CHEMISTRY LETTERS, pp. 1189-1190, 1994.

A Novel Homogeneous Liquid-liquid Extraction Based on Three-phase Formation with Perfluorosurfactant and Amine Compounds

Shukuro IGARASHI,*† Tohru KYUWA, Masaya MATSUURA, and Takao YOTSUYANAGI
Department of Molecular Chemistry and Engineering, Faculty of Engineering,
Tohoku University, Sendai, Miyagi 980

A new type of three-phase separation phenomenon was found by the charge neutralization of perfluorooctanate ion {PFOA$^-$, $CF_3(CF_2)_6$-COO^-} with amylammonium ion (R-N^+H_3). For example, a three-phase system was formed at pH=6.8 and $[PFOA]_T/[amine]_T$=0.5. The partition behaviors of solutes such as water-soluble porphyrin and compounds in vivo into each liquid phase were examined.

The charge neutralization of perfluorooctanate ion, induced some new types of homogeneous liquid-liquid extractions by phase separation. For example, aqueous PFOA$^-$ solution of a water-miscible organic solvent such as acetone, 1,4-dioxane, and tetrahydrofuran provides a pH-reversible phase separation system around pH=0.6, due to the pKa value of 1.0 (at I=0.1, 20 ℃) for HPFOA. It can be successfully applied to the ultra-high preconcentration of metal chelates and porphyrin compounds. A 10^4 hold concentration was achieved within 20 min by this method.1) In the case using quaternary ammonium ion (Q^+), we have found that the volume of the separated second phase remarkably changed depending not only upon the kinds of Q^+ ion and the amount of the PFOA$^-$-Q^+ ion pair, but also on temperature. Based on these findings, a new concentration method by the combined use of the phase separation and thermal transformation has been developed.2) Recently, we have studied the use of protonated amine compounds (R-N^+H_3) as a counter ion in order to induce pH-reversible phase separation around the neutral pH region. On the course of these studies, it was found that two kinds of water-immiscible liquid phases (second and third phases) were immediately formed from the homogeneous aqueous solution. Partition studies of solutes to each phase, revealed that this system can be used as a new three-phase homogeneous liquid-liquid extraction method for water soluble porphyrins and biochemically important compounds.

Standard procedure: A 5 cm^3 sample solution containing L-ascorbic acid, hemoglobin, and $\alpha, \beta, \gamma, \delta$-tetrakis(4-trimethylaminophenyl)porphine(TTMAPP), 5 cm^3 of 0.1 mol dm^{-3} PFOA aqueous solution prepared as previously described, and 5 cm^3 of the pH buffer solution (a mixture of 0.8 mol dm^{-3} boric acid, 0.2 mol dm^{-3} citric acid, and 0.35 mol dm^{-3} sodium phosphate solutions were added in order to adjust the pH to 6.8), are placed in a 30 cm^3 cylindrical glass vial fitted with a plastic cap. Five cm^3 of a 0.2 mol dm^{-3} amylamine aqueous solution was then added to the mixture. After gentle shaking, the mixture is allowed to stand for 30 min. The volume of the sedimented phase (second and third phases) is determined using a 0.1 cm^3 micro-syringe.

---

† Present address: Department of Materials Science, Faculty of Engineering,
Ibaraki University, 4-12-1 Nakanarusawa, Hitachi, Ibaraki 316.

Further, the extraction behaviors of the solute among the phases were evaluated spectrophotometrically.

The phase separation behaviors using forty kinds of protonated amine compounds were examined. The amylamine was chosen because of its clear-cut and smooth phase separation. The relationships among pH of aqueous phase after three-phase separation, the total concentration ratio of PFOA and amylamine, and the volume of each phase are shown in Fig.1. The region described by the slant line in Fig.1 indicates the zone of pH and the concentration ratio of PFOA and amylamine for the formation of the three-phase system. In the condition leading to almost the same volume of the second phase and the third phase (refer to the conditions shown in the standard procedure), the values of specific gravity of each phase were 1.00 in the aqueous phase, 1.22 in the second phase, and 1.41 in the third phase. Water content, measured by the Karl-Fischer titration (Mitsubishi Kasei Co., Type KF-01) was 44.0 wt% in the second phase and 13.1 wt% in the third phase. These results indicate that not only the charge neutralization of PFOA$^-$ with R-N$^+$H$_3$ but also the solvation of water and/or amine to the PFOA$^-$-Q$^+$ ion pair seem to play an important role in this phase separation.

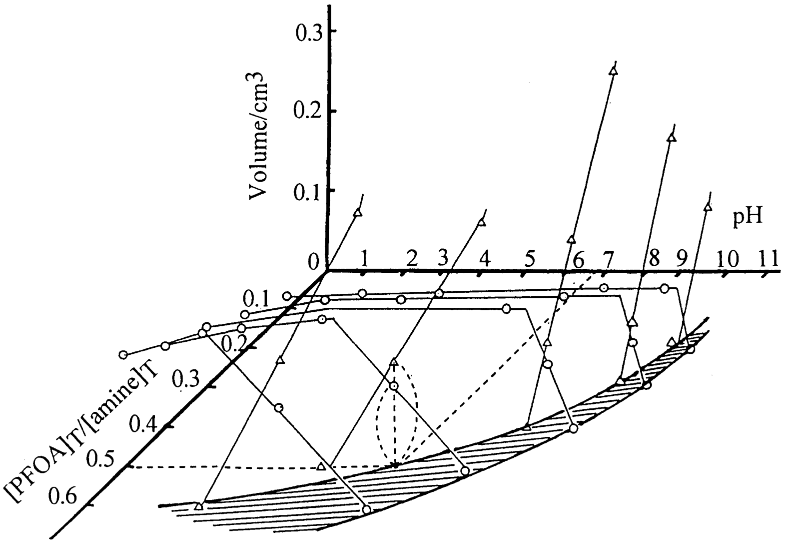

Fig.1. The relationships of pH, the total concentration ratio of PFOA and n-amylamine, and the volume of each sedimended phase.
—○—:data for the third phase, —△—:data for the second phase
$[PFOA]_T=2.4\times10^{-2}$ mol dm^{-3}, at 20 ℃.
Dashed line : pH=6.8, $[PFOA]_T/[amine]_T=0.5$,
volume ; 0.11 cm^3 (—○—), 0.14 cm^3 (—△—).

The partition behavior of solutes in each phase was also studied. Vitamin B$_{12}$ was distributed between the aqueous phase and the second phase. Crystal violet and α, β, γ, δ-tetrakis(1-methylpyridinium-4-yl)porphine were distributed in the second phase and the third phase, respectively. But, neither α, β, γ, δ-tetrakis(4-sulfophenyl)porphine nor L-ascorbic acid were extracted into the water-immisible phase. On the other hand, since TTMAPP and hemoglobin from calf blood were quantitatively distributed in the second phase and the third phase, respectively, the three components of L-ascorbic acid, hemoglobin, and TTMAPP were able to be separated into the aqueous, second and third phases, respectively using only a one-step process with the addition of amylamine to the PFOA solution.

In conclusion, this system provides a new homogeneous liquid-liquid extraction method, which will be useful for the separation of components in vivo, because the large water content of the three phases is expected to prevent their denaturing.

References

1) S.Igarashi and T.Yotsuyanagi, *Mikrochim. Acta*, **106**, 37 (1992).
2) S.Igarashi and T.Yotsuyanagi, Proceedings of the international solvent extraction conference, (ISEC'90), Elsevier, 1725 (1992).

(Received April 8, 1994)