

# Liquid–Liquid Equilibria and Partitioning of *o*-Chlorophenol in Ethylene Glycol Monobutyl Ether + Water, Diethylene Glycol Monohexyl Ether + Water, and Poly(oxyethylene(4)) Lauryl Ether + Water

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Liquid–liquid equilibria of ethylene glycol monobutyl ether (C<sub>4</sub>E<sub>1</sub>) + water and diethylene glycol monohexyl ether (C<sub>6</sub>E<sub>2</sub>) + water at atmospheric pressure were measured for temperature ranges of 322.8 K and 273.2 K to 382.5 K, respectively. The lower critical solution temperature (LCST) and upper critical solution temperature (UCST) of C<sub>4</sub>E<sub>1</sub> + water were determined to be 322.8 K and 402.8 K, respectively. The LCST of C<sub>6</sub>E<sub>2</sub> + water is 273.2 K, while the corresponding UCST does not exist. The equilibrium compositions of *o*-chlorophenol partitioning in the top and bottom phases of the three binary C<sub>4</sub>E<sub>1</sub> + water, C<sub>6</sub>E<sub>2</sub> + water, and poly(oxyethylene(4)) lauryl ether (C<sub>12</sub>E<sub>4</sub>) + water mixtures were also measured.

## Introduction

Above the cloud points of an aqueous solution containing a nonionic surfactant, the solution may separate into two phases—a dilute aqueous phase and a phase containing the surfactant in high concentration, which is sometimes called the coacervate phase. The concentration of the nonionic surfactant in the coacervate phase can be relatively high in general, e.g., 20 mass %. However, the concentration in the dilute phase is usually low, but generally greater than the critical micelle concentration (Corti et al., 1984). In this case, the lowest temperature at which the solution becomes cloudy and its corresponding concentration are referred to as the lower critical solution temperature (LCST). At sufficiently high temperature, the multiple phase solution may again become one phase; i.e. the system may show an upper critical solution temperature (UCST).

Cloud points of various types of nonionic surfactants in aqueous solutions have been reported in the literature (Sjöblom and Stenius, 1989). For some nonionic surfactants, the cloud point phenomena can occur without phase separation.

The organic solute present in the nonionic aqueous solution will concentrate in the coacervate phase after phase splitting. It has been observed that the concentration ratios of organic solute between the coacervate and the dilute phase exceed 10. The separation and purification process based on the coacervation phenomena is not well established.

In previous work, Lee and Lee (1995) measured the liquid–liquid equilibria for Triton X-100 + water as a function of pressure. In this study, the liquid–liquid equilibria (LLE) of the ethylene glycol monobutyl ether + water, diethylene glycol monohexyl ether + water, and poly(oxyethylene(4)) lauryl ether + water systems containing *o*-chlorophenol were measured as a function of temperature and the corresponding partition ratios were measured.

## Experimental Section

**Chemicals.** Ethylene glycol monobutyl ether of 99 mol % was obtained from Sigma. Diethylene glycol monohexyl

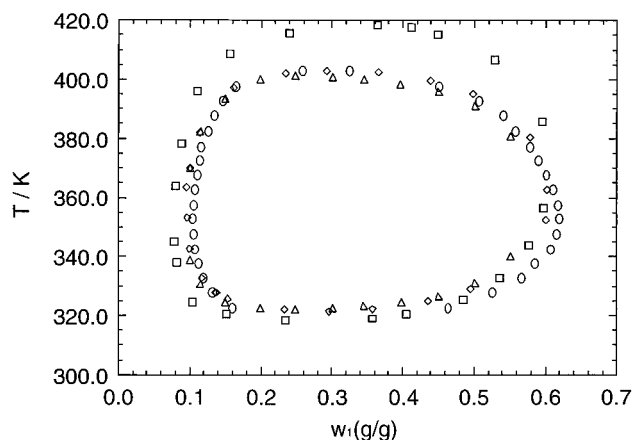
**Table 1. Temperature and Mass Fractions of Ethylene Glycol Monobutyl Ether and Diethylene Glycol Monohexyl Ether in the Top (*w<sub>T</sub>*) and Bottom Phases (*w<sub>B</sub>*) of Ethylene Glycol Monobutyl Ether (C<sub>4</sub>E<sub>1</sub>) (1) + Water (2) and Diethylene Glycol Monohexyl Ether (C<sub>6</sub>E<sub>2</sub>) (1) + Water (2)**

| C <sub>4</sub> E <sub>1</sub> + water |                          |                          | C <sub>6</sub> E <sub>2</sub> + water |                          |                          |
|---------------------------------------|--------------------------|--------------------------|---------------------------------------|--------------------------|--------------------------|
| <i>T</i> /K                           | <i>w<sub>T</sub></i> (T) | <i>w<sub>T</sub></i> (B) | <i>T</i> /K                           | <i>w<sub>T</sub></i> (T) | <i>w<sub>T</sub></i> (B) |
| 322.8                                 | 0.463                    | 0.160                    | 273.2                                 | 0.068                    | 0.020                    |
| 327.8                                 | 0.525                    | 0.132                    | 278.3                                 | 0.257                    | 0.017                    |
| 332.7                                 | 0.565                    | 0.119                    | 283.4                                 | 0.412                    | 0.014                    |
| 337.7                                 | 0.584                    | 0.112                    | 288.5                                 | 0.488                    | 0.014                    |
| 342.5                                 | 0.607                    | 0.107                    | 293.6                                 | 0.562                    | 0.013                    |
| 347.7                                 | 0.616                    | 0.105                    | 298.7                                 | 0.598                    | 0.013                    |
| 352.8                                 | 0.619                    | 0.103                    | 303.8                                 | 0.625                    | 0.013                    |
| 357.6                                 | 0.617                    | 0.105                    | 308.8                                 | 0.652                    | 0.013                    |
| 362.8                                 | 0.611                    | 0.107                    | 313.9                                 | 0.677                    | 0.013                    |
| 367.7                                 | 0.601                    | 0.111                    | 317.9                                 | 0.694                    | 0.013                    |
| 372.8                                 | 0.590                    | 0.113                    | 322.8                                 | 0.713                    | 0.012                    |
| 377.2                                 | 0.578                    | 0.116                    | 327.8                                 | 0.733                    | 0.012                    |
| 382.5                                 | 0.557                    | 0.125                    | 332.7                                 | 0.746                    | 0.012                    |
| 387.7                                 | 0.541                    | 0.134                    | 337.7                                 | 0.761                    | 0.011                    |
| 392.8                                 | 0.506                    | 0.146                    | 342.5                                 | 0.772                    | 0.011                    |
| 397.6                                 | 0.451                    | 0.165                    | 347.7                                 | 0.781                    | 0.011                    |
| 402.8                                 | 0.324                    | 0.258                    | 352.8                                 | 0.786                    | 0.011                    |
|                                       |                          |                          | 357.6                                 | 0.792                    | 0.010                    |
|                                       |                          |                          | 362.8                                 | 0.797                    | 0.010                    |
|                                       |                          |                          | 367.7                                 | 0.802                    | 0.010                    |
|                                       |                          |                          | 372.8                                 | 0.804                    | 0.010                    |
|                                       |                          |                          | 377.2                                 | 0.806                    | 0.010                    |
|                                       |                          |                          | 382.5                                 | 0.807                    | 0.010                    |

ether of 98 mol % was supplied by Aldrich and poly(oxyethylene(4)) lauryl ether was provided by Sigma. Double distilled *o*-chlorophenol (99.0 mol %) was given by Junsei. Acetonitrile (>99.8 mass %, gradient grade) was obtained from Merck and used as a mobile phase of the HPLC. Triple distilled water was used.

**Apparatus and Procedure.** The liquid–liquid equilibria of ethylene glycol monobutyl ether + water and diethylene glycol monohexyl ether + water were made at atmospheric pressure. The temperature of all samples was controlled by a water bath (Jeio Tech, MC-31) for low temperatures (273.2 K to 353.1 K) and a oil bath (HAAKE, N2) for high temperatures (353.1 K to 402.8 K). The bath temperatures were measured by a K-type thermocouple

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**Figure 1.** Liquid-liquid equilibria for the ethylene glycol monobutyl ether (1) + water (2) system at atmospheric pressure: (○) this work; (□) Chakhovsky, 1956; (△) Cox and Cretcher, 1926; (◇) Schneider, 1963.

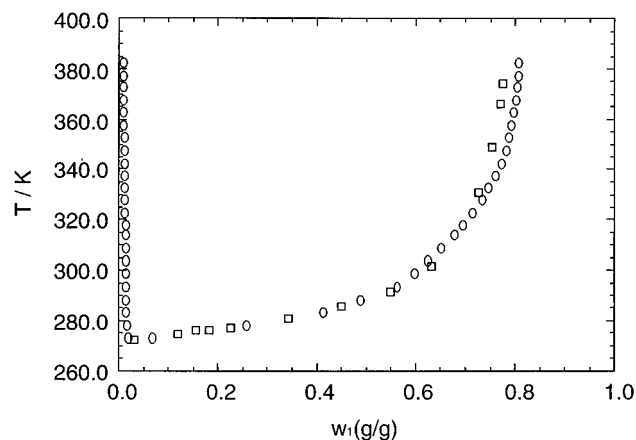
(Cole Parmer, 08532-31) and a thermometer (Cole Parmer, 89500-00) having a resolution of  $\pm 0.1$  K and an accuracy of  $\pm 0.7$  K.

For the liquid-liquid equilibria of the nonionic surfactant + water system, the aqueous solutions containing a nonionic surfactant of about  $10 \text{ cm}^3$  in the  $30 \text{ cm}^3$  test tubes were placed in the bath for 30 min. After the desired temperature was set, the samples were stirred. All samples usually split into two phases within 5 min. The equilibrium time of 4 h was confirmed by measuring the concentration of each phase as a function of time. After 4 h, the variances of the concentration with time are within  $\pm 0.0005$ . Samples in the top and bottom phases were collected using syringes with a volume of  $1 \text{ cm}^3$  in order not to disturb the equilibrium state.

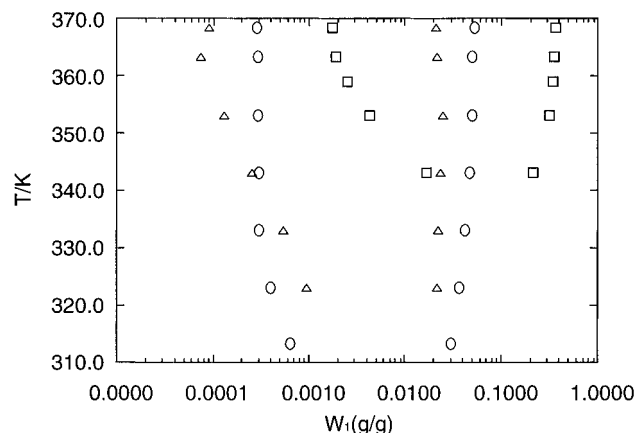
To examine the *o*-chlorophenol partitioning of the top and bottom phases,  $100 \mu\text{L}$  of *o*-chlorophenol was added to the total  $10 \text{ cm}^3$  of aqueous surfactant solution. The phase compositions were determined by an Abbe refractometer (Atago, 3T) for the binary nonionic surfactant + water system and HPLC (Waters, 501 pump, 486 Detector) for the ternary surfactant + water + *o*-chlorophenol system. The refractometer temperature was controlled by a water bath (HAAKE, N2) to within  $\pm 0.01$  K. The maximum experimental errors for the top and bottom phase analyses were less than 0.1 mass % for two binary systems. Acetonitrile + water (40:60 by volume) was used for the mobile phase of the HPLC. A  $\mu\text{Bondapak C}_{18}$   $125 \text{ \AA}$   $10 \text{ m}$  (Waters) column was used for this analysis. The flow rate of the mobile phase was  $0.9 \text{ cm}^3 \cdot \text{min}^{-1}$ .

## Results and Discussion

The liquid-liquid equilibrium data for the ethylene glycol monobutyl ether + water and diethylene glycol monoethyl ether + water at atmospheric pressure are presented in Table 1 and compared with the existing literature values (Cox and Cretcher, 1926; Chakhovsky, 1956; Schneider, 1963) in Figures 1 and 2, respectively. For the ethylene glycol monobutyl ether + water system, the LLE data of the present study show a small deviation from Cox and Schneider's data for the entire surfactant concentration and temperature between the UCST and LCST. Chakhovsky's data deviate significantly from the experimental LLE data of this study at high temperatures and particularly near the UCST. This deviation may be due to their experimental method. The methods used in the work of Cox and Schneider and Chakhovsky are similar. They determined the cloud point of weighted



**Figure 2.** Liquid-liquid equilibria for the diethylene glycol monoethyl ether (1) + water (2) system at atmospheric pressure: (○) this work; (□) Chakhovsky, 1956.



**Figure 3.** Partitioning of *o*-chlorophenol (1) in the three ethylene glycol monobutyl ether + water, diethylene glycol monoethyl ether + water, and poly(oxyethylene(4)) lauryl ether + water binary systems at atmospheric pressure: (□) poly(oxyethylene(4)) lauryl ether + water; (○) diethylene glycol monoethyl ether + water; (△) ethylene glycol monobutyl ether + water.

**Table 2. Temperature and Mass fractions of *o*-Chlorophenol in the Top ( $w_T$ ) and Bottom Phase ( $w_B$ ) of Ethylene Glycol Monobutyl Ether ( $C_4E_1$ ) (1) + Water (2), Diethylene Glycol Monoethyl Ether ( $C_6E_2$ ) (1) + Water (2) and Poly(oxyethylene(4)) Lauryl Ether ( $C_{12}E_4$ ) (1) + Water (2)**

| $C_4E_1$ + water |           |           | $C_6E_2$ + water |           |           | $C_{12}E_4$ + water |           |           |
|------------------|-----------|-----------|------------------|-----------|-----------|---------------------|-----------|-----------|
| $T/K$            | $w_1$ (T) | $w_1$ (B) | $T/K$            | $w_1$ (T) | $w_1$ (B) | $T/K$               | $w_1$ (T) | $w_1$ (B) |
| 323.1            | 0.0214    | 0.0010    | 313.2            | 0.0296    | 0.0006    | 343.1               | 0.2127    | 0.0167    |
| 333.1            | 0.0222    | 0.0005    | 323.1            | 0.0367    | 0.0004    | 353.1               | 0.3100    | 0.0042    |
| 343.1            | 0.0234    | 0.0003    | 333.1            | 0.0417    | 0.0003    | 359.2               | 0.3394    | 0.0025    |
| 353.1            | 0.0245    | 0.0001    | 343.1            | 0.0474    | 0.0003    | 363.3               | 0.3476    | 0.0019    |
| 363.3            | 0.0216    | 0.0001    | 353.1            | 0.0502    | 0.0003    | 368.5               | 0.3617    | 0.0017    |
| 368.5            | 0.0211    | 0.0001    | 363.3            | 0.0497    | 0.0003    |                     |           |           |
|                  |           |           | 368.5            | 0.0519    | 0.0003    |                     |           |           |

amount of water and nonionic surfactant solution visually by noting the temperature at which a solution heated above the cloud temperature lost its turbidity on cooling. The temperature at which the scale of the thermometer was visible in the solution was recorded as the cloud point. The heating and cooling rates were regulated to about  $1 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$  around the cloud point. However, we measured the phase behavior with direct sampling and analysis. The visual method can determine the cloud point at huge concentrations with some accuracy but is subject to error at low concentrations. Phase transition in a surfactant system can be very difficult to obtain accurately by a visual technique (McFann and Johnston, 1993). For the dieth-

ylene glycol monoethyl ether + water system, the experimental LLE data of this study show a slight deviation near the LCST and a large deviation at high temperatures when compared with Chakhovsky's data. Unfortunately, the LLE data in the water-rich phase having the very low surfactant concentration were not reported in the literature.

For these two systems, the top phases were the coacervate phase because the density of water is higher than that of the surfactant. The LCST and UCST of ethylene glycol monobutyl ether + water were found to be 322.8 K and 402.8 K, respectively. The LCST of diethylene glycol monoethyl ether + water was found to be 273.2 K, and the corresponding UCST does not exist. The concentration difference of diethylene glycol monoethyl ether between the dilute and coacervate phases increases with temperature.

The equilibrium partitioning of *o*-chlorophenol in the top and bottom phases of the binary ethylene glycol monobutyl ether + water, diethylene glycol monoethyl ether + water, and poly(oxyethylene(4)) lauryl ether + water mixtures are shown in Figure 3, and their values are listed in Table 2. The overall LLE behavior of these three systems seems to be very similar to that of the corresponding binary systems. The concentration differences of *o*-chlorophenol in the top and bottom phases for the two binary diethylene glycol monoethyl ether + water and poly(oxyethylene(4)) lauryl ether + water mixtures become large with increasing

temperature. The concentration differences of *o*-chlorophenol in the top and bottom phases for the binary ethylene glycol monobutyl ether + water mixtures show a maximum with increasing temperature. The concentration ratios of *o*-chlorophenol between the top and bottom phases range from 12 up to 245 for the three binary systems.

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