Removal of Volatile Organic Compounds from Contaminated Surfactant Solution using Co-Current Vacuum Stripping

Pornchai Suriya-Amrit, Suratsawadee Kungsanant, Boonyarach Kitiyanan

Abstract—There has been a growing interest in utilizing surfactants to separate the hydrophobic volatile organic compounds (HVOCs) from aqueous solution. One attractive process is cloud point extraction (CPE), which utilizes nonionic surfactants as a separating agent. Since the surfactant cost is a key determination, it is important that the surfactants are reused. This work aims to study the performance of the co-current vacuum stripping using a packed column for HVOCs removal from contaminated surfactant solution. The volatility and the solubility of HVOCs in surfactant system are determined in terms of an apparent Henry's law constant and a solubilization constant, respectively. Moreover, the HVOCs removal efficiency column is assessed in terms of percentage of HVOCs removal and the overall liquid phase mass transfer coefficient. The results show that, as K_{ow} increase, K_s also increase whereas H_{app} of the HVOCs are significantly decreased. The HVOCs removal for all solute were around 90%.

Keywords—Apparent Henry's law constant, Branched secondary alcohol ethoxylates, Vacuum Stripping

I. INTRODUCTION

THE emission of hydrophobic volatile organic compounds (HVOCs) from the petrochemical industry causes several environmental problems and health concerns. Since the HVOCs are suspected to be carcinogenic and mutagenic substances, even at very low concentration, a HVOCs treatment process is required to separate the HVOCs from the contaminated solution before discharging to a public water reservoir. Surfactant-based separation techniques have been proposed to economically eliminate these HVOCs since they are more effective in terms of both separation efficiency and energy than conventional techniques. Moreover, surfactants are generally more environmentally friendly than other conventional solvents utilized in liquid–liquid extraction. However, it could be seen that using surfactant to remove HVOCs from wastewater could produce high concentration of surfactant containing HVOCs. The method that uses to remove HVOCs from wastewater by using surfactant is cloud point extraction process (CPE) [1]-[4]. In some research found that more than 90 percent surfactant was in coacervate phase of the cloud point extraction techniques. Therefore, it is necessary to have another step to support in order to reuse the surfactant, which will make the process more economic attractive.

S. Pornchai, is with "The Petroleum and Petrochemical College, Chulalongkorn University", Pathumwan, Bangkok 10330, Thailand (e-mail: poch_sp88@hotmail.com),

K. Suratsawadee is with "Department of Chemical Engineering, Faculty of Engineering, Prince of Songkhla University"

K. Boonyarach is with "Center for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University", Bangkok 10330, Thailand
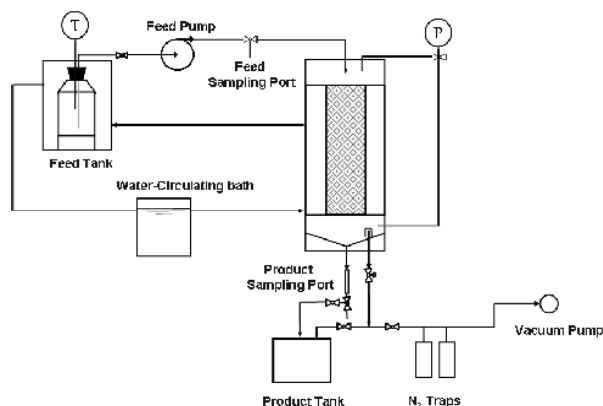
Generally, the separation technique of HVOCs from the aqueous solution could be done by many methods, for example, air stripping chamber [5]-[7], steam stripping chamber [8]-[10], and spraying [11]-[12]. These methods are highly effective and can be widely applied, for example, air stripping chamber is used to treat drinking water, wastewater and groundwater. Most of the chambers, the vapor flow in opposite direction of the liquid resulting in high efficient of convection. In the part of steam stripping chamber, it is often used by applying the waste steam from other production processes, which help to reduce production cost. In addition, this technique could be operated in small scale comparing to the air stripping chamber. The spraying is normally used to remove the HVOCs from water, since it contains high surface area and transfer rate. However, if all of the above mention methods are applied to remove the HVOCs from surfactant solution. The counter current flow of vapor and liquid inside the chamber can cause excessive foaming leading to overflow and failure in most applications. Moreover, as the surfactant is water soluble compound, using steam may require the subsequence separation of surfactant from contaminated water.

Vacuum stripping has been widely used for HVOC removal from contaminated water in chemical and petrochemical industries, such as the removal of butane [13] and refrigerants [11] from water in a desalting process [14], carbon dioxide and oxygen from water, HVOCs from water streams, and emulsified organic liquid from water. Generally, all of these processes are operated in counter-current mode because it provides a high mass transfer rate. In contrast, the mass transfer in a co-current process can be limited as a maximum of one transfer unit is possible before equilibrium is reached between the vapor and liquid phases. It was reported that the mass transfer coefficient of the counter-current flow in a packed tower was threefold higher than that of the co-current flow for carbon dioxide absorption into water [15]; in general, co-current separation efficiency is lower than that of a counter-current separation, making the latter process much less popular. However, flooding and limited liquid loading were found to be limitations of the counter-current operation, especially in a process containing surfactants [16]-[20]; thus, the co-current operation is suggested for use in recycling a contaminated surfactant solution.

Therefore, this research is aims to develop the packed column applying for separation of organic compounds from contaminated surfactant solution. The study will focus on the isolation of HVOCs in the group of aromatic and chlorinated hydrocarbons from the alcohol ethoxylates nonionic surfactant since the future trends in surfactant the AEs will be used more, due to its environmental friendly properties.

Fig. 1 Schematic of the vacuum stripping unit

II. EXPERIMENTAL

A. Materials

A Branched Secondary Alcohol Ethoxylates 2-(2,6,8-trimethylnonan-4-yloxy)ethanol, (Tergitol TMN-6) was use as the nonionic surfactant. Reagents grade benzene, toluene, and ethyl benzene used for this study were obtained from Sigma-Aldrich (Singapore).

B. Analytical Technique

The concentration of surfactant was measured by using a Total Organic Compounds (TOC 5000A, Shimadzu). The HVOC concentration was measured by a gas chromatograph with a flame ionization detector (Agilent technology, USA). Due to high volatility of the HVOC, a static headspace auto-sampler was used as sampler injection technique with no intervention of heavy nonionic surfactant molecule. A gas-tight syringe was used to collect product sampler solution from the vials in batch experiment and from the vacuum stripping unit in continuous operation. Then, 100 µl, of liquid sampler was transferred into the 20-ml glass vials with Teflon-coated septa and aluminum holed caps. The conditions of gas chromatograph for HVOC concentration determination were as following; stabile wax column, Agilent; carrier, helium with the flow rate of 15 mL/min; make up gas, ultra-pure nitrogen with the flow rate of 30 mL/min; oven temperature, $60^{\circ}C$ isothermal; injector temperature, $125^{\circ}C$; and detector temperature, $300^{\circ}C$. The standard quantitative calibrations were made to obtain HVOC concentration in liquid phase.

C. Determination of Solubilization Constant, K_s

The value of K_s can be obtained by using correlation of HVOCs partial pressure and apparent Henry's law constant in coacervate phase solution described as followings:

$$K_s = \frac{c_{sol}}{c_u c_m} \quad (1)$$

Where: $C_{sol} = C_{total\ solute} - C_u$, and $C_m = C_{totalsurfactant} - CMC$

$C_{total\ solute}$ is total organic solute concentration, and $C_{totalsurfactant}$ is total surfactant concentration. At low solute concentration, the value of K_s can be estimated as its infinite dilution value and is independent of solute concentration [19].

D. Determination of Apparent Henry's law Constant, H_{app}

Several identical 20-mL glass vials containing 4 mL of an aqueous solution containing the HVOC were prepared. The HVOC was protected from leakage by capping the vials with Teflon-coated septa and aluminum holed caps. The HVOC concentration was varied but was kept below its water solubility limit. After reaching equilibrium, the HVOC concentration in the headspace and liquid phases was analyzed by the gas chromatograph connected with the headspace auto-sampler. Finally, the equilibrium correlation between HVOC concentration in vapor and in liquid phases was obtained. For the surfactant-containing system, due to higher solubility in the surfactant solutions, the HVOC concentrations were varied from 100 to 2000 ppm. The experiments were conducted in a similar manner as those for the HVOC-water system.

Fig. 2 Liquid Distributor

E. Continuous Operation

According to Fig. 1, the pressure of the stripping unit was maintained under vacuum using the rotary vane pump. The operating temperature was controlled at $40^{\circ}C$ using the water circulating bath. After the column pressure was stable, 1.0 mL/min of the feed solution was pumped to the top of the column by the peristaltic pump pass through the liquid distributor as shown in Fig. 2. The viscous surfactant-containing liquid flew down along the packed column and was stored in the product tank. A vapor suction line was attached at the bottom of the stripping column to operate the column in co-current mode. At the end of line a cold trap was installed to prevent the rotary vane pump from liquid-induced damage. After reaching the steady state, the liquid sample was collected by a gas-tight syringe in the feed and product streams for HVOC concentration analysis.

In this work, the feed solution contained 2000 ppm of HVOC and 450 mM of surfactant concentration. The feed flow rate was fixed at 1.0 mL/min, the absolute column pressure is varied from 53 torr. The efficiency of stripping process was observed and reported in term of the overall liquid phase volumetric mass transfer coefficient (K_xa) and the percentage of HVOCs removal

III. RESULTS AND DISCUSSION

A. Vapor-Liquid Equilibrium

In order to assess the performance of stripping processes for removing HVOCs from surfactant solution, the partitioning behavior of HVOCs among vapor, aqueous, and micellar phase must be investigated via the modified equilibrium

partitioning in closed system (EPICS) method. Generally, the presence of the micellar phase significantly reduces the volatilization of HVOCs. Thus, the total amount of HVOC accumulated in micellar phase plays a significant role in process design. In this study, the volatilization and solubilization of HVOCs are reported in term of Henry's law constant and solubilization constant, respectively. The general properties of the studied HVOCs are shown in Table 1.

TABLE I
MOLECULARSTRUCTURES AND THE HENRY'S LAW CONSTANTS (H) OF THE SELECTEDAROMATICSOLUTES

HVOCs	Structure of VOCs	log octanol-water partition coefficient, log K_{ow}	Henry's law constant, H (atm/ppm)
BEN		2.13	1.1×10^{-04a}
TOL	CH$_3$	2.69	1.2×10^{-04a}
ETB	C$_2$H$_5$	3.15	1.5×10^{-04a}

B. The Partition Behavior

To determine the equilibrium time of the HVOCs' partitioning in aqueous and coacervate phase solution, the concentration of the HVOCs in vapor phase was measured as a function of time. For aqueous system, the solution with various HVOCs concentration was added in 20 mL headspace glass vials with Teflon-coated septa and aluminum holed caps. The vials will be placed in the headspace-GC oven controlled at 40°C. The sample in vapor phase was collected and automatically measured as a function of time. For surfactant system, the surfactant concentration in feed solution was maintained at 450 mM in every experiment. The coacervate solution with various HVOCs concentrations was added in 20-mL headspace glass vials with Teflon-coated septa and aluminum holed caps. The equilibrium time was obtained by using the method similar to that in the aqueous system. From experiment, it was observed that the equilibrium was reached around 30 minutes with shaking. In order to guarantee this experiment reached equilibrium system, the systems were operated to reach equilibrium for 60 minutes.
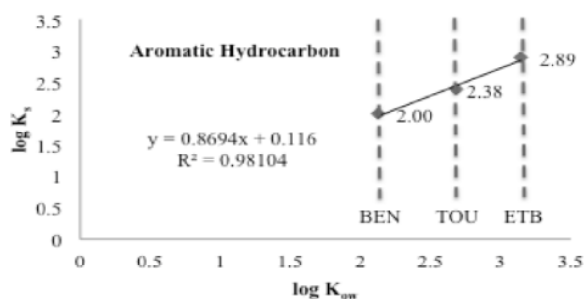

Fig. 3 Correlationbetweenoctanol-water partitioncoefficient (K_{ow}) andsolubilization constant (K_s)

TABLE II
HVOCs REMOVAL (%), SOLUBILIZATION CONSTANT (K_s), AND APPARENT HENRY'S LAW CONSTANT (H_{APP}) OF ALL STUDIED HVOCs

HVOCs	H_{app} (atm/ppm)	K_s (M^{-1})	Removal (%)
BEN	6.03×10^{-5}	1.80	98.9
TOL	3.98×10^{-5}	4.35	93.2
ETB	2.26×10^{-5}	14.10	89.8

C. Determination of Solubilization Constant, K_s

The solubilization, K_s was the ratio of the distribution of the solute between the micelles and the aqueous phase and was calculated via Eqs (1). The higher solubilizationis the higher HVOCs can be solubilized into micellar phase. The K_s was independent of surfactant concentration except the micellar structure change via concentration.

In this work, the solubilization constants of the HVOCs were conducted at 500-2000 ppm HVOCs in 450 mM tergitol TMN-6 at 40°C. The hydrophobicity of HVOCs is characterized by the octanol-water partition coefficient (K_{ow}) as shown in Table 1. The higher K_{ow} gave higher hydrophobic of solute and the more its tendency to solubilizein micelles which make the lower volatilization of HVOCs [2],[17],[18].

Fig. 3 presents the good linear logarithm correlation at equilibrium condition of aromatic hydrocarbon series. The r-square was 0.98104. The log K_s value was increase with the increasing of alkyl group of aromatic hydrocarbon (BEN>TOL>ETB). These phenomenon clearly confirm that the solubilization of HVOCs increase as a result of the increasing of the hydrophobic of HVOCs. This is because the surfactants can increase the mass transfer of the hydrophobic contaminant from bulk liquid phase by accumulating the hydrophobic compounds in micellar cores.

D. Determination of Apparent Henry's law Constant, H_{app}

Normally, the volatilization and Henry's law constant increases when the hydrophobicity and K_{ow} values increase in order to the increasing of the degree of alkylation as shown in Table I. Nevertheless, the Henry's law constant of ethyl benzene was highest over the other due to its easiness of volatility nature. The Henry's law constant data of benzene, toluene, and ethyl benzene are illustrated in Table I.

At concentration above CMC, the HVOCs in surfactant solution will be solubilized inside micelles, resulting in enhancing the solubility of HVOCs. The presence of micelles can decrease the volatilization of HVOCs which indicated in term of Henry's Law constant, so the Henry's Law constant must be modified to be "Apparent Henry's Law Constant" or H_{app}. The volatility of the HVOCs was conducted at 40°C by using 100-800 ppm HVOCs in water system and 500-2000 ppm HVOCs in 450 mM Tergitol TMN-6. The calculated apparent Henry's law constants of each solute were shown in Fig. 4. It should be noted that benzene has highest apparent Henry's law constant, so might be easiest to remove benzene from surfactant comparing with toluene and ethyl benzene.
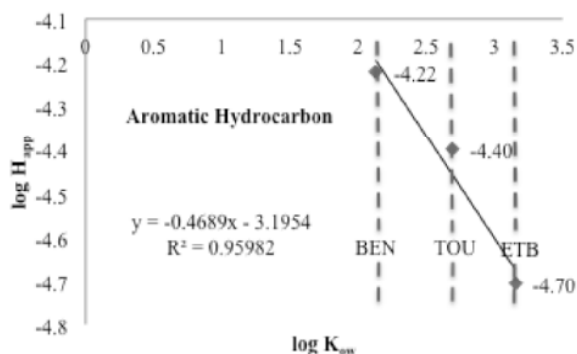
Fig. 4 Correlationbetweenoctanol-water partitioncoefficient (K_{ow}) and apparent Henry's law constant (H_{app})

All solute illustrate the decrease of H_{app} along the increasing of hydrophobicity which means that the less of volatilization of HVOCs, despite the fact that the H values increase along the hydrophobicity of solutes.

As investigated in the earlier, the increasing of hydrophobic of solutes (K_{ow}), the solubilization of HVOCs (K_s) increase, mean the less volatilization of HVOCs in nonionic surfactant solution. This result was conversely with the relationship between H and K_{ow} (Table.1). Therefore, the phenomenon of H_{app} to the degree of hydrophobicity, which show in Fig 4, can be indicated that the effect of solubilization plays an important role in of the volatility of HVOCs in surfactant solution. Figure also shows a good linear relationship between log K_{ow} and log H_{app} with the r-square was higher than 0.95.

E. Continuous Operation

The HVOCs removal (%) and $K_{ow}$for aromatic hydrocarbon is displayed in Table 2. Table 2 illustrates that HVOCs removal decrease in order; BEN>TOL>ETB. The efficiency of HVOCs removal is higher than 89 %. The greatest efficiency of vacuum stripping to remove HVOC is 98.9 % for BEN. This is because it has highest volatilization (H_{app}). On the other hand, the lowest efficiency is 89.8% for ETB due to the hardest to strip HVOCs from coacervate solution to vapor phase.

According toHVOCsremoval (%) andK_{ow}, the resultsclearly show that the higherK_{ow}givegreaterHVOCsremovalfrom the surfactant solution as a result of the highermass transfer rate.

The reason is thatanincrease in HVOCshydrophobicity affect in enhancingsolubilization of HVOCs in the surfactantmicelles.

IV. CONCLUSIONS

For the vapor-liquid equilibrium study, the volatilization and solubilization of HVOCs in coacervate phase of Tergitol TMN-6 were observed and reported in terms of apparent Henry's law constant (H_{app}), and the solubilization constant (K_s), respectively. The hydrophobicity of VOCs was reported via the octanol-water partition coefficient (K_{ow}). It was found that the K_s of HVOCs in coacervat solution increase with the increasing of K_{ow}, while the H_{app} decrease. This due to the tendency of HVOC to be solubilized in micelles. Subsequently, HVOC in HVOC-contaminated coacervate phase can be stripped out in the co-current vacuum packed

column at 40°C. The stripping column can be operated without significantly foaming and flooding. The maximun removal was benzene and the lowest removal was ethyl benzene. In addition, the HVOC removal and the mass transfer coefficient, K_xa, decrease as increasing of hydrophobicity or K_{ow} of HVOCs.

REFERENCES

[1] P. Trakultamupatam, J.F. Scamehorn, and S. Osuwan. (2002)."Removal of volatile aromatic contaminants from waste water by cloud point extraction,".Separation Science and Technology, 37(6), 1291-1305.
[2] P. Taechangam, J.F. Scamehorn, S. Osuwan, and T. Rirksomboon. "Effect of nonionic surfactant molecular structure on cloud point extraction of phenol fromwastewater,"Separation and Purification Technology,
[3] S. Sakulwongyai, P. Trakultamupatam, J.F. Scamehorn, S. Osuwan, and S.D. Christian (2000). "Use of a surfactant coacervate phase to extract chlorinated aliphatic compounds from water: Extraction of chlorinated ethanes and quantitative comparison to solubilization in micelles,"Langmuir, 16(22), 8226-8230.
[4] W. Kimchuwanit, S. Osuwan, J.F. Scamehorn, J.H. Harwell, and K.J. Haller (2000)."Use of acoacervatephaseto extract trichloroethylenefrom water,"Separation Science and Technology, 35(3), 1991-2002.
[5] S. Kutzer, H. Wintrich, and A. Mersmann (1995)."Air stripping - a method for treatment of wastewater,"Chemical Engineering and Technology, 18(3), 149-155.
[6] R.L. Gross, and S.G. TerMaath (1985)."Packed tower aeration strips trichloroethylene from groundwater,"Environmental Progress, 4(2), 119-124.
[7] V. Linek, J. Sinkule, and V. Janda (1998)."Design of packed aeration towers to strip volatile organic contaminants from water,"Water Researchs, 32(4), 1264-1270.
[8] O D Castillo, J. R. Guerrero-Medina, G. Lopez-Toledo, J. Rocha (2000)."Mathematical Evaluation of Activated Carbon Adsorption for Surfactant Recovery in a Soil Washing Process,"Ind. Eng. Chem. Res., 39(3) 731.
[9] Y. Hwang, G.E. Keller, and J.D. Olson (1992a). "Steam stripping for removal of organic pollutants from water1. Stripping effectiveness and stripping design,"Industrial and Engineering Chemistry Research, 31(7), 1753-1759.
[10] Y. Hwang, G.E. Keller, and J.D. Olson (1992a). "Steam stripping for removal of organic pollutants from water. 2. Vapor liquid equilibrium data,"Industrial and Engineering Chemistry Research, 31(7), 1760-1768.
[11] W.C. Lin, P.A. Rice, Y.S Cheng, and A.J. Barduhn (1977). "Vacuum stripping of refrigerants in water sprays,"AlChE Journal, 23(4), 409-415.
[12] M.N. Tackie, and P.A. Rice (1991). "Vacuum stripping of trichlorofluoromethane emulsions from water sprays,"Separation Technology, 1, 205-213.
[13] J.E. Bajolle, and , P.A. Rice (1971). "Vacuum Stripping of Butane from Water in a PackedColumn,"Chemical Engineering and Technology,9(4), 351-366.
[14] E.A. Rasquin, S. Lynn, and D.N. Hanson (1977). "Vacuum degassing of carbon dioxide and oxygen from water in packed column,"Industrial and Engineering Chemistry Fundamentals, 16(1), 103-108.
[15] A.LLydersen(1991). "Co-current vacuum de-aeration of water for injection into oil reservoirs,"Chemical Engineering Technology, 14(4), 248-252.
[16] R.E. Treybal (1981). Mass Transfer Operation. 3rd ed. Auckland: McGraw-Hill.

[17] S. Kungsanant, B. Kitiyanan, T. Rirksomboon, S. Osuwan, and J.F. Scamehorn (2008)."Toluene removal from nonionic surfactant coacervate phase solutions by vacuum stripping,"Separation and Purification Technology, 63(2), 370-378.

[18] S. Kungsanant, B. Kitiyanan, T. Rirksomboon, S. Osuwan, and J.F. Scamehorn (2009). "Volatileorganic compound removalfromnonionicsurfactantcoacervatephasesolutionsby co-currentvacuum stripping: Effect of surfactantconcentration, temperature, andsolute type,"Separation and Purification Technology, 66, 510-516.

[19] U.N. Choori, J.F. Scamehorn, J.F. O'Haver, and J.H. Harwell (1998). "Removal of volatile organic compounds from surfactant solutions by flashvacuum stripping in a packed column,"Ground Water Monitoring and Remediation, 18(4), 157-165.

[20] Mackay, D. (2006) Handbook of physical-chemical properties and environmental fate for organic chemicals, 2nd edition; CRC/Taylor & Francis: Florida.