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BENCH-SCALE APPLICATION OF SUPERCRITICAL FLUID EXTRACTION FOR THE REMOVAL OF PHENOL FROM AQUEOUS SOLUTION

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ABSTRACT

The supercritical fluid extraction of phenol, a common pollutant, from aqueous solutions is performed in a bench-scale extraction apparatus through the use of supercritical CO_2 at 150 bar and 45°C. The obtained results are satisfactory, and the influence of pressure and flow rate of supercritical CO_2, as well as the co-solvent effect, are examined. Finally, the LCVM (Linear Combination of Vidal and Michelsen) mixing rules model, an EoS/G^E (Equation of State/Gibbs free energy) one, thermodynamic model with new interaction parameters, combined with a simple mathematical one, is used successfully for the correlation of the experimental results by adjusting the overall volumetric mass transfer coefficients of the process.

Key Words: Supercritical fluid extraction; Flow rate; Pressure; Co-solvent; EoS/G^E model; Overall volumetric mass transfer coefficients

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INTRODUCTION

In recent years, the supercritical fluids (SCFs) have attracted substantial interest in the chemical engineering community due to the intense need for inexpensive, nontoxic solvents to overcome the problems created by the escalating costs of energy-intensive separation methods (e.g. distillation), the inability of traditional techniques to provide the separations needed for emerging new industries (microelectronics, biotechnology, etc.), and the safety and environmental restrictions associated with common industrial solvents. As a result, interest in supercritical fluid extraction (SFE) as a viable commercial separation technique has been renewed.

Recently, special attention has been given to the application of SFE in environmental control (1), where three major areas have been mainly studied: extraction of organic contaminants from water (2–6), extraction of organics from contaminated soil (6), and extraction of organics from adsorbents. This can be attributed to the fact that each year increasing amounts of hazardous wastes, mostly in the form of water contaminated with toxic organic compounds, are produced and cannot be treated satisfactorily by available conventional methods. Distillation and incineration are adequate for highly concentrated solutions, but both of them are energy intensive, while the latter also requires proper disposal of the solid residue (ash). Adsorption and biodegradation are preferable for very low contamination levels (ppm levels), while air stripping is most effective for volatile compounds. However, the regeneration of the adsorbent for the former case and the sludge disposal as well as the large time requirements for the latter one restrict the applicability of these methods. Finally, liquid extraction, although a viable technique, has limited use due to the presence of residual solvent in the processed water, the recovery of which is a very energy-consuming process.

Consequently, SFE appears to be an attractive alternative to the aforementioned methodologies, as it can remove a broad range of organic solutes from aqueous systems at low operating temperatures. SFE also employs nontoxic solvents, such as CO_2, that are easily removed from the final product.

The removal of phenol, a common toxic pollutant, from water with the help of supercritical CO_2 is examined in this study. The thermodynamic modeling and the design of the process have already been presented (7). The former was achieved with the use of an EoS/G^E (Equation of state/Gibbs free energy) model, the LCVM (Linear combination of Vidal and Michelsen mixing rules) (8) with satisfactory results. With this model, a unit for the SCF extraction of phenol from industrial wastewater was designed and the operating parameters of this unit were optimized. Although the application of SFE in the treatment of aqueous waste is feasible, the need for high pressures significantly increases the equipment cost. However, the use of an appropriate co-solvent, which increases the equilibrium coefficients, K, of the pollutant can decrease the cost considerably (3,6,7).

In this work, a bench-scale unit was used to study the removal of phenol from aqueous solutions and obtain water clear enough to be disposed into the sea. The maximum content of phenol in wastewater disposed in the Saronikos Bay (Greece) is not to exceed 0.5 ppm according to Greek regulations. The influence of pressure and flow rate of CO_2 is examined as well as the co-solvent effect. Moreover, the experimental data were correlated by a simple mathematical model combined with the LCVM model with the new interaction parameters of UNIFAC (7). The overall volumetric mass transfer coefficients are evaluated through this process.

EXPERIMENTAL

Apparatus

Figure 1 shows a schematic of the apparatus used in our experiments. The SFE 500 (SEPAREX Chimie Fine) unit is designed to conduct development research on a wide range of supercritical extraction applications. Many different solid and liquid raw materials can be tested in batch operation and the results obtained can be readily scaled up.

The apparatus is composed of a high-pressure vessel and two high-performance cyclonic separators with an internal volume of 18 ml each, operating at pressures up to 300 bar. The high-pressure vessel contains a 400-ml extraction

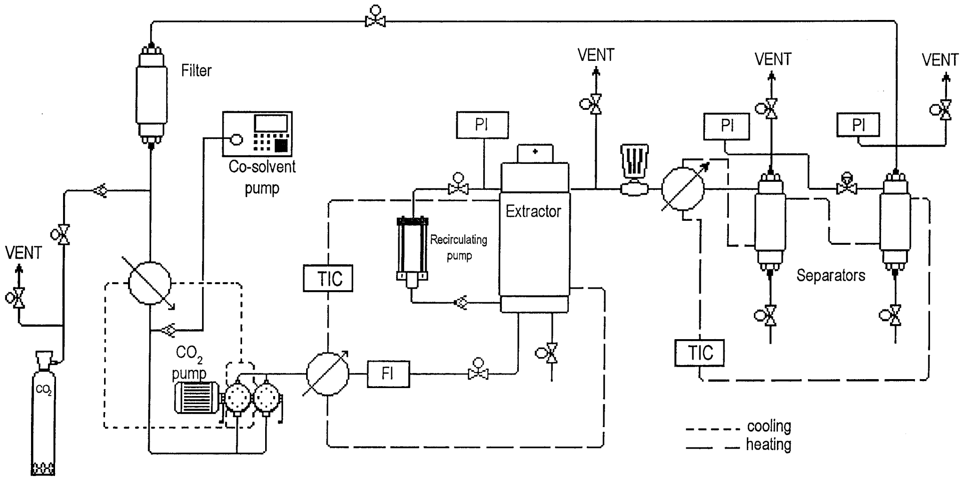

Figure 1. Flow diagram for the SFE 500 apparatus. PI: pressure indicator, FI: flow indicator, TIC: temperature indicator and control.

cylinder with ends closed with stainless-steel porous disks. A high-pressure membrane pump with jacketed heads for cooling, capable of a CO_2 flow rate of up to 5 kg/h, pressurizes the solvent, while a pneumatic pump may recirculate the SCF in the extractor. Furthermore, a co-solvent can be added in the system by a piston pump. A cooling system condenses CO_2, and two heating baths control the operating temperatures in the jacketed extractor and separators to a maximum of 70°C. Valves are used to regulate the pressure in the extractor and the separators, while a solvent mass flowmeter is placed just before the extractor. An electronic interface indicates the temperature, the density, the flow rate, and the mass of CO_2 passed through the extractor.

Materials

Liquid carbon dioxide with a purity of 99.5% at 49.5 bar (15°C) was purchased from Air-Liquide, Greece. High-performance liquid chromatography water and analytical reagent toluene were provided by LAB-SCAN. Solid phenol with purity 99.5% was purchased from Riedel-de Haen. Also, the helium (99.996%), synthetic air (99.998%), and hydrogen (99.96%) used in gas chromatography were supplied by Messer Griesheim GmbH.

Experimental Procedure

A solution of 1% phenol in water was prepared and fed into the extraction cylinder, which was filled with glass beads to ensure larger contact surface between the continuous phase (liquid) and the dispersed one (CO_2). In this way, the free volume of the extractor container is reduced by 50%. To prevent the dilation or overflow of the feed, the extraction basket was not filled to the top. Thus, approximately 100 g of the mixture were used in each experiment.

The two separators were operated at 35 ± 0.1°C and the solvent was not recycled. The pressure effect was studied at 45 ± 0.1°C and 1 ± 0.1 kg/h, the flow rate effect at 150 ± 1 bar and 45°C, and the co-solvent effect at 150 bar, 45°C, and 1 kg/h. Each experiment was ended when the desired amount of CO_2 had passed (± 0.1 kg). Then the extract and the residue were collected and analyzed.

Analysis

The analysis of the residue was conducted with a gas chromatography system (FISONS, 8000 Series) equipped with a flame ionization detector and a packed DB-WAX column. Helium (35 cm^3/min at 27 °C) was the carrier gas, and the detector temperature was 250°C. The oven temperature was constant at 140°C. Different reference curves have been prepared for the different concentration levels of phenol in water. The range of accuracy of these measurements varies from ± 1% to ± 5% as the concentration of phenol in water was decreased.

EXPERIMENTAL RESULTS

Determination of the Phenol-Removal Curve

To examine the feasibility of the process, the removal of phenol from aqueous solutions was studied thoroughly at 150 bar, 45°C, and 1 kg/h. The obtained results for phenol are presented in Fig. 2. The limiting phenol concentration (0.5 ppm) outlined by Greek regulations was reached after the consumption of approximately 7.5 kg CO_2.

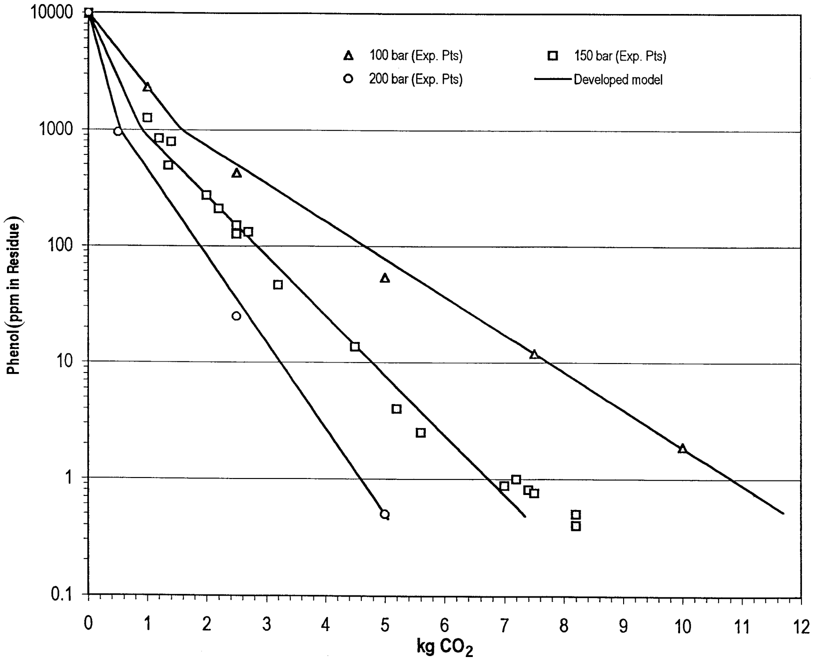

Figure 2. Pressure effect in the extraction rate of phenol. Exp. Pts., experimental data.

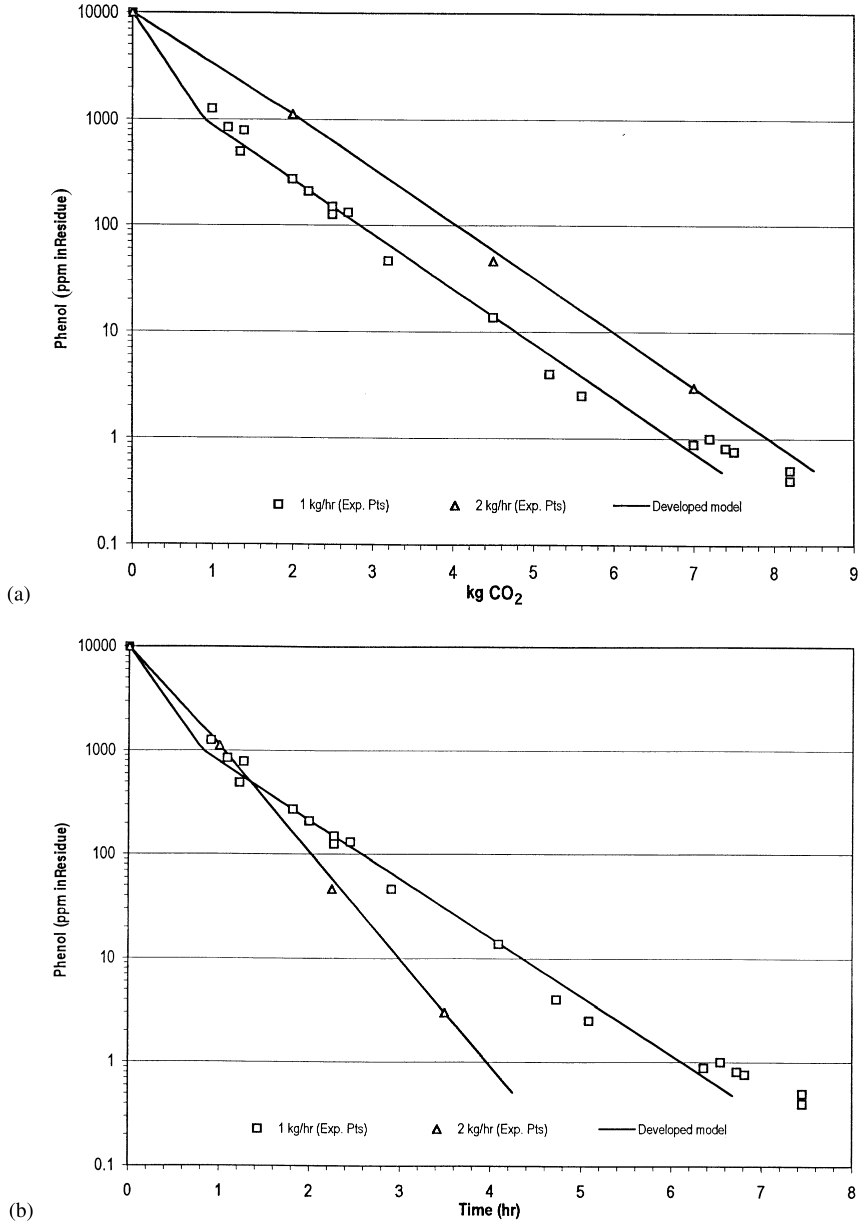

Figure 3. (a) Flow rate effect in the extraction rate of phenol with respect to CO_2 consumption. (b) Flow rate effect in the extraction rate of phenol with respect to time. Exp. Pts., experimental data.

Effect of Pressure

To examine the extraction pressure effect on the removal of phenol, two additional pressures were tested (100 and 200 bar). The three extraction curves for phenol are presented in Fig. 2. Pressure, as these curves indicate, is a very important parameter for extraction. It considerably increases the extraction rate due to the increase of the phenol solubility in CO_2. This phenomenon was more pronounced at lower pressures (100 to 150 bar). However, the increase of operating pressure leads to higher operating and equipment costs.

Effect of CO_2 Flow Rate

CO_2 flow rates of 1 and 2 kg/h were used to study the effect flow rate on the removal of phenol. In Fig. 3a, the phenol concentration in the residue is plotted versus CO_2 consumption (kg), and in Fig. 3b, it is plotted against time (h). The increase of the solvent flow rate resulted in an increase of the amount of phenol extracted with respect to time. Consequently, the productivity of the unit was increased. However, the associated increase in CO_2 consumption leads to increased operating costs. Therefore, the solvent flow rate should be optimized in each case with respect to the total cost (7,9).

Effect of Co-solvent

The LCVM model was used to select a proper co-solvent for study. Prediction results obtained with LCVM for several potential co-solvents showed that aromatic compounds were the most promising. These results were also supported by the literature (3). Toluene was finally selected because it is less hazardous than the other aromatics under consideration, such as benzene, chlorobenzene, etc. The extraction curve of phenol was determined at 45°C, 150 bar, and a solvent/co-solvent flow rate of 1 kg/h with 5% mol co-solvent. The results are presented in Fig. 4, which clearly shows that the use of a co-solvent led to an increase in the extraction rate. As a consequence of co-solvent use, the duration of the extraction was shortened and CO_2 consumption was decreased.

CORRELATION OF THE EXPERIMENTAL RESULTS

The Model

To describe the SFE of phenol in the extractor, a model was developed based on the assumption that no axial or radial distribution of the

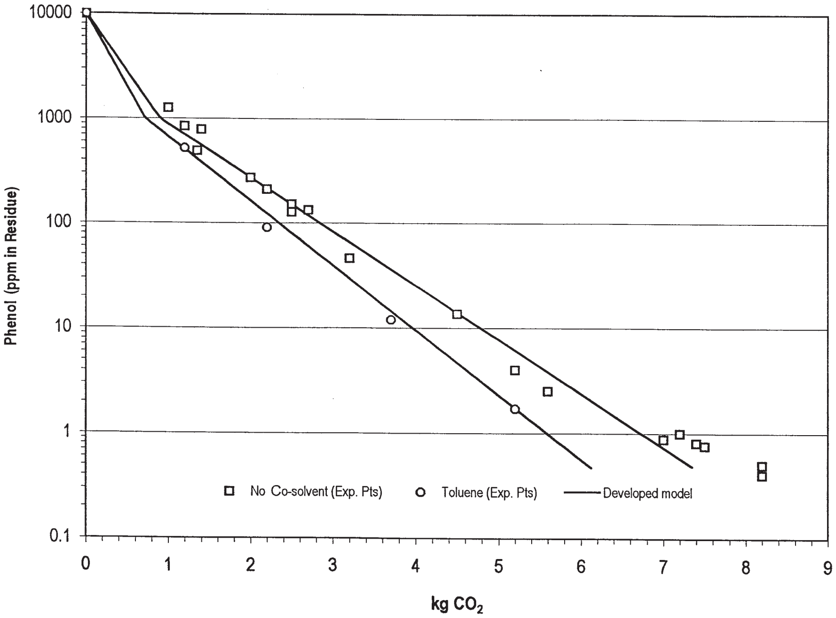

Figure 4. Prediction of co-solvent effect in the extraction rate of phenol. Exp. Pts., experimental data.

components existed. The mass balances in the extractor are presented as follows:

$$\frac{W}{\rho} \cdot y_i + V^{\text{vap}} \cdot \frac{dy_i}{dt} = J_i \tag{1}$$

$$V^{\text{liq}} \cdot \frac{dx_i}{dt} = -J_i \tag{2}$$

$$\alpha K_i \cdot (x_i - x_i^*) = J_i \tag{3}$$

$$x_i^* = \frac{y_i}{K_i^{\text{LCVM}}} \tag{4}$$

The symbols used are explained in the nomenclature at the end of this paper.

Equation (1) represents the mass transfer rate of component i in the vapor phase; Eq. (2) represents the mass transfer rate of component i in the liquid phase; Eq. (3) represents the mass transfer rate through the interface; and Eq. (4) represents equilibrium at the interface. By combining Eqs. (1–4), the following system of ordinary differential equations is obtained:

$$\frac{W}{\rho}\cdot y_i + V^{\text{vap}}\cdot\frac{dy_i}{dt} + V^{\text{liq}}\cdot\frac{dx_i}{dt} = 0 \tag{5a}$$

$$V^{\text{liq}}\cdot\frac{dx_i}{dt} = -\alpha K_i\cdot\left(x_i - \frac{y_i}{K_i^{\text{LCVM}}}\right) \tag{5b}$$

This system has a unique solution for the initial condition: $t = 0$, $x = x_0$, $y = y_0$, and it was solved by employing the Runge-Kutta-Verner (5th and 6th order) algorithm provided by the International Mathematical and Statistical Library. The only adjustable parameter of the model is αK_{ph}, as the parameters V^{vap}, V^{liq}, and K_i^{LCVM} are obtained from the LCVM model (8) as revised by Boukouvalas et al. (7).

LCVM has been proposed by Boukouvalas et al. (8) for the prediction of vapor-liquid equilibria of various systems. It is a very successful EoS/G^{E} model with a wide range of applicability. The main characteristic of this type of model is that the mixing rule for the attractive parameter a of the EoS is derived by setting the expression for G^{E}, obtained from the EoS, equal to that from an existing G^{E} model. The LCVM model combines the translated PR (Peng-Robinson) (Eq. 6), as it was modified by Magoulas and Tassios (10), with the original UNIFAC, a widely applicable G^{E} model, which is being updated and extended regularly (11), through the mixing rules presented in Eqs. (7) and (8):

$$P = \frac{\text{RT}}{V + \tau - b} - \frac{a}{(V + \tau)(V + \tau + b) + b(V + \tau - b)} \tag{6}$$

$$\alpha = \Sigma x_i\alpha_{\text{i}} + \left(\frac{\lambda}{A_v} + \frac{1-\lambda}{A_M}\right)\frac{G^{\text{E}}}{\text{RT}} + \frac{1-\lambda}{A_M}\Sigma x_i\ln\left(\frac{b}{b_i}\right) \tag{7}$$

with $\alpha = a/b\text{RT}$, $\lambda = 0.36$, $A_V = –0.623$, $A_M = –0.52$

$$b = \Sigma x_i b_i \tag{8}$$

More details about the development of LCVM, along with results of the model's behavior, are available in various publications (7,8,12–15).

Correlation Results

To describe the experimental results, the overall volumetric mass transfer coefficient of phenol had to be calculated, but because the coefficient value depends on the phenol concentration, it was not possible to describe the whole concentration range with a single value. Therefore, two overall volumetric

Table 1. Optimum Model Parameters at Different Pressures

Pressure (bar)	αK_{ph} $(x > x_c)$ (m³/s)	αK_{ph} $(x < x_c)$ (m³/s)
100	6.67E–08	2.71E–08
150	9.19E–08	3.88E–08
200	13.3E–08	5.44E–08

$x_c = 1000$ ppm

mass transfer coefficients were determined, one for high phenol concentration $(x > x_c)$ and another one for low $(x < x_c)$; x_c was set equal to 1000 ppm for all cases.

The optimum values for the mass transfer coefficients in the pressure-effect experiments are presented in Table 1. The order of magnitude of these coefficients, 10^{-8} m³/s, is in agreement with the results noted in literature (16) for packed towers. The correlation of the experimental results is satisfactory, as shown in Fig. 2. Because of the increased extraction rate, the αK_{ph} values increased with respect to pressure. The mass transfer coefficients corresponding to the high concentration region of the extraction curve were higher than those of the second part.

The effect of solvent flow rate was also described satisfactorily. The results obtained are presented in Table 2 and Figs. 3a and 3b. Due to insufficient number of experimental data available to represent the first region of the extraction curves, no safe conclusions can be reached about the values of αK_{ph}. For the second region, αK_{ph} increased with the flow rate.

Finally, by assuming that these coefficients are not affected by the presence of the co-solvent (the amount of toluene in the system is not significant), prediction of the extraction curve for phenol was attempted. The prediction results are presented in Fig. 4, and they are very satisfactory.

Table 2. Optimum Model Parameters at Different Flow Rates

Flow rate (kg/h)	αK_{ph} $(x > x_c)$ (m³/s)	αK_{ph} $(x < x_c)$ (m³/s)
1	9.19E–08	3.88E–08
2	6.47E–08	7.08E–08

$x_c = 1000$ ppm

CONCLUSIONS

The removal of up to 0.5 ppm phenol from water succeeded in a bench-scale unit through the use of supercritical carbon dioxide. The effects of parameters, such as total amount of CO_2 consumed, pressure, solvent flow rate, and co-solvent were also examined.

The extraction pressure is a very important design parameter because its increase leads to the increase of the phenol extraction rate, but at the expense of the capital cost.

By increasing the solvent flow rate, lower extraction times were achieved, which is important because the productivity of the unit is also increased. However, at the same time the CO_2 consumption increases too, and consequently, the operating cost becomes higher.

Co-solvent is another significant operating parameter. It can make the extraction more effective and less expensive.

A simple mathematical model based on the mass balances in the extractor, combined with a successful thermodynamic model, was developed to describe the process. Successful results were obtained by adjusting only the overall volumetric mass transfer coefficient.

NOMENCLATURE

αK	overall volumetric mass transfer coefficient (m^3/s)
b	EoS parameter
G^E	Gibbs Excess free energy
J_i	Mass transfer rate of component i (kg/s)
K_i^{LCVM}	distribution coefficient of component i
P	pressure (bar)
R	gas constant (m^3 bar/kmol·K)
t	time (s)
T	temperature (K)
V	molar volume (m^3/kmol)
V^{liq}	liquid volume (m^3)
V^{vap}	vapor volume (m^3)
W	CO_2 mass flow rate (kg/s)
x_i^*	concentration of the liquid-fluid interface, which is to be at equilibrium with the fluid phase y_i (kg/m^3)
x_i	liquid concentration of component i (kg/m^3)
y_i	vapor concentration of component i (kg/m^3)

Greek symbols

α	EoS parameter
λ	LCVM parameter
ρ	solvent density (kg/m^3)
τ	volume translation ($m^3/kmol$)

Subscripts

c	phenol concentration controlling the transition in the extraction curve
i	component i
ph	phenol

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