This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

## Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

# Membrane Extraction of Phenol With Linear Monoalcyl Cyclohexane

Slavica M. Stevanović[a]; Milan V. Mitrović[b]; Yakov I. Korenman[c]
[a] DEPARTMENT OF ANALYTICAL CHEMISTRY, FACULTY OF TECHNOLOGY AND METALLURGY, UNIVERSITY OF BELGRADE, BELGRADE, YUGOSLAVIA [b] INSTITUTE OF GENERAL AND PHYSICS CHEMISTRY, BELGRADE, YUGOSLAVIA [c] DEPARTMENT OF ANALYTICAL CHEMISTRY, STATE TECHNOLOGICAL ACADEMY OF VORONEZH, VORONEZH, RUSSIA

Online publication date: 03 August 1999

**To cite this Article** Stevanović, Slavica M. , Mitrović, Milan V. and Korenman, Yakov I.(1999) 'Membrane Extraction of Phenol With Linear Monoalcyl Cyclohexane', Separation Science and Technology, 34: 4, 651 — 663

**To link to this Article: DOI:** 10.1081/SS-100100672

**URL:** http://dx.doi.org/10.1081/SS-100100672

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION SCIENCE AND TECHNOLOGY, **34**(4), pp. 651–663, 1999

# Membrane Extraction of Phenol with Linear Monoalcyl Cyclohexane

SLAVICA M. STEVANOVIĆ*
DEPARTMENT OF ANALYTICAL CHEMISTRY
FACULTY OF TECHNOLOGY AND METALLURGY
UNIVERSITY OF BELGRADE
KARNEGIJEVA 4, P.O. BOX 494, YU-11000 BELGRADE, YUGOSLAVIA

MILAN V. MITROVIĆ
INSTITUTE OF GENERAL AND PHYSICS CHEMISTRY
YU-11000 BELGRADE, YUGOSLAVIA

YAKOV I. KORENMAN
DEPARTMENT OF ANALYTICAL CHEMISTRY
STATE TECHNOLOGICAL ACADEMY OF VORONEZH
PROSPECT REVOLUTION 19, 394 000 VORONEZH, RUSSIA

## ABSTRACT

The membrane extraction of phenol with linear monoalcyl cyclohexane (lMACH) as an organic solvent was studied. The organic/water distribution coefficient was obtained simply by equilibrating an aqueous solution of phenol with lMACH in a separatory funnel at room temperature. The mass transfer coefficient of phenol in the solvent extraction process was determined using the method of defined interface surface area. The membrane extraction of phenol was carried out in a commercial capillary dialyzer with a membrane surface area of 1.2 $m^2$. It was shown that a relatively high extraction efficiency could be achieved (over 90%) in spite of a relatively low distribution coefficient for the observed system (0.27) when the flow rate of the organic phase was higher than the flow rate of the aqueous solution of phenol.

*Key Words.* Membrane extraction; Phenol; Linear monoalcycyclohexane; Hollow fiber

---

*To whom correspondence should be addressed.

## INTRODUCTION

Phenol and phenolic derivates are chemical products commonly found in aqueous effluents from various industries. Concentrations of phenol in wastes of this kind vary in a wide range from several ppm to 2–3% (1). Removal of phenol from wastewaters has been accomplished by means of various purification techniques that involve extraction, adsorption, evaporation, or biological processes. One of the most widely used methods of removing phenol from concentrated waste streams is solvent extraction using polar organic solvents (2). An important disadvantage of this method is emulsion formation that may increase the organic loading of the treated stream, requiring additional cleanup. The membrane extraction process shows certain advantages over classical solvent extraction (a smaller amount of extracting agent, negligible loss of organic solvent, impossible formation of stable emulsion). A very large surface area per unit volume can be achieved using microporous hollow fiber extractors, which enables high separation factors, although the mass transfer coefficient is not usually high (3, 4). Moreover, in hollow fibers the two fluid flows are almost completely independent which precludes flooding, loading, or channeling (5). Hollow-fiber-shaped membranes enable construction of parallel-flow or crossflow multiphase contractors for integrated extraction–stripping (pertraction) processes (5, 6).

The primary aim of our work was to test the suitability of linear monoalcyl cyclohexane (lMACH) as an organic extractant for phenol, and the suitability of polysulfone fibers so that a special module for multistage membrane pertraction could be designed since, in our opinion, it is the optimal way for phenol removal from wastewaters. Although it has a rather low distribution coefficient compared to some polar solvents, lMACH was chosen because it has several important advantages as an extragent for phenol, especially if the membrane extraction, or even better, membrane pertraction is applied. First, it is completely nontoxic and not harmful for the environment in any way, so the recovery of residual dissolved solvent is avoided. Second, it is practically immiscible with water, and if a membrane contactor is applied it is impossible that a water–lMACH emulsion will be formed. Third, it is very convenient for multistage membrane pertraction where the stripping is performed with an alkaline solution (our paper in the preparation) since it is also immiscible with such a solution. Further, stronger solvents may require more chemically resistant fibers (e.g., polypropylene) which are generally hydrophobic. We chose polysulfone for the hollow fibers because of its hydrophilicity, so that the water–lMACH contact will be at the organic side of the membrane surface. We expect this will lower the overall mass transfer resistance for phenol, since the highest resistance will be in the organic phase based on the low organic/water distribution coefficient of phenol.

## EXPERIMENTAL

Three kinds of experiments were performed: distribution coefficient measurements, mass transfer coefficient measurements, and permeation measurements.

All experiments and solutions were maintained at room temperature (21°C).

### Distribution Coefficient Measurements

The organic/water distribution coefficient of phenol was obtained simply by equilibrating an aqueous solution of phenol (p.a. Merck) with lMACH in a separatory funnel at room temperature. In general, it took about 5 minutes to reach an equilibrium condition. The range of phenol concentration in distilled water was 5–100 mg/dm$^3$. The pH values of aqueous solutions varied from 2 to 10. The hydrogen ion concentration in the aqueous phase was controlled by adding $H_3PO_4$ or $NH_3$, and it was measured using a pH-meter (Iskra, MA 5475). The extractant phase was pure lMACH (TMF Laboratories, Belgrade) and lMACH 1:1 in gasoline (medical pure).

### Mass Transfer Coefficient Measurements

The mass transfer coefficient of phenol in the extracting process was determined using the constant interfacial area method (7). The measurements were carried out in the constant interfacial area apparatus (Lewis-type cell) shown in Fig. 1. It is made of Pyrex glass with an interfacial area of 47.75 cm$^2$. The stirrer blades were symmetrically located with respect to the interface, and the stirrer was driven using a Labo-stirrer model “Iskra” 450. In our study of the kinetics of extraction the stirring speed was varied from 50 to 200 rpm and the initial phenol concentration in aqueous solution was varied from 10 to 100 mg/dm$^3$ at pH 6.0.

### *Procedure*

First, an aqueous solution of 100 cm$^3$ volume was placed in the cell, and then an equal volume of organic solution was carefully poured into the cell along the interior wall of the cell. By doing this, the disturbance at the interface was minimized. Then the mass transfer of phenol from the aqueous phase to the organic phase started. A sample (0.5 cm$^3$) was taken at a certain time interval from the aqueous phase and analyzed.

### Permeation Measurements

The membrane extraction of phenol was carried out in a commercial capillary dialyzer (HEMOFARM, Vršac) (8) with the characteristics summarized in Table 1.

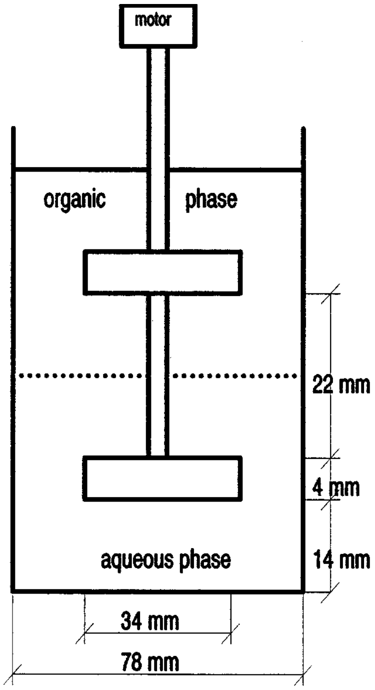

FIG. 1 A scheme of the constant interfacial area cell. Inter-facial area = 34.64 $cm^2$, and volume of organic phase (or aqueous phase) = 100 $cm^3$.

The experiments were carried out for a range of flow rates for a countercurrent feed/organic flow. A feed solution that contained 1.06 $mmol/dm^3$ phenol (pH 6.0) flowed around the capillaries, and the extractant phase (pure lMACH) flowed countercurrently through the capillaries.

TABLE 1
Characteristics of the HEMOFARM Capillary Dialyzer

| Parameter | |
|---|---|
| Internal module diameter (m) | 0.030 |
| Fiber length (m) | 0.23 |
| Membrane area ($m^2$) | 1.2 |
| Number of fibers in the module (—) | 6000 |
| Membrane material | Polysulfone |
| Membrane porosity (—) | 0.65 |
| External fiber diameter (μm) | 225 |
| Internal fiber diameter (μm) | 200 |

## Analysis

The concentration of phenol in the aqueous phase was measured spectrophotometrically by Specol (Carl Zeiss, Jena) at a wavelength of 510 nm after a complex with 4-aminoantipyrine and $K_3[Fe(CN)_6]$ was formed (9). The concentration of phenol in the organic phase was calculated using the material balance.

# RESULTS AND DISCUSSION

## Distribution Coefficients

The distribution coefficient of phenol as a function of the concentration of phenol in the aqueous phase and the pH of the aqueous phase is shown in Fig. 2 for the extractant lMACH. Inspection of the figure reveals that the distribution coefficient of phenol is practically independent on the initial concentration. However, it is dependent on the pH of the aqueous phase and has its maximum at pH 6.0 ($m = 0.27$). These results are not consistent with the expected data according to the literature (2), but they are real, and we believe that the explanation deals with the ionic strength and interphase surface tension of the solutions, and requires a more detailed analysis. However, this is

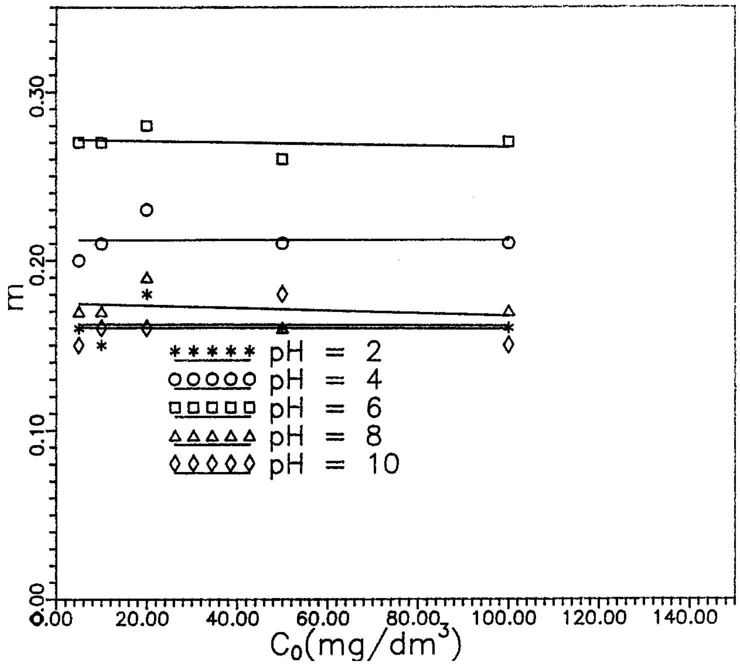

FIG. 2 Distribution coefficient of phenol as a function of the concentration of phenol in the aqueous phase for a range of pH; extractant lMACH.

not relevant to our present research, since we performed all experiments at the same pH value (6.0). The same behavior was shown for an extraction system of phenol in aqueous solution/lMACH in gasoline (1:1), but a lower value for distribution coefficient was obtained ($m = 0.17$). On the basis on distribution coefficient data, pure lMACH was chosen as the extractant in further examinations.

## Mass Transfer Coefficients

Typical experimental data of the time-dependent concentration of phenol in a kinetic run of the extraction process in the cell are shown in Fig. 3.

The mass transfer coefficient, $K$, can be calculated from the experimental data of the distribution coefficient (Fig. 2) and experimental data of the time-dependent concentration of phenol (Fig. 3) by using the Wang–Hu equation (7):

$$\left\{\frac{m}{mf+1}\ln\left[\frac{\left(\frac{C_{\mathrm{a}}}{C_{\mathrm{a},0}}-\frac{1}{mf+1}\right)}{\left(\frac{mf}{mf+1}\right)}\right]\right\} = -(KA)\cdot t \tag{1}$$

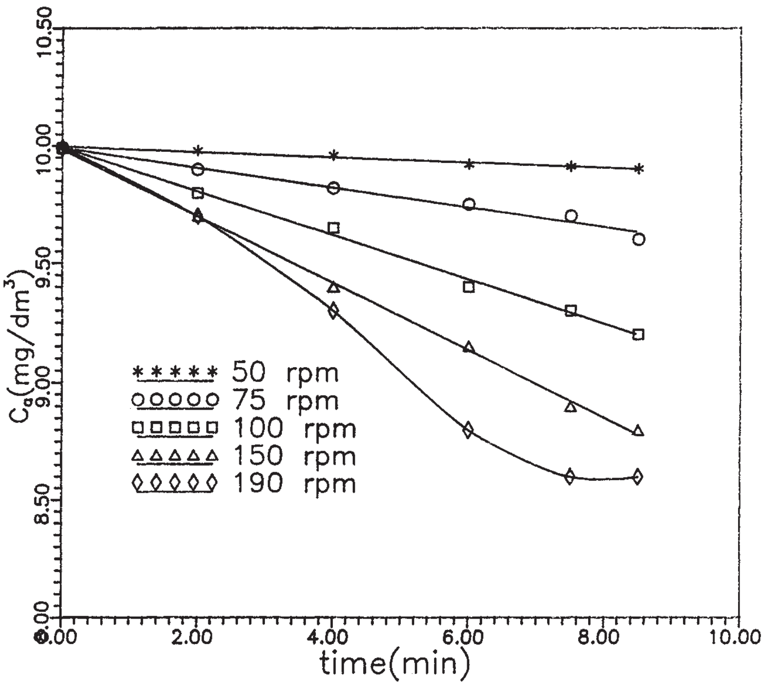

FIG. 3 The change in the concentration of phenol in the aqueous phase as a function of time: $C_0 = 10$ mg/dm$^3$, pH 6, and extractant lMACH.

where $f$ is the volume ratio of the organic phase to the aqueous phase ($V_o/V_a$), $C_a$ is the bulk concentration of phenol in the aqueous phase in time $t$, and $C_{a,0}$ is the initial concentration of phenol in aqueous phase, so for $t = 0$, $C_a = C_{a,0}$. In general, Eq. (1) is derived assuming that an equilibrium state is built up on the organic–aqueous interface, and considering a constant value for the distribution coefficient of phenol $m$, which is independent on the concentration of phenol in the aqueous phase, as it is in the present system. It was also assumed that $f$, $m$, and $K$ values are independent of time. By letting the left side of Eq. (1) be $Y$, a plot of $-Y$ value vs time exhibits a straight line with a slope of $KA$, as shown in Fig. 4. $A$ is defined as the interfacial area per unit volume of the organic phase. This slope is used to calculate the mass transfer coefficient of phenol between the lMACH and aqueous phase. It is obvious from Fig. 4 that the mass transfer coefficient strongly depends on the stirring speed. At stirring speeds over 190 rpm the interfacial surface was significantly disturbed, so that the area was not defined and constant any more. For that reason only the well-defined regime (up to 190 rpm) was observed. The highest value for $K$ ($0.97 \times 10^{-3}$ cm/s) was obtained at 190 rpm. In the simplest terms, this coefficient should equal the diffusion coefficient, which is around $10^{-5}$ cm$^2$/s for small solutes (for phenol in lMACH, $D = 0.88 \times 10^{-5}$ cm$^2$/s) (10), divided by the boundary layer thickness, around $10^{-2}$ cm (11). This gives a value close to the highest one observed.

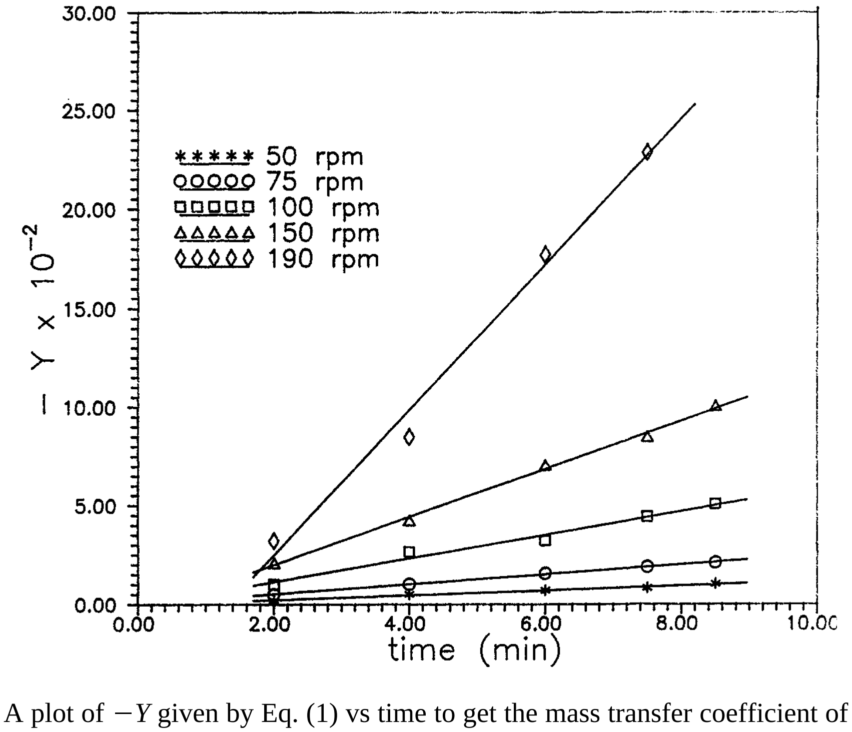

FIG. 4 A plot of $-Y$ given by Eq. (1) vs time to get the mass transfer coefficient of phenol at various stirring speeds.

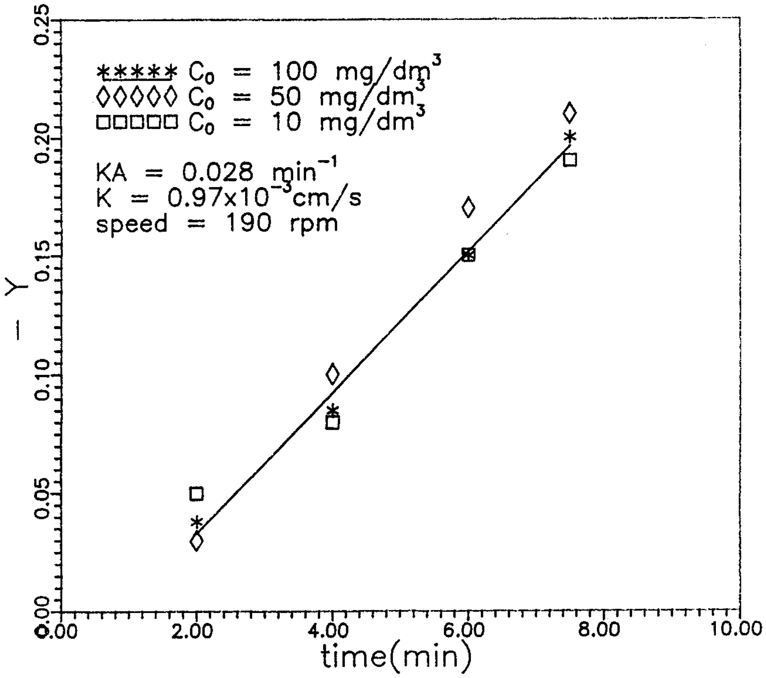

FIG. 5 A plot of $-Y$ given by Eq. (1) vs time to get the mass transfer coefficient of phenol for different initial phenol concentrations.

It is also found that this mass transfer coefficient is insensitive to the initial concentration of phenol in the aqueous phase, as shown in Fig. 5.

## Membrane Extraction

Investigation of membrane extraction of phenol from aqueous solutions with the extractant lMACH by using the hollow fiber membrane extractor reveals that a change in the feed flow rate (aqueous solution) does not affect the bulk concentration of phenol in raffinate when the flow rate of the organic solution is kept constant. However, an increase in the flow rate of the organic extractant decreases the bulk concentration of phenol in the raffinate. That means that almost all the resistance to mass transfer is located at the organic boundary layer. The efficiency of membrane extraction of phenol, defined by the equation

$$E\,(\%) = \frac{Q_E \cdot C_E}{Q_F \cdot C_{F,0}} = \left(1 - \frac{C_R}{C_{F,0}}\right) \qquad (2)$$

is presented in Fig. 6 as a function of feed and extract flow rates ($Q_F$ and $Q_E$). In Eq. (2), $C_R$ and $C_E$ are the bulk concentrations of phenol in the water raffinate and organic extract, respectively, and $C_{F.0}$ is the initial feed concentration of phenol.

Inspection of Fig. 6 reveals that a significantly higher efficiency can be obtained when the organic flow rate is higher than the feed flow rate. An efficiency of 90% was obtained when this ratio was 5:1. Furthermore, from experimental observation, no emulsion formation occurred during the operation.

The overall mass transfer coefficient can be calculated from these concentration measurements by using a transfer unit analysis. The capillary dialyzer used can be considered to be an extraction column where the raffinate and extract phases flow countercurrently as schematically presented in Fig. 7. The membrane is used to separate the water and lMACH phases. The feed, the aqueous solution of phenol, enters the column at the rate $R_1 = 24.42$ mol/h (0.44 $\text{dm}^3$/h) and a concentration of phenol $C_{R1} = 1.06 \times 10^{-3}$ mol/$\text{dm}^3$ around the fibers, and leaves the column at the other end with rate $R_2 = 22.22$ mol/h (0.4 $\text{dm}^3$/h) and concentration of phenol $C_{R2} = 0.101 \times 10^{-3}$ mol/$\text{dm}^3$. The extractant, lMACH, enters the column countercurrently at the rate $E_2 =$ 6.02 mol/h (1.8 $\text{dm}^3$/h) and a concentration of phenol $C_{E1} = 0$ inside the fibers, and leaves the column at the other end with rate $E_1 = 4.68$ mol/h (1.4 $\text{m}^3$/h) and concentration of phenol $C_{E1} = 0.213 \times 10^{-3}$ mol/$\text{dm}^3$. Since the principal diffusional resistance lies in the *E* phase (*m* small and constant), the

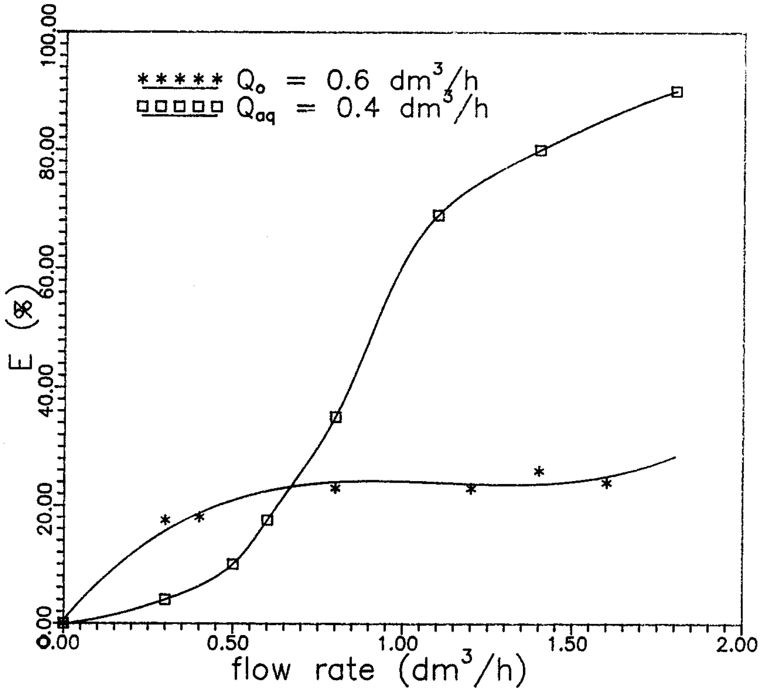

FIG. 6 Efficiency of membrane extraction of phenol as a function of feed and extractant flow rates for initial feed concentration of phenol, $C_0 = 100$ mg/$\text{dm}^3$.

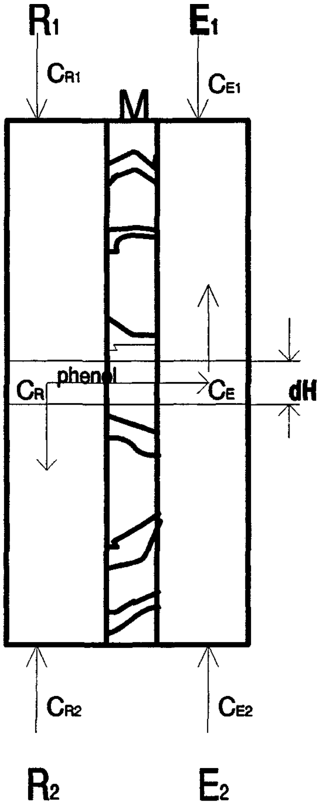

FIG. 7 Membrane extraction with continuous countercurrent contact.

following equation is used to determine the overall mass transfer coefficient of phenol in the *E* phase, $K_E$ (12):

$$K_E = \frac{E \cdot N_{tOE}}{H \cdot A(1 - x_E)_{OM} C_{Eav} S} \tag{3}$$

where $N_{tOE}$ is the number of transfer units; *H* is the column height (module length); $A = 4/d$ is the interfacial surface area per unit volume of column, where *d* is the internal diameter of the fiber; *S* is the cross-sectional area perpendicular to the diffusional direction (effective membrane surface); $C_{av}$ is the average extract concentration of phenol; and *x* is the mole fraction of phenol in solution. Subscripts E, O, and M indicate extract, overall, and mean, respectively. For very dilute solutions and constant *m*, $(1 - x_E)$ is near unity, and *R* and *E* are substantially constant. The equation for $N_{tOE}$ then becomes approximately

$$N_{tOE} = \frac{1}{1 - \frac{mE}{R}} \ln\left[\left(1 - \frac{mE}{R}\right)\left(\frac{x_{E1} - mx_{R2}}{x_{E2} - mx_{R2}}\right) + \frac{mE}{R}\right] + \frac{1}{2}\ln\frac{1 - x_{E2}}{1 - x_{E1}} \tag{4}$$

and by rearrangement of Eq. (3) becomes

$$\frac{E \cdot N_{\mathrm{tOE}}}{C_{\mathrm{Eav}}} = K_{\mathrm{E}} \cdot A \cdot S \cdot H \tag{5}$$

Since in practice there are always slight variations in $E$ and $R$ (in the present case as a consequence of pressure drop in the hollow-fiber module), somewhat more precise results are obtained by using values of these quantities at the dilute end of the system ($E_2$ and $R_2$), since the transfer units are ordinarily concentrated at this end. As $x_{\mathrm{E2}} = 0$, the last right-hand part of the equation becomes zero. Thus,

$$N_{\mathrm{tOE}} = \frac{1}{1 - \dfrac{mE_2}{R_1}} \ln\left[\left(1 - \frac{mE_2}{R_1}\right)\left(\frac{x_{\mathrm{E1}} - mx_{\mathrm{R2}}}{-mx_{\mathrm{R2}}}\right) + \frac{mE_2}{R_1}\right] \tag{6}$$

Using Eqs. (5) and (6) and experimental data, and adopting the same assumptions as above that values of $m$, $K$, and $E_2/R_1$ are independent on time, we plotted the term $EN_{\mathrm{tOE}}/C_{\mathrm{Eav}}$ vs time. Using an arithmetic average rather than a logarithmic average for $C_{\mathrm{Eav}}$, in order to simplify the calculation, is justified by the fact that an error of no more than 1.5% is incurred, which is about the same as the experimental error. The slope of the straight line presented in Fig. 8 is

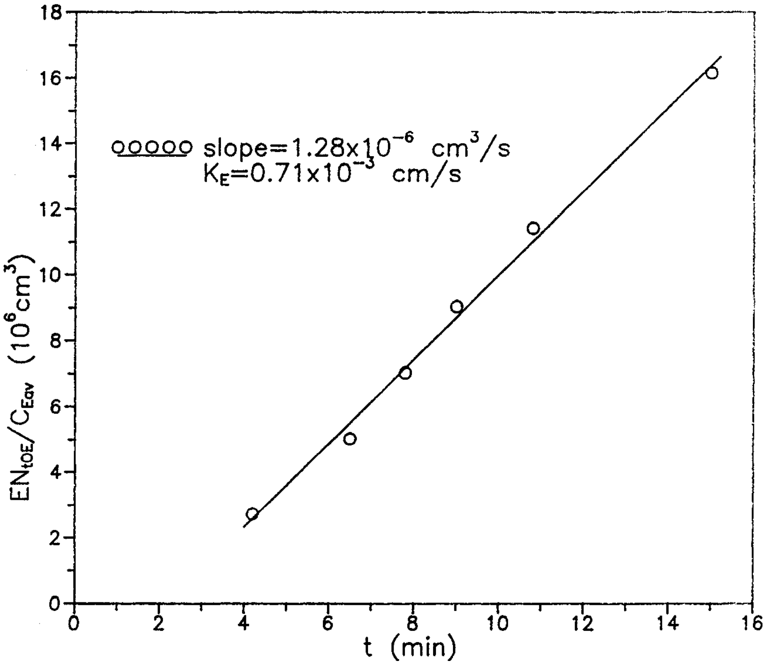

FIG. 8 A plot of $EN_{\mathrm{tOE}}/C_{\mathrm{Eav}}$ vs time to get the mass transfer coefficient of phenol at an initial feed concentration $1.06 \times 10^{-3}$ mol/dm$^3$.

$K_E \cdot A \cdot S \cdot H$, from which the mass transfer coefficient was calculated. The mass transfer coefficient could be calculated from data like those in Fig. 8 because we know the surface area per volume $A$ ($= 4/d$). The value obtained for $K_E$ is $0.71 \times 10^{-3}$, which is of the same order of magnitude as the value for $K$ obtained with Lewis's cell. The number of mass transfer units for a time of 1 hour is $N_{tOE} = 5$. Although the experiments were not performed in order to develop correlations for contactor design nor to analyze the mass transfer mechanisms, but to test the lMACH as a carrier and polysulfone fibers as the hydrophilic membrane phase for a pertraction process, the results presented above are sufficiently reliable to support the conclusion that the analyzed process is diffusional controlled, with the main resistance in the organic boundary layer in the case where a hydrophilic membrane is used. The membrane apparently offers no resistance due to ultrafiltration; otherwise it would presumably retard the mass transfer coefficient.

## CONCLUSIONS

This membrane extraction technique proved that the solvents such as lMACH, with a very low distribution coefficient, can be successfully used in the removal of phenol from water without any of the operational problems characteristic for conventional dispersion-based processes. In addition, this process completely avoids the additional contamination of treated waters. It is also concluded that the membrane extraction of phenol with lMACH is a diffusion-limited process, and the main resistance is in the organic boundary layer. When a hydrophilic membrane is used, membrane resistance seems to be significantly reduced. Considering the very low distribution coefficient of lMACH, it might be even better used as a carrier in the multistage membrane pertraction of phenol, and that will be the subject of our further research.

## ACKNOWLEDGMENT

The authors are grateful to the Serbian Scientific Council for financial support.

## REFERENCES

1. L. Boyadzhiev and S. Alexandrova, *Sep. Sci. Technol.*, *27*, 1307 (1992).
2. Y. I. Korenman, *Extraction of Phenols*, Volgo-Viatsk Pub. House, Gorky, 1977.
3. R. Prasad and K. K. Sirkar, *AIChE J.*, *34*, 177 (1988).
4. L. Dahuron and E. L. Cussler, *Ibid.*, *34*, 130 (1988).
5. A. Onjia, Z. Juric, S. Stevanovic, and M. Mitrovic, *J. Serb. Chem. Soc.*, *61*(3), 173 (1996).

6. S. Stevanovic, A. Onjia, and M. Mitrovic, "Pertraction of Solutes in Double Hollow-Fiber Membrane Pertractors," in *AIDIC Conference Series*, ERIS C.T. S.r.l., Milan, Italy, Vol. 1, 1995, p. 221.
7. M. L. Wang and K. H. Hu, *J. Chin. Inst. Chem. Eng.*, *23*(1), 9 (1992).
8. S. Stevanovic, D. Markovic, M. Mitrovic, and Y. I. Korenman, *Zh. Prikl. Khim.*, *67*(10), 1743 (1994).
9. B. Ettinger, C. C. Ruchhoft, and R. J. Lishka, *Anal. Chem.*, *23*, 1783 (1951).
10. R. H. Perry and C. H. Chilton, *Chemical Engineers Handbook*, 5th ed., McGraw-Hill, Tokyo, 1979.
11. V. G. Levich, *Physicochemical Hydrodynamics*, Prentice-Hall, New York, NY, 1962.
12. R. E. Treybal, *Mass Transfer Operations*, 3rd ed., McGraw-Hill, New York, NY, 1980.

*Received by editor October 17, 1997*
*Revision received June 1998*

PAGE 664 IS BLANK

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Downloaded At: 11:15 25 January 2011

# Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

**Order now!**

Reprints of this article can also be ordered at

http://www.dekker.com/servlet/product/DOI/101081SS100100672