SUPERCRITICAL FLUID EXTRACTION OF ETHYLENE OXIDE FROM ITS AQUEOUS SOLUTION

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The mutual solubility of ethylene oxide and supercritical carbon dioxide was studied at T = 308 K in the pressure range P = 4.2-20 MPa, and the phase distribution of ethylene oxide in the water-ethylene oxide-supercritical carbon dioxide system was investigated at T = 308 and 323 K and P = 7.3-20.0 MPa.

INTRODUCTION

Ethylene oxide is a large-scale product of ethylene-based heavy organic synthesis. Recovery of ethylene oxide from its aqueous solution is one of the most energy-intensive unit processes, most of the energy being consumed at the stage of distillation separation of water and ethylene oxide [1]. This is the reason why reducing energy consumption in this process is of particular interest to researchers and process engineers. Bhise and Hoch proposed to recover ethylene oxide by sub- or supercritical fluid extraction with carbon dioxide [2-6]. Sub- or supercritical carbon dioxide and aqueous ethylene oxide are brought in contact in a countercurrent extraction column. No less than 90% of ethylene oxide is extracted into carbon dioxide, whereas the water content of the extract does not exceed 1 wt %. Ethylene oxide can be separated from its mixture with carbon dioxide by distillation. Bhise and Hoch did not rule out using a cosolvent (in particular, fin-butane) in the distillation column for reducing the column-top temperature.

The purpose of this work was to obtain reliable experimental data on the mutual solubility of ethylene oxide and the extracting fluid and on the phase distribution of ethylene oxide in the water-ethylene oxide-supercritical carbon dioxide system. These data are necessary to set up material and heat balance equations for the extraction cycle and to design a supercritical fluid extraction process.

1 - MATERIALS AND METHODS

An experimental apparatus for batch extraction (Fig. 1) was used to treat one part of the initial mixture with one part of a fluid. The apparatus and the measurement procedures were described in detail earlier [7].

A setup for circulation extraction (Fig. 2) [8] was used for fluid extraction in the pressure range 7.5-35 MPa and the temperature range 293-473 K. The flow circulation is achieved by a MK-80-3.5/350 booster diaphragm compressor *3* (AO Kazan'kompressormash, Kazan, Russia), which is able to compress gases up to 35 MPa. In order to maintain a constant extract flow rate and eliminate the flow pulsations induced by the diaphragm motion, the gas is pumped by the compressor into receiver *4*. The working pressure of the extract is set with an accuracy of ± 0.1 MPa with an ADN-I 0063M1 pressure regulator 5 (AO Kazan'kompressor-I mash, Kazan, Russia). The pressures in the extractor and the separator

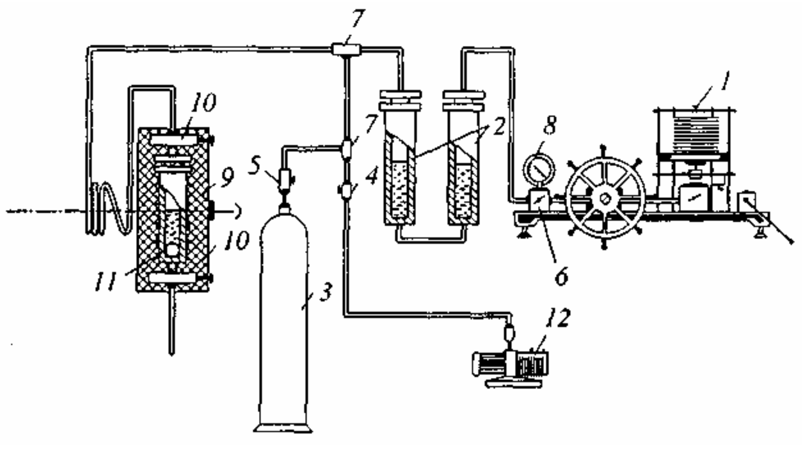

Figure 1: Batch extraction apparatus: (/) MP-2500 deadweight pressure gauge, (2) intermediate vessels, (3) cylinder with the extract, (4-6, 10) high-pressure valves, (7) T-junction, (8) standard pressure gauge, (9) high-pressure heat-insulated autoclave, (11) ball, and (72) vacuum pump.

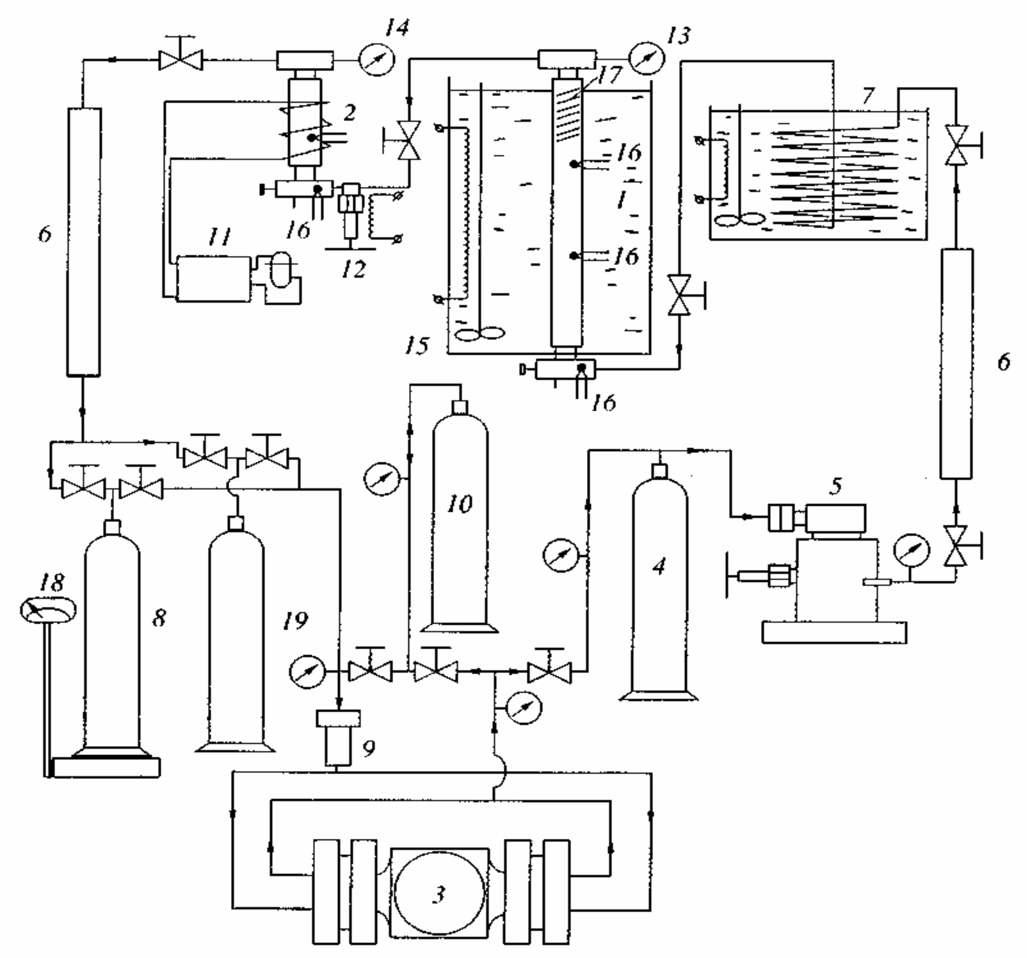

Figure 2: Setup for circulation extraction

are measured with standard pressure gauges *13* and *14.* Through a drying filter *6,* the gas enters heat exchanger *7,* where it is heated to a temperature $T > T_{cr}$, then the fluid flows in extractor *1,* where it is bubbled through a portion of the initial mixture. The extractor is thermostated with an accuracy of ±0.05 K in a bath *15*. The fluid temperature in the extractor and the gas temperature in the separator are measured with an accuracy of ±0.1 K, with under study through the walls of the apparatuses with the use of special sealing plugs. For better mass transfer, the extractor is randomly packed with stainless-steel rings 3 mm in diameter. Entrainment of the liquid by the flowing extract is prevented with a louver-type inertial drop catcher *17* placed in the upper part of the extractor. In separator *2,* the components dissolved in the fluid are recovered by reducing the pressure and the temperature of the flow to the values that are subcritical for the extract. For this purpose, the solution is flowing through a heated throttle valve *12* at the inlet of the separator. The separator itself is cooled with a coolant coming from thermostat *11* equipped with a cooling unit. Extract-free carbon dioxide flows through a drying filter and is admitted into the receiving cylinder *8.* The maximum pressure in the receiving cylinder is 1.5 MPa. Since the compression ratio of the compressor is 5, the pressure of 35 MPa in the receiver is produced in two steps with the use of an intermediate cylinder *19.* First, the recovered carbon dioxide from the receiving cylinder is pumped through a fine filter *9* into an intermediate cylinder *10* up to a pressure of 5-7.5 MPa, and only thereafter the receiver *4* is filled to a pressure of 25-35 MPa with the extract pumped from the intermediate cylinder.

The amount of compressed extract in the receiver enables one to maintain the required flow rate for several hours, and, thereby, attain an extract-to-mixture weight ratio of the order of 10^2 and up. If necessary, the pressure in the receiver can be boosted without interference in the process, which can thus be performed for as long as is desired. The amount of extract having passed through the mixture being separated is estimated with the use of an electronic balance *18.* The receiving cylinder *8* is placed on the balance pan, and the cylinder is weighed before and after extraction with an accuracy of ±0.025 kg.

2 – EXPERIMENTS AND RESULTS

We studied the mutual solubility of ethylene oxide and supercritical carbon dioxide in a batch extractor at T = 308 K and P = 4.2-20 MPa. The results of our study are presented in Figs. 3 and 4.

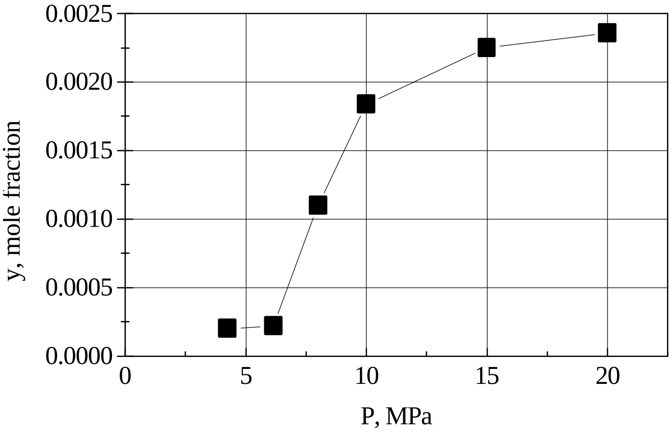

Figure 3: Solubility (mole fraction) y of ethylene oxide in supercritical carbon dioxide as a function of pressure.

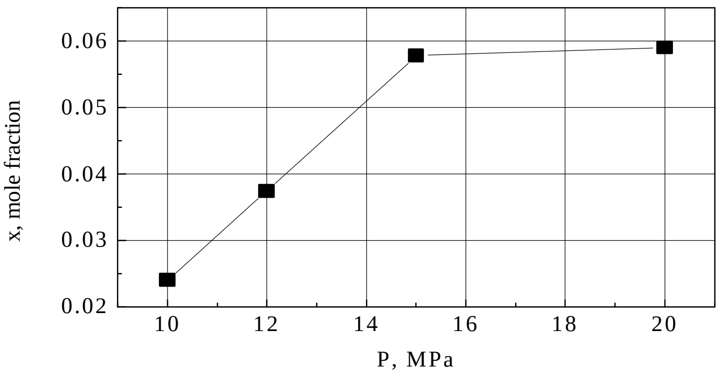

Figure 4: Solubility (mole fraction) *x* of supercritical carbon dioxide in ethylene oxide as a function of pressure

The mutual solubility increases rapidly with increasing pressure. The largest values of the derivative $(\partial y/\partial P)_T$ are observed within a relatively narrow pressure range in the vicinity of the critical pressure of the pure fluid. This finding is fully consistent with predictions [9] based on the theory of solubility in liquid-supercritical fluid systems. The range of state parameters where $(\partial y/\partial P)_T$ changes drastically is the optimal for the supercritical extraction process, which involves fluid extraction at $P > P_{cr}$ and extract separation recovery at $P < P_{cr}$. The temperature 308 K is optimal for supercritical fluid extraction with carbon dioxide, since as the temperature recedes from the critical temperature of the extract, the dissolving power of the extract decreases and the energy consumption increases (Fig. 5).

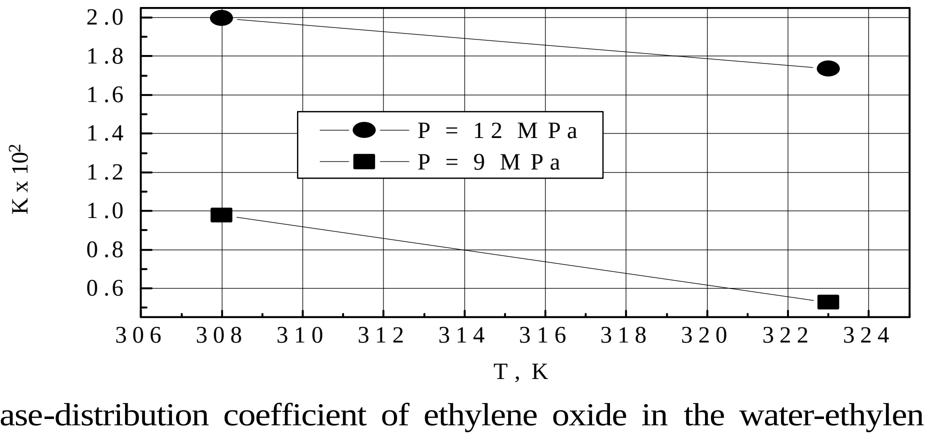

Figure 5 Phase-distribution coefficient of ethylene oxide in the water-ethylene oxide-supercritical carbon dioxide system as a function of temperature at P = 9 and 12 MPa.

A measure of the selectivity of an extract fluid (ability to extract the desired component from the original mixture) is the phase-distribution coefficient. The phase distribution of ethylene oxide in the water-ethylene oxide-supercritical carbon dioxide system at T = 308 and 323 K and P = 7.3-20.0 MPa was studied in a circulation extractor. All the experiments were carried out at the same mass flow rate of carbon dioxide. The results of these experiments are presented in Figs. 5 and 6.

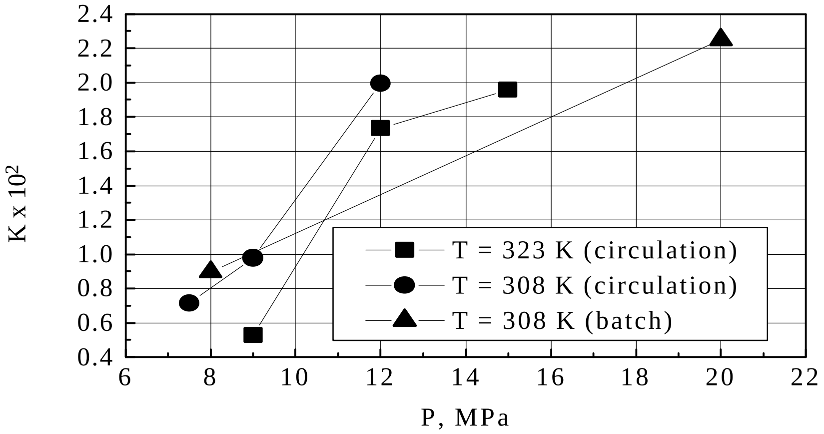

Figure 6: Phase-distribution coefficient of ethylene oxide in the water-ethylene oxide-supercritical carbon dioxide system as a function of pressure at T = 308 and 353 K for the circulation and T = 308 K for batch extractors

Figure 6 shows the distribution-coefficient isotherms at 308 and 353 K. Note the agreement between the data obtained at 308 K in the batch and circulation extractors. One can see that the pressure dependence of the phase-distribution coefficient is qualitatively similar to that of the ethylene oxide solubility in supercritical carbon dioxide. As the pressure is raised, the phase-distribution coefficient increases. Furthermore, there is a narrow pressure range where the phase-distribution coefficient rises particularly sharply.

The temperature 308 K is optimal for supercritical fluid extraction with carbon dioxide, since as the temperature recedes from the critical temperature of the extract, the dissolving power of the extract decreases and the energy consumption increases (Fig. 7). As the temperature is increased above the critical temperature of pure carbon dioxide, the phase-distribution coefficient decreases (Fig. 7). This means a decrease in the selectivity of the extract with respect to the desired component.

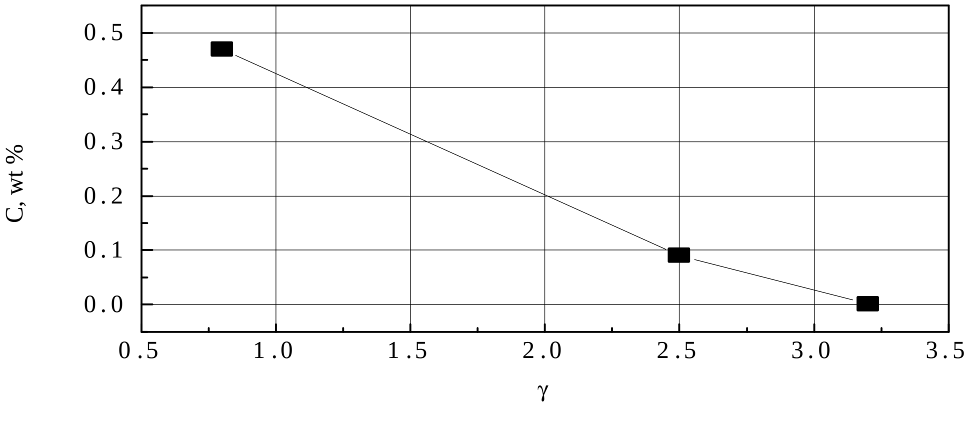

Figure 7: Concentration C of ethylene oxide in the raffinate as a function of the weight ratio (γ) of the extract to the original solution in the extraction of ethylene oxide from its aqueous solution at T = 308 K and P = 9 MPa.

The amount of extract required to completely separate ethylene oxide from its aqueous solution can be estimated from the phase-distribution coefficient. This inference agrees with the results of the experiments in which we varied the weight ratio of the extract to the original solution (Fig. 7).

CONCLUSION

Thus, our study demonstrated that the phase-distribution coefficient and, accordingly, the efficiency of fluid extraction of ethylene oxide from its aqueous solution depend strongly on the process parameters. The data obtained can be used to optimize energy consumption in the supercritical fluid extraction of ethylene oxide from its aqueous solutions with the aim of replacing the extremely energy-intensive distillation process.

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