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INFLUENCE OF CONTINUOUS AQUEOUS PHASE ON THE PREPARATION AND STABILITY OF COLLOIDAL LIQUID APHRONS

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ABSTRACT

Colloidal Liquid Aphrons (CLAs) were prepared from various solvents such as nonpolar hydrocarbons, alcohols, and amines. The influence of surfactant type and concentration on CLA preparation were studied and maximum phase volume ratio (PVR: volume ratio of the dispersed solvent phase to the water phase) was also investigated. The CLA preparation from nonpolar hydrocarbons or alcohols was possible with a high PVR regardless of surfactant type. However, stable CLA preparation was possible using cationic or nonionic water-soluble surfactant in case of a basic solvent. Since solvent recovery is as important as selection of solvent in CLA-based process design, the stability of CLAs in a

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given dispersion was quantified from released solvent volume when CLAs broke up. The effect of surfactant types, concentrations, and solvent types were investigated under various continuous phase conditions. Equation of pseudo-first-order-reaction kinetics was found well to fit the data only when the CLA was made from kerosene or ionic strength of continuous phase was very low.

Key Words: Colloidal liquid aphron; Stability; Solvent; Surfactant

INTRODUCTION

Colloidal liquid aphrons (CLAs) consist of a micron-sized solvent droplet surrounded by a thin, aqueous, soapy-film and are stabilized by nonionic or ionic surfactants which are chosen on the basis of their solubility in the solvent and soapy-film (1). Since CLAs have been shown to possess many useful properties, including large interfacial area and high stability, separation processes have been recognized as potential application areas of aphrons (2). The CLAs have been successfully applied to the extraction of antibiotics, organic pollutants such as organic dyes, immobilization of enzymes, and toxicity reductions in the downstream separation of fermentation products biotechnology (3–7). Colloidal gas aphrons (CGAs) are analogous to CLAs except that they contain gas phase inside the aqueous soapy film. Similarly, CGAs have been investigated for use in flotation processes for the removal of organic pollutants and clarification of biological media (8–11). Especially, predispersed solvent extraction (PDSE) process is an innovative technology that recent advances have improved upon the conventional solvent extraction process (12). In this process, the organic phase is processed into polyaphrons then predispersed solvents are recovered by CGA flotation. The CLAs will remain as discrete entities over a long period and do not undergo coalescence as does a conventional emulsion. It is important to note that these CLA-based technologies are at the expense of leaving residual solvent and surfactant in the pregnant phase containing substances to remove. However, since the ratio of extracting solvent to pregnant solution can be very low in PDSE, the amount of residual surfactant released from CLA can be negligible. Thereby the solvent recovery is important and rate-controlling step in the PDSE process. While flotation with CGA proved to be effective in CLA recovery, better recovery techniques for dispersed solvent in the aqueous phase would be needed over CGA flotation. Residual solvent removal becomes a necessity for the successful application of these technologies.

A basic knowledge about stability of aphrons would be very valuable for the optimization of aphron-based processes and provide useful information for the design of process equipment. For CGAs, the effect of surfactant type, concentration and pH of continuous phase and additives such as enzymes, polymers, and salts on the CGA half-life was studied (13,14). Matsushita et al. (13) and Sebba (1) also studied the influence of the above factors on the stability of CLAs and provided useful information on the preparation of polyaphrons. However, previous reports on the stability of CLAs have focused on the stability of isolated CLAs for a limited number of organic solvents. Recently, Lye and Stuckey studied the stability of CLAs when dispersed in various continuous phases (15). Scarpello and Stuckey investigated stability of CLAs that were prepared using an Aliquat 336/*n*-octanol/Softanol 120 solvent phase and proposed a semi-empirical design equation for prediction of CLA half-life (16).

In this study, CLAs were prepared with various solvents, surfactants, and phase volume ratio (PVRs). The stability measurements for CLA were presented in terms of solvent volume release from aphrons and half-life. The effect of surfactant types, concentrations, and solvent types on the stability of the CLAs was investigated. In addition, the influence of continuous aqueous phase property on stability of dispersed CLA was discussed.

EXPERIMENTAL

Materials

A number of solvents commonly used in solvent extraction in biotechnology were tested to form CLAs. The solvents used in this work were 1-hexanol (>98%, Aldrich, St. Louis, MO), 1-octanol (>%99, Sigma, Milwaukee, WI), 1-decanol (>99%, Junsei, Japan), *n*-hexane (99%, Sigma, Milwaukee, WI), *n*-octane (99%, Aldrich, St. Louis, MO), iso-octane (99%, Aldrich, St. Louis, MO), kerosene (Aldrich, Milwaukee, WI), trioctylamine (TOA, Sigma, Germany), tripropylamine (TPA, Aldrich, Milwaukee, WI) and Aliquat 336 (Aldrich, Milwaukee, WI).

Tergitol 15-S-3 (Aldrich, St. Louis, MO) was used as oil-soluble surfactant. The water-soluble surfactants used were sodium dodecylbenzene sulfonate (SDBS, Aldrich, Milwaukee, WI), hexadecyl trimethyl ammonium bromide (HTAB, Sigma, Denmark) and Brij35 (Sigma, USA).

The CLA was prepared by following steps. A stable-foam was obtained by mixing of an aqueous phase containing the desired concentration of water-soluble surfactants. To the foaming solution, the organic solvent containing 0.1% (w/v) Tergitol 15-S-3 was gradually added. The CLAs were prepared from various solvents and surfactants. Correctly formed CLA had a creamy-white appearance and showed no signs of phase separation over a period of months. To characterize the CLA formed, the volume ratio of the dispersed organic phase to the continuous phase was defined as PVR.

$$\mathrm{PVR} = \frac{V_\mathrm{o}}{V_\mathrm{w}} = \frac{\text{Dispersed Organic Solvent Phase Volume}}{\text{Continuous Aqueous Phase Volume}} \tag{1}$$

Stability Measurement

Prepared CLAs were dispersed in standard solution of pH 4 and pH 9 (Junsei) to investigate the effect of continuous phase pH on stability. Similarly, ionic strength of continuous phase was adjusted using NaOH (Aldrich), KOH (Aldrich), NaCl (Aldrich) and KCl (Junsei). Each adjustor of ionic strength was dissolved in deionized water at 25°C with the desired concentration.

To determine the stability, the CLAs were dispersed in a conditioned continuous aqueous phase. Upon the cessation of mixing, buoyancy forces will cause the CLAs to rise to the surface and then coalesce. Creaming is defined as a process where flocculated CLAs rise to the surface by a difference in density of the two phases. Creaming of the dispersed CLAs to the surface is prevented by a continuous gentle mixing of dispersion. In a typical experiment, 5 mL of a CLA phase was dispersed in 50 mL of the desired continuous phase. When CLAs were dispersed in a water phase that had different conditions from aqueous soapy shell, a solvent layer that was released from CLAs break-up was developed on the surface of the water phase. The released solvent volume from CLA was used to obtain a measure of stability. Three samples were taken per experiment with the same condition and the mean value was used.

RESULTS AND DISCUSSION

Preparation of Colloidal Liquid Aphrons from Different Solvent and Surfactants

The CLAs were prepared from various solvents and surfactants. The CLAs were made using surfactant concentration of 4 g/L in the aqueous phase, and 0.1% (v/v) of Tergitol 15-S-3 in the organic solvent phase. The results are presented in Table 1. The maximum obtainable PVR obtained was varied according to the solubility of solvent in water and the charge of the surfactant. Very stable CLAs were produced with nonpolar solvents regardless of the charge of water-soluble surfactants. In the case where anionic surfactant, SDBS, was used for aqueous soapy shell, the more stable CLAs that were made from alcohols

Table 1. Preparation of CLA from Different Solvents and Surfactants

Solvent	Solubility in Water (wt%)[a]	SDBS (4 g/L) PVR_{max} Obtained	HTAB (4 g/L) PVR_{max} Obtained	Brij35 (4 g/L) PVR_{max} Obtained
n-Hexane	0.00123	>32	>32	>32
n-Octane	6.6×10^{-7}	>32	>32	>32
Iso-Octane	0.00024	>32	>32	>32
Kerosene	—	>32	>32	>32
1-Hexanol	0.706	10	7	4
1-Octanol	0.0538	13	10	9
1-Decanol	—	14	9	11
TOA		—	>32	>32
TPA		—	27	>32
Alliquat 336/1-octanol mixture[b]		—	8	7

Organic soluble surfactant: Tegitol 15-S-3 (0.1% w/v).

[a] Values taken from Ref. (17).

[b] Concentration: 0.25 mol/kg.

were obtained with higher PVRs compared with CLAs containing cationic (HTAB) or nonionic surfactant (Brij35). The maximum obtainable PVR did not exceed 15 when CLAs were made from alcohols. Though 1-octanol and 1-decanol are insoluble in water, HTAB and Brij 35 are soluble in alcohols. In addition, alcohols have polarities that cause an interaction with outer aqueous soapy shells. Accordingly, high PVR cannot be obtained with alcohols.

The CLAs were not formed with TOA or TPA at the time when a cationic surfactant, such as SDBS, was used as water-soluble surfactant because of the basicity of amine solvent that tend to draw electrons. However, CLAs could be made with TOA or TPA using foamed water that is made of HTAB or Brij35. Aliquat 336 was tested with a mixture of 1-octanol due to relatively high viscosity. Therefore, these results show that CLA preparation can be affected not only on the properties of the solvent but also on aqueous soapy shell.

The influence of water-soluble surfactant concentration was investigated (Table 2). The water-soluble surfactant does not have an influence on the preparation of CLA that was made from kerosene. The higher PVR was obtained with 1-octanol that had lower solubility in water than 1-hexanol. When CLAs are generated using water-soluble surfactant of 4 g/L through 8 g/L, the concentration of the surfactant has no significant effect on the PVR_{max}. The addition of 1–4 g/L surfactant solution results in increased PVR. It was found that the maximum PVR could be changed with the different concentration of water-soluble surfactant in CLA preparation.

Table 2. Effect of Water-Soluble Surfactant Concentration on PVR_{max}

Concentration of Surfactant (g/L)	Kerosene			1-Hexanol			1-Octanol		
	SDBS	HTAB	Brij35	SDBS	HTAB	Brij35	SDBS	HTAB	Brij35
1	>32	>32	>32	6.5	3	3	11	4.5	6.5
2	>32	>32	>32	10	4	3	16	5	8
4	>32	>32	>32	10	7	4	16	10	9
6	>32	>32	>32	9.5	6	3.5	16	12	9.5
8	>32	>32	>32	9	6	3.5	15	13	9.5

Effect of Organic Solvent and Continuous Water Phase on the Stability of CLA

Isolated CLAs are usually characterized by PVR. For the value of PVR, prepared aphrons would have different packing and properties in polyaphron phases. In order to determine the effect of PVR on the stability, CLAs were manufactured with kerosene and these were dispersed in a standard solution of pH 4. During experiments, it was observed that a clear solvent layer developed on the surface of the dispersion phase, and the turbidity of the dispersion phase decreased. The volume of the solvent layer was measured and shown in Fig. 1. A plot of $\ln(V/V_0)$ against time yields a straight line as shown in Fig. 1. The kinetics of coalescence process of CLAs were proposed to follow pseudo-first-order-reaction kinetics, namely,

$$\frac{V(t)}{V_0} = \exp(-kt) \tag{2}$$

where $V(t)$ is the remained volume of CLAs, k is a first order rate constant, and t is the time elapsed (15).

The mean CLA half-life exhibited its maximum at PVR of 19. The stability of CLA was increased below the PVR of 19. Above the PVR of 19, isolated CLAs maintain stability, but CLAs when disperse in the phase that has a different condition from soapy shell rapidly lose equilibrium. The aqueous soapy shell of CLA becomes thin and the CLA is destabilized as the PVR of CLA rises.

The TOA/1-octanol mixtures were chosen as solvent in order to investigate the stability of CLAs made from different solvents. These CLAs can be used in the biological product separation (7). Figure 2 shows that the stability of CLA decreases with increasing TOA concentration in the mixture. The most stable CLA were obtained with CLA formulated with 1-octanol. Even though CLAs

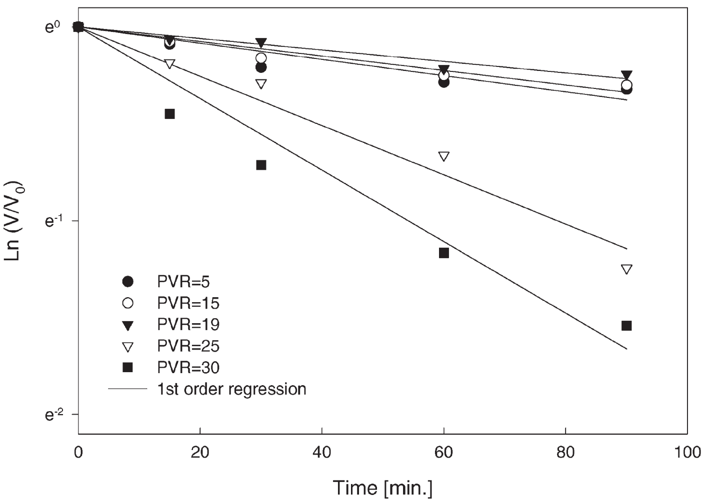

Figure 1. Plot of pseudo-first-order-reaction kinetics for CLAs break-up with time (Kerosene CLA; water soluble surfactant: SDBS 4 g/L; continuous phase pH = 4).

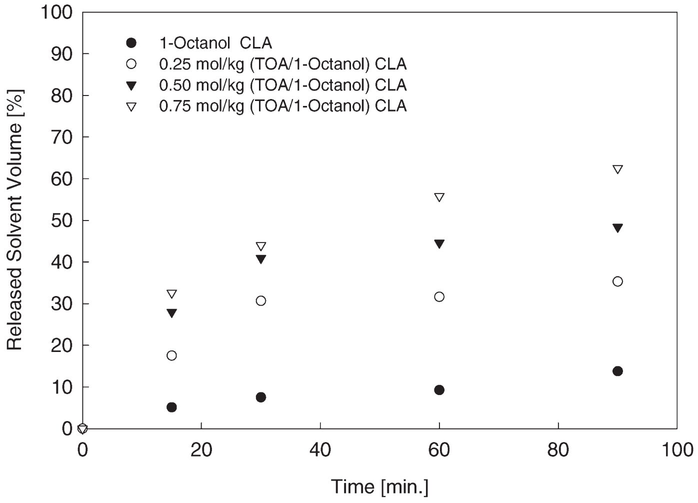

Figure 2. Effect of TOA concentration on the stability of 1-octanol CLA (PVR = 5, water soluble surfactant: SDBS 4 g/L; continuous phase pH = 9).

could not be formed alone with TOA when SDBS was used as water-soluble surfactant, stable CLAs could be formed with mixture of TOA/1-octanol.

It was possible to characterize stability by a pseudo-first-order-reaction kinetics in case of kerosene CLA and 1-octanol CLA. However, it was impossible in the case of CLA prepared with mixture of TOA/1-octanol. As the concentration of TOA increased, the stability of the CLAs decreased. It is due to the basicity of the solvent mixture. The organic solvents were surrounded with negative charged surfactant, the CLAs made from the basic solvent were destabilized. Both surfactant and solvent tend to obtain electrons. The stability of the CLAs depends on the PVR, in addition, is influenced by the composition of solvent phase of aphrons.

The influence of pH on the stability is shown in Fig. 3. The CLAs were made using water-soluble surfactant concentration of 4 g/L in the aqueous phase. The more stable CLAs were obtained with SDBS than with HTAB. The CLAs with SDBS were destabilized by the excess hydrogen ions in the dispersed phase at low pH values. Excess hydrogen ions lead to protonation of the head-group of the SDBS located at the outer soapy-shell interface. This would reduce the energy barrier to droplet coalescence and the polarity of the surfactant monomers (15). At pH 9, CLAs were stabilized by the surface charge repulsion of the outer soapy-shell consisting of SDBS. The stability of the CLAs containing HTAB rapidly decreased according to the variation of pH in the continuous phase. Since HTAB is stable in acid solution, a bilayer of surfactant molecules in outer-soapy shell is destabilized. Therefore, CLAs containing HTAB are more stable at pH 4 than at

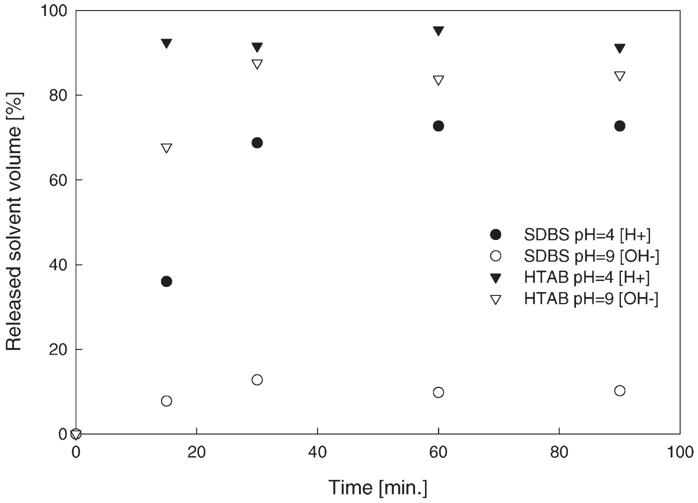

Figure 3. Effect of continuous water phase pH on stability of 1-Hexanol CLA (PVR = 5).

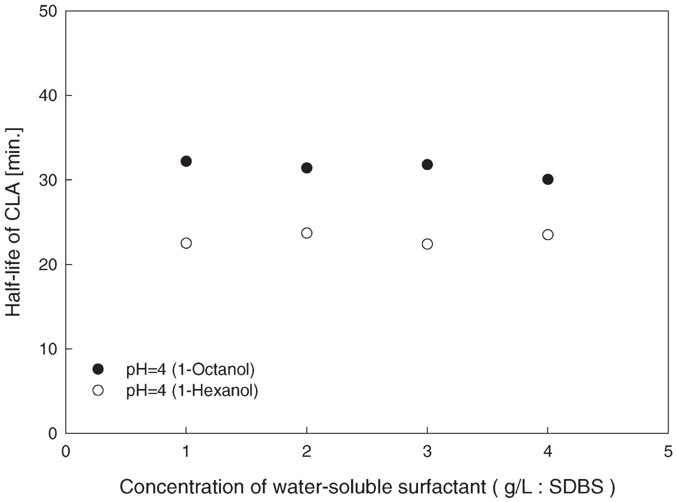

Figure 4. Effect of water-soluble surfactant concentration on half-life of 1-octanol and 1-hexanol CLAs (PVR = 5; continuous phase pH = 4).

pH 9. While CLA was stably dispersed in case of pH 7 and little solvent layer was observed on the surface of the dispersion phase. Upon the cessation of mixing, the CLAs rise to the surface and then coalesce. The volume of the reformed CLAs were larger than that of the CLAs prior to dispersion because the dispersed polyaphrons reform with an equilibrium PVR regardless of their initial PVR (15).

The effect of water-soluble surfactant concentration in the aqueous phase of CLA on half-life is shown in Fig. 4. The CLAs were made from different concentration of SDBS then dispersed in standard solution of pH 4. From Eq. (2), a first order half-life can be calculated from,

$$t_{1/2} = \frac{\ln 2}{k} \tag{3}$$

The half-life of the CLA does not change significantly over the course of the experiment. These results show that CLA preparation with low concentration of water-soluble surfactant is possible.

Effect of Ions Contained in the Continuous Phase

The effect of ionic strength in the continuous phase on the stability of CLA is shown in Fig. 5. The CLAs were immediately destroyed when CLAs were

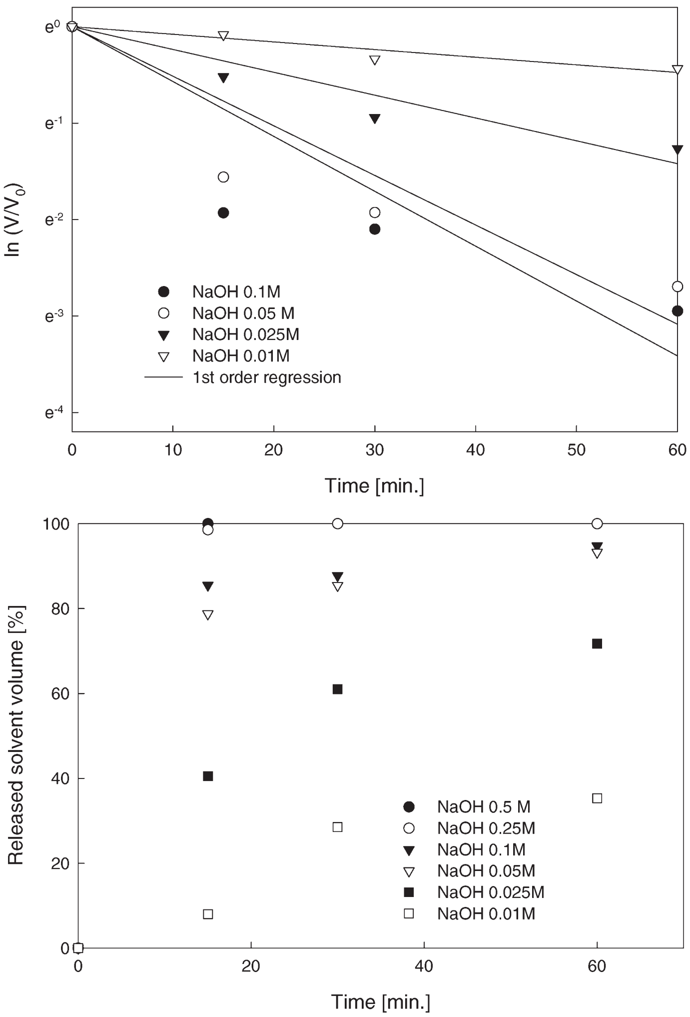

Figure 5. Plot of pseudo-first-order-reaction kinetics (top) and released solvent volume (bottom) with different ionic concentration (1-octanol CLA, PVR = 5, water-soluble surfactant: SDBS 4 g/L).

dispersed over 0.25 *M* NaOH solution. The CLAs containing SDBS become unstable with increasing NaOH concentration. Equation of pseudo-first-order-reaction kinetic was found to fit the data well only when the concentration of NaOH was below 0.025 *M*. In addition, Eq. (2) did not agree with the experimental data when the CLAs were instantly destabilized. For instance,

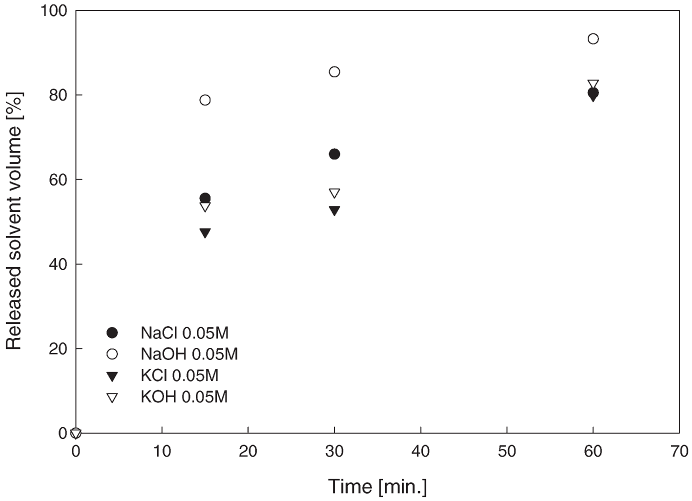

Figure 6. Effect of ionic strength on stability of 1-octanol CLA (PVR = 5, water-soluble surfactant: SDBS 4 g/L).

stabilities of 1-hexanol CLAs with HTAB in Fig. 3 do not agree with the pseudo-first-order-reaction kinetics, while those with SDBS fit well. Accordingly, CLAs are destabilized with different mechanisms according to the condition of the dispersed phase. At high concentration of NaOH, flocculation/coalescence of CLAs occur in addition to CLA break-up (16).

Figure 6 represents the effect of salt in the continuous phase on the stability of CLA. The salts used were NaCl, NaOH, KCl, and KOH. It was observed that relatively low stability of the CLAs dispersed in continuous phases contained sodium cation. In case of SDBS, sodium ions are counter-ion of surfactant with anionic hydrophilic head group that could combine more rapidly than other cation with surfactant head-group. This would reduce the stability of outer soapy shell.

CONCLUSION

Several solvents commonly used in biotechnology for the downstream extraction process were tested to form CLAs. The results show that CLA with nonpolar hydrocarbon solvent can be formulated with PVR over 32, while PVR_{max} are relatively low in case of the CLA prepared from alcohols. According to the change of solvents and surfactants used to prepare CLAs, obtainable PVR was varied. Amine-based CLAs can be produced with a very high PVR by mixing of amines with other solvents that reduce basicity. In addition, CLA comprised of an amine can be made with cationic or nonionic water-soluble surfactant. The stability of the CLAs was influenced by the PVR and nature of the continuous phase in which they were dispersed. The state of dispersed phase has more serious influence on the stability of CLA than that of the organic solvent used for preparation of the CLAs. Although pseudo-first-order kinetics model is useful for a measure of CLA stability, this model cannot be applied when destabilization of CLAs occurs immediately.

NOTATION

k	first order rate constant
t	time
$t_{1/2}$	half-life
V_o	volume of organic solvent in CLA preparation
$V(t)$	remained volume of CLAs
V_w	volume of continuous phase in CLA preparation
V_0	initial volume of polyaphrons dispersed in aqueous phase

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REFERENCES

1. Sebba, F. *Foams and Biliquid Foams: Aphrons*; Wiley: New York, 1987.
2. Sebba, F. Predispersed Solvent Extraction. Sep. Sci. Technol. **1985**, *20*, 331–334.
3. Lye, G.J.; Stuckey, D.C. In *Separations for Biotechnology III*; Pyle, D.L., Ed.; SCI Publishing: London, UK, 1994; 280.
4. Zhang, C.; Valsaraj, K.T.; Constant, W.D.; Roy, D. Studies in Solvent Extraction Using Polyaphrons. I. Size Distribution, Stability, and Flotation of Polyaphrons. Sep. Sci. Technol. **1996**, *31*, 1463–1482.
5. Lee, D.W.; Hong, W.H.; Hwang, K.Y. Removal of Organic Dye from Water Using Predispersed Solvent Extraction. Sep. Sci. Technol. **2000**, *35*, 1951–11962.
6. Lye, G.J.; Pavlou, O.P.; Rosjidi, M.; Stuckey, D.C. Immobilization of *Candida cylindracea* Lipase on Colloidal Liquid Aphrons (CLAs) and

Development of a Continuous CLA-Membrane Reactor. Biotechnol. Bioeng. **1996**, *51* (1), 69–73.

7. Hong, Y.K.; Lee, D.W.; Lee, P.C.; Hong, W.H.; Chang, H.N. Extraction of Lactic Acid With Colloidal Liquid Aphrons and Comparison of Their Toxicities With Solvents Without Surfactant on the Viability of *Lactobacillus rhamnosus*. Biotechnol. Lett. **2001**, *23*, 983–988.
8. Roy, D.; Valsaraj, K.T.; Kottai, S.A. Separation of Organic Dyes from Wastewater by Using Colloidal Gas Aphrons. Sep. Sci. Technol. **1992**, *27*, 573–588.
9. Caballero, M.; Cela, R.; Perez-Bustamente, J.A. Studies on the Use of Colloidal Gas Aphrons in Coflotation and Solvent Sublation Processes. A Comparison with the Conventional Techniques. Sep. Sci. Technol. **1989**, *24*, 629–640.
10. Save, S.V.; Pangarkar, V.G. A Model for Harvesting of Microorganisms Using Colloidal Gas Aphrons. J. Chem. Technol. Biotechnol. **1994**, *61*, 367–373.
11. Save, S.V.; Pangarkar, V.G. Harvesting of *Saccharomyces cerevisiae* Using Colloidal Gas Aphrons. J. Chem. Technol. Biotechnol. **1995**, *62*, 192–199.
12. Michelsen, D.L.; Ruettimann, K.W.; Hunter, K.R.; Sebba, F. Feasibility Study on Use of Predispersed Solvent Extraction/Flotation Techniques for Removal of Organics from Wastewaters. Chem. Eng. Commun. **1986**, *48*, 155–163.
13. Matusushita, K.; Mollah, A.H.; Stuckey, D.C.; del Cerro, C.; Bailey, A.I. Predispersed Solvent Extraction of Dilute Products Using Colloidal Gas Aphrons and Colloidal Liquid Aphrons: Aphron Preparation, Stability and Size. Colloids Surf. A **1992**, *69*, 65–72.
14. Save, S.V.; Pangarkar, V.G. Characterization of Colloidal Gas Aphrons. Chem. Eng. Commun. **1994**, *127*, 35–54.
15. Lye, G.J.; Stuckey, D.C. Structure and Stability of Colloidal Liquid Aphrons. Colloids Surf. A **1998**, *131*, 119–136.
16. Scarpello, J.T.; Stuckey, D.C. The Influence of System Parameters on the Stability of Colloidal Liquid Aphrons. J. Chem. Technol. Biotechnol. **1999**, *74*, 409–416.
17. Riddick, J.A.; Bunger, W.B.; Sakano, T.K., (Eds.) *Organic Solvnets: Physical Properties and Method of Purification*; Wiley: New York, 1986; Vol. 2.

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