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Effective Separating Agents for Extractive Distillation of a Propylene Oxide–Methanol Mixture

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Abstract—The activity coefficients at infinite dilution were determined and used for estimating the maximum selectivity of twenty different separating agents for the propylene oxide–methanol pair formed during propylene oxide synthesis. Protic and aprotic solvents were compared in terms of their effectivity. A relationship between the maximum selectivity and physicochemical properties of the solvent was established.

Keywords: propylene oxide, methanol, activity coefficients, selectivity
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Propylene oxide is an important industrial product of the main organic synthesis. The implementation of the technology of propylene oxide production in a methanol medium [1] on a heterogeneous catalyst by propylene oxidation with hydrogen peroxide [2, 3] (HPPO, Hydrogen Peroxide to Propylene Oxide, technology) or by direct oxidation of propylene with oxygen and hydrogen [4] raises a number of difficulties.

When the reaction is carried out in methanol the separation of a propylene oxide–methanol mixture by simple distillation is not possible because of the formation of a tangential azeotrope (96.9 wt % propylene oxide, 3.1 wt % methanol) [5]. A number of patents [6–9] describe methods for separating propylene oxide from methanol and other impurities. Among them a method for purification of low-molecular-weight olefin oxides, including propylene oxide, is suggested by extractive distillation with glycols (ethylene glycol, propylene glycol) and glycol ethers (ethylene glycol monomethyl ether or diethylene glycol monomethyl ether) [6]. Also, complex mixtures of solvents are suitable as separating agents, e.g., a mixture consisting of water (70–90 wt %), 1,2-propylene glycol (1–15 wt %), propylene glycol monomethyl ether (5–20 wt %), and dipropylene glycol (0.5–2 wt %) [7]. Separation of methanol and propylene oxide from a reaction mixture can be achieved via extractive distillation with nonvolatile hydroxy-containing polar solvents acting as the separating agent [8]. This method proved to be useful for removing carbonyl compound impurities from a mixture with propylene oxide. In the method of separation of propylene oxide from methanol, described in [9], the separating agents used are water, propylene glycol, and a mixture thereof.

Published data [6–9] indicate that the most effective separating agents for extractive distillation of the propylene oxide–methanol pair are protic solvents forming strong hydrogen bonds with methanol [10]. The physicochemical properties of propylene oxide and methanol suggest that highly basic aprotic solvents are also suitable for their separation.

Making a justified choice of the selective separating agent requires conducting time-consuming laborious experiments using special equipment for vapor–liquid equilibrium studies [11]. The search for optimal separating agent can be substantially simplified if the selectivity of solvents is assessed by a method based on gas-liquid chromatography [12, 13] which allows estimating the selectivity of the solvent at infinite dilution for the components of the mixture being separated in the selective solvent. The most important point in determining the limiting activity coefficients

Table 1. Physicochemical properties of the solvents

Solvent no.	Separating agent	DN,[a] kJ/mol (DN^N) [10, 17, 18]	AN^{Nb} [10, 19]	Et(30),[c] kJ/mol [10, 20]	bp, °C [21]
1	Dimethylsulfoxide	124.9 (0.77)	19.3	189.0	189
2	Ethylene glycol	86.7 (0.534)	42.8	235.9	197
3	*N*-Methylpyrrolidone	114.4 (0.704)	13.3	176.8	206
4	Morpholine	–	17.5	171.8	129
5	1,4-Butylene glycol	–	–	224.2	228
6	Diethylene glycol	–	–	225.4	245
7	Triethyl phosphate	108.9 (0.67)	–	174.7	215
8	1,2-Propylene glycol	–	9.9	226.7	189
9	*N,N*-Dimethylformamide	111.5 (0.685)	16	183.5	153
10	Trimethyl phosphate	96.4 (0.59)	–	182.7	193–194–197
11	Furfuryl alcohol	–	–	210.8	244–245
12	Cyclohexanol	81.7 (0.502)	–	196.5	160
13	Tetraethylene glycol dimethyl ether	–	–	–	275
14	γ-Butyrolactone	75.4 (0.464)	–	–	204–205
15	Ethylene glycol dimethyl ether (diglyme)	–	–	161.7	162
16	Triethylene glycol dimethyl ether (triglyme)	–	–	163.0	216
17	Benzoic acid nitrile	49.9 (0.31)	15.5	173.9	191
18	Nitrobenzene	18.4 (0.11)	–	172.6	210
19	Undecane	0	–	125.7	196
20	Pentadecane	0	–	129.9	270

[a] Gutmann donor number. [b] Acceptor number. [c] Dimroth-Reichardt solvent polarity parameter.

and the selectivity of solvents in separation of a propylene oxide–methanol mixture is to establish a relationship between the selectivity and physicochemical characteristics of the separating agent. In particular, this concerns the relationship between the maximum selectivity of the separating agent with respect to the propylene oxide–methanol system, on the one hand, and the basicity and acid properties of the solvent, on the other.

To elucidate the physicochemical nature of the optimal separating agent for the propylene oxide–methanol pair we used the gas-chromatographic method, and for comparison of the separating agents in terms of their effectivity, the maximum selectivity S_{max}. The activity coefficients at infinite dilution in the solvents tested were calculated on the basis of the gas-chromatographic data [14–16]. For physicochemical properties of the solvents, see Table 1.

Table 2 lists the calculated specific retention volumes and activity coefficients of methanol and propylene oxide at infinite dilution for the separating agents tested, as well as the selectivity of the latter. The specific retention volumes in the solvents were calculated by formula (1) [22]:

$$V_g^0 = F\cdot(\tau/m)\cdot(273.15/T_f)\cdot(3/2)\{[(P_i/P_0)^2 - 1]/[(P_i/P_0)^3 - 1]\} \times\{[P_0 - P(H_2O)]/P_0\}, \quad (1)$$

where F is the carrier gas flow rate, cm^3/s; τ, retention time, s; m, mass of the solvent in the column, g; T_f, column temperature, K; P_0, column outlet pressure, Pa; P_i, column inlet pressure, Pa; and $P(H_2O)$, saturated water vapor pressure at temperature T_f, Pa.

Table 2. Specific retention volumes and limiting activity coefficients of methanol and propylene oxide in the solvents and selectivity of the separating agents

Separating agent	Specific retention volume, cm^3/g		Limiting activity coefficients		Selectivity of separating agent S_{max}
	propylene oxide V_{g1}^0	methanol V_{g2}^0	propylene oxide γ_1^∞	methanol γ_2^∞	
Dimethylsulfoxide	146	3558	2.79	0.49	5.72
Ethylene glycol	98	2271	5.23	0.96	5.44
N-Methylpyrrolidone	137	2694	2.35	0.51	4.64
Morpholine	107	2105	3.41	0.74	4.62
1,4-Butylene glycol	90	1679	3.95	0.90	4.41
Diethylene glycol	82	1517	3.68	0.84	4.38
Triethyl phosphate	89	1419	1.99	0.53	3.76
1,2-Propylene glycol	103	1583	4.08	1.12	3.63
N,N-Dimethylformamide	169	2500	2.59	0.74	3.49
Trimethyl phosphate	130	2080	1.04	0.47	2.22
Furfuryl alcohol	49	420	6.61	3.28	2.01
Cyclohexanol	119	920	2.68	1.47	1.82
Tetraethylene glycol dimethyl ether	187	820	0.77	0.74	1.03
γ-Butyrolactone	244	768	1.52	2.05	0.74
Ethylene glycol dimethyl ether (diglyme)	245	769	0.96	1.31	0.73
Triethylene glycol dimethyl ether (triglyme)	247	675	0.72	1.13	0.64
Benzoic acid nitrile	354	302	0.96	3.21	0.30
Nitrobenzene	240	189	1.08	5.82	0.19
Undecane	85	28	2.41	30.67	0.08
Pentadecane	74	20	4.61	71.77	0.06

The activity coefficients at infinite dilution γ_i^∞ in the solvent were calculated by formula (2) [23]:

$$\gamma_i^\infty = (273.15 \cdot R)/(M \cdot P_i^0 \cdot V_g^0), \quad (2)$$

where R is universal gas constant; P_i^0, saturated vapor pressure of the test component at temperature T_f, Pa; and M, molar mass of the solvent, g/mol.

The selectivity of the separating agent at infinite dilution in the propylene oxide–methanol system was calculated as the ratio of the limiting activity coefficients using formula (3):

$$S_{max} = \gamma_{\mathbf{I}}^\infty / \gamma_{\mathbf{II}}^\infty, \quad (3)$$

where $\gamma_{\mathbf{I}}^\infty$ and $\gamma_{\mathbf{II}}^\infty$ are the limiting activity coefficients of propylene oxide **I** and methanol **II**, respectively.

Separating agents possessing high solubility are used for extractive distillation. The activity coefficients presented in Table 2 indicate that virtually all solvents tested possess high solvency with respect to the propylene oxide–methanol system and should form homogenous systems, since $\gamma_i^\infty \leq 5$. A series of limiting activity coefficients of methanol (γ_i^∞) in a number of solvents are given in the reference book [24], and those for propylene oxide were determined for the first time.

The interaction in the separating agent–methanol system is determined by a number of specific (hydrogen bonding) and nonspecific (electrostatic) solvation factors. The results reported in [25] suggest that the main contribution to selectivity comes from the ability of the separating agent molecules to form stable hydrogen bonds with methanol. Proceeding from the assumption of Lewis acid-base interaction (donor-acceptor interaction), the solvation in the separating agent–methanol system can be assessed with the use of model systems characterizing the donor or acceptor properties of the separating agent.

The model of acid-base interaction involving an aprotic solvent treats the separating agent, an aprotic solvent, as the electron pair donor (D), and methanol with one coordination site (methanol possesses high acceptor properties: AN 41.3 [19]), as acceptor (A). The Lewis basicity parameters of the separating agents can be described by Gutmann donor number (DN) [10].

The interaction of the separating agent with methanol is described by reaction (4):

$$\mathrm{D:} + \mathrm{A} \rightleftarrows \mathrm{DA}. \quad (4)$$

It may be assumed that an increase in the donor number of an aprotic solvent will cause strengthening of the bond in the separating agent–methanol complex.

The dependence plotted in Fig. 1 confirms the assumption on the selectivity at infinite dilution to depend on the donor number of the separating agent in the methanol–propylene oxide system and is fairly adequately described by Eq. (5) or, in the logarithmic form, by Eq. (6):

$$S_{max} = S^0_{max} \cdot e^{0.035DN}, \quad (5)$$

$$\ln (S_{max}) = 0.035 \cdot DN - 2.64. \quad (6)$$

where S^0_{max} is the maximum selectivity of the separating agent with DN = 0 kJ/mol (undecane).

Using the above dependence it is possible, basing on the donor numbers of the separating agents, to choose among them the separating agent matching the required selectivity.

According to published data, protic solvents are supposed to be applied as separating agents. Most protic solvents possess acceptor properties. The acceptor power of separating agents is described by various scales [26]: AN, Et(30), and other. Among them, the Et(30) Dimroth-Reichardt energy parameter

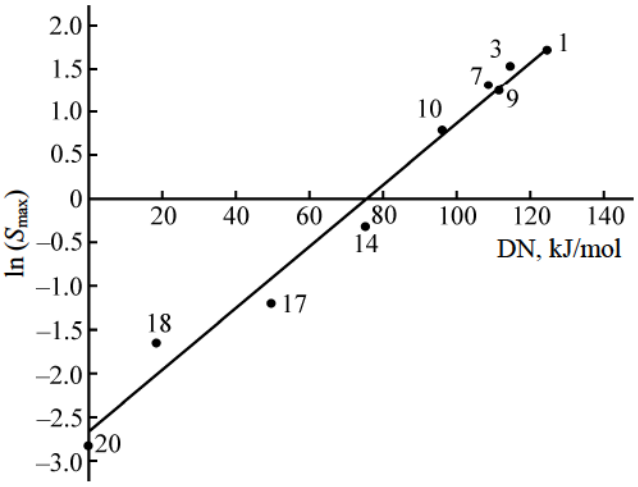


Fig. 1. Correlation diagram of ln (S_{max}) with the donor number (DN) of aprotic solvent (R 0.993). Point numbers correspond to solvent numbers in Table 1.

scale may be used to describe the acidity of the separating agent.

Here, we evaluated the capability of a number of protic solvents for selective separation of the propylene oxide–methanol pair.

The experimental points on the plot (Fig. 2) constitute a regular pattern showing how the selectivity of the separating agent (a protic solvent) varies with the Et(30) Dimroth-Reichardt parameter, which is satisfactorily described by an exponential function equation (7):

$$S_{max} = S^0_{max} \cdot e^{0.035Et}, \quad (7)$$

where S^0_{max} is the maximum selectivity of the potential separating agent with Et(30) = 0 kJ/mol.

Equation (7) implies that an increase in Et(30) (acceptor ability) of the separating agent causes the selectivity of separation to increase.

Linear anamorphosis of exponential dependence (7) appears as follows:

$$\ln (S_{max}) = 0.035Et - 6.56. \quad (8)$$

The established relationship (7) quantitatively confirms that the selectivity of a protic solvent is related to the parameter Et(30) of the separating agent in the propylene oxide–methanol system. The increase in Et(30) of the separating agent leads to increased interaction between the separating agent and methanol.

High selectivity of protic separating agents is apparently due also to hydrogen bonding via interactions of the oxygen atom of the separating agent

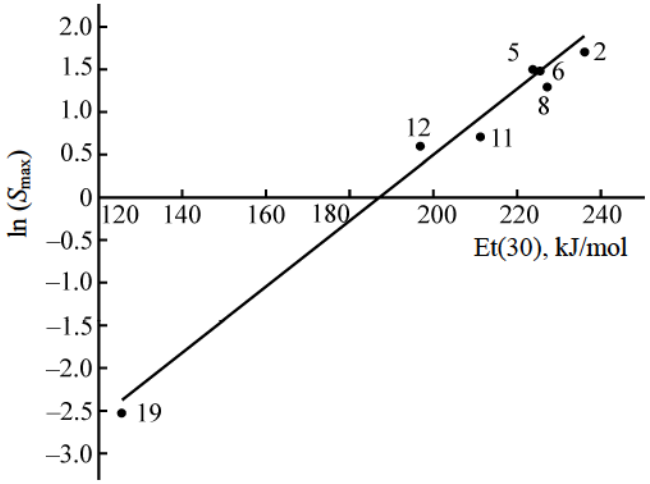


Fig. 2. Correlation diagram of ln (S_{max}) with Et(30) Dimroth–Reichardt parameter for protic solvents (R 0.970). Point numbers correspond to solvent numbers in Table 1.

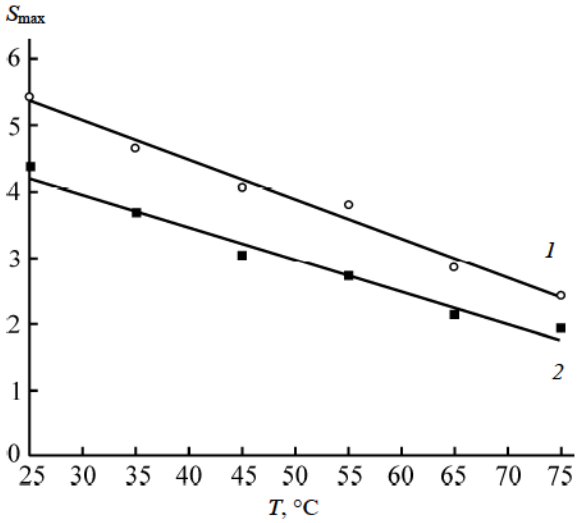


Fig. 3. Temperature dependence of the selectivity of separating agents for (*1*) ethylene glycol (R 0.992) and (*2*) diethylene glycol (R 0.985).

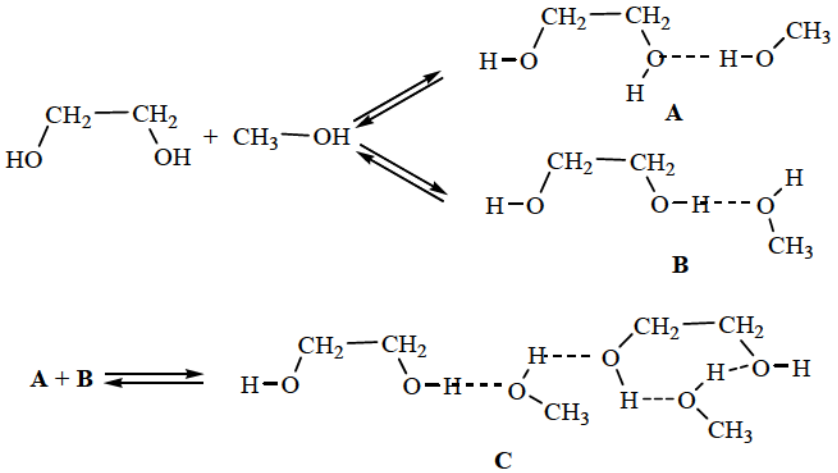
with the hydrogen atom in the hydroxy group of methanol (**A**) and of the oxygen atom in methanol with the hydrogen atom in the separating agent (**B**), which may result in the formation of a complex with an intricate composition (**C**) (Scheme 1).

In terms of the Lewis theory of donor-acceptor interaction, the stability of the separating agent–methanol complex is determined by the strength of the coordination bond between the electron pair donor and the electron pair acceptor. Consequently, with increasing energy of interaction in the separating agent–methanol system the transition of the electron pair from donor to acceptor becomes more favorable by energy. Therefore, the interaction between the donor and acceptor molecules occurs as a result of the neutralization of the base with the acid.

The selectivity of a protic solvent tends to increase with increasing number of hydroxy groups in its molecule, as evidenced by the selectivity S_{max} at infinite dilution, obtained experimentally for a diol, 1,4-butylene glycol (4.41), and a monoatomic alcohol, cyclohexanol (1.82).

The nonideality of the systems decreases with increasing temperature, resulting in a lower selectivity of the separating agents due to decreased stability of the separating agent–methanol complex. In this

Scheme 1.



connection, it is important to determine the temperature range within which a decrease in S_{max} is not essential for the technology of separation of the methanol–propylene oxide pair.

We examined the temperature dependence of the selectivity of the separating agent for the most selective protic solvents, ethylene glycol (S_{max} 5.44) and diethylene glycol (S_{max} 4.38),.

As seen from the dependence plotted in Fig. 3, the selectivity of the separating agents tends to decrease with increasing temperature; over the 25–45°C range it does not substantially change. The latter fact is important in terms of industrial implementation of the extractive distillation process for separation of the propylene oxide–methanol pair. The supply of the separating agent at a temperature from 25 to 45°C will provide efficient separation of methanol from propylene oxide.

The dependences obtained in this study are suitable for theoretical estimation of the selectivity of the separating agent with respect to the propylene oxide–methanol pair subjected to extractive distillation. The use of separating agents characterized by $S_{max} > 1$ will allow obtaining high-purity propylene oxide via extractive distillation.

EXPERIMENTAL

The study was carried out on a Tsvet-800 chromatograph in the isothermal mode (t_i 25°C, a flame ionization detector, carrier gas helium, a 1 m × 3 mm column). Silanized CHEZASORB AW-HMDS 0.25–0.36 mm served as the solid carrier. To achieve concentrations close to infinite dilution state of the sample in the solvent, the amount of the sample injected was varied in the 0.1–1 μL range. Symmetrical peaks and the fact that the retention time was independent of the concentration of the sample injected were indicative of an equilibrium sorption process [22]. The saturated vapor pressures for methanol and propylene oxide were calculated using the Antoine correlation, based on the reference data [21].

The solvents acting as the stationary liquid phase were applied on a solid carrier in the amount of 20–25 wt % by the procedure from [27]. The relatively nonvolatile analytically pure grade solvents were dried using KA-U synthetic zeolites.

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