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# Removal of an Organic Dye from Water Using a Predispersed Solvent Extraction

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## ABSTRACT

The removal of Solvent Yellow 1 in a range from 0.25 to 10 ppm by weight from an aqueous solution using a predispersed solvent extraction (PDSE) was investigated and compared with conventional solvent extractions in batch mode. Colloidal liquid aphrons (CLAs) made out of kerosene were used as a predispersed organic solvent. To form CLAs, Tergitol 15-S-3 and sodium dodecylbenzene sulfonate were used as oil-soluble and water-soluble surfactants, respectively. The ratio of solvent volume to pregnant solution volume was less than 0.025. The efficiency of the extraction with CLAs can be higher than that of a single-staged conventional extraction process with a shorter contact time. The recovery of used CLAs with a colloidal gas aphrons (CGAs) flotation was measured using different surfactants. CLAs with an extremely large surface area can also reduce processing time and energy cost. PDSE is therefore a promising process for the removal of organic materials from water.

## INTRODUCTION

Solvent extractions are used for the purification, enrichment, separation, and analysis of various components in mixtures. These are based on the principle that a solute can distribute itself in a certain ratio between two immisci-

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ble solvents. Therefore, the selection of both a diluent and extractant determines the equilibrium for a given system, and the efficiency of the extraction process depends on its mass transfer rates. The conventional process includes intensive mixing or considerable contact time in order to achieve a sufficient mass transfer. The requirements for an extensive time, energy consuming mixer/settler, along with a high solvent consumption, are limiting factors for the wide application of conventional solvent extractions. One novel technique that can circumvent these drawbacks is the PDSE process that employs aphrons.

Some potentialities have been proposed for the application of aphrons in the separation process. "Aphron" is defined as a distinct unit of fluid, encapsulated by a thin soapy film of another fluid (1). Photomicrographs of aphrons are presented in Fig. 1. The average diameter of a colloidal gas aphron (CGA) is 25–150 μm. Colloidal liquid aphron (CLA) is similar to CGA, except that the inner gas phase is replaced with the solvent phase and its average diameter is submicron to 50 μm. Both CGA and CLA have demonstrated many unique and attractive properties. The most striking features of aphrons are both good stability and colloidal properties. CGAs do not coalesce so therefore can be pumped as easily as water. Properly made CLAs can be stored in stoppered bottles for years, without visible deterioration, and CLAs can also be stably dispersed in water (2).

There have been a number of reported applications for CGA (3–11). Some preliminary studies have shown that applications with CGA can be used for the removal of organic dye and metal from water (3–6). Caballero et al. (7) studied coflotation and solvent sublation processes with CGA, and Roy et al. (8) compared a conventional surfactant solution with CGA suspension in a soil washing process. Some investigators have also used it to harvest microorganisms (9, 10) and for protein recovery (11). Yet only a few preliminary studies have shown that CLAs can be applicable for the removal of organics from wastewater (12, 13).

Predispersed solvent extraction (PDSE), which uses CLAs as a predispersed solvent, was first proposed by Sebba (1). The PDSE process is applicable with a low solvent/water ratio for the treatment of wastewater that contains a low solubility, hydrophobic compound (12, 13). CLAs are precomminuted micron-sized organic solvents, thereby exposing an enormously increased interfacial area where a transfer of solute from one phase to another can occur very rapidly with a minimum energy requirement. Although the solvent is usually lighter than water and would be expected to rise, this is also very time consuming because of the small size of CLA. The used solvent is usually recovered by flotation using CGAs. When a CGA dispersion is added to an aqueous solution, the CGA rises due to the normal buoyancy force, and a CLA's rise velocity is further enhanced when CGAs combine

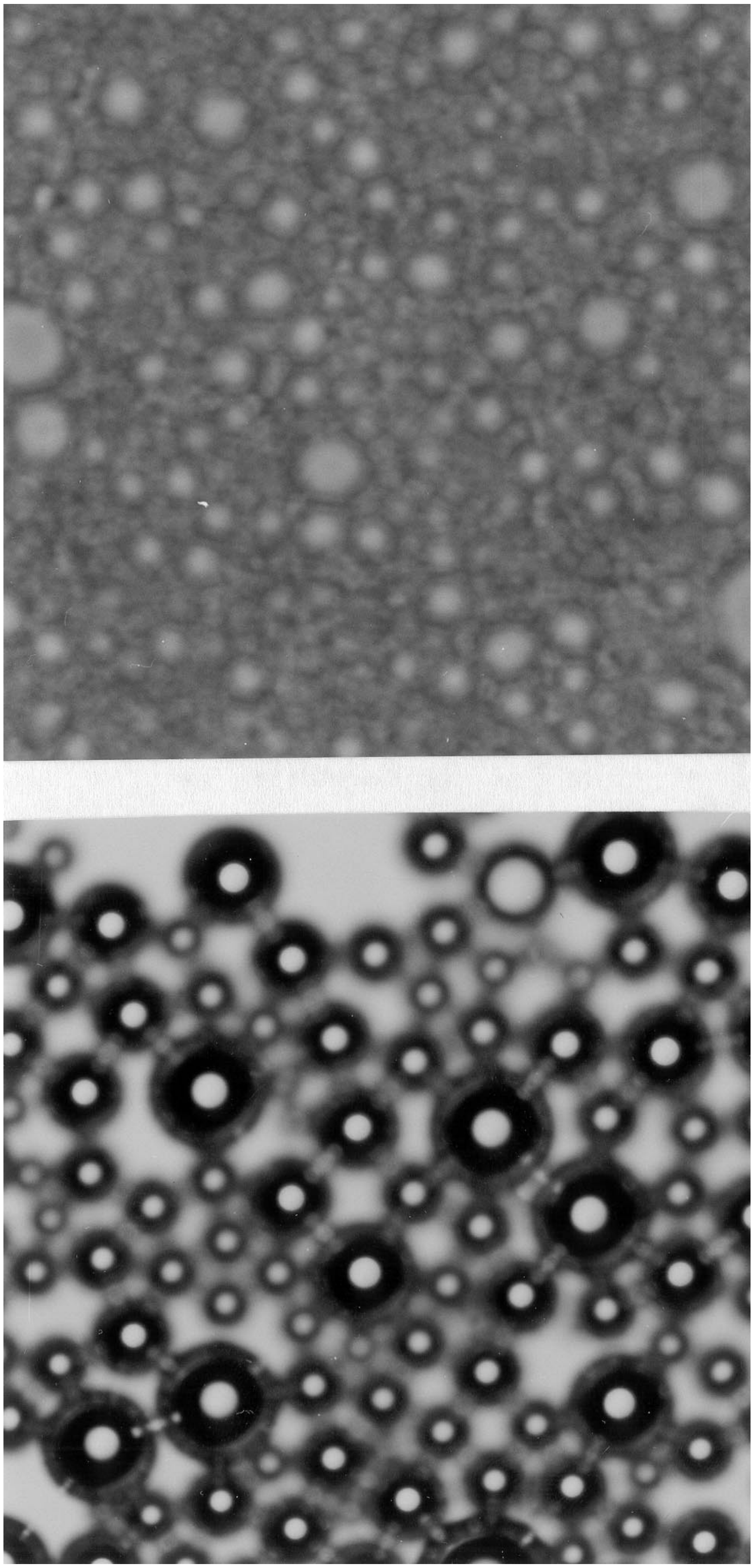

FIG. 1 Photomicrograph of CGAs made out of HTAB solution (left) and CLAs made out of kerosene (right).

with CLAs. Since CGAs have considerable mechanical strength and a large surface area as compared with gas bubbles, the use of CGAs is effective for the recovery of solvents after extraction.

In this study the removal of an organic from water with PDSE was investigated and then compared with conventional solvent extractions. Kerosene was chosen as the organic solvent for CLA, and Solvent Yellow 1 was used as the organic compound because of its ease in analysis. The initial concentration of Solvent Yellow 1 in the aqueous solution was below 10 ppm, while the ratio of extracting solvent to pregnant solution was less than 0.025. The recovery of predispersed solvents with CGA flotation was also considered.

## EXPERIMENTAL

### Materials

Kerosene obtained from Aldrich Chemical Co. was used as the organic solvent, and the aqueous solution was prepared with distilled water. Tergitol 15-S-3 was used as the oil-soluble surfactant, and sodium dodecylbenzene sulfonate (SDBS) as the water-soluble surfactant to form CLA. CLAs were prepared by the following steps. A stable foam was obtained by mixing an aqueous phase containing 4 g/L of SDBS. To this foaming solution, kerosene containing 0.01% (v/v) of Tergitol 15-S-3 was then gradually added. CLAs have a creamy appearance. The phase volume ratio (PVR) is defined as follows, which characterizes CLA (2):

$$\mathrm{PVR} = \frac{\text{Dispersed solvent phase volume}}{\text{Continuous phase volume}} \tag{1}$$

CGAs were made from a water-soluble surfactant solution based on Sebba's method (14). This consisted of a high-speed mixer and a fully baffled cylindrical reactor. The level of the surfactant solution was initially adjusted to a few centimeters above the spinning disk. The aqueous solution was then stirred at 6000 rpm. The properties of the surfactants are listed in Table 1. Solvent Yellow 1 [*p*-phenyl-azoaniline ($C_{12}N_{11}H_3$), Sigma Chemical Co.] was chosen as a organic solute.

### Equipment

PDSE experiments were conducted in an apparatus shown in Fig. 2. The column consisting of acrylonitrile has dimensions of 10 cm i.d. and 40 cm height. The operation was of a batch mode. Various amounts of Solvent Yellow 1 solution were placed in the column. A given volume of CLA was diluted with water 1:1 (v/v), and it was then introduced into the column through the bottom. The CGA dispersion prepared in the generator was then

TABLE 1
The Properties of Surfactants Used

| Surfactant | | MW/CMC (mM) | Charge |
|---|---|---|---|
| | *Water-soluble (CGA/CLA)* | | |
| Sodium dodecyl benzene sulfonate (SDBS) | $C_{12}H_{25}O_6H_4SO_3Na$ | 348.5/1.5 | Anionic |
| Hexadecyl trimethyl ammonium bromide (HTAB) | $C_{19}H_{42}NBr$ | 364.5/0.9 | Cationic |
| Polyoxyethylene sorbitan monooleate (Brij 35) | $C_{12}H_{25}(OCH_2CH_2)_nOH$, $n = 23$ | −1200/0.06 | Nonionic |
| | *Oil soluble (CLA)* | | |
| Tergitol 15-s-3 | | 336/NA | Nonionic |

pumped into the base of the column by using a peristaltic pump. Flow rates of both CLA and CGA were 20 mL/min. A thin layer of solvent at the surface of the aqueous solution was finally taken, and the recovered solvent volume was measured.

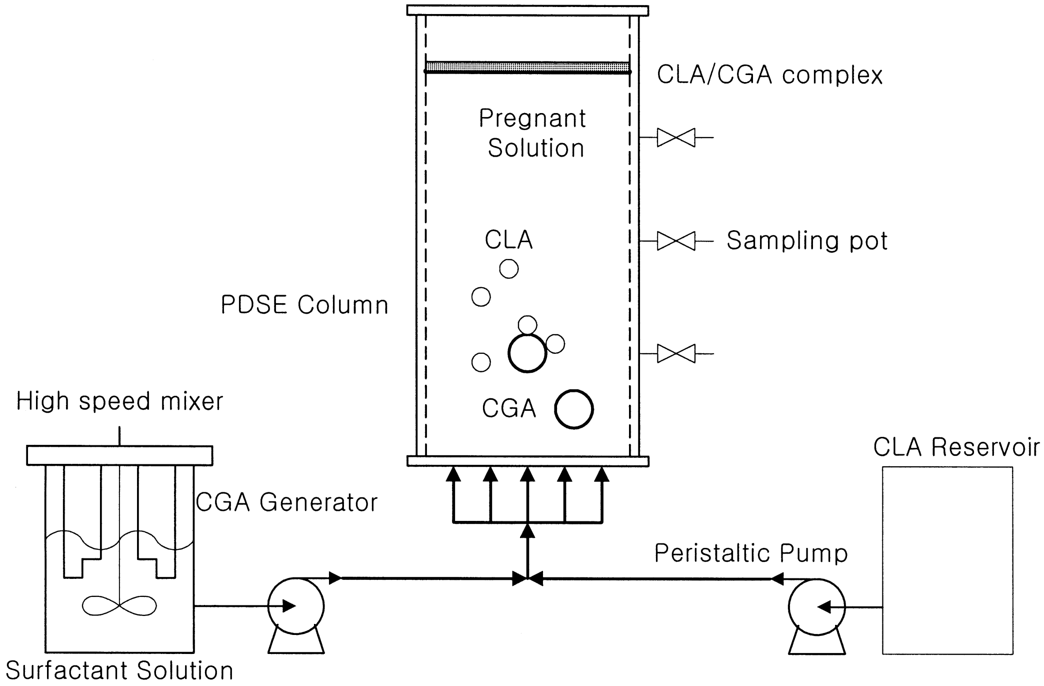

FIG. 2 Schematic diagram of experimental apparatus.

## Analysis

The organic solvent phase was considered for analysis. The sample taken at the top of the pregnant solution was centrifuged, and then the concentration of Solvent Yellow 1 in the kerosene was measured using a HP 8542A diode array spectrophotometer. To compare the performance of PDSE with that of conventional solvent extractions, we measured the distribution coefficient of Solvent Yellow 1 in the kerosene/water system under various conditions.

## RESULTS AND DISCUSSION

### Extraction Efficiency of PDSE

Several extractions with PDSE/CGA flotation tests were examined, and the extraction efficiency ($E_0$) was defined as follows (12):

$$E_0 = \frac{\text{Concentration of organic phase with PDSE}}{\text{Equilibrium concentration of organic phase with conventional solvent extraction}} \tag{2}$$

$E_0$ represents the efficiency of PDSE as compared to the maximum removal at equilibrium that can be attained using straight solvents in the mixer-settler process.

Figure 3 illustrates the effects of settling time on both solvent recovery and extraction efficiency. The system was allowed to settle without flotation. During these experiments 12.5 mL of CLAs with PVR 19 and 2500 mL of 5 ppm aqueous solution were used. Without intense mixing of the solvent with water, most of extraction was achieved by the simple contact of CLAs with a pregnant solution over a short time. After settling for ca. 6 hours, the settling time had little effect on the solvent recovery and extraction efficiency. Zhang et al. (15) reported that the average size distribution of CLAs in water became smaller as time elapsed. Finally, small-sized CLAs floated to the surface of the pregnant solution more slowly, therefore extended settling times are needed without CGA flotation.

CLAs that were formulated with different PVRs were also prepared and examined. CLAs with a PVR above 10 show flow characteristics corresponding to a Bingham-plastic fluid, and those with an increasing PVR show more gel-like properties. The effects of PVR change on extraction efficiency without flotation is shown in Fig. 4. After feeding of the CLAs/water mixture was completed, the mixture was then allowed to settle for 20 minutes. The total aqueous solution volume with concentration used was 2500 mL and 0.5 ppm, respectively. To compare a straight solvent with CLA, kerosene with the same volume of CLA was introduced at the bottom under the same conditions. The extraction efficiencies shown were markedly poorer, as can be seen in Fig. 4.

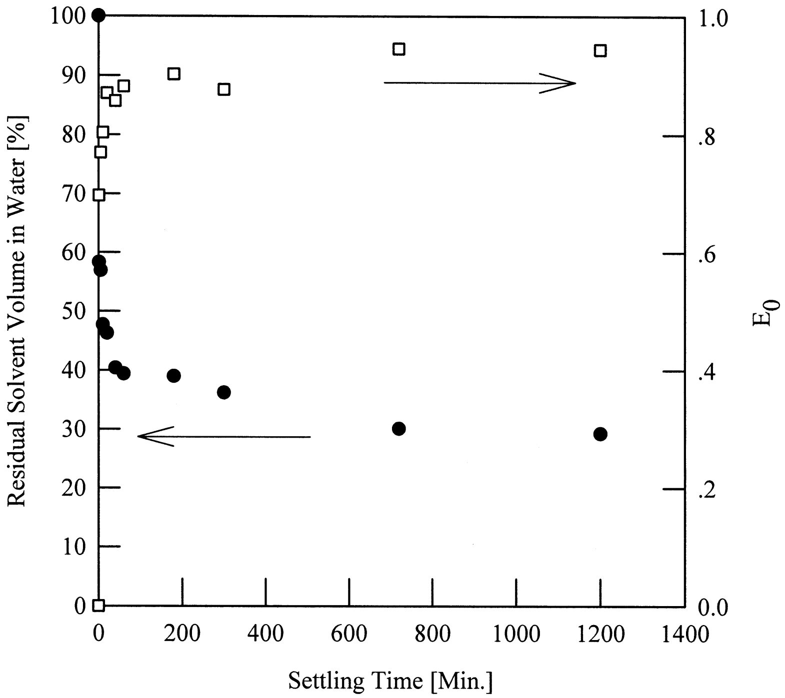

FIG. 3 Settling time effect on the solvent recovery and extraction efficiency.

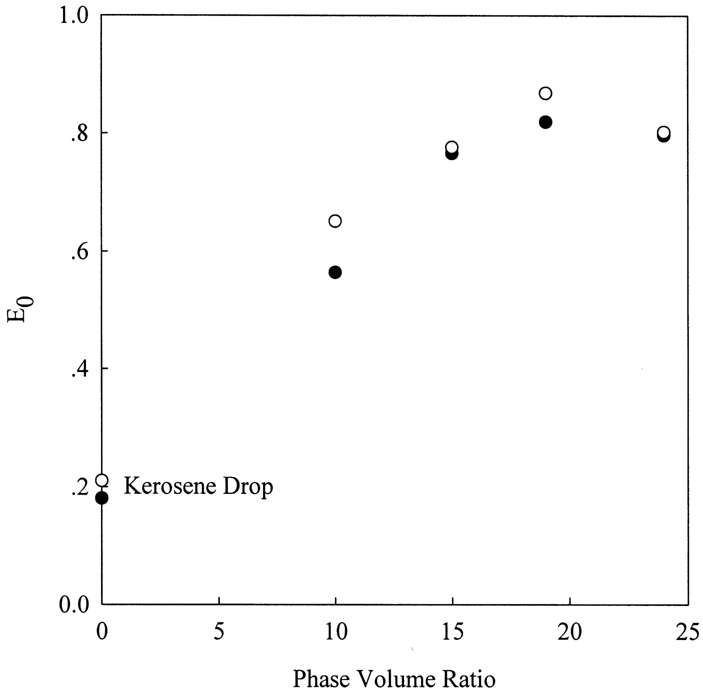

FIG. 4 Effect of PVR on the extraction efficiency: (●) CLA 10 g, (○) CLA 5 g.

These results indicate that the precommunited solvent with a vastly increased interfacial area can achieve an enhanced mass transfer rate. The maximum extraction efficiency was shown in the case of CLAs with a PVR of 19. These can be concluded to be due to the stability of CLA and flow characteristics. The PVR of 19 is reported to be ideal for the production of a stable CLA (2). When CLAs with a low PVR were introduced to the column, we observed that the released oil phase formed large droplets, and CLAs with a PVR above 19 also behaved like a gel, therefore barely dispersing in pregnant phase, so the effective mass transfer area was reduced.

## Organic Solvent Recovery with CGA Flotation

Flotations using SDBS, HTAB, and Brij 35 as the surfactants for the generation of CGAs were carried out in order to determine their effects on CLA recovery. The total aqueous phase volume was 2500 mL, and 25 mL of CLAs were introduced to the column. CGA dispersions were supplied at a flow rate of 20 mL/min, and then each system was allowed to settle for 20 minutes. Samples (50 mL) were taken at the surface of the aqueous phase, and the solvent phase was separated using a centrifuge. The experiments were repeated three times, and the averaged results are presented. As can be seen from Fig. 5, flotation with CGAs increased the solvent recovery. Zhang et al. (15) ex-

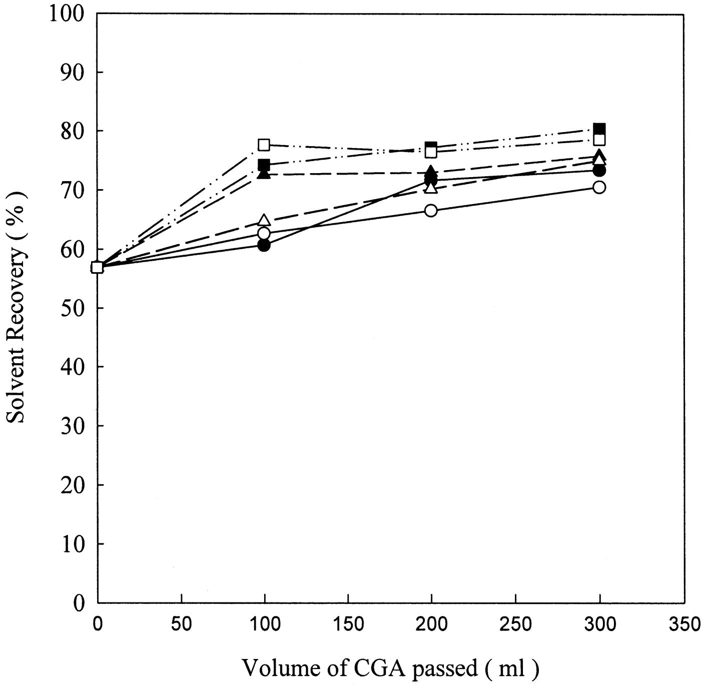

FIG. 5 Solvent recovery for CGA flotation with various surfactants: (●) SDBS (600 ppm: negative-ionic), (○) SDBS (1200 ppm), (▲) HTAB (600 ppm: positive-ionic), (△) HTAB (1200 ppm), (■) Brij 35 (600 ppm: nonionic), (□) Brij 35 (1200 ppm).

plained the dispersed solvent recovery with CGA flotation by coulombic attraction between the collectors (CGAs) and the colligends (CLAs). The continuous phase of CLA contained anionic surfactants (SDBS). The CGA made from a cationic type worked more effectively than the CGA made from anionic type. In this study, CGA from Brij 35 removed solvents most efficiently. As was shown by Chaphalkar (16), CGA generated from nonionic surfactants had a smaller diameter as compared to CGA from ionic surfactants, and the increase in surfactant concentration also reduced the mean diameter of the CGA. We can give the outline of the CLA recovery with CGA flotation by stating that the surface areas provided by CGAs played an important part in addition to the surface charges of both CGA and CLA. In increasing the amount of CGA dispersion, the surface areas that CLAs could attach to were also increased, so that the solvent recovery increased. Although CGA flotation enhances the recovery of solvents in an aqueous solution, more efficient techniques for recovering residual solvents from a pregnant solution have to be considered.

## Mass Transfer in PDSE

Figure 6 shows the effects of contact time, and then compares the extraction efficiency with and without flotation using CGAs made from Brij 35. The con-

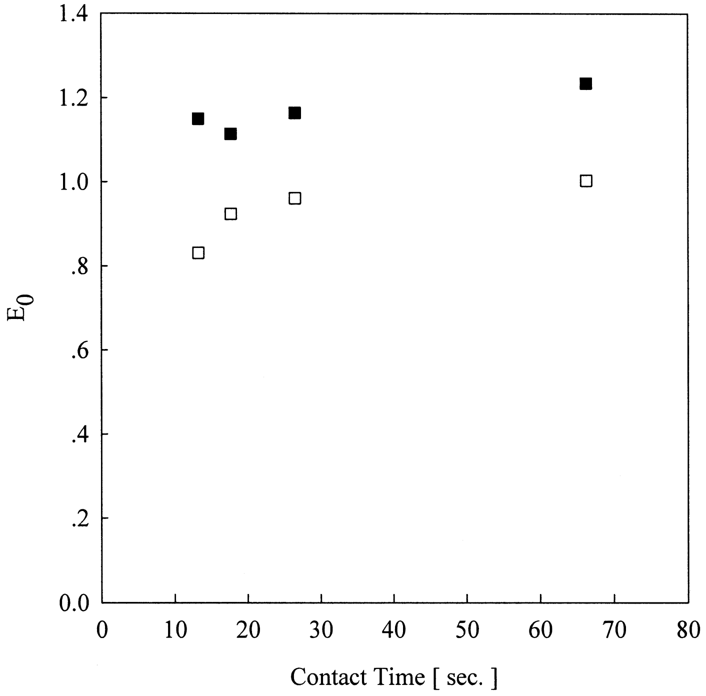

FIG. 6 Contact time effect on the extraction efficiency: (□) without CGA flotation, (■) with CGA flotation.

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tact time of CLAs with pregnant solution was calculated from the rise velocity of the CLAs/CGA complex. The rise velocity of a single CLA is negligible as compared to that of the CLAs/CGA complex (13). The diameter of CLA and CGA were assumed to be 10 μm and 100 μm, respectively. The pregnant solution volume was varied within 500 to 2500 mL, and the volume of CLAs used was constant. In all cases the concentration of initial pregnant solution was 1 ppm. The filled symbols indicate cases of PDSE/CGA flotation. Extraction efficiency was increased with a CGA flotation. Though water is the continuous phase when CLAs are added to the water, practically it does not immediately break up into individual drops. Flotation with CGAs also disperses CLAs well into the pregnant solution, thereby increasing the surface areas that can be available for mass transfer. Also, the number of CLAs that leave the pregnant solution also increases, with the overall process removal further increasing.

The initial solute concentration effects on the process are presented in Fig. 7. The feed solution was 2500 mL, and CLAs with a PVR of 19 were used. The experimental results show that the initial solute concentration does not affect the extraction efficiency. As was shown in Fig. 6, CGA flotation enhanced the extraction efficiency. Values of $E_0$ larger than 1 were obtained with PDSE/CGA flotation, as shown in Figs. 6 and 7. In conventional solvent ex-

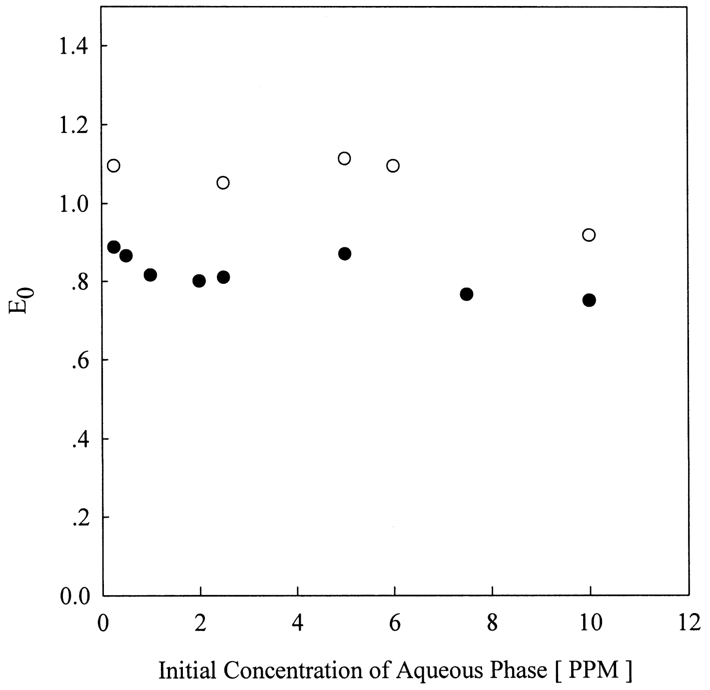

FIG. 7 Initial solute concentration effect on the extraction efficiency: (●) without CGA flotation, (○) with CGA flotation.

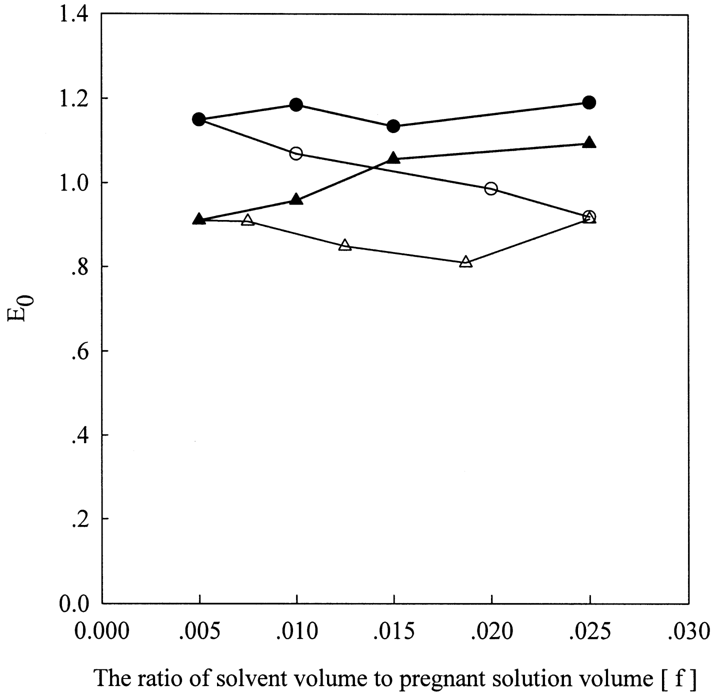

FIG. 8 Extraction efficiency according to the method by which CLAs were supplied: (△) without CGA flotation (continuous CLA feed), (○) with CGA flotation, ▲ without CGA flotation (discontinuous CLA feed), (●) with CGA flotation.

traction the mass transfer from the pregnant solution to solvent continues until equilibrium is established. However, in PDSE the mass transfer occurs between CLA and only a part of pregnant solution volume (2). Therefore, flotation of CGAs increases the solvent's recovery and also aids CLAs to disperse in the pregnant solution. If CLAs are well dispersed, then there are an enormous number of CLAs, all following one another, with each effectively removing the solute.

Figure 8 shows the extraction efficiency according to the method of CLA supplied to the pregnant solution. The ratio of solvent volume to pregnant solution volume was defined as $f$. A comparison was made between the case where the extraction solvent was used in one large volume and the case where the solvent was used in several divided volumes. In addition, the amount of CLAs being fed with a constant pregnant solution volume was changed. The pregnant solution was 2500 mL, and originally contained 1 ppm of Solvent Yellow 1. The open symbols and filled symbols represent the experimental data, followed by continuous and discontinuous CLA supply to the column, respectively. When CLAs were supplied discontinuously to the column, the same volume of CLAs were then further divided into 12.5 mL, and each volume of CLAs was then supplied to the column after a settling time of 10 minutes. An increase of CLA in quantity with a discontinuous supply makes PDSE more efficient. A divided supply of CLAs makes all CLAs following one another possible. It is similar to a washing process. It is more efficient to wash a few times with the liquid divided into small volumes, than only once with the full volume of liquid. In addition to the solvent's recovery, the method of solvent supply also has an important effect upon process efficiency. A divided supply of CLA is easily applicable to the PDSE process compared with conventional mixer-settler processes.

## CONCLUSION

Extraction rates with CLA were enhanced with the result of increased surface area. An extraction efficiency above 0.7 was attained with short hold-up times. The flotation of CLAs with CGAs also gives higher extraction efficiency than a conventional mixer/settler extraction process and further increases the solvent's recovery. PDSE is a rate-controlled process that is influenced by the solvent's recovery. The recovery of CLA depends not only on the surface charges of both CGA and CLA, but also on the surface areas provided by CGA. The PDSE process can achieve very quick extraction using simple equipment without intensive mixing. PDSE looks promising as a means for extending the conventional solvent extraction processes.

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