Holdup and Solvent Extraction Characteristics in Electrostatic Liquid-Liquid Contactor

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Various attempts have been made to enhance mass-transfer efficiencies in mass-transfer processes dealing with liquid drops. Generally, such enhancement can be obtained by producing a larger interfacial surface area for diffusion and a higher degree of turbulence within and around drops for eddy diffusion. The requirement for making turbulence coupled with a larger interfacial surface area is difficult, because these features are incompatible in the sense that small drops neither have high relative velocities nor do they exhibit marked internal circulation patterns. The application of an electric field as a technique to overcome these problems has been proposed by Thornton (1968). Many investigators have experimentally studied the effects of the electric field on the rates of mass transfer in a liquid-liquid system and have suggested that the application produced significant increases in the mass-transfer coefficients. Novel liquid-liquid contactors have been actively developed by many researchers (Bailes and Stitt, 1987; Scott and Wham, 1989; Gu, 1990). Recently, a unique contactor with a pair of inclined parallel plate electrodes was developed by our research group (Yoshida et al., 1986, 1988; Yamaguchi, 1993). It was quantitatively shown that the contactor had some favorable characteristics for liquid dispersion, mixing of the liquid phases, and phase separation, but the holdup fraction of the dispersed phase was low. In the present study, an unconventional contactor has been developed to aim at increasing the dispersed-phase holdup (Yamaguchi and Kanno, 1995). The electrodynamic and mass-transfer characteristics of the contactor were examined.

Experimental Apparatus and Procedures

The novel liquid-liquid contactor is shown in Figure 1. The test contactor made of transparent acrylic resin is 90 mm in ID and 150 mm in height. The contactor is equipped with two electrodes: a rod electrode and a plate electrode are fixed at the top and bottom of the contactor. The rod electrode made of 5-mm-dia. copper is pointed at one end and connected to a high voltage generator (Brandenburg 2807R). The plate electrode is made of stainless steel and electrically grounded through an electrometer (Takeda Rikken TR8651) for measuring the electric current between the electrodes. The rod electrode is removable and so the distance between the electrodes is variable. An aqueous phase and an organic phase were supplied continuously from each reservoir into the contactor using peristalic pumps, respectively. Both phases were discharged at given flow rates by the pumps to maintain each of the phases at a given level. The contactor contains three phases: an aqueous phase at the bottom; a gaseous phase at the top; and an organic phase located between the aqueous and gaseous phases. When the DC voltage was applied above a certain value to the rod electrode, a corona discharge was generated from the electrode and formed an electrostatic field in the organic phase through the gaseous phase. As the field strength approached a certain value, the interface between the aqueous and organic phases began to move with small fluctuations due to the field-induced stress. With increasing voltage, the fluctuations became waves having conical crest-like shapes of various scales. At an applied voltage higher than the critical one, aqueous droplets were violently ejected from the tips of the waves into the organic phase (Figure 1). The moving behavior of the droplets in the electric field followed this sequence: (1) The droplets having induced charge were ejected from the tip of the waves into the organic phase (drop formation); (2) They rose against gravity toward the interface between the organic and gaseous phases because of the Coulomic force as the interaction of the charge of the droplet with the electric field. After they contacted the interface and their polarity were changed to the opposite charge, they fell through the organic phase on the aqueous phase (cross-current contacting, agitation of the organic phase); (3) The droplets collided with the aqueous phase and instantaneously coalesced with it because the droplets and the aqueous phase have opposite charges (phase separation).

In the hydrodynamic experiment, distilled water was used as a dispersed phase and three kinds of the organic solvents were prepared as a continuous phase: SOLVESS 150, ISOPAR M, and ISOPAR E (Exxon Chemicals). Di(2-ethylhexyl) phosphoric acid (D2EHPA; Daihachi Chemicals Inc.) was used as an extractant and played a role to vary the electrical properties ot the continuous phase. In the mass-transfer experiment, the aqueous solution was prepared with the

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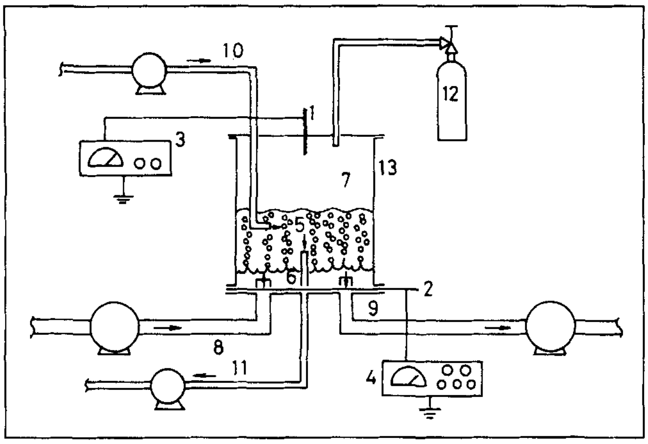

Figure 1. Experimental apparatus.

(1) Rod electrode; (2) plate electrode; (3) high voltage generator; (4) electrometer; (5) continuous phase; (6) aqueous phase; (7) gaseous phase; (8) aqueous phase supply; (9) aqueous phase discharge; (10) continuous phase supply; (11) continuous phase discharge; (12) nitrogen gas vessel; (13) test contactor.

concentration of 0.5 mmol/L by dissolving zinc sulfate in distilled water. The continuous phase was prepared by diluting D2EHPA in ISOPAR M at 0.024, 0.12 and 0.3 mol/L in monomeric D2EHPA concentration. The physical properties of the liquids used are listed in Table 1.

The holdup fraction of the dispersed phase was measured by a batch method: each constant volume of the water phase (dispersed phase) and an organic phase (continuous phase) was fed to the contactor, and the dispersed phase was perfectly dispersed into the continuous phase by applying a high voltage. The ratio of the volume of the dispersed phase to the total volume of both phases was defined as the holdup fraction of the dispersed phase. The voltage at which the dispersed phase just began to settle on the lower plate electrode with decreasing voltage was measured and defined as the minimum voltage during which a constant holdup fraction was maintained. Using this procedure, the relation between the holdup and the applied voltage was examined in detail under various operating conditions as a fundamental characteristic of electrodispersion of the aqueous phase.

Size distribution of the droplets were examined as follows. The droplets in the contactor were sampled with the continuous phase in a petri dish where a thin film of a liquid paraffin dissolved surfactant (Span 80) was prepared. Because the droplets were quickly covered by surfactant and could not move due to high viscosity of the liquid paraffin, droplet-droplet coalescence in the dish was prevented and the native size of the droplets in the contactor could be obtained. They were quickly recorded using the video recorder through photomicrography and measured.

Mass-transfer characteristics in the contactor were examined using solvent extraction of the zinc-D2EHPA system. In the forward extraction experiment, an aqueous solution of 0.5 mmol/L zinc as the dispersed phase and an ISOPAR M containing D2EHPA as the continuous phase were used, respectively. After the flows of both phases attained at steady state, the aqueous phase was sampled at the outlet of the contactor and analyzed for zinc using an atomic absorption spectrophotometer. In the experiment, the pH in the aqueous phase was not controlled using buffer solutions. While in the backward extraction experiment, the aqueous sulfate solution as the dispersed phase and the ISOPAR M containing Zn-D2EHPA complexes as a continuous phase were prepared, respectively. The experimental procedure and the measurement of zinc concentrations were the same as those in the forward extraction experiment.

Results and Discussion

Holdup fraction of the dispersed phase

The effects of various operating parameters on the holdup Φ were examined on SOLVESSO 150, ISOPAR M, and ISOPAR E. The parameters are height of the gaseous phase L_0 (m), the continuous phase L_C (m), and the applied voltage E_P (V). In Figure 2 are shown the experimental results, in which Φ is plotted vs. E_P for different continuous phase. It is found that each of Φ increases with an increase in E_P. The voltage required to obtain the equivalent Φ for different continuous-phase increases with increasing density difference between the dispersed and continuous phases. However, Φ for all the continuous phases approach the same values at an applied high voltage. This will mean that liquid dispersion in the region of applied high voltage is dominated by an electric force irrespective of the physical properties of the continuous phase. The influence of D2EHPA concentration C_{RH} (mol/L) in ISOPAR M on the holdup was also examined because it has significant effects on the electrical properties of the continuous phase as a foreign material and is an important parameter in practical solvent extraction. Increasing C_{RH} causes a reduction in the dispersed-phase holdup. It is a reason why the field induced stress acting on the surface of aqueous phase decreases with an increase in C_{RH} which results in enhancing electrical conductivity.

Table 1. Physical Properties of Liquid Used at 25°C

Liquid	Density kg/m^3	Interfacial Tension mN/m	Viscosity mPa·s	Dielectric Constant pF/m	Electrical Conductivity nS/m
water	998	—	1.01	718.0	8.6×10^4
ISOPAR E	718	21.9	0.668	17.4	1.3
ISOPAR M	786	42.3	2.67	18.0	0.05
ISOPAR M + 0.024 mol/L D2EHPA	787	18.5	2.75	18.1	0.30
ISOPAR M + 0.12 mol/L D2EHPA	789	18.3	2.78	18.2	1.3
ISOPAR M + 0.3 mol/L D2EHPA	794	17.9	2.96	18.6	18.0
SOLVESS 150	890	21.1	1.13	20.9	8.8

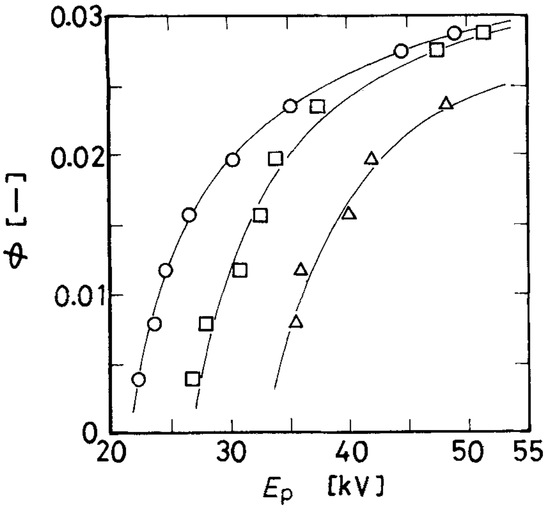

Figure 2. Effect of physical properties of continuous phase on holdup fraction of dispersed phase under applied voltage and in the absence of mass transfer.

Conditions: $L_o = 60$ mm; $L_c = 40$ mm; $C_{RH} = 0$ mol/L; ○: water/SOLVESS 150; □: water/ISOPAR M; △: water/ISOPAR E.

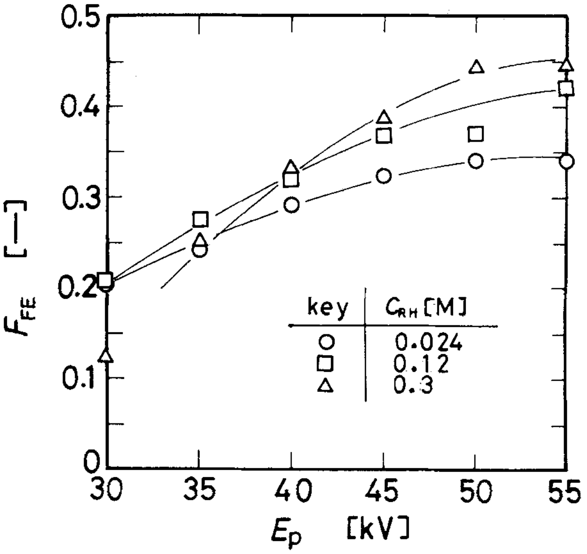

Figure 3. Effect of D2EHPA concentration on forward extraction efficiency of zinc in the electric field for the system of $ZnSO_4$ solution/D2EHPA/ISOPAR M.

Conditions: $L_o = 60$ mm, $L_c = 40$ mm, $L_d = 15$ mm, pH = 4.1, $Q_c = Q_d = 1$ mL/s.

Size distribution of the droplets

The size distribution and the Sauter mean diameter of the droplets d_{32} were greatly different with different continuous phases. They were obtained by the applied voltage of up to 50 kV for each of continuous phases as follows: $d_{32} = 0.7–0.9$ mm for SOLVESS 150; $d_{32} = 0.2–0.5$ mm for ISOPAR E; $d_{32} = 0.4–1.0$ mm for ISOPAR M. They will result from electrically aided coalescence-redispersion behavior of the droplets depending on physical properties of the continuous-phase and the holdup characteristics. From the results of the dispersed-phase holdup and the droplet size, ISOPAR M was chosen as a suitable continuous phase for examination of the electrohydrodynamic and mass-transfer characteristics.

Droplet velocity in the electric field could not be obtained because of their complex motion which accompanied the coalescence-redispersion of the droplets.

Solvent extraction of zinc

Mass-transfer efficiency was evaluated by the forward extraction degree of zinc; $F_{FE} = (C_{in} - C_{out})/(C_{in} - C^*)$. Examples of the experimental results are shown in Figure 3 in which F_{FE} is plotted vs. E_P with C_{RH} as a parameter for the selected conditions shown in the figure. F_{FE} increases with an increase in E_P. This is due to the violent turbulence of the aqueous phase induced by dispersing or coalescing from/with the aqueous phase, which results in enhancing the mass transfer at the interface between both phases and the violent mixing of both phases by the higher relative velocity of the droplets resulting in a decreasing diffusional resistance of zinc around the droplets. With increasing C_{RH}, F_{FE} also increased though the holdup decreased. This is because D2EHPA molecules adsorbed on the surface of the droplets and the interface between both phases increase with increasing C_{RH} and the frequency of the interfacial reaction between zinc and D2EHPA molecules. Increasing flow rate of the aqueous phase resulted from decreasing of F_{FE} because of the residence time decreasing the aqueous phase. In the backward extraction, the effects of the applied voltage and the flow rate of aqueous phase on the extraction degree showed similar results obtained in the forward extraction. However, generally the backward extraction efficiency was better than the forward one because the continuous phase was purified with the removal of zinc in the continuous phase and the electrical dispersion of the aqueous phase into the continuous phase improved. This result is one of the distinguishing characteristics in the present contactor which is much more useful for removal of the contamination from the organic phase. All the experimental results in electrohydrodynamics and mass transfer are found elsewhere (Kanno, 1992). It was found that the application of an electric field makes possible the direct supply of electrical energy to mass-transfer operations of two-phase liquid systems without the need to use any mechanical and moving parts.

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Notation

C_{in} = inlet concentration of zinc in aqueous phase, mol/L
C_{out} = outlet concentration of zinc in aqueous phase, mol/L
C^* = equilibrium concentration of zinc in aqueous phase with *Zn*-D2EHPA concentration in continuous phase, mol/L
L_d = height of aqueous phase, m
Q_c = volumetric flow rate of continuous phase, m^3/s
Q_d = volumetric flow rate of aqueous phase, m^3/s

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