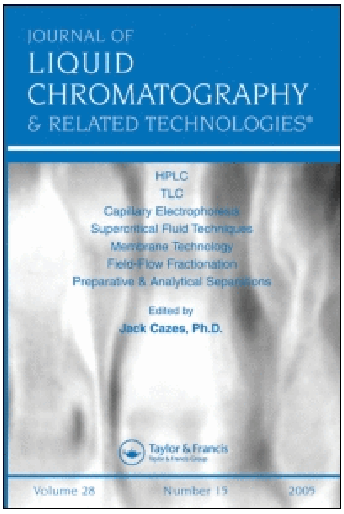

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Extraction of Nonionic Surfactants from Waste Water Using Centrifugal Partition Chromatography

Randy A. Menges[a]; Tracy S. Menges[a]; Gary L. Bertrand[a]; Daniel W. Armstrong[a]; Larry A. Spino[b]
[a] Department of Chemistry, University of Missouri-Rolla, Rolla, Missouri [b] Shell Development Company, Houston, Texas

To cite this Article Menges, Randy A. , Menges, Tracy S. , Bertrand, Gary L. , Armstrong, Daniel W. and Spino, Larry A.(1992) 'Extraction of Nonionic Surfactants from Waste Water Using Centrifugal Partition Chromatography', Journal of Liquid Chromatography & Related Technologies, 15: 15, 2909 — 2925

To link to this Article: DOI: 10.1080/10826079208016356

URL: http://dx.doi.org/10.1080/10826079208016356

JOURNAL OF LIQUID CHROMATOGRAPHY, 15(15&16), 2909-2925 (1992)

EXTRACTION OF NONIONIC SURFACTANTS FROM WASTE WATER USING CENTRIFUGAL PARTITION CHROMATOGRAPHY

RANDY A. MENGES[1], TRACY S. MENGES[1], GARY L. BERTRAND[1],
DANIEL W. ARMSTRONG[1]*, AND LARRY A. SPINO[2]
[1]*Department of Chemistry*
University of Missouri-Rolla
Rolla, Missouri 65401
[2]*Shell Development Company*
Houston, Texas

ABSTRACT

A novel method for the extraction of nonionic surfactants from waste water is described which uses centrifugal partition chromatography (CPC). The extractant is the liquid stationary phase of the CPC apparatus, and the raffinate serves as the mobile phase. Partition coefficients (K) of nonionic surfactants were measured between water and several common organic solvents to determine the best extractant. The effect of salt concentration on K is examined. Extractions are demonstrated which remove a nonionic surfactant from a relatively large volume of simulated waste water into a relatively small volume

*To whom correspondence should be sent.

of ethyl acetate extractant. In order to assess the viability of this method, nonylphenol ethoxylate (NPEO) was chosen because of its UV absorbance characteristics.

INTRODUCTION

Surfactants are used in large volumes in consumer detergents and toiletries, in commercial cleaners and as industrial process aids. After use, surfactants are discharged to sewage treatment plants, septic tank systems, industrial biotreaters, or more directly to the environment. Understanding the fate of surfactants after discharge, and the exposure of natural organisms to them, are important elements in an environmental safety assessment supporting their use. Analyses of trace surfactants and their metabolites in environmental water samples, sludges and sediments are needed to provide the raw data on real world exposure for such an assessment.

Nonionic surfactants, particularly those containing a polyoxyethylene chain as the hydrophile, are important in detergents, cleaners, and process aids. The most important classes are linear alcohol ethoxylates (AEO) and alkylphenol ethoxylates (APEO). $RO(CH_2CH_2O)_nH$ and $RC_6H_4O(CH_2CH_2O)_nH$ are the general chemical formulas for AEO and APEO, respectively. The R-group can be either linear or branched and may contain 8 to 16 carbon atoms, and n can be an average of 5 to 18 ethoxylate units even though commercial ethoxylated nonionic surfactants contain measureable amounts of ethoxymers that range from n=0 to n=18+. AEO and APEO compose a large percentage of the world's nonionic surfactant market. Approximately 40% of all household detergents that can be purchased in U.S. supermarkets contain nonionic surfactants as a major active constituent, and over 60% of all surfactants used in industrial applications are nonionic. APEO have been used extensively as the main active component in institutional and industrial surface cleaners (1,2).

Analysis of environmental samples involves two key steps, extraction and quantitation. This paper explores the feasibility of using Centrifugal Partition Chromatography (CPC) for the extraction step. An aromatic nonionic, nonylphenol ethoxylate (NPEO), was chosen for this exploratory phase to simplify quantitation due to its UV absorbance. Extension to alcohol ethoxylates and other nonionics is planned in the next phase.

Analytical extraction procedures have been developed for APEO in aqueous environmental solutions (3) and in sewage sludges (4,5,6). The extraction of APEO from water involves the use of ethyl acetate as the extractant and the addition of salts to the aqueous raffinate. The two liquids are placed in a sublator apparatus (7) and a stream of nitrogen is purged through the liquids to enhance the extraction of the surfactants (8). The extraction of APEO from sewage sludge is performed by a modified soxhlet extraction with methylene chloride as the extractant (4). Quantitation of APEO in waste water or sewage sludge has been done by liquid or gas chromatography after using these extraction procedures (5,8). Spectroscopic methods to quantitate aromatic-containing nonionic surfactants have been published which use UV absorbance or fluorescence (9-12).

CPC is a form of liquid-liquid counter current chromatography which uses centrifugal force to retain a liquid stationary phase. The CPC apparatus can be described as automated 50 μl liquid-liquid extraction chambers connected in series. Many applications of CPC have been reported, including separations and octanol-water partition coefficient measurements (13,14). This work describes a novel method for extracting nonionic surfactants from waste water and concentrating them in an extractant. The extractant is a liquid which is used as the stationary phase of the CPC, and the "waste water raffinate" is the mobile phase. This allows a continuous extraction of new raffinate into a relatively small volume of extractant. The extractant can easily be recovered from the CPC by reversing the direction of flow. To determine the best extractant to use in the CPC extractions, the partition coefficients of NPEO between various organic solvents and water were determined. The effect of salt on the partition coefficient was also examined. In order to assess the viability of this method, nonylphenol ethoxylate (NPEO) was used as a model APEO in this study because of its UV absorbance characteristics.

EXPERIMENTAL

Materials

Nonylphenol ethoxylate (NPEO) used had the domestic trade name of IGEPAL® CO 630 (Rhone-Poulenc). The molecular formula for this NPEO is $C_9H_{19}C_6H_4O(C_2H_4O)_nH$. It has an average molecular weight of 616 and the C_9 alkyl moiety is highly branched. Nonylphenol ethoxylates contain a wide range of ethoxylate groups per hydrophobe (n=0 and up). This particular NPEO contains an average of nine ethoxymers. Hexane, octanol and ethyl acetate of Omnisolv grade were obtained from EM Science, Gibbstown, NJ. The water was distilled, then passed through a Barnstead D8922 cartridge to trap organics and filtered with a 0.45 µm porous nylon 66 membrane to remove particulates. The sodium chloride was purchased from Sigma.

Centrifugal Partition Chromatograph

The centrifugal partition chromatograph (CPC) apparatus was a model NMF-LLN, Sanki Laboratory, Mount Laurel, NJ. The "column" may be composed of 1 to 12 cartridges, model 250W, connected in series. Each cartridge has 400 chambers in which to perform liquid-liquid extractions. One cartridge has an internal volume of approximately 20 ml; therefore, the CPC may have a total internal volume of up to 240 ml and 4,800 liquid-liquid extraction chambers connected in series. These cartridges and the basic operation of the CPC apparatus have been thoroughly discussed (15). A single Shimadzu, Columbia, MD, model LC-6A reciprocating piston pump was used. Flow rates from 0.1 to 9.9 ml/min can be used. A CPC model FCU-V valve assembly was used to control the direction of the flow in the CPC. The extraction of NPEO from waste water was conducted in the descending mode (*i.e.*, the direction of mobile phase flow was from the "top" of the column to the "bottom"). However, if an extractant is used which has a density greater than the raffinate, the ascending mode should be used. The column effluent was manually collected and analyzed for NPEO. The mobile phase and the stationary phase solvents must be mutually presaturated prior to the CPC extraction (15). The NPEO spiked water was prepared by presaturating water or salt solutions with ethyl acetate and then adding approximately 10-15 mg/L of NPEO. After extraction of the raffinate, the mass of NPEO in the extractant and the column effluent was measured, and mass balances were obtained.

Partition Coefficient Measurement

The partition coefficients of the nonionic surfactant between various organic solvents were measured using a shake-flask technique. Aqueous solutions of NPEO were prepared in the concentration range of ca. 5 ppm to 200 ppm. 20 ml of each aqueous NPEO solution was pipetted into a 40 ml vial. Approximately 20 ml of organic solvent was poured into the vial and a screw cap with a teflon lining was placed on the vials. These vials were then vigorously shaken for approximately 5 min and sonicated for 30 min. The procedure was repeated, except this time 20 ml of organic NPEO solution was pipetted into the vial, and then distilled water was added. The partition coefficient values obtained were the same using either method, but the shake-flask experiments with the NPEO starting in the organic phase formed less emulsion. The vials were then centrifuged at 4000 RPM for 20 min at 23° C using a Sorvall model RC5C centrifuge. Aliquots of each phase were drawn and the concentration of NPEO was measured spectroscopically. Additional shake-flask experiments were performed using the ethyl acetate/water system to study the effect of salt on the partition coefficient. These followed the same procedure except that the concentration range of the NPEO was from 50 ppm to 1200 ppm and sodium chloride solutions (0, 0.5, 1.0, and 2.0 M) were used as the aqueous phase.

Quantitation of Nonionic Surfactant

UV absorbance has been used previously to quantitate octyl phenol ethoxylate (11). NPEO was quantitated using an Hitachi model U-2000 UV spectrophotometer or a Perkin-Elmer LS-5 fluorescence spectrophotometer. NPEO has absorbance maxima at 222 nm and 275 nm and an emission band at 310 nm. Standard solutions were prepared by weighing NPEO in 500 ml volumetric flasks. Serial dilutions were made into 100 ml volumetric flasks. Ethyl acetate, hexane, and octanol were presaturated with water to prepare the organic standards and water or aqueous salt solutions were presaturated with the respective organic solvent prior to making the aqueous standards. All absorbance and fluorescence measurements were made in 1 cm quartz cuvettes. In the hexane/water and octanol/water systems, the concentration of the NPEO was determined by UV absorbance at 222 nm. Ethyl acetate has a UV cut-off of 255 nm; therefore, the NPEO was quantitated in the organic phase of the ethyl acetate/water system using UV absorbance at 275 nm. The aqueous phase NPEO concentration for the ethyl acetate/water system was quantitated using fluorescence detection. 275 and 310 nm were used as the excitation and emission wavelengths, respectively, and the slit widths were set at 15 and 5 nm, respectively.

RESULTS AND DISCUSSION

The use of UV absorbance or fluorescence measurements to quantitate NPEO in the hexane/water and octanol/water solvent systems proved to be adequate for the concentration ranges used in this study. The molar absorbtivity of NPEO at 222 nm was determined in solutions of hexane saturated with water, water saturated with hexane, octanol saturated with water, and water saturated with octanol. The values are 9720, 10190, 11080, and 12930 $Lmol^{-1}cm^{-1}$, respectively. The detection limit at 222 nm was determined to be ca. 0.5 mg/L. The molar absorbtivity of NPEO in ethyl acetate solution saturated with water at 275 nm was determined to be 1640 $Lmol^{-1}cm^{-1}$, and, within experimental error, this value was not affected by the saturation of the ethyl acetate with different concentrations of salt solutions. The detection limit at 275 nm was ca. 3 mg/L. The concentration of NPEO in water saturated with ethyl acetate was determined by fluorescence. The standard curve for the fluorescence of NPEO in ethyl acetate was linear over the concentration range of 0.3 to 88 mg/L.

Table I. Partition Coefficients of Nonylphenyl ethoxylate[a]

Organic Solvent	K	Standard Deviation
hexane	1.4	0.1
octanol	11.4	3.0
ethyl acetate	53.9	0.9

[a] between the organic solvent and water

Partition coefficients (K) were calculated using the equation

$$K = \frac{[\mathrm{NPEO}]_{\mathrm{organic}}}{[\mathrm{NPEO}]_{\mathrm{aqueous}}}$$

Table I lists the partition coefficient of NPEO between water and three organic solvents: ethyl acetate, hexane and octanol. These three organic solvents were chosen because ethyl acetate is used as the solvent in many extractions of nonionic surfactants from waste water, and the partition coefficients of surfactants in hexane/water and octanol/water solvent systems are used in studies of the hydrophilic-lipophilic balance of surfactants. From the data in Table I, it is clear that NPEO has a high affinity for ethyl acetate although it is not clear at this time if there is a significant partitioning difference between the wide variety of ethoxymers present in NPEO. The standard deviation of the octanol/water partition coefficient is high because only low concentrations of NPEO (<50 mg/L) could be used in the shake flask experiments. Higher concentrations in the octanol/water shake-flask experiments resulted in a persistent emulsion layer being formed. The hexane/water partition coefficient of NPEO has

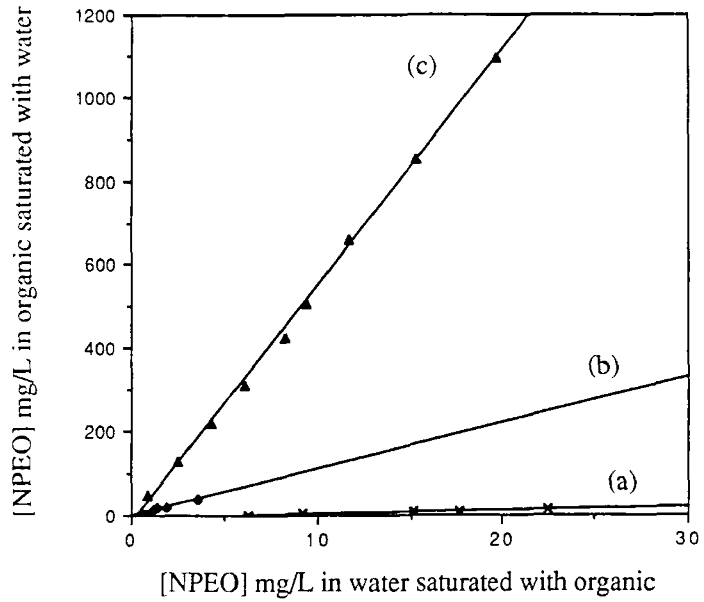

Figure 1. Partition isotherm for NPEO between water and (a) hexane, (b) octanol, and (c) ethyl acetate. The slope represents the partition coefficient (K) for NPEO in each solvent system.

been shown in the literature to decrease above its cmc (11,16). Figure 1 shows the partition isotherms of NPEO for the three aqueous/organic solvent systems used. The slope of the isotherm is equal to K. In the concentration ranges examined, the K for all three solvent systems appears to be constant; however, in this study, the concentration in the hexane/water system did not exceed the cmc reported in the literature, and only the K for low NPEO concentrations was determined for the octanol/water system. Because the K for NPEO in the hexane/water and octanol/water systems were small, the use of these solvents was not pursued further.

Table II. Effect of Salt on the K of Nonylphenol ethoxylate in an Ethyl Acetate/Aqueous Solvent System

[NaCl] M	K	Standard Deviation
0.0	53.9	0.9
0.5	71.2	1.2
1.0	76.0	2.5
2.0	147.0	6.6

Ethyl acetate exhibited the highest selectivity for the NPEO and was chosen as the extractant for the CPC extraction experiments. Additional shake-flask experiments were performed to study the effect of salt on K in the ethyl acetate-water system. Table II list the partition coefficients of NPEO between ethyl acetate and varying concentrations of NaCl aqueous solutions. The increase in K with increasing salt concentration is a typical salting-out effect. This effect is not entirely understood, but it is known that both the surfactant and the ethyl acetate are salted-out of the aqueous phase.

CPC Extraction Experiments

Figure 2 shows the fraction of NPEO in the raffinate unextracted by the CPC as a function of the effluent volume for two CPC extraction experiments. Both extractions were performed under the same conditions except for the number of cartridges used for the column. Extraction (b) was performed using 3 cartridges in the CPC (column volume is 60 ml

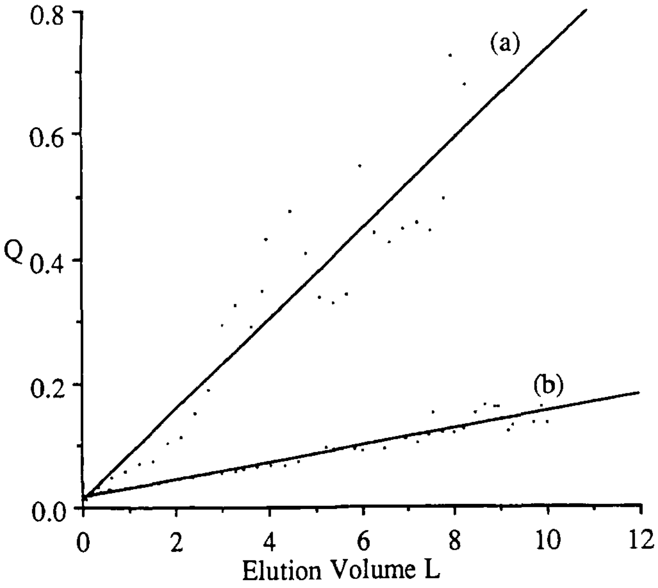

Figure 2. Comparison of the extraction of NPEO using 1 and 3 cartridges. Both of the extractions were done using a flow rate of 5 ml/min, 600 RPM, and 23°C. Curve (a) was done with 1 cartridge, V_T = 20mL, $V_{extractant}$ =10 mL and curve (b) was done with 3 cartridges, V_T = 60mL, $V_{extractant}$ =30 mL. The $[NPEO]_{initial}$ were 14.2 mg/L and 16.5 mg/l, respectively. $Q=[NPEO]_{effluent}/[NPEO]_{initial}$ and represents the fraction unextracted.

with 30 ml of the extractant ethyl acetate). Extraction (a) was performed using only 1 cartridge (column volume 20 ml, and 10ml of extractant). After 5 liters of raffinate were pumped through the CPC column, the CPC using 3 cartridges was still removing approximately 92% of the NPEO from the mobile phase; however, the extraction being done with 1 cartridge was removing only 62.5% of the NPEO from the mobile phase. This shows that increasing the volume of extractant and the number of extractions (*i.e.*, increasing the number of cartridges) increases the percentage of NPEO extracted from the raffinate.

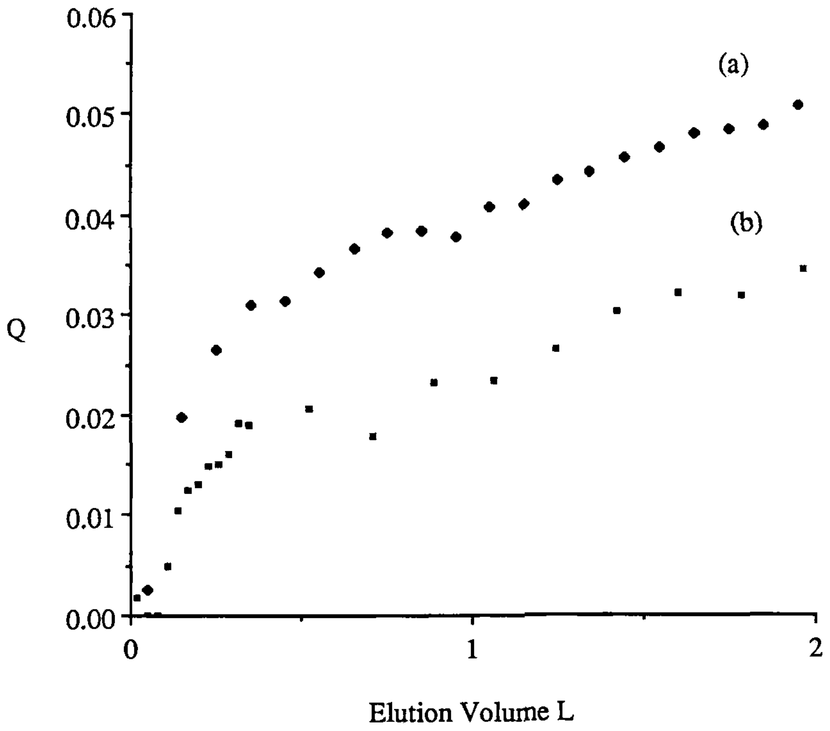

Figure 3. Comparison of the extraction of NPEO at different flow rates. Curve (a) is for a flow rate of 5 mL/min and (b) is for 3 mL/min. Both extractions were done at 600 RPM and 23°C with 6 cartridges, V_T =120mL, $V_{extractant}$ = 60 mL. The $[NPEO]_{initial}$ were 12.3 mg/L for curve (a) and 16 mg/L for curve (b).

Figure 3 shows the fraction of NPEO unextracted from the raffinate as a function of eluant volume for two different flow rates. Curve (a) is for 5 ml/min and curve (b) is for 3 ml/min. After 2 liters of raffinate were pumped through the CPC column, 95% of the NPEO was still being extracted from the stream for a flow rate of 5 ml/min, but if the flow rate was reduced to 3 ml/min, 97% could be extracted. Of course, decreasing the flow rate increases the total extraction time.

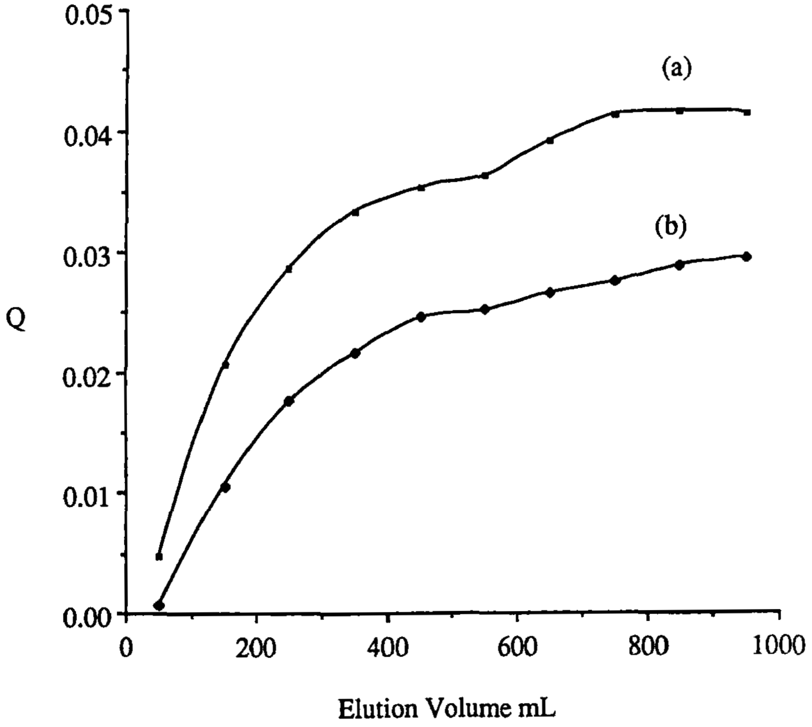

Figure 4. Effect of salt on the extraction of NPEO by the CPC. Curve (a) shows the extraction done without the addition of salt to the raffinate, and curve (b) shows the extraction done with the addition of 1.0 M NaCl to the raffinate. Both extractions were done with 6 cartridges, 5 mL/min, 23°C and 600 RPM with $[NPEO]_{initial}$ equal to 11.6 mg/L.

Table II shows that the K of NPEO between ethyl acetate and water increases with increasing salt concentration; therefore, we examined the effect that the concentration of salt in the raffinate had on the CPC extraction. Figure 4 shows extractions performed with no salt (a) and with 1.0 M NaCl (b). All other conditions were held constant. After extracting 1 liter of raffinate, 95.8 and >97% of the NPEO was still being removed

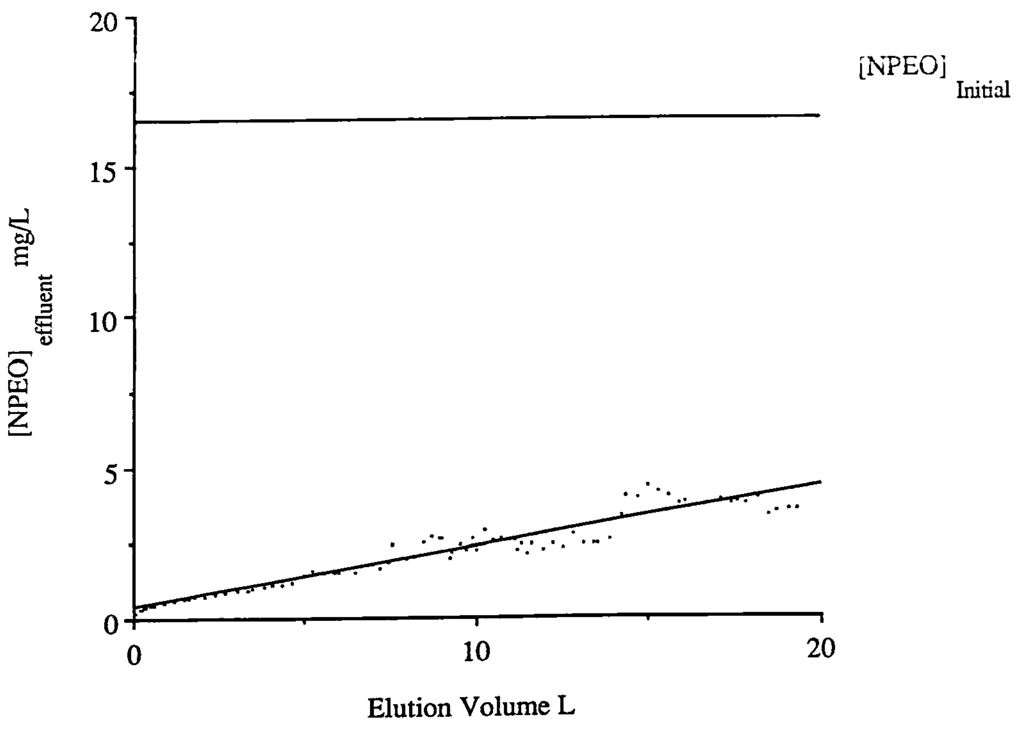

Figure 5. Effluent concentration profile for a 20 liter CPC extraction experiment. The extraction was performed using 3 cartridges, ca. 30 mL of extractant, 5 mL/min, 600 RPM, 23°C, and $[NPEO]_{initial}$ =16.5 mg/L.

from the raffinate, respectively. Obviously, salt increases the efficiency of the extraction of the NPEO into ethyl acetate.

Figure 5 shows the eluant concentration of NPEO as a function of the effluent volume. The column consisted of 3 cartridges and contained only 30 ml of ethyl acetate extractant. The flow rate was 5 ml/min. 20 liters of waste water was extracted, and at the end of the experiment, >75% of the NPEO was still being removed. Overall, >86% of the NPEO present in the raffinate was extracted. 285 mg of NPEO was concentrated into 30 ml of ethyl acetate extractant. Clearly, CPC offers the advantage of concentrating materials of interest into tens of milliliters of solvent rather than hundreds of milliliters required by solvent sublation techniques.

This technique may be a viable approach to remove nonionic surfactants from waste water. Although this method was only shown to be effective for liter quantities of waste water, it serves as a good model for possible larger scale industrial processes. In fact, much larger CPC apparatuses are available for larger counter current extractions. One area of caution that one must be aware of is that of "column flooding". When a relatively high concentration of surfactant has been extracted into the stationary phase, the possibility of forming an emulsion increases. If an emulsion forms between the stationary phase and mobile phase, the raffinate is pumped out of the column. When the emulsion band is eluted a large peak is observed on the detector. Naturally this leads to a large decrease in the volume of the stationary phase. It is difficult to predict when or if flooding will occur. It depends on the nature and concentration of the surfactant, the nature of the stationary and mobile phase solvents, as well as the instrumental parameters (*e.g.*, spin rate, flow rate, cell geometry, etc). Fortunately, if flooding occurs, it is relatively late in the extraction experiment. Currently, estimations of flooding points must be done empirically.

The addition of salt to the raffinate is a common technique to increase extraction efficiency. Caution should be exercised when using very high salt concentrations in the mobile phase for CPC. The rotary seals of the CPC unit do not seem to be adversely affected by low salt concentrations. Using 1M NaCl raffinate as the mobile phase, we did not experience any failures of the rotary seals; however, they should be rinsed clean of any solid residue after use. High salt or buffer concentrations often leave solids that can scratch the surface of rotary seals.

CONCLUSION

The CPC proved to be a very effective tool for the extraction of nonylphenol ethoxylates from water. This technique may be a viable method with which to also remove similar amounts of nonionic surfactants from waste water. Empirically, we have described factors which affect extraction efficiency including: extractant volume, number of extractions, flow rate of the raffinate, salt effects, and partition coefficients. Work is currently underway to provide a more accurate theoretical description of this process and to apply CPC to nonaromatic surfactants, such as linear alcohol ethoxylates.

ACKNOWLEDGEMENT

Support of this work by Shell Development Company is gratefully acknowledged.

REFERENCES

1. Layman, P.L.; *Chem. Eng. News*, Jan. 23, (1984), 17-49.

2. Layman, P.L.; *Chem. Eng. News*, Jan. 20, (1986), 21-42.
3. McEvoy, J. and Giger, W.; *Environ. Sci. Technol.*, **20**, (1986), 376-83.
4. Stephanon, E. and Giger, W.; *Environ. Sci. Technol.*, **16** (11), (1982), 800-805.
5. Marcomini, A. and Giger, W.; *Anal Chem.*, **59**, (1987),1709-15.
6. Kubeck, E. and Naylor, C. G.; *JAOCS*, **67**, (1990), 400-405.
7. Boyer, S. L., Guin, K. F., Kelley, R. M., Mausner, M. L., Robinson, H. F., Schmitt, T. M., Stahl, C. R. and Setzborn, E. A., *Environ. Sci. Technol.*, **11**, (1977), 1167.
8. Ahel, M. and Giger, W.; *Anal Chem.*, **57**, (1985), 2584-90.
9. Crisp, P.T., Eckert, J.M., Gibson, N.A., and Wester, I.S.; *Anal Chim. Acta.*, **123**, (1981), 355-57.
10. Favretto, L., Stancher, B., and Tunis, F.; *Analyst*, **105**, (1980), 833-40.
11. Greenwald, H.L., Kice, E.B., Kenly, M., and Kelly, J.; *Anal Chem.*, **33**, (1961), 465-68.
12. Holt, M. S., McKerrell, E. H., Perry, J. and Watkinson, R. J.; *J. of Chromatogr*, **362**, (1986), 419-424.
13. Menges, R.A., Bertrand, G.L., and Armstrong, D.W., *J. Liq. Chromatogr.*, **13**(15), (1990), 3061-77.
14. Cazes, J. and Nunogak, K., *American Laboratory*, February, 1987, 126-142.
15. Berthod, A. and Armstrong, D.W., *J. Liq Chromatogr*, **11**(3), (1988), 547-66; **11**(3), (1988), 567-83; **11**(6), (1988), 1187-1204; **11**(7), (1988), 1457-74.
16. Warr, G.G., Grieser, F., and Healy, T.W., *J. Phys. Chem.*, **87**, (1983), 4520-24.