Entrainer selection for separating tetrahydrofuran/water azeotropic mixture by extractive distillation

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A B S T R A C T

The mixture of tetrahydrofuran (THF) and water is a minimum boiling azeotrope due to the strong hydrogen bond effect. Some entrainers with different molecular structures which can potentially disrupt hydrogen bonds have been used to improve the relative volatility of THF–water system. After cautiously screening, we find that dimethyl sulfoxide (DMSO) as a hydrogen bond breaker is more effective to break the azeotrope than 1, 2-propanediol proposed by Songlin Xu etc. To validate our viewpoint, the vapor–liquid equilibrium (VLE) data of the two ternary systems: THF (1) + water (2) + 1, 2-propanediol (3) and THF (1) + water (2) + DMSO (3) were measured at 101.32 kPa. And these data are also valuable for the design of extractive distillation process. The nonrandom two-liquid (NRTL) model was applied to correlate the binary and ternary VLE data.

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1. Introduction

THF is extensively used as reagent or solvent in organic chemistry. It can mix well with the vast majority of organic solvents. Unfortunately, THF and water can form a minimum boiling azeotrope at atmospheric pressure, 63.5 °C, containing 83.69% THF in mole fraction [1]. This may be caused by the strong hydrogen bond effects between THF and water. So it is difficult to obtain high purity THF from the mixture by conventional distillation or rectification. To date, many methods have been used to break the azeotrope. For instance, M. Seiler broke the azeotrope successfully by applying hyperbranched polyesters and hyperbranched polyesteramide [2], while Lu Jie etc. did a lot of investigation on various membranes in pervaporation [3,4]. However, these processes have not been put into use widely, and extractive distillation is still a common method to separate this azeotropic mixture [5–8]. A suitable entrainer can reduce the apparatus investment and energy consumption apparently. Thus, selecting an appropriate entrainer is a vital point for the extractive distillation of THF.

In the process of research, we find that for this strong polar system, hydrogen bonds play a key role in forming the azeotrope. So the azeotrope can be effectively broken if an entrainer can disrupt hydrogen bonds between THF and water. Therefore, the relative volatility between the components will increase obviously. According to this perspective, a series of entrainers are selected including

glycols, amides, sulfocompound etc. which potentially disrupt hydrogen bonds and increase the relative volatility of the mixture. Their selectivities are investigated respectively. Then the effects of the entrainers with different molecular structures on the hydrogen bonds are explored in detail. After cautiously screening, more effective entrainer dimethyl sulfoxide (DMSO) is selected. Hydrogen bond effect widely exists in strong polar azeotropic system, so our analysis will give some enlightenment on entrainer selection of other strong polar azeotropic system similar with THF–water system.

1, 2-propanediol had been proposed as an entrainer for separating the mixture by Xu and Wang [5]. Their results were obtained via a HYSYS simulation but the relevant VLE data did not provided. In this paper, we explored the separation effects of 1, 2-propanediol and DMSO seriously by investigating the phase equilibrium behaviors of the two ternary systems: THF (1) + water (2) + 1, 2-propanediol (3); THF (1) + water (2) + DMSO (3) and measuring the VLE data at 101.32 kPa since these data are also pivotal for design of extractive distillation process.

2. Materials and methods

2.1. Chemicals

THF, DMSO, 1, 2-propanediol, dimethylacetamide (DMAC) and dimethyl formamide (DMF) are supplied by Sinopharm Group CO. Ltd. The purities of all reagents are confirmed to be analytical grade by chromatography. The water used in experiments is deionized water which is prepared by our laboratory.

2.2. Apparatus and procedure

We employed equilibrium still (manufactured by NGW, Wertheim, Germany) described by Hunsmann [9] to implement vapor–liquid equilibrium tests. The capacity of the still is about 100 mL and it is equipped with a reflux condenser. A proper amount of ternary mixture was injected in the still, and heated until the whole system reached equilibrium. This process usually lasted about 1 h. Then samples from the top and bottom of the still were taken to analyze the contents. We applied a quartz thermometer to measure the equilibrium temperature and a manostat to regulate the system pressure.

The contents of the samples were analyzed by an Agilent 7890A gas chromatograph (GC). We adopted the thermal conductivity cell detector, a 30 m, 0.320 mm i.d., 0.25 μm, capillary column and programmed heating-up to obtain perfect peak of each component. We set oven start temperature as 372.15 K, maintained 3.5 min, then increased by 50 K/min to 473.15 K and stay 7 min. Moreover, we set injector and detector temperatures as 493.15 K and 523.15 K respectively.

3. Results and discussion

3.1. Entrainer selection

Entrainer selection is the key point for the extractive distillation technique. Selectivity is the main evaluation index of separation effect, which is defined as

$$S_{i,j} = \alpha_{i,js}/\alpha_{i,j} \tag{1}$$

where $\alpha_{i,j}$, and $\alpha_{i,js}$ are the relative volatilities of the two key components before and after the entrainer added. We can suppose the vapor as an ideal behavior at atmospheric pressure. So, VLE equation [10] can be simply rewritten as

$$py_i = \gamma_i x_i p_i^{sat} \tag{2}$$

where x_i and y_i are the mole fractions of component i in the vapor and liquid phase respectively containing entrainer; γ_i represents the activity coefficient of component i; p is the total pressure of the equilibrium system; p_i^{sat} is the saturated vapor pressure of pure component i at system temperature. We can approximate $\alpha_{i,j}$ at 1 for the system is binary azeotrope. In addition, p_i^{sat}/p_j^{sat} is a constant, therefore

$$S_{i,js} = \alpha_{i,js} = \frac{Y_i/X_i}{Y_j/X_j} = \frac{\gamma_i p_i^{sat}}{\gamma_j p_j^{sat}} \tag{3}$$

The mole fractions X_i, Y_i are on entrainer-free basis, which can be obtained through phase equilibrium experiments. Activity coefficient γ_i can be correlated using the thermodynamic model [11]. In this paper, we use NRTL to correlate VLE data since it gives better agreement with the experimental results.

As mentioned above, strong hydrogen bond effect between THF and water causes the azeotrope. But we find that the hydrogen
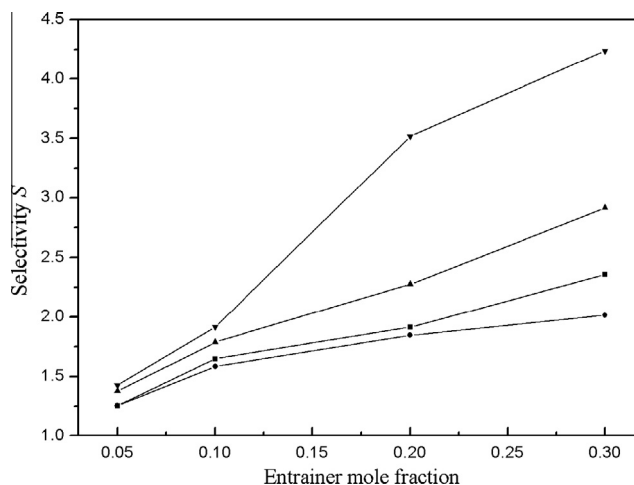

Fig.1. Selectivities of different entrainers varying entrainer mole fraction ●, DMF; ■, DMAC; ▲, 1, 2-propanediol; ▼, DMSO.

bond effect between THF and water will be decreased when following conditions emerge: (1) The entrainer can only form hydrogen bonds with one of the azeotropic components; (2) The entrainer forms much stronger hydrogen bonds with one component than the other. By this way the relative volatility between THF and water can be sufficiently increased thanks to the addition of entrainer and the separation becomes feasible. Based on this view, a series of potential entrainers were selected to implement vapor–liquid equilibrium tests and the basic information of the entrainers was listed in Table 1. Each experiment was repeated three times to eliminate contingency. The selectivity of each entrainer with different entrainer contents was figured out and shown in Fig. 1. Obviously, sorting the entrainers by selectivity

Table 2
VLE data for THF (1) + water (2) system at 101.3 kPa.

T/K	x_1	Y_1^{exp}	Y_1^{cal}	REy_1
366.76	0.003	0.257	0.245	4.707
357.14	0.008	0.480	0.467	2.726
347.65	0.024	0.660	0.654	0.937
343.15	0.050	0.733	0.726	0.989
340.65	0.066	0.750	0.755	0.704
339.45	0.090	0.787	0.781	0.781
338.95	0.160	0.800	0.802	0.235
338.70	0.237	0.809	0.810	0.074
338.19	0.341	0.827	0.820	0.841
338.14	0.464	0.857	0.824	3.860
338.16	0.680	0.857	0.844	1.564
338.15	0.790	0.869	0.861	0.938
338.05	0.851	0.891	0.879	1.349
338.15	0.913	0.911	0.915	0.393
339.26	0.958	0.958	0.946	0.475

The relative error of y_1 : $REY_1 = |Y_1^{exp} - Y_1^{cal}|/Y_1^{exp} \times 100$.

Table 1
Basic information of selected entrainers [12].

Entrainers	DMSO	1,2-Propanediol	DMAC	DMF
Molecular structure	$(CH_3)_2S = O$	$HOCH_2CH_2CH_2OH$	$CH_3CON(CH_3)_2$	$HCON(CH_3)_2$
Molecular weight	78.13	76.09	87.12	73.10
Boiling point (101.3 kPa) T/K	462.15	460.45	439.25	426.15
Densities(298.15 K) ρ/(g cm^{-3})	1.0958	1.0381	0.9366	0.9487
Dipole moment (303.15 K) μ/(10^{-3}C·m)	13.34	7.51	12.41	12.88
Evaporation heat Hm/(kJ mol^{-1})	52.92	538.1	52.3	47.545