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Experimental Justification of the Effectivity of the Separating Power of Solvents for Extractive Distillation of the Propylene Oxide–Methanol Binary System

V. N. Klementyev[a] and V. V. Potekhin[b]

[a] *St. Petersburg State Institute of Technology (Technical University), Moskovskii pr. 26, St. Petersburg, 190013 Russia*
e-mail: kvn@technolog.edu.ru

[b] *Joint-Stock Company Himtek Engineering, ul. Akademika Pavlova 5, str. B, St. Petersburg, 197022 Russia*

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Abstract—Highly selective protic and aprotic solvents were compared in terms of their effectivity as extractive distillation agents for the propylene oxide–methanol system. Separating agents were chosen on the basis of their solubility data. A relationship between the capacity of the separating agent and the degree of extraction of propylene oxide was established.

Keywords: propylene oxide, methanol, degree of extraction, solubility, solvent capacity

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Propylene oxide is an important product of organic synthesis underlying manufacture of substances possessing valuable properties essential for various industrial applications, in particular, of polyols (60–70%) used in the production of polyurethane plastics, propylene glycol (20%), surfactants, etc. The world annual propylene oxide production is about 10 mln tons [1].

Commercial production of propylene oxide is based primarily on the chlorohydrin and hydroperoxide technologies [2, 3]. Each of them has advantages and disadvantages [4], while the main quality criterion for propylene oxide is a high, no lower than 99.5 wt %, purity of the target product. The composition of the impurities and the technology used for isolation of propylene oxide from the reaction mixture are factors determining the economic efficiency of the process. Therefore, the propylene oxide preparation technology in which propylene reacts with a "pure" epoxidizing agent of inorganic nature, e.g., hydrogen peroxide [5], has a considerable merit [6].

In 1983, new Ti-containing synthetic zeolites, titanium silicates (TS-1, TS-2) with ZSM-5 or MFI structure, were obtained by EniChem (Italy) [7]. Titanium silicates react with hydrogen peroxide to form reactive titanium-hydrogen peroxide complexes. This property of titanium silicate molecular sieves gave an impetus for development of olefin epoxidation catalysis [8]. In 1991, propylene oxide was prepared by TS-1-catalyzed direct epoxidation of propylene with hydrogen peroxide [9]. The reaction selectivity was 97% at 97% hydrogen peroxide conversion.

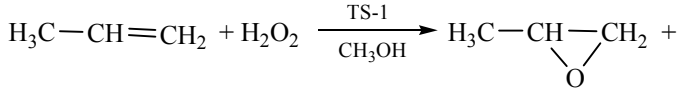
In 2006, BASF AG and Dow Chemical Co. launched a joint project to produce propylene oxide from propylene and hydrogen peroxide at the site of BASF in Antwerp. In 2009, the joint activities by BASF, Dow Chemical, and Solvay culminated in putting into operation the first large-scale production of propylene oxide by the new HPPO (Hydrogen Peroxide to Propylene Oxide) technology.

Direct epoxidation of propylene with hydrogen peroxide over TS-1 heterogeneous catalyst [reaction (1)] is carried out in a methanol medium [10]. Depending on the epoxidation conditions, the resulting reaction product has the following composition: propylene oxide 10–15%, methanol 50–60%, water 10–30% [11, 12], reaction by-products 2–3%. The latter include methoxypropanols and 1,2-propylene glycol formed by reactions (2) and (3).

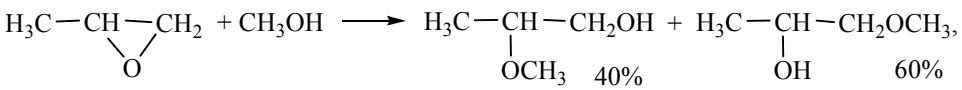
Table 1. Parameters of the separating agents

Exp. no.	Separating agent	Selectivity, S_{max} [a]	Hildebrand solubility parameter δ, $kJ^{0.5}\,cm^{1.5}$
1	Water[b]	16.8	47.9
2	Dimethylsulfoxide	5.72	26.5
3	Ethylene glycol	5.44	32.4
4	*N*-Methylpyrrolidone	4.64	24.9
5	Morpholine	4.62	22.3
6	Diethylene glycol	4.38	31.7
7	1,2-Propylene glycol	3.63	27.9
8	*N,N*-Dimethylformamide	3.49	24.6

[a] Data from [21]. [b] Water selectivity was calculated on the basis of the vapor-liquid equilibrium data for water–methanol and water–propylene oxide systems [26] by the technique described in [17, 21].



(1)



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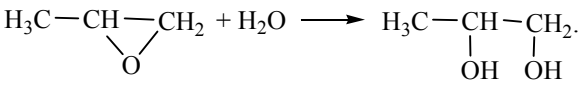

(3)

Simple distillation at atmospheric pressure does not allow the isolation of propylene oxide from the reaction mixture with purity better than 99.5 wt % because of the formation of a tangential methanol–propylene oxide azeotrope [13] comprising 96.9 wt % of propylene oxide. Hence, the search for and development of economically and technologically effective methods for separation of propylene oxide from its mixture with methanol is of key importance.

Propylene oxide–methanol mixtures can be separated by liquid-liquid extraction using water and a saturated paraffin hydrocarbon [14], e.g., octane [15], or C_8–C_{20} hydrocarbons [16].

Impurities are removed from propylene oxide by extractive distillation. Advantages offered by this separation technology include the possibility to use solvents in high concentrations (75–90 wt %) on all the column plates, which increases the separation selectivity and efficiency [17]. The main problem with application of extractive distillation is that of choosing an effective separating agent. The currently available publications describe the use of water [18, 19], as well as of glycols and their ethers [20] for this purpose.

The aim of this study was to experimentally verify the suitability of solvents with preset selectivity parameters for separation of a propylene oxide–methanol mixture by extractive distillation to produce propylene oxide with purity no lower than 99.5 wt %.

Table 1 and 2 present the experimental and calculated data for the selective solvents chosen. For comparison of the solvents differing in the nature and properties, a constant (1 : 1) ratio of the separating agent to the feed was used.

Knowing the acidity or basicity of a solvent it is possible to estimate its maximum selectivity for separation of the propylene oxide–methanol pair [21]. The highest selectivity can be exhibited by both protic and highly basic aprotic solvents. There is a limited choice of solvents potentially suitable for extractive distillation of the propylene oxide–methanol pair. On the one hand, a candidate solvent (separating agent) must have a high selectivity, and, on the other hand, it must possess sufficient dissolving power with respect to methanol and propylene oxide to prevent phase separation in liquid heterogeneous systems on the distillation column plates. Thereby, possible decrease

Table 2. Composition of the distillates and degree of extraction of propylene oxide

Component	Experiment no.[a]							
	1	2	3	4	5	6	7	8
Propylene oxide, wt %	98.18[b]	99.9	99.9	99.9	99.9	99.9	99.9	99.9
Degree of extraction of propylene oxide, weight fraction	0.99	0.92	0.97	0.96	0.96	0.97	0.98	0.99

[a] The experiment no. corresponds to the solvent no. in Table 1. [b] The rest is water.

in effectivity of the separating agent because of reduction in the relative volatility of the components of the pair to be separated will be avoided [22].

The Hildebrand–Semenchenko solubility rule states that mutual solubility is the higher the closer the solubility parameters [17]. We estimated the solubility of the separating agents using the Hildebrand parameter δ [23, 24]:

$$\delta = [(\Delta H_v - RT)/V_m]^{1/2}. \quad (4)$$

Here, ΔH_v is the molar vaporization enthalpy, kJ mol^{-1}; R, universal gas constant; V_m, liquid molar volume, cm^3 mol^{-1}; and T, temperature, K.

Easy experimental determination of the solubility makes the method of choosing separating agents based on their solubility data convenient. In this case, the temperature dependence of the solubility of the separating agent should be taken into account [25].

The separating agents listed in Table 1 cause the relative volatility of the propylene oxide–methanol system to significantly shift toward lower volatility of methanol, as indicated by the selectivities of the separating agents chosen. However, choosing the separating agents based solely on the maximum selectivity is incorrect and can lead to poor distillation column performance, since the selectivities were estimated under conditions close to infinite dilution of the system components in the solvent. The latter should possess good dissolving powers for the components of the pair to be separated so as to ensure effective mass exchange at a preset consumption of the separating agent under extractive distillation conditions.

According to the Hildebrand parameter values, good dissolving powers for both methanol and propylene oxide can be expected for all the solvents among those tested by us for which δ is close to the solubility parameter of methanol (δ = 29.9 kJ$^{0.5}$ cm$^{1.5}$) and propylene oxide (δ = 19.1 kJ$^{0.5}$ cm$^{1.5}$).

The data in Table 2 confirm nearly complete removal of methanol, whose proportion in the distillate was reduced to trace amounts, for the entire series of the experiments.

Of all the solvents listed in Table 1, water has the highest selectivity. When water is used as separating agent, extraction of propylene oxide from its mixture with methanol is the most complete. However, the distillate contains water (1.82%) because of the formation of a propylene oxide–water azeotrope [26]. The water content of >0.01% in commercial propylene oxide is unacceptable, since the presence of water significantly affects the quality of the materials to be produced subsequently from propylene oxide. Consequently, an additional drying procedure should be initiated for water removal. Despite high activity coefficients of propylene oxide in water (γ^{∞} = 35.71) and high selectivity of water (S_{max} = 16.8) its use as separation solvent is impractical. Furthermore, the presence of water may cause phase separation in the liquid on the column plates (for solubility parameters of water and the components being separated, see Table 1).

In case of extractive distillation with morpholine as separating agent (exp, no. 5), the latter passes into the distillate as the degree of extraction of propylene oxide increases.

Based on the experimental data on the propylene oxide isolation by extractive distillation and the theoretical δ values for the solvents chosen, ethylene glycol, diethylene glycol, 1,2-propylene glycol, dimethylsulfoxide, *N*-methylpyrrolidone, and dimethylformamide can be recommended for separation of the propylene oxide–methanol pair by extractive distillation. With these solvents there will be no phase separation on the internal mass-transfer of the distillation column. At the same time, a disadvantage of DMSO consists in its low decomposition temperature. The temperature of the thermal degradation onset for

Table 3. Activity coefficient of methanol and capacity of the separating agents

Separating agent	Activity coefficient of methanol [21], γ_i^∞	Capacity of solvent, $C_{i,S}$
Water	1.93	0.52
Dimethylsulfoxide	0.49	2.04
Ethylene glycol	0.96	1.04
N-Methylpyrrolidone	0.51	1.96
Morpholine	0.74	1.35
Diethylene glycol	0.84	1.19
1,2-Propylene glycol	1.12	0.89
N,N-Dimethylformamide	0.74	1.35

DMSO is 150°C [27], and at the boiling point (189°C) the extent of decomposition is 6% [28].

Since methanol and propylene oxide are polar substances, it is necessary to take into account the interaction in the methanol–solvent–propylene oxide ternary system, along with the solubility parameter. To this end we used the capacity parameter ($C_{i,S}$) [29] [Eq. (5)]:

$$C_{i,S} = 1/\gamma_i^\infty, \quad (5)$$

where i refers to the solute, and γ_i^∞ is the activity coefficient at infinite dilution.

It might be expected that smaller activity coefficients lead to strong interactions in the methanol–solvent and propylene oxide–solvent systems. However, solvents possessing high selectivities often have low capacities which are most often neglected or used as a secondary option at best.

In our case, there is a satisfactory correlation (R = 0.96) between the capacity of the solvent and the degree of extraction of propylene oxide (Fig. 1).

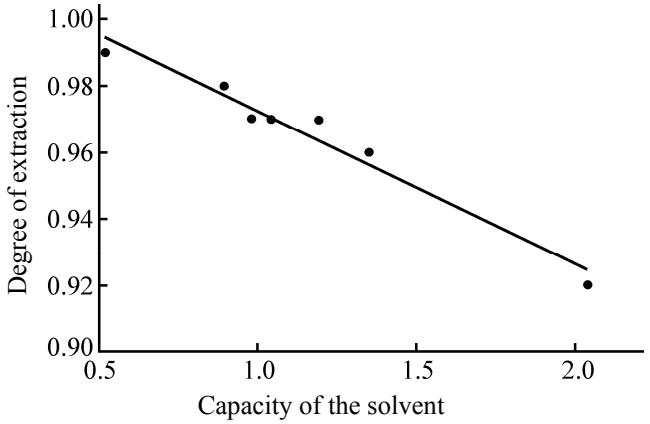

Fig. 1. Degree of extraction vs. capacity of the separating agent.

The experimental data (points) in Fig. 1 can be satisfactorily described by linear equation (6):

$$\omega = -0.046C_{i,S} + 1.02, \quad (6)$$

where ω is the degree of extraction.

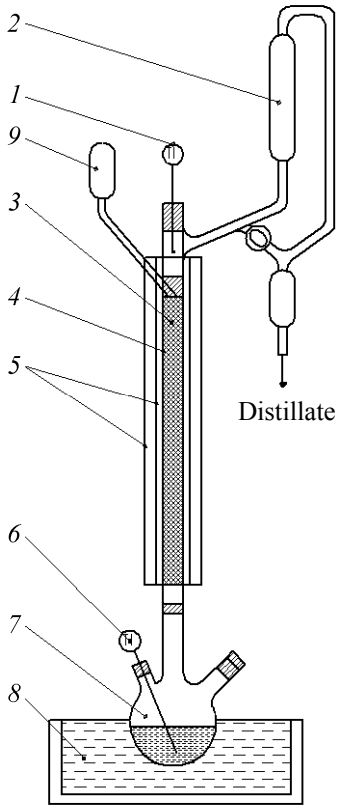

Fig. 2. Schematic diagram of the laboratory distillation column: (*1*) column top thermometer, (*2*) distillation column head, (*3*) random packing, (*4*) distillation column sidebar, (*5*) thermostatic jacket, (*6*) column bottom thermometer, (*7*) column bottom, (*8*) bath (heat carrier, heating element), and (*9*) separating agent feeding reservoir.

The practical significance of Eq. (6) consists in that, if the solvent has a high selectivity, this factor is not the only and sufficient criterion for separating agent to be regarded as suitable for effective isolation of propylene oxide by extractive distillation: The knowledge of the solvent capacity is essential.

The selectivity at infinite dilution S_{max} serves as the main choosing criterion in evaluation of candidate separation solvents for extractive distillation [21]. In practice, the concentrations in the system are far from those in the state of infinite dilution. However, some solvents can show maximum selectivity when at intermediate concentrations [30].

In choosing a solvent as separating agent, account should be taken not only of the nonvalent interactions between the solvent and propylene oxide but also of a high chemical reactivity of propylene oxide [31–33], associated with possible opening of the oxirane ring.

Our experiments showed that extractive distillation enables isolation of propylene oxide with 99.9 wt % purity compliant with the modern propylene oxide quality criteria. According to the totality of the characteristics determined, of all the solvents tested by us the best separating power for the propylene oxide–methanol pair is exhibited by ethylene glycol and DMF.

EXPERIMENTAL

Propylene oxide was separated from the experimental mixtures on a laboratory batch distillation column at atmospheric pressure. The composition of the experimental mixture was close to the azeotrope: propylene oxide 95%, methanol 4.5%, impurities 0.5%. The setup is shown schematically in Fig. 2. A glass column of 21 mm internal diameter was filled with Levin's spiral-prismatic packing material; the packed bed height was 850 mm. The solvents used as separating agents are listed in Table 1.

The distillate and the bottom product were analyzed by gas-liquid chromatography on a Tsvet 800 chromatograph (a 20 m×0.25 mm quartz capillary column, PEG-20M stationary phase). Chromatographic conditions: nitrogen carrier gas, evaporator temperature 250°C, column oven temperature 50°C (isotherm), a flame ionization detector, sample volume 1 μL.

The water content of the mixtures was determined by Fisher's method on a Expert 007M instrument.

The degree of extraction of propylene oxide was calculated by formula (7)

$$\omega = m_2/m_1, \quad (7)$$

where m_1 and m_2 are the weights, g, of propylene oxide in the initial mixture and distillate, respectively.

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