Effects of Solution Physical Properties on Separation Characteristics in Ultrasonic Atomization

Keiji Yasuda1*, Eiji Fujimori1, Yoshiyuki Bando2, Soyoko Yamaguchi2, Masaaki Nakamura2 and Yasuhiro Kawase3

1Waste Treatment Facility, Nagoya University, Nagoya
2Department of Chemical Engineering, Nagoya University, Nagoya
3Nippon Refine Co. Ltd., Tokyo
yasuda@nuce.nagoya-u.ac.jp

Abstract

In order to clarify the separation mechanism in ultrasonic atomization, the effects of solution physical properties on separation characteristics were examined. For the aqueous solutions of monohydric alcohols, the content in accompanying liquid was higher than that in residual solution. For the aqueous solutions of di-, tri-hydric alcohols and amides, however, the content in accompanying liquid was lower. It is considered that the hydrophilic and hydrophobic properties of molecule strongly govern the separation characteristics. The separation mechanism was modeled, and the surface solute amount in droplet was estimated.

1. Introduction

When the high power ultrasound irradiates the liquid, small liquid droplets are generated from the liquid surface. This phenomenon is called as ultrasonic atomization [1].

Recently, it has been reported that ethanol is concentrated from the aqueous solution by ultrasonic atomization [2-4]. Since ultrasonic atomization scarcely accompanies the phase change, this is a great advantage comparing with the distillation operation. Therefore, the method has been applied to the concentration of ethanol in Japanese sake. Sato et al. [2] have studied the effects of initial content and temperature in bulk solution on the concentration characteristics. With decreasing temperature in bulk solution, the content in droplet increased and the droplet amount decreased. D. M. Kirpalani and F. Toll [3] investigated the ultrasonic fountain jet, which was the source of atomization. In the fountain jet, the temperature was higher and the ethanol content was lower than those in bulk solution. They considered that the formation of alcohol-rich droplet was due to the corollary effects of the surface excess on ultrasonic cavity and the alcohol vaporization during cavity collapse.

However the separation mechanism in ultrasonic atomization is still unclear. The ultrasonic atomization occurs from the liquid surface. It is considered that the separation characteristics are governed by adsorption behavior of solute on liquid surface.

In this study, the aqueous solutions of alcohols, amides, carboxylic acids and inorganic salts were used. The separation characteristics and droplet diameter distribution in ultrasonic atomization were measured. The separation mechanism was modeled, and the surface solute amount in droplet was estimated.

2. Experimental

Figure 1 shows the outline of experimental apparatus. The apparatus consisted of a cylindrical and transparent vessel made of polyvinylchloride resin, an ultrasonic oscillator and a constant temperature bath. The diameter and height of vessel were 100 and 550 mm, respectively. An ultrasonic oscillator with 20 mm in diameter was set at the center of vessel bottom. The ultrasonic frequency was 2.4 MHz and the electric power was 18 W. The carrier gas was air and flowed through the vessel to accompany the atomized droplets. The inlet and outlet of carrier gas were attached on the wall of vessel. The diameters of gas inlet and outlet were 20 mm. The heights from the vessel bottom to the centers of gas inlet and outlet were 200 and 500 mm, respectively. The superficial velocity of carrier gas was...
0.16 m/s.

As the sample, the aqueous solutions of methanol (MeOH), ethanol (EtOH), 1-propanol (PrOH), propylene glycol (Pr(OH)2), formamide (MeCONH2), acetamide (EtCONH2), acetic acid (Me(COOH)), propionic acid (Et(COOH)) and inorganic salts (Li2SO4, Na2SO4, K2SO4, Rb2SO4 and Cs2SO4) were used. The sample temperature was 283 K. After ultrasonic atomization, the content of residual liquid was measured using the gas chromatography with TCD detector (GC390, GL Science Inc.). The content in accompanying liquid and the liquid flow rate were calculated from the material balance. The diameter distribution of atomized droplet was measured by using a laser light scattering (SPR7340, Nikkiso Co., Ltd.).

3. Results and Discussion

Droplet diameter distribution

For sample we used, the probability of droplet diameter based on volume is well expressed by the following normal distribution;

\[ q_{3i} = \frac{1}{\sqrt{2\pi} \sigma} \exp \left\{ - \frac{(d_i - d_{3m})^2}{2\sigma^2} \right\} \]  \hspace{1cm} (1)

where \(d_i\) (m) is the droplet diameter, \(d_{3m}\) (m) is the median droplet diameter based on volume and \(\sigma\) (m) is the standard deviation.

Lang [5] has proposed the theoretical equation describing the effects of ultrasonic frequency \(f\) (Hz), surface tension in bulk liquid \(\sigma\) (N/m) and liquid density in bulk liquid \(\rho\) (kg/m\(^3\)) on the diameter of droplet ultrasonically atomized. The liquid viscosity was excluded in his equation, but in our experiment the median droplet diameter based on volume decreased with increasing viscosity in bulk solution. So, we modified Lang’s equation as follows;

\[ d_{3m} = 2.8 \left( \frac{\sigma}{\rho f^2} \right)^{0.2} (\mu / \mu_w)^{0.18} \] \hspace{1cm} (2)

where \(\mu\) and \(\mu_w\) (Pa·s) are the viscosities of bulk solution and water. The calculated results agree with the measured data within an error of \(\pm\) 20 %.

From the droplet diameter distributions measured under different conditions, the standard deviation was obtained by using Eq. (1). The standard deviation was expressed by means of the physical properties of bulk solution as follows;

\[ \sigma = 4.6 \times 10^5 f^{-0.41} \rho^{-0.50} \mu^{-0.18} \] \hspace{1cm} (3)

The calculated results reproduce the measured data within an error of \(\pm\) 30 %.

3.1. Separation characteristics

Figure 2 shows the effect of solute molar fraction in residual solution on solute molar fraction in accompanying liquid for aqueous solution of monohydric alcohols. The solute molar fraction in residual solution is the average value of those before and after atomization. For all data, the accompanying liquid is concentrated. The solute molar fraction in residual solution increases with increasing solute molar fraction in residual solution. At the same solute molar fraction in residual solution, the solute molar fraction in accompanying liquid for 1-propanol is the highest and that for methanol is the lowest.

Figure 3 shows the effect of hydroxyl function number in the solute molecule on solute molar fraction in accompanying liquid. For propylene glycol and glycerol, the solution did not atomize at high solute molar fraction in residual solution. The accompanying liquid for aqueous solutions of propylene glycol and glycerol is diluted. At the same solute molar fraction in residual solution, the solute molar fraction in accompanying liquid for glycerol is the lowest.
For several alcohol aqueous solutions, the liquid flow rate is plotted against viscosity in residual liquid as shown in Fig. 4. The liquid flow rate decreases with increasing viscosity in residual liquid.

Figure 5 shows the solute molar fraction in accompanying liquid of aqueous solutions of amides and carboxylic acids. The solute molar fractions in residual solutions were 0.1 ± 0.01. For amides (formamide and acetamide), the solute molar fraction in accompanying liquid is slightly lower than that in residual solution. From data in Fig. 3 and 4, it is considered that the hydrophilic and hydrophobic properties of molecule strongly govern the separation characteristics in ultrasonic atomization. On the other hand, for carboxylic acids (acetic acid and propioloc acid), the molar fraction in accompanying liquid is the same as that in residual solution. We measured that the separation characteristics in ultrasonic atomization for aqueous solutions inorganic salt (Li2SO4, Na2SO4, K2SO4, Rb2SO4 and Cs2SO4) and the molar fraction in accompanying liquid was the same as that in residual solution. These results indicate that ionized molecules in water are not separated by ultrasonic atomization.

3.2. Modeling of concentration mechanism

In our previous paper [4], the attachment of a demister reduced the flow rate of accompanying liquid, but enriched the ethanol content in accompanying liquid. This result suggests that the specific surface area of droplet governs the separation characteristics in ultrasonic atomization. We ignore the vaporization and the droplet cohesion, and simply model the atomized droplets to consist of solute shell on its surface and solution core. We assume that the surface solute amount on shell is independent on droplet diameter and that the content in core is the same as that in bulk solution. For concentration, the surface solute amount \( s \) (mol/m\(^2\)) is estimated from the molar balances of solvent and solute in atomized droplet as follows;

\[
C_{A H2O} \Sigma \pi n_i d_i^{3/6} = C_{R H2O} \Sigma \pi n_i \delta_i^{3/6} / 6 \quad (4),
\]

\[
C_{A C} \Sigma \pi n_i d_i^{3/6} = s \Sigma \pi n_i \delta_i^{3/6} / 6 \quad (5),
\]

where \( C_{A H2O} \) (mol/m\(^3\)) and \( C_{A C} \) (mol/m\(^3\)) are the molarities of solvent and solute in accompanying liquid, \( C_{R H2O} \) (mol/m\(^3\)) and \( C_{R C} \) (mol/m\(^3\)) are the molarities of solvent and solute in residual solution, \( n_i \) is the number of droplet and \( \delta_i \) (m) is the diameter of core of droplet. In the case of dilution, the subscript of H2O is interchanged with that of C.

For aqueous solutions of alcohols and amides, Table 1 shows the droplet diameter, standard deviation, solute molar fraction in accompanying liquid and surface solute amount with the molecular volume. The solute molar fractions in residual solutions were 0.1 ± 0.01. The droplet diameter and standard deviation were estimated from eqs (1) and (2). The minus value of surface solute amount indicates that the shell consists of water. For same hydrophilic substituents, the values of surface solute amount are almost the same.

![Figure 4: Plot of liquid flow rate against viscosity in residual liquid](image)

![Figure 5: Solute molar fraction in accompanying liquid of aqueous solutions of amides and carboxylic acids](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \delta m ) [( \mu m )]</th>
<th>( \nu \times 10^6 ) [-]</th>
<th>( X_A ) [-]</th>
<th>( s \times 10^2 ) [mol/m(^2)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me(OH)</td>
<td>5.3</td>
<td>2.7</td>
<td>0.25</td>
<td>0.51</td>
</tr>
<tr>
<td>Et(OH)</td>
<td>4.4</td>
<td>3.0</td>
<td>0.32</td>
<td>0.44</td>
</tr>
<tr>
<td>Pr(OH)</td>
<td>4.0</td>
<td>3.3</td>
<td>0.34</td>
<td>0.37</td>
</tr>
<tr>
<td>Pr(OH)(_2)</td>
<td>4.4</td>
<td>2.3</td>
<td>0.04</td>
<td>-3.90</td>
</tr>
<tr>
<td>Pr(OH)(_3)</td>
<td>4.8</td>
<td>2.0</td>
<td>0.00</td>
<td>-7.60</td>
</tr>
<tr>
<td>H(CONH(_2))</td>
<td>5.9</td>
<td>2.7</td>
<td>0.08</td>
<td>-1.30</td>
</tr>
<tr>
<td>Me(CONH(_2))</td>
<td>5.2</td>
<td>2.6</td>
<td>0.08</td>
<td>-1.30</td>
</tr>
</tbody>
</table>
Langumir [6] has reported the potential energies when 1 mol of solute molecules move from bulk to surface in aqueous solution. The potential energies of solute molecule estimated the sum of all substituents in molecule. The potential energies of hydrophilic substituents of OH, (OH)₂, (OH)₃ and (CONH₂) are 0.24, -0.29, -0.83, -0.13 J/mol, respectively.

The surface solute amounts in Table 1 are plotted against potential energies of substituents of OH, (OH)₂, (OH)₃ and (CONH₂) as shown in Fig. 6. The surface solute amount increases with increasing potential energies of hydrophilic substituents. The separation characteristics in ultrasonic atomization are dominated by interaction amounts between water and hydrophilic substituent of solute.

4. Conclusions

The effects of solution physical properties on separation characteristics were examined. The separation mechanism was modeled, and the surface solute amount in droplet was estimated. The following facts were clarified:

1. The liquid flow rate decreases with increasing viscosity in accompanying liquid.
2. For the aqueous solutions of monohydric alcohols, the accompanying liquid is concentrated. On the other hand, di-, tri-hydric alcohols and amides, the accompanying liquid is diluted.
3. The ionized molecules in water are not separated by ultrasonic atomization.
4. The separation characteristics in ultrasonic atomization are dominated by interaction amounts between water and hydrophilic substituent of solute.

5. References