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Recovery of Alcohol Ethoxylates Nonionic Surfactant using Co-Current Vacuum Stripping

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Cloud point extraction (CPE) has shown to be an effective technique to remove organic compounds from contaminated water using nonionic surfactant as a separating agent. To make this process more economically attractive, the spent nonionic surfactants should be recycled and reused. This work utilized a packed column operated under vacuum in co-current mode to remove the volatile organic compounds (VOCs) from the secondary alcohol ethoxylates, AEs, coacervate solution. The co-current operation can effectively avoid plugging, excessive foaming, and flooding. The selected volatile organic contaminants are aromatic hydrocarbons such as benzene, toluene, and ethylbenzene. The hydrophobic properties of the VOCs are described by an octanol-water partition coefficient (K_{ow}). The results show that as the K_{ow} increases, the K_s substantially increases while the H_{app} of the VOCs significantly decreases. The reduction of VOCs volatilization is possibly due to greater partitioning of the VOCs into surfactant micelles. The similar trend is also observed in the continuous operation. The results show that as the K_{ow} increases, the percentage of VOCs removal and the K_xa decrease due to the VOCs' hydrophobic effect. The removal percentages of the VOCs vary from 60 to 90%. The R^2 of the log-log and semi-log relationships between K_{ow} and studied parameters are observed in the range of 0.96-0.99.

Keyword: Nonionic Surfactant, VOCs, Co-current Vacuum Stripping, Cloud point extraction

INTRODUCTION

For the past several years, the gravity of the problem with contamination in ground, surface, and waste water by volatile organic compounds (VOCs) has become increasingly evident. The sources of these VOCs can be varied: leaking underground storage tanks, poor disposal practices, application to soil for agricultural purposes, or an accidental spill of VOCs. These compounds also cause health problems even though they are present in the system at very low concentration. The economic removal of these compounds is needed for safety and public health reasons [1]. The cloud point extraction process (CPE) has been proposed for the treatment of contaminated water because it consumes little energy and, generally the surfactant used in the process is biodegradable and not harmful to the environment. This process utilizes a nonionic surfactant as separating agent. Separation is conducted by taking advantage of the cloud point phenomenon that occurs when a nonionic surfactant solution is heated beyond its cloud point temperature. The CPE in rotating disc contactor (RTC) shows excellent performance over a traditional liquid-liquid extraction because it could operate with high efficiency, at low cost, and in a sustainable manner [2] - [4].

To make the CPE more economically attractive, the surfactants have to be recovered and reused. Since these organic solutes have high volatility, vacuum stripping has been proposed to be the promising technique to remove the VOCs from the surfactant solution [5] - [7].

In previous studies, the co-current vacuum stripping in a packed column was successfully applied for the removal of VOCs from alkyl phenol ethoxylates (APEs) coacervate phase solution without flooding and plugging [6] – [7]. In this work, this process is further studied for the removal of VOCs from alcohol ethoxylates (AEs) coacervate phase solution. The AEs surfactant is selected because of its environmental benefits while the APEs is suspected to cause endocrine disruption. In addition, the equilibrium studies and the efficiency of vacuum stripping are discussed.

MATERIAL

The secondary alcohol ethoxylates (AEs), Tergitol 15-S-7 ($C_{11\text{-}15}H_{23\text{-}31}O(CH_2CH_2O)_7.3H$), was purchased from Union Carbide and was used as the nonionic surfactant. AEs has an alcohol group located at various positions along the chain of 11–15 carbon atoms with an average ethylene oxide number of 7.3. Reagent grade benzene with 99.8% purity, toluene and ethylbenzene with 99.5% purity were purchased from J.T. Baker (Phillipsburg, NJ, USA). All chemicals were used as received. Deionized water was used for the solution preparation.

APPARATUS

A cylindrical stripping column constructed of acrylic fiber with a diameter of 2.5 in. and a height of 12 in., has an acrylic water jacket 5 in. in diameter. The stripping column was packed with 5x5 mm glass Raschig ring. The feed tank is a 9 in. height and 4 in. diameter vessel made of glass with a 6.5-in. diameter acrylic water jacket. The product tank is 6 in. in height and 6 in. in diameter and made of stainless steel. The system is maintained under vacuum conditions by a rotary vane pump. A peristaltic pump was used to transfer feed solution into the stripping column. The operating temperature was controlled using a water circulating bath.

The diagram of the vacuum stripping unit is shown in Fig. 1 [6].

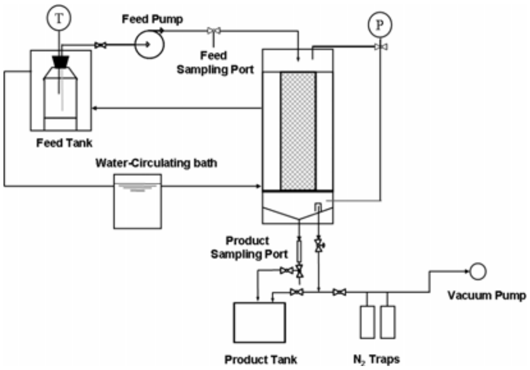

Figure 1. Co-current Vacuum Stripping Unit

EXPERIMENTAL

Equilibrium time determination

The partitioning of the VOCs in water and coacervate phase solution was observed by modification of the method called the equilibrium partitioning in closed systems (EPICS) [8]. The operating temperature was controlled at 40 °C for all experiment runs [7].

The partitioning of VOCs in aqueous phase solution was measured by adding 4 mL of the water containing the VOCs in several identical 22-mL glass vials with Teflon-coated septa and aluminum holed caps. The vials were placed in an isothermal chamber of the headspace autosampler kept at 40 °C. Then, the vapor sample in the headspace was automatically collected and analyzed in a gas chromatograph. The equilibration time of the VOCs in the system was determined from the progression of VOC concentration with time. For the surfactant-containing system, the partitioning of VOCs in coacervate phase solution is observed by the same method.

Equilibrium data determination

Several identical 22-mL glass vials of VOCs in aqueous solution were prepared using the same method as that in equilibrium study. After reaching equilibrium, the VOC concentrations in the headspace and in the liquid phase were analyzed by the gas chromatograph connected to the headspace autosampler. Finally, the vapor-liquid equilibrium correlations for the VOCs were obtained. For the surfactant-containing system, the experiments were conducted in a similar manner as those for the VOC-water system. The data from this experiment were utilized to calculate the apparent Henry's law constant (H_{app}) and the solubilization constant (K_s) [6]. These parameters respectively represent the volatility and solubility of the VOCs in the surfactant solution.

Continuous Operation

The pressure inside the system was maintained under vacuum during the operation by using the rotary vane pump. The operating temperature was controlled using the circulating water bath at a constant temperature of 40 °C. After the column pressure was stable, 1.0 mL/min of the feed solution was pumped onto the top of the column by the peristaltic pump. The viscous surfactant solution flowed down along the packed column and was stored in the product tank. A vapor suction line was attached to the bottom of the stripping column to operate in co-current mode. A cold trap was installed to prevent the rotary vane pump from liquid-induced damage. The vacuum stripping packed column reached steady state within 90 minutes. The liquid sample was collected using a gas-tight syringe from the feed and product streams for VOCs removal efficiency evaluation.

In this work, the feed flow rate was fixed at 1.0 mL/min, the absolute column pressure is maintained at 59 torr, and the number of distributor holes was three. The aromatic hydrocarbons studied here are benzene (BEN), toluene (TOL), and ethylbenzene (ETB). The efficiency of the stripping process was observed and reported in terms of the VOCs removal (%) and the overall liquid phase volumetric mass transfer coefficient (K_xa) [6].

RESULTS AND DISCUSSION

Equilibrium study

The hydrophobicity of VOCs is described in terms of the octanol-water partition coefficient (K_{ow}). Generally, the higher the K_{ow}, the more hydrophobic the solute is and the more it has a tendency to solubilize in micelles which make the lower volatilization of VOCs to the vapor phase [9]-[10]. The properties of the aromatics VOCs are described in Table 1.

Table 1: The VOCs Properties

VOCs	Log K_{ow}	Henry's law constant, H (atm/ppm)
BEN	2.13	1.1×10^{-04} [11]
TOL	2.69	1.2×10^{-04} [12]
ETB	3.15	1.5×10^{-04} [11]

According to the equilibration time study, the observed equilibration time of the VOCs in water and coacervate system was around 30 minutes with shaking. In order to guarantee that the systems reached equilibrium these were operated for 60 minutes per run.

Fig. 2 and Fig. 3 show that as the value of K_{ow} increases due to the increasing degree of alkylation, the values of H and K_s increase while the H_{app} decreases. It can also be observed that H_{app} differs from H by at least one order of magnitude. It might be implied that the reduction in the VOCs volatilization could be caused by the greater tendency of the VOCs to partition into the surfactant micelles.

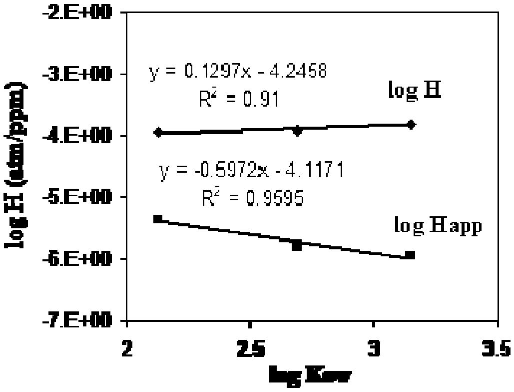

Figure 2. Henry's Law Constant (H, ♦) and Apparent Henry's Law Constant (H_{app}, ■) of the VOCs at Equilibrium Condition (450 mM AEs, 40 °C)

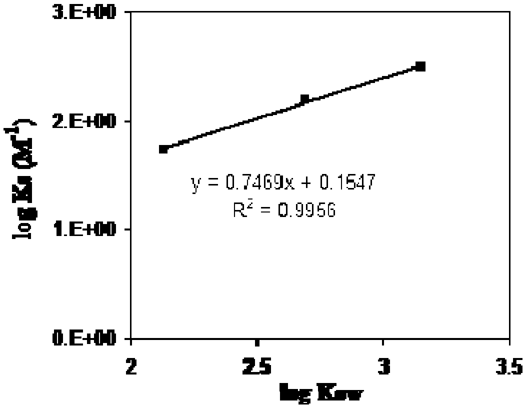

Figure 3. The Solubilization Constants of the Correlation the VOCs at Equilibrium Condition (450 mM AEs, 40 °C)

The log-log correlations between H, H_{app}, and K_s and K_{ow} show a good linear relationship. The R^2 values of each correlation are higher than 0.90. These results indicate that the greater value of K_{ow} of VOCs can show both their greater hydrophobicity and their greater tendency to solubilize into the micellar phase.

Continuous Operation

The stripping column was operated in co-current mode with 1.0 mL/min feed flow rate at 59 absolute torr column pressure and 40°C using 3-hole distributor [6]-[7]. During operation, there was no significant foaming and plugging of coacervate solution observed in the stripping column. The VOC removal (%) and the overall liquid phase volumetric mass transfer coefficient (K_xa) of the VOCs are shown in Fig. 4 and Fig. 5, respectively.

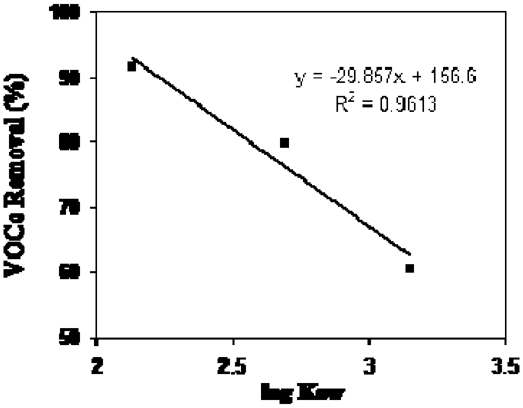

Figure 4. The Correlation between VOCs Removal (%) and log K_{ow} (2000 ppm VOCs in 450 mM AEs, 40 °C)

It can be seen that the percentage of VOC removal and the K_xa decrease with increasing K_{ow}. The removal of VOCs decreases according to the order BEN>TOL>ETB. In addition, the R^2 of the semi-log relationships between the K_{ow} and the percentage of VOCs removal and the K_xa are 0.96 and 0.98, respectively. It is clearly noted that the increase in the VOCs hydrophobicity enhances solubilization of VOCs in the surfactant micelles leading to the decrease in VOCs stripping performance.

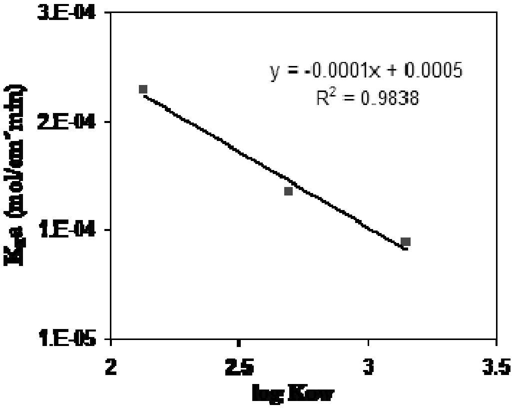

Figure 5. The Correlation between K_xa (mol/cm^{3}min) and log K_{ow} (2000 ppm VOCs in 450 mM AEs, 40 °C)

CONCLUSION

The co-current vacuum stripping using a packed column at controlled 40°C was successfully used for aromatic VOC removal from AEs solution. The consistency of the results obtained from equilibrium and continuous studies show that the increase in the VOC hydrophobicity could facilitate VOC solubilization in surfactant micelles which cause a reduction in VOCs volatilization and the VOC stripping efficiency in a packed column. Overall, the efficiency of VOCs removal was higher than 60% for all solutes. Moreover, the log-log and semi-log plots between the K_{ow} and the studied parameters show good linear relationships. These correlations support that K_{ow} could be applied for predicting VOCs stripping performance. Similar studies using other hydrophobic solutes are recommended.

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REFERENCES

1) P. Hunter and S.T. Oyama: Control of Volatile Organic Compound Emissions (2000).
2) P. Trakultamupatam, J.F. Scamehorn, and S. Osuwan: Sep. Sci. Technol. **37** (2002) 1291.
3) P. Trakultamupatam, J.F. Scamehorn, and S. Osuwan: Sep. Sci. Technol. **39** (2004) 479.
4) P. Trakultamupatam, J.F. Scamehorn, and S. Osuwan: Sep. Sci. Technol. **39** (2004) 501.
5) U.N. Choori, J.F. Scamehorn, J.F. O'Haver, and J.H. Harwell: Ground Water Monit. Rem. **18** (1998) 157.
6) S. Kungsanant, B. Kitiyanan, T. Rirksomboon, S. Osuwan, and J.F. Scamehorn: Sep. Purif. Technol. **62** (2008) 370.
7) S. Kungsanant, B. Kitiyanan, T. Rirksomboon, S. Osuwan, and J.F. Scamehorn: Sep. Purif. Technol. **66** (2009) 510.
8) J. Jiang, L.M. Vane, and S.K. Sikdar: J. Membr. Sci. **136** (1997) 233.
9) J. Li and B. Chen: J. Colloid Interf. Sci. **263** (2003) 625.
10) P. Taechangam, J.F. Scamehorn, S. Osuwan, and T. Rirksomboon: Sep. Sci. Technol. **43** (2008) 3601.
11) G.A. Robbins, S.Wang, and J.D. Stuart: Anal. Chem. **65** (1993) 3113.
12) L.M. Vane and E.L. Giroux: J. Chem. Eng. Data **45** (2000) 38.