Size Distribution of Droplets in Two Liquid-phase Mixture Compared between Liquid Spraying and Mechanical Stirring

Taisuke SHIMOGOUCHI,***† Hirochika NAGANAWA,** Tetsushi NAGANO,** Bernd GRAMBOW,** **** and Yuichiro NAGAME* **

*Graduate School of Science and Engineering, Ibaraki University, Mito, Ibaraki 310-8512, Japan

**Advanced Science Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, Japan

***Asaka Riken Co., Ltd., 47 Aza Maseguchi, Kanaya, Tamura, Koriyama, Fukushima, 963-0725, Japan

****SUBATECH (IMT Atlantique, CNRS-IN2P3, University of Nantes), 44307 Nantes, France

† To whom correspondence should be addressed.

E-mail: ptshimogouchi@asaka.co.jp
Abstract

A new liquid-liquid extraction method, called the “emulsion flow” method, is expected to realize an ideal liquid-liquid extraction by controlling emulsion generation and separation using liquid spraying only by solution sending. In order to understand the mechanism of the emulsion control in the emulsion flow method, the size distribution of droplets in two liquid-phase mixtures was compared by using originally designed apparatus 1) for the case of liquid spraying and 2) for the case of mechanical stirring. We demonstrate that the size distribution of droplets generated near a mixing device (a nozzle for liquid spraying or an impeller head for mechanical stirring) determines the phase separation property.

Keywords: Emulsion flow method, emulsion control, droplet size distribution, liquid-liquid extraction, liquid spraying, mechanical stirring
Introduction

Liquid-liquid extraction (solvent extraction) is an important technology in industries and analytical chemistry for collecting and separating target components dissolved in an aqueous solution by using an organic solvent immiscible with water. Recently, a new liquid-liquid extraction method, called the “emulsion flow” method, has been developed at Japan Atomic Energy Agency (JAEA).\(^1\)-\(^{10}\) The emulsion flow method, due to the lowest cost, the easiest handling, the highest level in efficiency, compactness and safety, in comparison with conventional methods, mixer-settler, pulse column, spray column, centrifugal extractor, etc., and eco-friendliness, has attracted attention in industries and has been expected to bring innovation to liquid-liquid extraction technologies.\(^{11}\)

Apparatus based on the emulsion flow method can realize an ideal liquid-liquid extraction with its high ability for two-liquid-phase mixing to reach an emulsion by spraying micrometer-sized droplets of an organic phase into the counter-current flow of an aqueous phase only by feeding solutions. At the same time, the emulsion in the apparatus disappears rapidly and perfectly by drastically changing the area of cross-section in the vessel structure where the flow of the emulsion passes through. This indicates an excellent ability of the apparatus for controlling the mixing two liquid phases into an emulsion and of their subsequent separation from the emulsion.

On the other hand, the mechanism of emulsion control (controlling emulsion generation and separation) in the emulsion flow method is still unclear. In the present study, we focus to the size distribution of the droplets in the mixture of an aqueous and an organic phase. In particular, we take note of the difference from the mixture obtained by mechanical stirring, which is the most popular method for the two liquid-phase mixing in industries, to clarify what is superior to the conventional methods using mechanical stirring such as mixer-settler. From
previous studies on the liquid-liquid mixing by mechanical stirring, it is known that droplet-size
distribution can affect the kinetics of extraction and phase separation.\textsuperscript{12-18} The droplet-size
distribution in the emulsion generated by liquid spraying is compared in the present study with
that generated by mechanical stirring using originally designed apparatus for droplet
observation. The difference in phase separation properties between the two types of emulsion
is investigated.

\section*{Experimental}

\textit{Apparatus originally designed for observing droplets}

Figure 1(a) and 1(b) show two apparatus originally designed and fabricated for observing
droplets generated by liquid spraying and by mechanical stirring, respectively. The shape and
volume of main body vessel and piping structures of these apparatus are the same. The height,
width and depth of each vessel shown in Fig. 1(a) and 1(b) are 390 mm, 153 mm and 48 mm,
respectively. The vessel of these apparatus is divided into two parts with a partition board.
One is the mixer part (the cross sectional area is 2300 mm$^2$) for mixing an aqueous and an
organic phase and the other is the settler part (the cross sectional area is 4600 mm$^2$) for
separating these phases from each other. The emulsion generated in the mixer part transfers to
the settler part through a passing hole created in the partition board. In both apparatus, an
aqueous phase is introduced from the upper side of the vessel and circulated in the vessel while
an organic phase is introduced from its lower side and circulated in a similar manner.

Two nozzles are installed in the mixing part of the apparatus shown in Fig. 1(a). The
upper nozzle for introducing an aqueous phase is a polypropylene hollow cylinder with one end
closed having 12 holes of 0.5 mm diameter. The lower nozzle for spraying an organic phase is
a bell-shaped glasswork having a face of a sintered-glass plate whose maximum pore size is 0.04 - 0.05 mm. Meanwhile, an impeller device is set in the mixing part of the apparatus shown in Fig. 1(b). The impeller head is a disk having six vertical grooves on its underside, and the diameter and the height are 30 mm and 10 mm, respectively. The impeller head is located at the middle of the mixing part that is just the position of an interface between the aqueous and the organic phase.

Experiments to observe droplets

The vessel of the two apparatus shown in Fig. 1(a) and 1(b) is filled with 2 L of deionized water as an aqueous phase and 2 L of Shellsol D70 (Shell Chemicals) whose density is 0.796 g mL$^{-1}$ as an organic phase. The feed rate of the aqueous phase and that of the organic phase are the same at 100 mL min$^{-1}$ and each of the two liquid phases is circulated in the vessel of these apparatus. The rotation speed of the impeller in the apparatus of Fig. 1(b) is set at 1000 rpm. The droplet observation was carried out after 20 min operation of each apparatus reaching a stationary state.

Observation of droplets with a high-speed camera

The observation of droplets in two liquid-phase mixing and the phase separation was conducted from the outside, as is shown in Fig. 2, by using a high-speed camera (High-speed microscope VW-9000, Keyence Corporation) having a camera unit (VW-600C) and high-performance zoom lens (VH-Z20R). A micro-ruler (MR-4, Kenis Co., Ltd.) was used for the calibration in measuring the droplet diameter. Video images were captured under the condition that lens magnification and depth of field were ×200 and 0.44 mm, respectively. The number of droplets in a fixed volume (0.76 mm$^3$) defined by calibrated height and width and depth based on the depth of field (1.14 mm × 1.52 mm × 0.44 mm) was obtained. Size
distribution of droplets was determined by measuring the diameter of 2000 droplets in a number of such fixed volumes so as to obtain statistically reliable data for the droplet-size distribution. Droplets on the boundaries of fixed volumes are treated as follows. When more than one-third of a droplet sticks out of a fixed volume, the droplet is not counted as being included in the fixed volume. From the limitation of the machine performance (magnification limit, etc.), droplets whose diameter is less than 0.02 mm in an emulsion are hardly observed.

Results and Discussion

Figure 3 shows the two observational apparatus in operation, indicating observation points. Point A is near the mixing device (the lower nozzle or the impeller head). Point B is before the passing hole in the mixer part. Point C is after the passing hole in the settler part. Point D is defined just before an interface between an emulsion and an aqueous phase in the settler part. Point E is after the interface in the settler part. The droplets generated in the mixer part transfer from point A to point E in the settler part along its flow direction shown in Fig. 3. As is seen from Fig. 3, phase separation in the settler part is greatly different between these two apparatus. In the liquid spraying-type apparatus, the aqueous phase in the settler part is very clear. On the other hand, in the mechanical stirring-type apparatus, too much oil droplets transfer into the aqueous phase in the settler part, and then, the interface position is lowered; it seems that the inflow of oil droplets into the aqueous phase causes an increase in the volume of emulsion in the settler part.

Figure 4 shows the droplet-observation results at points A, B, C, D, and E in the case of liquid spraying, and those in the case of mechanical stirring are shown in Fig. 5. The frequency distribution, that is a value obtained in volumetric basis, is indicated as a function of droplet diameter. As is seen from Fig. 4, the droplet-size distribution at the point of A is very
sharp. In contrast, in the case of mechanical stirring, the droplet-size distribution at point A (near the impeller head) is broad, as is shown in Fig. 5. In short, nearly mono-dispersed droplets having uniform size are generated by liquid spraying at around the lower nozzle, meanwhile, by mechanical stirring, poly-dispersed droplets of various sizes are generated at around the impeller head.

At point E in the case of liquid spraying shown in Fig. 4, it was impossible to obtain observation data because no droplets were found; the aqueous phase in the settler part is always clear with no oil droplets. In the course of growing to be an emulsion, nearly mono-dispersed droplets generated at point A (near the lower nozzle) are densified and coalesce to each other randomly and consequently to reach an emulsified condition at point B. That is to say, such coalescence occurring at random makes the size of droplets larger and their size distribution broad. On the other hand, in the comparison of the data at point B and point C, the droplet-size distributions before and after the passing hole are found to be not much different. Even for the droplets reached point D located just before the interface between the emulsion and the aqueous phase, their size distribution is not much changed.

In the case of mechanical stirring shown in Fig. 5, an emulsified condition is observed already at the starting point near the impeller head namely point A. The emulsified condition is basically kept at points B and C, whereas, the rate of the droplets smaller than 0.2 mm at points B and C becomes somewhat higher than that at point A. More precisely, the volumetric frequency of the smaller-sized droplets at point C is slightly larger than that at point B, i.e., the smaller-sized droplets are gradually increased from point A to point C along the droplet-flow direction shown in Fig. 3. In contrast, at points D and E, the droplet-size distribution is drastically changed and is largely shifted into much smaller sizes, which is quite different from the case of liquid spraying. Sharply peaked volumetric frequency as a function of droplet diameter appears at around 0.1 mm in the observation result at point D and at around 0.05 mm
in the observation result at point E. Also, it is noteworthy that point D in the case of mechanical stirring is situated lower than point D in the case of liquid spraying. When such smaller-sized droplets in large numbers cross over an original interface in the settler part, the original interface disappears and another interface is newly created at the same time. In addition, a part of the smaller-sized droplets leaks out into the aqueous phase in the settler part, as is shown in the observation result at point E. The smaller in the size of droplets, the smaller the buoyant force that is the major force to promote the coalescence of droplets. Therefore, such small-sized droplets drift around the interface without their coalescence, which is deeply related to backmixing.\textsuperscript{19, 20} This is quite a contrast to the case of liquid spraying where no droplets were observed at point E; besides, droplets smaller than 0.2 mm were hardly seen at point D in the case of liquid spraying. The apparatus shown in Fig. 1(b) can be operated under a controlled condition to suppress the smaller-sized-droplet generation, however, the machine performance declines significantly in accordance with a low impeller rotation speed and a low feed rate, which will be described in detail separately in another report.

Such a great difference between the case of liquid spraying and that of mechanical stirring can be seen more clearly by superimposing the results obtained at points B, C and D together, as is shown in Fig. 6, and by comparing these figures. In the case of liquid spraying, the volumetric frequency distribution as a function of droplet diameter is not much changed along the droplet-flow direction from point B to point D through point C, as is seen from Fig. 6 (a). In contrast, in the case of mechanical stirring, the droplet-observation result is drastically changed when the droplet flow reaches point D, as is seen from Fig. 6 (b). This means the accumulation of small-sized droplets around the interface between the emulsion and the aqueous phase.

The difference in phase separation between liquid spraying and mechanical stirring is schematically shown in Fig. 7. The emulsion grown from mono-dispersed droplets generated
by liquid spraying is easily and clearly separated into the two liquid phases, whereas, the emulsion grown from poly-dispersed droplets generated by mechanical stirring is hard to be clearly separated into the respective phases.

**Conclusions**

The difference in size distribution of droplets between liquid spraying with nozzles and mechanical stirring with an impeller has been investigated by using originally designed respective apparatus composed of two parts (a mixer part and a settler part) for the observation of droplets. The droplet observation with a high-speed camera was carried out at 5 points (A and B in the mixer part and C, D and E in the settler part) along the droplet-flow direction in these apparatus. We clarified that the size distribution of droplets generated near a mixing device (a lower nozzle or an impeller head) determines the phase separation feature.

In the case of liquid spraying, mono-dispersed droplets generated near the lower nozzle are densified and coalesce to each other at random and consequently to reach an emulsified condition. In the process of generating an emulsion, such random coalescence makes the droplet size larger and the size distribution broad. On the other hand, the droplet-size distribution in the emulsion thus generated is not much changed from the mixer part through to the end of the emulsion area, i.e., an interface in the settler part. Notably, aqueous phase in the settler part is always clear with no oil droplets, which enables to achieve clear and rapid phase separation with almost no droplets smaller than 0.2 mm just before the interface (at point D in Fig. 4).

In contrast, in the case of mechanical stirring, the droplets smaller than 0.2 mm generated near the impeller head in the mixer part are transferred along the droplet-flow direction without their coalescence and accumulated in the interface; the smaller in the droplet size, the more
difficult to coalesce to each other. Therefore, the frequency distribution of such smaller-sized droplets increases explosively at an observation point just before the interface. In addition, the smaller in the droplet size, the easier to cross over the interface and consequently the smaller-sized droplets leak out into the aqueous phase in the settler part with making it very cloudy.

From the viewpoint of phase separation, we concluded that liquid spraying in liquid-liquid mixing is much superior to mechanical stirring.

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Figure Captions

Fig. 1 Apparatus originally designed and fabricated for observing droplets generated by (a) liquid spraying (aqueous and organic droplets are indicated by blue and yellow circles, respectively) and by (b) mechanical stirring (aqueous or organic droplets are indicated by green circles), respectively.

Fig. 2 Illustration of experiments to observe droplets generated by liquid spraying and by mechanical stirring with a high-speed camera (green shadowed part indicates emulsion).

Fig. 3 Droplet-observation apparatus in operation, indicating observation points together with the droplet-flow direction.

Fig. 4 Droplet-observation results in the case of liquid spraying at point A (near the lower nozzle), point B (before the passing hole in the mixer part), point C (after the passing hole in the settler part), point D (just before an interface between an emulsion and an aqueous phase in the settler part) and point E (after the emulsion-aqueous phase interface in the settler part), respectively.

Fig. 5 Droplet-observation results in the case of mechanical stirring at point A (near the impeller head), point B (before the passing hole in the mixer part), point C (after the passing hole in the settler part), point D (just before an interface between an emulsion and an aqueous phase in the settler part) and point E (after the emulsion-aqueous phase interface in the settler part), respectively.
Fig. 6 Droplet-observation results in the case of (a) liquid spraying and (b) mechanical stirring at point B, C and D superimposed together.

Fig. 7 Illustration of the difference in phase separation between liquid spraying and mechanical stirring.
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