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Effects of Surface Activities of Extractants on Drop Coalescence and Breakage in a Mixer-Settler

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This work focuses on the relationship between surface activities of extractants and drop coalescence and breakage. Drop size distribution and Sauter mean diameter have been measured in one stage of a mixer-settler extraction column for three different liquid−liquid systems as functions of flow rate of dispersed phase, agitation speed, and concentration of extractants. Effects of drop coalescence on drop size have been investigated for three different types of extractants. The results show that the difficulty in occurrence of drop coalescence greatly influences the drop distribution pattern. The Sauter mean diameter for these three extractant systems increases linearly with the holdup of dispersed phase in the mixer and slopes of lines for these three systems are similar. Extractants have the ability to inhibit or promote drop coalescence by their surface activities. For coalescence inhibitors the data of drop size plotted versus interfacial tension fall on the same line, while the drop size measured for coalescence promoter is larger than the line.

Introduction

A number of relationships have been proposed to describe the effects of column geometry, agitation conditions, and physical properties of the liquid−liquid system on the drop size. Zhou and Kresta[1] summarized the diverse correlations proposed by many investigators. It should be noted that most authors agree on the effect of Weber number on drop size, while the observed holdup effects of dispersed phase on the drop size are different, depending on the authors. This fact suggests that the drop coalescence behavior depends on the liquid−liquid systems investigated and physicochemical properties of liquid−liquid systems play an important role in controlling the drop size. Some investigators focused their attention on the effect of interfacial tension and direction of mass transfer on drop size.[2−5] However, there have been few studies concerning the inherent physicochemical properties of solutes to influence the drop coalescence and breakage. Ban et al.[6] succeed in quantitative prediction of the drop coalescence behavior in the toluene + acetone/water system from the viewpoint of mass transfer. They are also successful in qualitative prediction of drop coalescence behavior of industrial extractant and surfactant systems.[7] The former treatment is essentially based on the effects of mass transfer at interphase on coalescence time between two droplets. In the latter HLB (hydrophile−lipophile balance) of various extractants is proposed to be a key parameter for predicting the drop coalescence behavior.

The objective of this work is to take one step more into the understanding of the drop coalescence effects on drop size in an extraction column. Special attention has been paid to the role of surface activities of extrac-
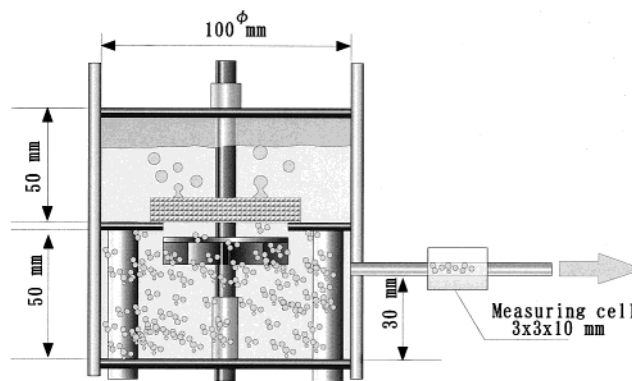

Figure 1. One stage of a mixer-settler extraction column.

tants on the relationship between drop size and drop coalescence behavior via surface activities of extractions. The drop size of a dispersed phase has been measured in a single-stage mixer-settler column for five different systems having various properties of surface activities, for example, TOPO (tri-*n*-octylphosphine oxide), TOA (trioctylamine), PC88A (2-ethylhexyl-phosphonic acid mono-2-ethylhexyl ester), D2EHPA (di(2-ethylhexyl) phosphoric acid), and LIX860IC (5-dodecylsalicylal-doxime).
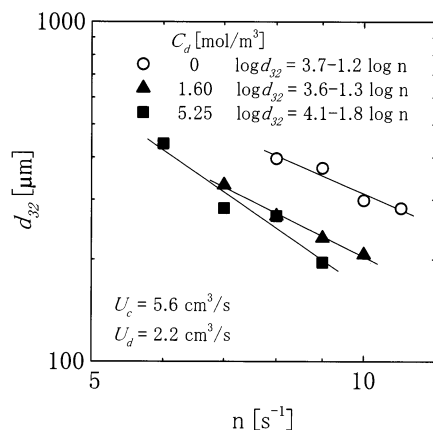
Experimental Section

One stage of the mixer-settler column used is 100 mm in diameter and 100 mm in height. A single stage of the column (see Figure 1) consists of a lower mixer part and an upper settler part, and a drop coalescer is set between them. This column is entirely made of acryl resin. The coalescer is a three-dimensional lattice made of glass fiber mesh coated with PTFE. A six-blade lifter turbine is installed in the mixer. Aqueous phase (continuous phase) is led to the bottom of mixer through two pipes (not shown in Figure 1) and is discharged from the bottom of the settler through two downspouts. Organic phase (dispersed phase) is also introduced from

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Figure 2. Sauter mean drop size in binary (heptane–water) and ternary systems (heptane + TOPO–water).

Figure 3. Effect of the extractants concentration on average coalescence time in water/heptane + various extractant systems.[7]

the bottom of the mixer and is drawn out from the top of the settler.

A direct photographic method through the column wall is not proper for measuring drop size for high holdup conditions in the column. Liquid samples in the mixer are drawn out through a pipe connected to the rectangular measuring cell. The pipe is made of glass with an inner diameter of 3 mm and the rectangular cell is made of $3 \times 3 \times 10$ mm acryl resin. The location of the suction probe is on the wall and 30 mm above the bottom of the mixer part. The drops were photographed through the measuring cell. No drop coalescence was observed in the cell wall. If drops coalesce, the impact of coalescence deforms the drops. Deformed drops were not observed except for extremely large drops. Uniform and "quasi-laminar" flow of each drop in the cell may prevent collision of drops. The volume of dispersed phase as well as the total amount of the liquid sample was measured to determine the holdup of the dispersed phase. The dispersed phase was heptane and the continuous phase was deionized water. TOPO, TOA, D2EHPA, LIX860IC, and PC88A were used as model extractants. These extractants were dissolved into the dispersed phase. After the column was filled with the continuous phase, the dispersed phase was introduced into the column. After agitation for 20 min to attain steady state, drop size and holdup were measured as functions of the extractant concentration, flow rate of the dispersed phase, and agitation speed.

Results and Discussion

Drop Size in Binary and Ternary Systems. The Sauter mean diameters, d_{32}, for the binary and ternary systems are plotted versus agitation speed, n, in Figure 2 where C_d is the concentration of TOPO. According to the Kolmogoroff theory of isotropic turbulence,[8] drop size depends on $We^{-0.6}$, that is, $n^{-1.2}$. For the binary system and the lower concentration of TOPO in the ternary system this dependence agrees with classical theory. At a high concentration of TOPO, as will be discussed in the next section, the breakage effect is dominant. For this system the dependence is different from the theory. A similar dependence of We has been reported by Konno and Saito[9] and Takahashi and Takeuchi.[10] These results show that the Kolmogoroff theory is unsuccessful in estimating drop size in the situations investigated.

Drop Size Distribution in Three Different Systems. Prior to this work, a study was carried out to
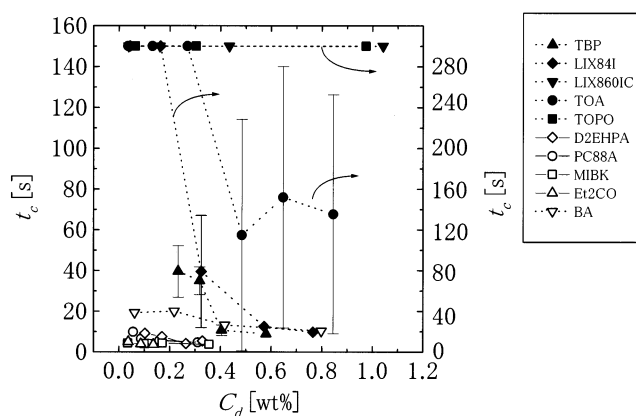
clarify the relationship between the drop coalescence behavior and surface activities of extractants.[7] Drop coalescence in a liquid–liquid system was monitored for 10 systems containing industrial extractants, for example, PC88A, D2EHPA, TBP (tri-n-butyl phosphate), MIBK (methylisobutyl ketone), LIX84I (2-hydroxy-5-nonylactophenone oxime), LIX860IC, TOA, Et2CO (diethyl ketone), BA (benzoylacetone), and TOPO. Coalescence times of two droplets of heptane growing at the adjacent glass nozzles standing in parallel were measured. Average coalescence times, t_c, plotted versus extractants concentration (wt %) for various extractants are reproduced in Figure 3 for ease of comprehension. Coalescence time equal to 300 s means that the droplets do not coalesce in the time of measurement.

The values of t_c for PC88A and D2EHPA are quite small, even at their low concentrations. TOPO and LIX860IC show no drop coalescence in the concentration range measured. While TOA shows no drop coalescence in the concentration ranges up to 0.27 wt %, the coalescence occurs at concentrations higher than 0.48 wt %. PC88A and D2EHPA work as a coalescence promoter, while TOPO and LIX860IC work as a coalescence inhibitor. TOA has both abilities. Generally, the presence of surface-active substance retards droplets from coalescing. This is because the interfacial tension gradient, which is produced from the concentration difference induced in the film by natural drainage, opposes the film drainage. However, the coalescence time for extractants except for TOPO and LIX860IC decreases with increasing extractants concentration. A similar result has been reported when a solute is transferred from the dispersed phase to the continuous phase.[6] As a result of slight solubility of these materials into water, the mass-transfer effect of these extractants may promote drop coalescence. Hydrophobicity of TOPO reflected in HLB values is the highest among the extractants investigated in this work; LIX860IC has the largest HLB value, which is well above the critical value.[7] If the HLB of the extractant contained in a heptane/water system is above the critical value, coalescence seldom occurs. This is actually the case for LIX860IC. These extractants show no effect on the drop coalescence. Extractants having an optimal hydrophilicity enhance the drop coalescence. PC88A and D2EHPA have optimal hydrophilicity. TOA has slightly higher hydrophilicity than TOPO. However, hydrophilicity of TOA is the lowest among the other extractants except for TOPO. This property of TOA leads to prevention of the drop coalescence at its low concentration and
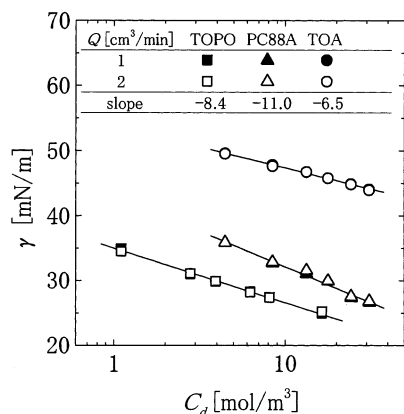
Figure 4. Interfacial tension of the heptane−water system plotted versus extractant concentration in heptane.
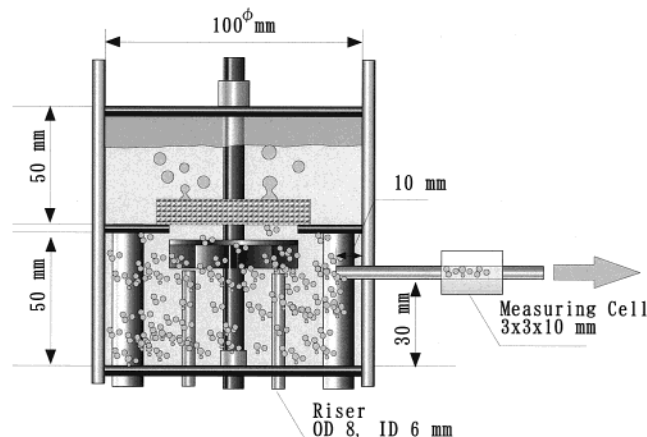
induces the coalescence at high concentration. Although TOA cannot be recognized as a coalescence promoter such as PC88A because of a high standard deviation in coalescence time as shown in Figure 3, it is apparent that TOA enhances drop coalescence at its high concentration.

In the above experiment, focus is on the drop coalescence behavior. For shedding light on the drop breakage behavior, interfacial tensions in heptane/water systems containing the extractants were measured by the drop weight method. The experimental procedure is described in our early paper.[6] The results are shown in Figure 4 where Q represents the feed flow rate to the nozzle-producing drop. The extractant concentration is based on the assumption that the extractants are insoluble in water. In all systems, interfacial tensions, which are independent of feed flow rate, decrease linearly with log C_d. The slopes for three extractant systems are provided in Figure 4. Interfacial tension for TOA shows the highest value while the slope is the lowest among the three systems, and for PC88A and TOPO interfacial tensions are low and the slopes are higher than those for TOA. These results mean that droplets in TOA systems are hard to break, while droplets in PC88A and TOPO systems are easy to break. As can be seen in Figures 3 and 4, TOA has the concentration-dependent drop coalescence ability and the low breakage ability, PC88A has the high coalescence and breakage abilities and TOPO has the low or no coalescence and high breakage abilities.

Drop size distributions in three different extractant systems are shown in Figure 5. The values of N and C_d in Figure 5 represent the number of droplets counted and extractant concentration in dispersed phase, respectively. U is the volumetric flow rate. The value of U_d equal to 1.4 cm³/s is the lowest value in this work and it means that the holdup of the dispersed phase in the range from 0.09 to 0.18 is quite low. In the case of TOPO, which works as a coalescence inhibitor, the decrease of frequency in drop size distribution with the drop size is observed as shown in Figure 5a. The highest frequency corresponds to the minimum drop size observable. As shown in Figures 3 and 4, TOPO shows no coalescence and has strong surface activities. The distribution for TOPO shows that the droplets undergo breakage. On the other hand, for PC88A working as a coalescence promoter (see Figure 3) the drop size distribution has a peak and is nearly symmetric. In the case of low concentration of TOA where it works as a coalescence inhibitor (see Figure 3), the distribution
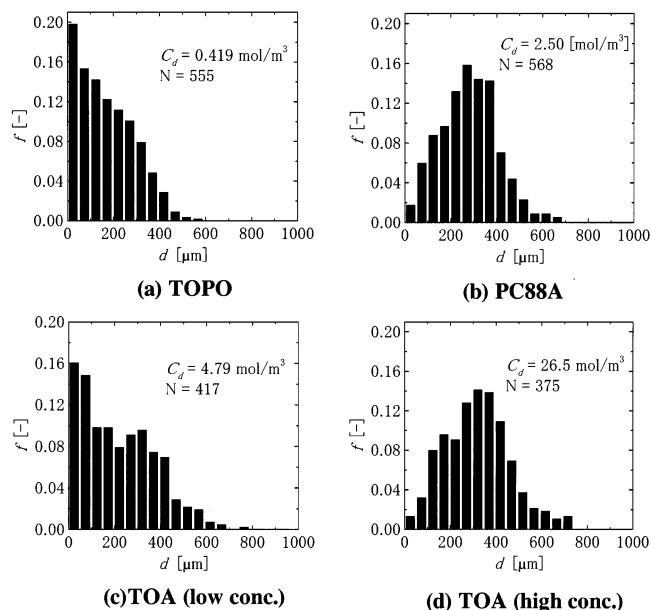
Figure 5. Drop size distributions in water/heptane + (a) TOPO, (b) PC88A, (c) TOA (low concentration), and (d) TOA (high concentration) systems. $U_d = 1.4$ cm³/s, $U_c = 5.6$ cm³/s, and $n = 8$ s⁻¹.


Figure 6. One stage of a mixer-settler extraction column with double risers.

pattern resembles that for TOPO, while at high concentration where TOA works as a coalescence promoter the distribution pattern is similar to that of PC88A. The distribution for TOA at low concentration, in which no drop coalescence is observed, is similar to that for TOPO. TOA at high concentration has coalescence ability, though the ability is lower than that for PC88A. The distribution for TOA resembles that for PC88A. Thus, the resemblance in Figure 5 demonstrates that the drop coalescence greatly influences the distribution pattern. Systems controlled by the coalescence process have generally a bimodal distribution. However, for PC88A and TOA at high concentrations the distributions deviate from a bimodal pattern. These results will be discussed in more detail later.

Similar experiments were carried out in the column with double risers for other extractant systems, for example, LIX860IC and D2EHPA, which work as a coalescence inhibitor and promoter, respectively. The column with double risers is described in Figure 6. The location of the suction probe is 10 mm inside the wall to diminish the end effect of wall on drop size. The column with double risers has higher throughput than
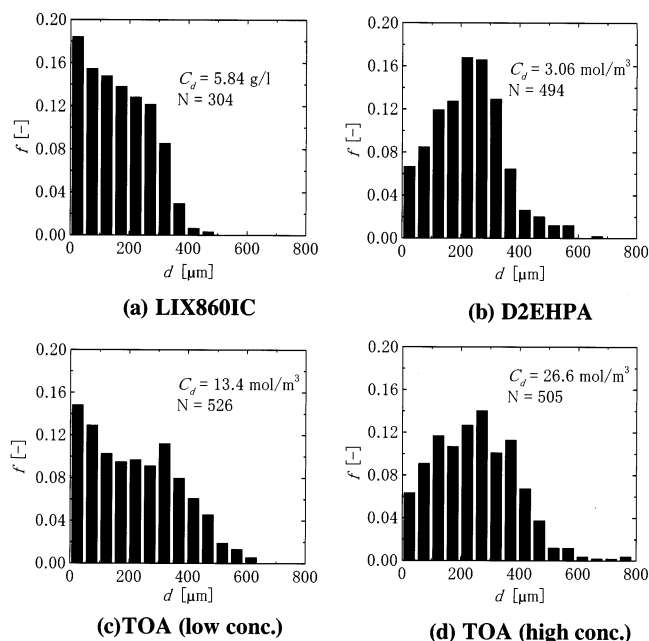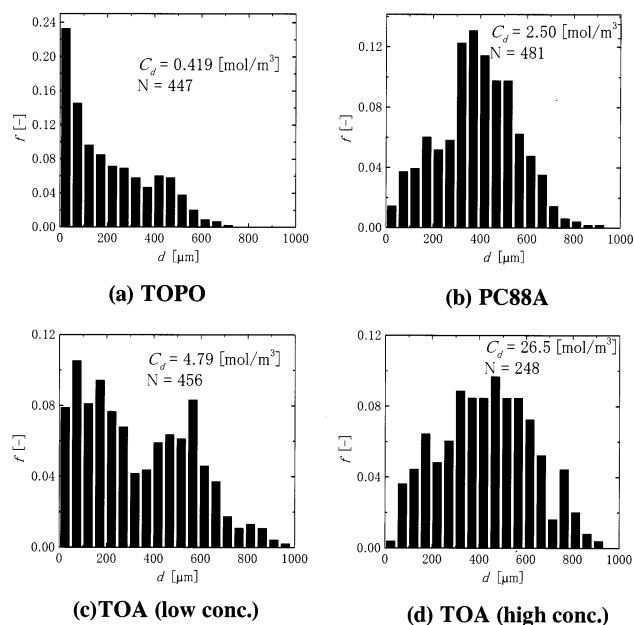
Figure 7. Drop size distributions in water/heptane + (a) LIX860IC, (b) D2EHPA, (c) TOA (low concentration), and (d) TOA (high concentration) systems in the column with double risers. $U_d = 1.4$ cm^3/s, $U_c = 5.6$ cm^3/s, and $n = 8$ s^{-1}.


Figure 8. Drop size distributions in water/heptane + (a) TOPO, (b) PC88A, (c) TOA (low concentration), and (d) TOA (high concentration) systems in the column with a single riser. $U_d = 3.7$ cm^3/s, $U_c = 5.6$ cm^3/s, and $n = 8$ s^{-1}.

Figure 9. Relationship between Sauter mean diameter and holdup in water/heptane + various extractant systems, $n = 8$ s^{-1}.

the column with a single riser.[11,12] Experimental results given in Figure 7 show a similar distribution pattern obtained for the column with a single riser, although experimental conditions are different. LIX860IC, which works as a coalescence inhibitor, shows a distribution pattern similar to that of TOPO, while D2EHPA, which works as a coalescence promoter, shows one similar to that of PC88A. Similar results are obtained for TOA. These findings demonstrate that the distribution pattern depends on the coalescence property of extractants, irrespective of the kind of extractant and the internal structure of the column.

In Figure 8 is given the distribution for four different systems at $U_d = 3.7$ cm^3/s. The holdup in the mixer is high and the high holdup enhances mechanically the coalescence frequency of droplets. TOPO shows a small second peak at about 450 μm as shown in Figure 8a. Though high holdup promotes drop coalescence, the second peak is quite small as a result of the low coalescence and high breakage abilities inherent to TOPO. The distribution for PC88A is nearly symmetric and is broader than that at $U_d = 1.4$ cm^3/s given in Figure 5b. High coalescence and breakage abilities inherent to PC88A lead to one-peak distribution. TOA at low concentration, given in Figure 8c, has a bimodal distribution, as is often seen. On the other hand, TOA at high concentration has a broad and nearly symmetric distribution, even though the second peak may be seen at about 800 μm in Figure 8d. The breakage ability for TOA is different from that for PC88A and TOPO. TOA at low concentration shows no drop coalescence like TOPO, while TOA at high concentration has coalescence ability, which is lower than that for PC88A. Systems having coalescence ability, but are different in terms of breakage abilities, show a symmetric peak even in high holdup conditions. However, the distribution pattern of the systems without coalescence ability is dependent on breakage ability. These results mean that the distribution pattern depends not on mechanical effects but on intrinsic surface activities inherent to each extractant;
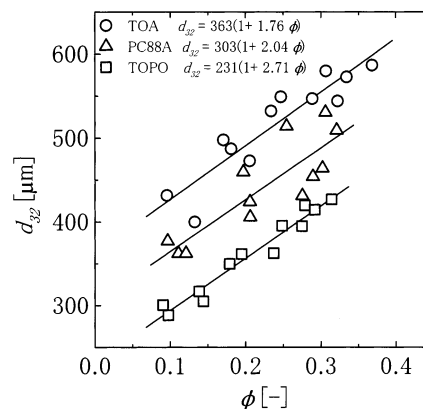
if this does not hold, all systems in high holdup conditions must show a bimodal distribution. Such a bimodal distribution can be produced for the systems with low or no coalescence and low breakage abilities in high holdup conditions.

Sauter Mean Diameter in Three Different Systems. Figure 9 represents the relationship between Sauter mean diameter and holdup in the column with a single riser. The holdup was changed by changing the flow rate of the dispersed phase from 1.4 to 3.7 cm^3/s. Drop sizes for TOA are the highest value among the three systems. This result reflects the highest interfacial tension of TOA. As a whole, the magnitude of the Sauter mean diameter corresponds to that of the interfacial tension in each extractant system. The Sauter mean diameter increases linearly with the holdup for all systems and the slopes of these lines are all in the range 620−640 μm. The higher the coalescence ability, the larger the degree of data scattering. At low concentration PC88A has a slope of about 930 μm, a value much steeper than that represented by the line in Figure 9. However, if the slopes for PC88A are averaged over a wide concentration rage, the line is similar to those of TOA and PC88A. This result contradicts our expectation
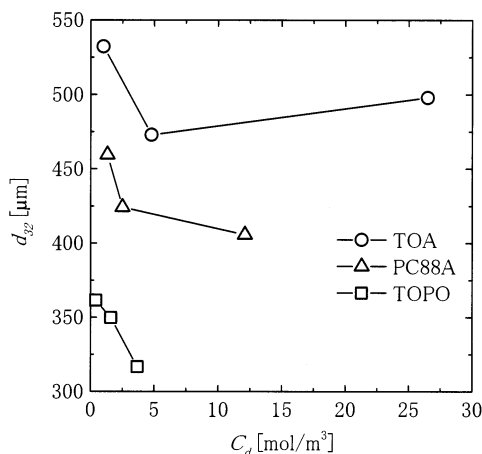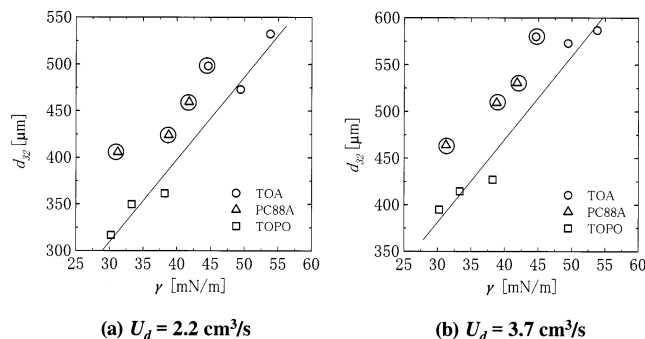
Figure 10. Relationship between Sauter mean diameter and extractant concentration in water/heptane + various extractant systems, $U_d = 2.2$ cm³/s, $U_c = 5.6$ cm³/s, and $n = 8$ s⁻¹.

(a) $U_d = 2.2$ cm³/s   (b) $U_d = 3.7$ cm³/s

Figure 11. Relationship between Sauter mean diameter and interfacial tension in water/heptane + various extractant systems, $n = 8$ s⁻¹. (The symbol O represents data of coalescence promoters.)

that the slope will be inversely proportional to the coalescence time; thus, PC88A will show the highest slope as a reflection of its shortest coalescence time among the three. Coalescence frequency increases with an increase in holdup. Thus, the Sauter mean diameter for PC88A having the highest coalescence ability should increase synergistically with the increase in holdup in any concentration. Consideration of the coalescence effect of these extractants alone is unsuccessful for interpreting these results. Thus, we should consider the breakage effect of these extractants. In what follows, the relationship between the Sauter mean diameter and coalescence and breakage abilities will be discussed.

Figure 10 shows an example of the relationship between Sauter mean diameter and extractant concentration. The concentration range for TOPO is very limited since turbidity appears at high concentration. The turbidity may correspond to extremely small droplets. Sauter mean diameters for both TOPO and PC88A decrease with the increase in the concentration, while the one for TOA goes down and up slightly or levels off with the concentration. Similar results are obtained at different flow rates of the dispersed phase. The coalescence behavior for PC88A is independent of the concentration as shown in Figure 3, although PC88A has a very short coalescence time. Additionally, a considerable decrease in interfacial tension for PC88A with concentration is observed. Such surface activities of PC88A cause a moderate decrease in the drop size with the concentration. TOPO shows no drop coalescence and the lowest interfacial tension. As a result, the drop size for the TOPO system decreases steadily with concentration. On the other hand, the drop coalescence for TOA occurs at high concentration, while at low concentration no drop coalescence is observed. TOA shows the highest interfacial tension. Due to these properties of TOA, the drop size shows a decrease followed by an increase with the concentration. The relationship between drop size and concentration can be explained on the basis of the dependence of interfacial tension and coalescence time on the concentration. In other words, drop size is a result of the competition between coalescence and breakage effect.

Examples of relations between Sauter mean diameter and interfacial tension measured are shown in Figure 11. Fitting of the data of drop size in coalescence inhibitor systems, that is, TOPO and TOA systems at low concentration leads to the lines in Figure 11. The

data enclosed with a circle represent the systems in which coalescence is promoted, as shown in Figure 3. In both parts a and b of Figure 11 drop sizes in coalescence inhibitor systems fall on the same line, while drop sizes in coalescence promoter systems, that is, PC88A and TOA at high concentration, are obviously above the line. These results show that in coalescence inhibitor systems consideration of interfacial tension permits estimation of drop size, while in the case of coalescence promoter systems, estimation of drop size should be done after considering intrinsic physicochemical properties inherent in each extractant.

Conclusion

Drop size of dispersed phase was measured in a single-stage mixer-settler column. For the binary system and at lower concentration of TOPO in the ternary system, the dependence of drop size on Weber number agrees with classical theory. At a high concentration of TOPO where the breakage effect is dominant, however, the dependence is different from the theory.

Drop size distribution depends on coalescence behavior of extractants. In coalescence inhibitor systems the frequency of drops decreases with the increase of drop size, while in the case of coalescence promoter systems the drop size distribution is nearly symmetric. Similar results were obtained irrespective of the kind of extractant and internal structure of the column. In high holdup conditions TOPO shows a moderate decrease in frequency of drops with an increase in drop size as can be seen in low holdup conditions. PC88A and TOA at high concentration have a broad and nearly symmetric distribution in both low and high holdup conditions. TOA at low concentration shows a typical bimodal distribution. Low or no coalescence and low breakage abilities inherent to each extractant in high holdup conditions form a bimodal distribution.

Drop size distribution is mainly determined by surface activity inherent to the extractant and not by the mechanical effects. This study shows that the drop size should be estimated by taking account of drop coalescence and breakage effects caused by surface properties of extractants.

Notation

C = solute concentration, mol/m³, wt %
d = drop diameter, μm
d_{32} = Sauter mean diameter, μm
D = impeller diameter, m

f = fraction of drop number for a definite small range Δd, dimensionless

n = agitation speed, s^{-1}

Q = feed flow rate to the nozzle-producing drop, cm³/min

t_c = coalescence time, s

U = volumetric flow rate, cm³/s

We = Weber number = $\rho_c n^2 D^3 / \gamma$, dimensionless

Greeks

γ = interfacial tension, mN/m

ρ = density, kg/m³

ϕ = holdup of dispersed phase, dimensionless

Subscripts

c = continuous phase

d = dispersed phase

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