entangled with each other to form a network structure[6]. The solution shows the viscoelasticity like polymers on macroscopical. At the same time, The system has achieved a dynamic balance through the rupture and the reorganization[7].

The ‘‘chemical’’ interactions between the amines and the acids are stronger than the ‘‘physical’’ interactions When amines extract acids from their aqueous solution. In 1995, Wang[8] reported that a chemical reaction took place between TOA and sulfuric acid and five compounds is formed. In 2010, Martak et al.[9] suggested the possible chemical structure of the TOA with 5-methyl-2-pyrazinecarboxylic acid (MPCA) and TOA with sulfuric acid complex. The possible structures model had been proposed with the increase of the concentration of sulfuric acid in the solution. After that, Qiu[10,11]took account of the bridging effect of the water molecule in viscoelastic scum combined the above mentioned model. According to Qiu’s model, all molecules are ideally involved in chemical
structure formation. However, not all of molecules participate in the chemical structure formation in the real situation, and the specific chemical structure is not ideal. She also proposed that the aggregation models of TOA-sulfuric acid-water with different molar ratios by fourier transform infrared spectroscopy (FTIR)[12]. It is necessary that more characterization methods are needed to support this view.

Recently, Molecular dynamics (MD)[13] is used to study the degree of action between molecules and the structure of the aggregating system. The results could provided through the microscopic phenomena simulation which are difficult to acquire by experiment[14].

In the present paper, the viscosity of the system of TOA mixed with sulfuric acid and water is investigated through experiment. Subsequently, the molecular structure and relative properties of involving materials were analyzed by quantum chemical calculation. Moreover, molecular dynamics calculations of the viscoelastic system of TOA mixed with sulfuric acid and water in different mole ratios was discussed.

2. Materials and methods

2.1 Materials
The TOA and sulfuric acid with analytical purity were purchased from Beijing Chemical Factory, China. The deionised water was produced in the Laboratory Centre of University of Science and Technology Beijing, China.

2.2 Experiments
In the study, the 50% sulfuric acid (weight percent) was prepared by dissolving pure sulfuric acid in the deionized water. Four 10 ml-beakers were prepared and 5 ml TOA was added into them separately. Then 0.5 ml, 1 ml, 1.5 ml, 2 ml, 50% sulfuric acid (wt.%) were introduced and mixed with 5 ml TOA respectively at room temperature. The corresponding molar ratio of sulfuric acid to TOA were 0.6, 1.0, 1.4, 1.8, and the molar ratio of water to TOA were 1.76, 2.94, 4.11, 5.29, respectively.

The viscosity of TOA–H₂SO₄–H₂O mixture was determined using a laboratory rotational viscometer (Brookfield DV2T, USA) connected through USB to a personal computer to record and store the data using the RheocalcT software at the ambient temperature.

2.3 Quantum chemical calculation and molecular dynamics (MD) details
The molecule geometries of TOA, H₂SO₄, H₂O were optimized by the B3LYP/6–31G (d,p) method employing the Gaussian 03 suite of programs. Molecular electrostatic static potential (ESP) analysis was done using GaussView 5.0 for prediction of nucleophilic and electrophilic sites.

Molecular dynamics simulations were done using the forcite module of Material Studio 8.0.

Step 1: Building cubic cells.

Four simulation cubic boxes were constructed using the Amorphous cell module at a temperature of 300 K. The number of molecules used in the simulations is reported in Table 1.

| Concentration (molar ratio) | Value |
|-----------------------------|-------|
| 1:0.6 | 1:1.0 | 1:1.4 | 1:1.8 |
| Number of trioctylamine | 20 | 20 | 20 | 20 |
| Number of sulfuric acid | 12 | 20 | 28 | 36 |
| Number of water | 36 | 60 | 84 | 104 |
Step 2: MD simulation.

Dynamic simulation was performed at 300 K. The cells were subjected to 100000 dynamic steps of 1 fs each at the NPT ensemble to determine their density. This stage was followed by an NVT ensemble refinement stage of 100 000 dynamic steps and a data collection stage of an additional 400 000 NVT steps.

All MD simulations were conducted using the forcite module with the COMPASS II (condensed-phase optimized molecular potentials for atomistic simulation studies) force field. The electrostatic term was considered using Ewald and vander Waals terms using atom-based summation methods with an accuracy of 103 kcal/mol. The repulsive cutoff for the vander Waals term was 12.5 Å. For NPT molecular dynamic simulations, the Nose thermostat and Berendsen barostat were chosen.

Step 3: Analysis.

The resulting dynamic trajectories were analyzed using forcite module analysis tools.

3. Results and discussion

3.1 Viscosity

The obtained values of viscosity at 298 K are presented in Figure 1. The viscosity of the system rises along with the increases of the molar ratio of sulfuric acid to TOA. When the ratio is 1.8, the viscosity of the system is as high as 1528 cP. It may be explained that with the increase of molar ratio of sulfuric acid to TOA, more and more aggregates are generated in the system. Aggregation has become more serious attributes to the strength effects of sulfuric acid and TOA in the system.

![Fig. 1. The viscosities of TOA–H2SO4–H2O mixtures at room temperature](image)

3.2 Quantum chemical calculation

3.2.1 Solvation free energy

Solvation is an important process during dissolution and solvation free energy can be used to reflect hydrophobicity of extractants. Solvation free energy is the change in single point energy when a molecule is transferred from a vacuum (or the gas phase) to a certain solvent. The solvation free energy of species i (ΔE_{sol}^i) is defined as:

\[ ΔE_{sol}^i = E_{sol}^i - E_{vac}^i \]

where \( E_{vac}^i \) is the single point energy of species i in vacuum and \( E_{sol}^i \) is the single point energy in solution.

When the value of \( ΔE_{sol}^i \) is positive, it means that the substance is difficult to dissolve in aqueous phase. It is clearly found that the calculated solvation free energy of TOA is 0.006 kcal·mol⁻¹ from Table 2. It theoretically proved that the amine with long alkyl chain possess the excellent hydrophobicity.
Table 2. Solvation free energy (kcal.mol⁻¹) of TOA

|        | $E_{\text{sol}}$ | $E_{\text{val}}$ | $\Delta E$ |
|--------|------------------|------------------|------------|
| Sulfuric acid | -1000.120        | -1000.126        | 0.006      |
| TOA    |                  |                  |            |
| Water  |                  |                  |            |

3.2.2 Molecular electrostatic potential (MEP)

Since amine acts as the nucleophilic reagent when extracting a certain acid, it is essential to investigate TOA reactive site. The calculation of molecular electrostatic potential (MEP) gives insight of reactivity, and the surface minimum of MEP reveals sites for electrophilic attack. As shown in Figure 2, the surface minimum of MEP for TOA extractants is located at the nitrogen atom. Based on this result, we can deduce that the nitrogen atom of the TOA could be the nucleophilic reactive site. It means that TOA will act with sulfuric acid or water in the extraction process.

![Fig. 2. Total electron density surface mapped with the surface of molecular electrostatic potential](image)

3.3 MD simulation

3.3.1 Three-Dimensional Bonding Model for TOA–sulfuric acid–water system of various molar composition.

The three-dimensional Bonding Model for TOA–sulfuric acid–water system of various molar composition is shown in Figure 3. It is shown that each different molar ratio systems have several kinds of groups with a circle. Each group is composed of intermolecular hydrogen bonds. The meaning of these groups is as follows:

- A–TOA and sulfuric acid, B–TOA and water molecules, C–sulfuric acid and water molecule, D–sulfuric acid itself, E–the bulk–like water, F–the free water

As can be seen in the figure 3, there are six types of groups with hydrogen bonding at the molar ratio of sulfuric acid to TOA of 0.6, 1.0 and 1.4 except 1.8. The hydrogen bond exit in the form of $\cdots$N···H–O–S, $\cdots$N···H–O–H, H–O···H–O–S, $\cdots$S=O···H–O–S, H–O···H–O–H seperately. There is no free water molecular in the molar ratio of 1.8. The amount of free water gradually decreases with the proportion of sulfuric acid increases. In other words, more and more water moleculars patecipates the hydogen bond interations. Subsequently, all of the water molecules are involved in the formation of network structure by hydrogen bonds at 1.8. Because of this, the mixture changed more viscous.
Fig. 3. Three–Dimensional Bonding Model for TOA / sulfuric acid / water system of various molar composition between TOA and sulfuric acid. (a) 1 : 0.6 (b) 1 : 1 (c) 1 : 1.4 (d) 1 : 1.8.

Fig. 4. The largest cluster for TOA / sulfuric acid / water system of various molar composition between TOA and sulfuric acid; a-1.4, b-1.8.

3.3.2 Radial distribution function
Radial Distribution Function (RDF): The radial distribution function (RDF, also referred to as the Pair correlation function) gives a measurement that the probability of the presence of an atom at the origin of an arbitrary reference frame. There will be an atom with its center located in a spherical shell of infinitesimal thickness at a distance from the reference atom. RDF may serve as a tool to estimate intermolecular interactions like hydrogen bonding. The values of RDF for TOA and water, TOA and sulfuric acid are shown in Figure 5.
The RDF value between TOA and water is the greatest when the molar ratio of sulfuric acid to TOA is 0.6 from figure 5(a). The value becomes smaller as the ratio increases. This shows that when the molar ratio of sulfuric acid and water to TOA is low, the action between TOA and water predominates. On the contrary, it can be seen that the RDF value between TOA and sulfuric acid is the smallest when the molar ratio of sulfuric acid to TOA is 0.6 from figure 5(b). With the increased of the molar ratio, the RDF value of TOA and sulfuric acid is increased as well. This means the action between TOA and sulfuric acid is predominant when the ratio is 1.8.

In addition, the action between TOA and water molecule takes place at a constant distance regardless of the molar ratio of sulfuric acid and water to TOA, but the action between TOA and sulfuric acid molecules shows that the higher the molar ratio of sulfuric acid and water to TOA is, the smaller the distance and the stronger the binding force is. It also shows that the higher the molar ratio of sulfuric acid and water to TOA, the more it shifts from the physical action to the chemical action.

![Graphs](image)

Fig. 5. Radial Distribution Function for TOA / sulfuric acid / water system (a) TOA and water (b) TOA and sulfuric acid and in the condensed phase at 300 K.

4. Conclusions

The aggregation system formed by the mixture of the sulfuric acid aqueous solution and TOA at the different molar ratio is studied. The intermolecular interaction for three-tuple model of TOA–H$_2$SO$_4$–H$_2$O is discussed according to the quantum chemical calculation and MD simulation. It is denoted that the viscosity of the system increases with the increase of sulfuric acid and water by the experiment. The value of viscosity is responsive to the degree of aggregation. The simulations shows that the interaction between TOA and water was predominated by hydrogen bonds when the molar
ratio of sulfuric acid and water to TOA is comparatively low. When the ratio is high, the interaction of TOA and sulfuric acid will play a leading role through protonation.

References
[1] C. Hanson, A.N. Patal, J. Appl. Chem. Biotechnol 19, 20-24(1969)
[2] K. A. Allen, J. Phys. Chem 60, 239-245 (1956)
[3] K. A. Allen, J. Phys. Chem 60, 943-946 (1956)
[4] H. Fu, Y. Li, Y. Song, J. Li, Z. Wang, L. Zhao, J. Mol. Liq 230, 329-336 (2017)
[5] J. Zhao, H. Yu, Colloids Surf., A 513, 274-279 (2017)
[6] C. Zheng, H. Lu, L. Wang, Z. Huang, J. Dispersion Sci. Technol 38, 1330-1335 (2017)
[7] M. I. Martinez-Espinoza, M. Maccagno, S. Thea, M. Alloisio, Appl. Surf. Sci 427, 724-732 (2018)
[8] M. Wang, Y. Lin, B. Liu, Ind. Eng. Chem. Fundam 34, 1302-1309 (1995)
[9] J. Marták, L. u. Kubíšová, S. t. Schlosser, J. Chem. Eng. Data 55, 3578-3589 (2010)
[10] X. Qiu, Z. Chang, H. Zhou, W. Li, B. Dong, Sep. Purif. Technol 86, 137-142 (2012)
[11] H. Cao, X. Wu, Z. Chang, W. Li, B. Dong, Q. Jin, Sep. Purif. Technol 145, 98-103 (2015)
[12] X. Qiu, Z. Chang, W. Li, H. Zhou, B. Dong, L. Qiao, Sep. Purif. Technol 95, 196-201 (2012)
[13] S. R. P. Bandlamudi, M. J. Cooney, G. L. Martin, K. M. Benjamin, Ind. Eng. Chem. Fundam 56, 3040-3048 (2017)
[14] X. Wu, Z. Chang, B. J. Blamo, J. Yuan, H. Uslu, W. Li, C. Ryong, Fluid Phase Equilib 449, 167-174 (2017)