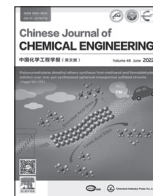




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Full Length Article

Mechanism analysis of solvent selectivity and energy-saving optimization in vapor recompression-assisted extractive distillation for separation of binary azeotrope



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ABSTRACT

Octane and *p*-xylene are common components in crude gasoline, so their separation process is very important in petroleum industry. The azeotrope and near azeotrope are often separated by extractive distillation in industry, which can realize the recovery and utilization of resources. In this work, the vapor–liquid equilibrium experiment was used to obtain the vapor–liquid equilibrium properties of the difficult separation system, and on this basis, the solvent extraction mechanism was studied. The mechanism of solvent separation plays a guiding role in selecting suitable solvents for industrial separation. The interaction energy, bond length and charge density distribution of *p*-xylene with solvent are calculated by quantum chemistry method. The quantum chemistry calculation results and experiment results showed that *N*-formylmorpholine is the best solvent among the alternative solvents in the work. This work provides an effective and complete solvent screening process from phase equilibrium experiments to quantum chemical calculation. An extractive distillation simulation process with *N*-formylmorpholine as solvent is designed to separate octane and *p*-xylene. In addition, the feasibility and effectiveness of the intensified vapor recompression assisted extraction distillation are also discussed. In the extractive distillation process, the vapor recompression-assisted extraction distillation process is globally optimal. Compared with basic process, the total annual cost can be reduced by 43.2%. This study provides theoretical guidance for extractive distillation separation technology and solvent selection.

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1. Introduction

The separation of aromatic hydrocarbon and aliphatic hydrocarbon mixtures is important in the petroleum industry and has been widely paid attention in the world [1]. Octane and *p*-xylene (PX) are two important chemical raw materials. PX is widely used in coatings, medicine and other fields. Octane is mainly used as a component of solvent gasoline, industrial gasoline, also used in organic synthesis. These two substances are common components in crude gasoline, so their separation process is very important in petroleum industry. However, the boiling points of octane and PX are very close, so the difficulty of separation is greatly increased. Distillation technology is widely used in azeotrope separation process

to solve the problem of difficult separation of aliphatic hydrocarbon and aromatic mixture [2,3].

The traditional separation method is difficult to effectively separate azeotrope, and the special distillation methods commonly used in industry, such as extraction distillation [4], pressure-swing distillation [5] and azeotropic distillation [6]. Extractive distillation can increase the relative volatility of components by adding solvent to improve the separation efficiency. Zhao *et al.* [7] separated ethanol, water and toluene with glycerol as solvent and found that extractive distillation was the most economical. Luyben *et al.* [8] used pressure-swing distillation and extractive distillation to separate acetone/methanol system, and found that extractive distillation has higher economic value and more stable dynamic control.

In extractive distillation, selecting suitable solvent is the key to achieve high efficiency and low energy consumption separation [9]. Based on quantum chemistry calculation, the relationship

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between the relative volatility and the interaction between molecules was explored from the molecular level. Firstly, Gaussian 09 W was used to calculate the molecular conformation and conformation energy of monomer and combination structure. By calculating the conformational energy between molecules, the interaction between each solvent and azeotrope can be predicted quantitatively. Based on DMOL³ module and density functional theory (DFT), the molecular conformation was optimized by COSMO-SAC model and GGA/VWN-BP function, and finally the bond length and electron density between solvent and azeotrope were obtained [10]. The bond length and electron density between solvent and azeotrope can qualitatively analyze the interaction between molecules. Felipe *et al.* [11] proposes a theoretical method based on DFT and COSMO-RS calculations to predict selectivity in the solvent extraction of lanthanum and cerium, by using β -diketones as the extractant and kerosene or imidazolium-based ionic liquids as the diluent. The results indicate that the theoretical selectivity trends agree closely with the experimental results, demonstrating the applicability of this method. Gao *et al.* [12] used COSMO-RS model to screen an appropriate ionic liquid to separate the binary azeotrope of ethyl acetate and ethanol and [OMIM][BF₄] was selected. The Quantum Mechanics calculations and molecular dynamics simulation are performed to study the interactions between the solvent molecules and [OMIM][BF₄], in order to investigate the separation mechanism at the molecular level. This predictive method has immense potential as a practical tool providing valuable insights into the design of extractants. And the quantum chemical prediction method can better predict the extraction ability of solvent. In this work, possible intermolecular interactions are determined by the bond length, interaction energy and electron density between the selected solvent and PX.

In extractive distillation, the most worth research is how to save energy and reduce cost after determining the appropriate solvent. Although distillation technology is widely used in separating azeotropic system, the main obstacle is high energy consumption. It is an inevitable trend to develop extractive distillation energy saving process [13,14]. The common distillation energy saving processes include thermal coupling process [15], thermal integration process [16] and vapor recompression-assisted process [17] *etc.* In this work, heat integration process and vapor recompression-assisted process are selected according to the heat load and flows temperature of the basic process. The heat integration scheme process is a very effective energy saving method, which has been studied by many scholars [18–21]. In the process of distillation, the unnecessary heat loss will be greatly reduced and the energy will be greatly saved if the flow that needs to be cooled can be used to heat the bottom of the column. The vapor recompression-assisted process compresses and raises the temperature of steam at the top of the column. The steam that reaches the required temperature and pressure becomes the high-quality heat source of the reboiler at the bottom of the column. Luo *et al.* [22] found that the bioethanol purification process using heat pump assisted extractive distillation can save energy by nearly 40% and reduce total annual cost (TAC) by 24%. Papers [23–25] have shown that the performance and effectiveness of enhanced self-heat recuperation with vapor recompression arrangement was prevailed over than that either with the integrated condenser/reboiler exchanger and both with simple stream-effluent economizers.

The traditional solvent screening methods are mostly based on experience and experiment, which cannot study the extraction mechanism of solvent. However, the study of extraction mechanism is very important for solvent selection. The bond length and electron cloud density are used to qualitatively judge the formation of hydrogen bonds between components. The interaction energy is used to quantitatively analyze the intensity of intermolecular interaction. The accuracy of the calculation results is

verified by phase equilibrium experiments. In this work, a feed preheating-heat pump extractive distillation process with the intensified vapor recompression assisted process is designed by using the best solvent—taking the separation of PX and octane as an example. The economic cycle iteration method [26,27] is used to optimize the strengthening scheme, and the TAC of the process is calculated to evaluate its economic performance. This study provides an idea for the separation of near boiling point system and azeotrope by extractive distillation.

2. Vapor Liquid Equilibrium Experiment

In extractive distillation, vapor–liquid equilibrium (VLE) data is the basic data for design and optimization of process [28,29]. Therefore, the VLE properties of the difficult system were obtained by VLE experiment. The dimethyl sulfoxide (DMSO), PX, butyl butyrate, octane and cyclohexanol were purchased from Aladdin. The isobaric VLE experiment of binary system was carried out in an improved rose equilibrium kettle. In this work, the contents of different reagents in vapor and liquid phase of DMSO(1) + PX(2), PX(1) + butyl butyrate(2), octane(1) + butyl butyrate(2) and octane(1) + cyclohexanol(2) were determined by GC-14C. In order to eliminate the measurement error, all samples were tested three times, and the average value of each sample was used for correlation regression.

2.1. Experimental data and calculation

For the four binary systems of DMSO(1) + PX(2), PX(1) + butyl butyrate(2), octane(1) + butyl butyrate(2) and octane(1) + cyclohexanol(2), the isobaric VLE data at 101.3 kPa are listed in Tables S1–S4, and the *T*-*x*-*y* diagrams are plotted in Figs. S1–S4 (in Supplementary Material). As shown in Figs. S1–S4, this indicates that there is no azeotropic behavior between the selected solvent and binary mixture, and the selected solvent can be considered as the solvent for extractive distillation.

2.2. Thermodynamic consistency test

In this work, the thermodynamic consistency of VLE data of four binary systems DMSO(1) + PX(2), PX(1) + butyl butyrate(2), octane(1) + butyl butyrate(2) and octane(1) + cyclohexanol(2) is evaluated by using the Van Ness method [30]. It is expressed by Eqs. (1) and (2).

$$\Delta P = \frac{1}{N} \times \sum_{i=1}^N \Delta p_i = \frac{1}{N} \times \sum_{i=1}^N \left| \frac{p_i^{\text{cal}} - p_i^{\text{exp}}}{p_i^{\text{exp}}} \right| \quad (1)$$

$$\Delta y = \frac{1}{N} \times \sum_{i=1}^N \Delta y_i = \frac{1}{N} \times \sum_{i=1}^N |y_i^{\text{cal}} - y_i^{\text{exp}}| \quad (2)$$

where p_i^{exp} and y_i^{exp} stand for the experimental pressure and mole fraction data in the vapor phase, respectively. p_i^{cal} and y_i^{cal} stand for the calculated pressure and mole fraction of the vapor phase by the NRTL, UNIQUAC and Wilson model, respectively. The criterion to judge whether the experimental data pass the thermodynamic consistency test is that the calculated values of Δy and ΔP are less than 0.01. The results of ΔP and Δy by van Ness test are presented in Table S5. Therefore, it was concluded that the experimental VLE data are in good thermodynamic consistency.

2.3. VLE data correlation

The VLE data for the four binary mixtures (DMSO(1) + PX(2), PX(1) + butyl butyrate(2), octane(1) + butyl butyrate(2) and octane(1) + cyclohexanol(2)) were correlated using NRTL, UNIQUAC and

Wilson model. According to the research of Renon and Prausnitz [31], the non-randomness parameter (α_{ij}) of NRTL model is set as 0.3.

Eq. (3) is the maximum likelihood objective function, which can be used to represent the binary interaction parameters of the models.

$$OF = \sum_{i=1}^N \left[\left(\frac{T_i^{\text{exp}} - T_i^{\text{cal}}}{\sigma^T} \right)^2 + \left(\frac{p_i^{\text{exp}} - p_i^{\text{cal}}}{\sigma^p} \right)^2 + \left(\frac{x_i^{\text{exp}} - x_i^{\text{cal}}}{\sigma^x} \right)^2 + \left(\frac{y_i^{\text{exp}} - y_i^{\text{cal}}}{\sigma^y} \right)^2 \right] \quad (3)$$

The root-mean-square deviations [32] (RMSD) and average absolute deviation (AAD) for the temperature (T_i) and the vapor phase composition (y_i) were calculated following the Eqs. (4)–(7). These two values can be used to compare the experimental data with the calculated values.

$$\text{RMSD}(T_i) = \left(\sum_{i=1}^N (T_i^{\text{exp}} - T_i^{\text{cal}})^2 / N \right)^{0.5} \quad (4)$$

$$\text{RMSD}(y_i) = \left(\sum_{i=1}^N (y_i^{\text{exp}} - y_i^{\text{cal}})^2 / N \right)^{0.5} \quad (5)$$

$$\text{AAD}(T_i) = \sum_{i=1}^N |T_i^{\text{exp}} - T_i^{\text{cal}}| / N \quad (6)$$

$$\text{AAD}(y_i) = \sum_{i=1}^N |y_i^{\text{exp}} - y_i^{\text{cal}}| / N \quad (7)$$

Table S6 shows the correlated binary interaction parameters of Wilson, UNIQUAC and NRTL models and the values of RMSD and AAD for the four binary systems. The values of RMSD and AAD for the mole fraction of vapor phase are less than 0.009 and 0.008, respectively. And the values of RMSD and AAD for temperature are less than 0.74 K and 0.62 K, respectively. The results indicate that the three models can be used to regress the isobaric VLE data.

2.4. The relative volatility

The purpose of adding the solvent is to change the relative volatility between the components and make it deviate from $\alpha = 1$ as much as possible. The relative volatility expression is as follow:

$$\alpha = \frac{y_A/y_B}{x_A/x_B} = \frac{\gamma_A P_A^0}{\gamma_B P_B^0} \quad (8)$$

where α is the relative volatilization; y and x are composed of vapor and liquid phases respectively; P_A^0 and P_B^0 refer to the saturated vapor pressure of pure component A and B under system operation; γ_A and γ_B refer to the activity coefficients of components A and B in liquid phase. Table S7 shows the contents of vapor and liquid phases of PX/octane under different compositions.

Fig. 1 shows the effect of different solvents on the composition of PX-octane with different feed molar ratios. According to the degree of deviation from the diagonal, the separation effects of cyclohexanol, butyl butyrate, DMSO, EGME and NFM are studied. As shown in Fig. 1, the x -axis is liquid phase mole fraction of octane. The y -axis is the vapor phase mole fraction of octane, and the vapor and liquid phases mole fraction of octane changes with the addition of solvent. It can be seen from Fig. 1 that the curve deviates furthest from $\alpha = 1$ when NFM as solvent. This indicates that the enhancement of relative volatility by using NFM as solvent is more attractive to PX-octane. The effect of DMSO on relative volatility is less than NFM. The butyl butyrate has the least effect on the relative volatility and the curve deviates nearest from $\alpha = 1$. According to the calculation results of relative volatility,

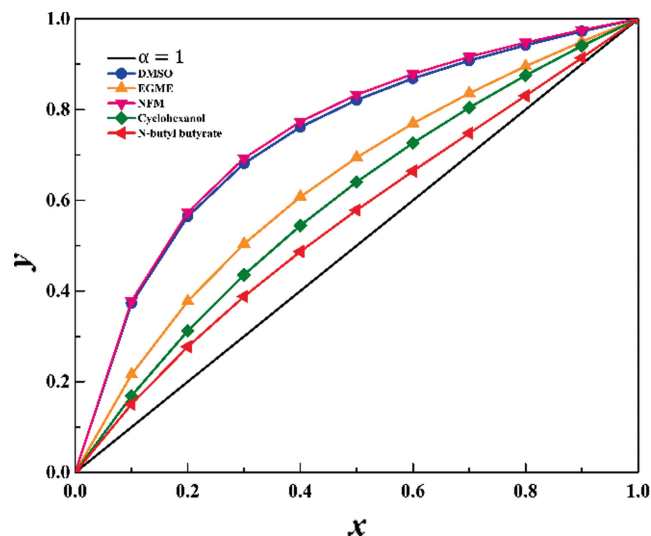


Fig. 1. The y - x diagram under DMSO, 2-methoxyethanol (EGME), cyclohexanol, butyl butyrate and N -formylmorpholine (NFM).

DMSO, EGME and NFM were selected as potential solvents, and the interaction between them and azeotrope was analyzed by quantum chemical calculation.

3. Quantum Chemical Calculation

3.1. Bond length

Quantum chemistry uses quantum mechanics to study a variety of problems. With the development of computer science, it has been applied to chemistry, medicine, food and other fields. It makes up for the deficiency of the traditional experimental means, and makes people more deeply study and understand the nature of the structure and properties of various substances. Gaussian is one of the earliest quantum chemistry calculation programs. It supports a variety of quantum chemistry calculation theories and calculation methods, and can realize geometric structure optimization, chemical bond energy calculation and other functions. The quantum chemical simulation calculation of solvent molecules and PX molecules by using Gaussian program (the calculation method is same as Section 3.2). The optimal configuration of the combinatorial structure of solvent and PX is obtained, and the bond length is obtained under the combinatorial structure.

Through bond length analysis, there is a certain interaction between hydrogen atoms in PX and oxygen atoms in DMSO, EGME and NFM. The optimal configuration and bond length of the three combinatorial structures in Fig. 2 show that the distance between hydrogen atoms in PX and oxygen atoms in DMSO, EGME and NFM are 2.243, 2.475 and 2.214. The van der Waals radius of hydrogen and oxygen are 1.20 and 1.52, and the sum of van der Waals radius of hydrogen and oxygen is 2.72. We can see that the distances between hydrogen atom in PX and oxygen atom in DMSO, EGME and NFM are smaller than the sum of van der Waals radius of corresponding atom. The results showed that there are strong interactions between PX and DMSO, EGME and NFM, respectively. And the hydrogen bond between hydrogen atom in PX molecule and oxygen atom in DMSO is the strongest.

3.2. Interaction energy

In addition to the analysis of bond length, the interaction energy can also be used to analyze the interaction between molecules. The

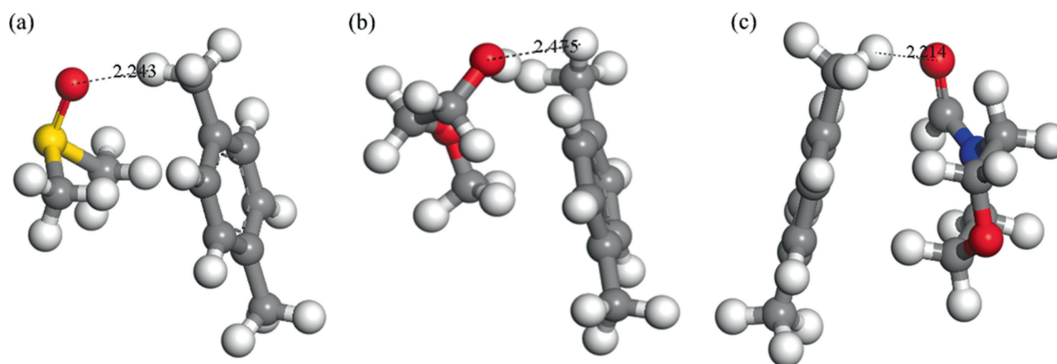


Fig. 2. Hydrogen bond lengths for DMSO, EGME and NFM (a) PX-DMSO, (b) PX-EGEM, (c) PX-NFM.

difference between combinatorial structure and monomer energy is commonly used to express the bond energy between molecules. Li *et al.* [33] studied the interaction between serine and water by quantum chemistry method, calculated the hydrogen bond energy between serine and water, and obtained the most stable existence form of serine water complex; Wang *et al.* [34] analyzed the binding energy of organic solvent, ionic liquid and acetic acid–water system by Gaussian. The results showed that DMSO and [BMIM] [BDP] had better extraction effect on the separation of acetic acid–water system. It provides theoretical guidance for the effective separation of acetic acid–water system and provides a certain reference for the selection of the best entrainer. The calculation of interaction energy is divided into three steps. First, the initial combinatorial structure produced by the gentor/genmer component of the molclus; Then, the quantum chemical program MOPAC and Gaussian [35,36] are used to optimize in sequence, and a batch of structures with lower energy were obtained by screening the results; After that, the molecular conformation and interaction energy of monomer and combinatorial structures were calculated by Gaussian program. It is necessary to optimize all the molecules individually, and then to optimize the combined structure. Calculation formula of interaction energy [37] as follow:

$$\Delta E = E_{AB} - E_A - E_B \quad (9)$$

The E_A is the lowest conformational energy of component A; E_B is the lowest conformational energy of component B; E_{AB} is the lowest conformational energy of binary system.

Hydrogen bond energies greater than 0.015 a.u. are generally considered to be stronger. We can see from the above Table S8 that the interaction energy of DMSO, EGEM, NFM and PX is more than 0.015 a.u. And the interaction energies of the DMSO/EGME/NFM are -0.044 , -0.041 and -0.07 a.u., respectively. The results show that the hydrogen bond energy between PX and NFM is stronger than DMSO and EGEM. Compared with DMSO and EGEM, NFM can better separate PX/octane. Through the interaction energy analysis, the role of bond energy is explored from the molecular level, which provides theoretical support for the effective separation of PX/octane by NFM.

3.3. Charge density distribution

This work studied the total charge density distribution and deformation charge density distribution [38] between DMSO/EGEM/NFM and PX to analyze whether there is hydrogen bond between them. The total charge density between PX and DMSO/EGEM/NFM are shown in Fig. 3, and the deformation charge density between PX and DMSO/EGEM/NFM are shown in Fig. 4.

When the Isovalue is 0.15, the link is still obvious, this indicates that a strong hydrogen bond may be formed between solvent and PX. For PX, DMSO and EGEM can clearly see the link of $C-H \cdots O$ when Isovalue reaches 0.1, and the connection disappears when the Isovalue exceeds 0.1. Only when the Isovalue of NFM reaches 0.25, the link of $C-H \cdots O$ is still obvious. This result can explain that all three solvents have extraction ability in extractive distillation, among which the extraction ability of NFM is the strongest.

The same results can be obtained from the deformation charge density analysis in Fig. 4. The receiving electron region around O atom is red and the electron loss area around H atom is blue. Six carbon atoms on the benzene share a large π bond. The electrons are all concentrated on the carbon rings. The hydrogen atoms become “bare” protons, if the solvent can provide electrons, and hydrogen on the benzene can be used as the acceptor of electrons. The results are shown in Fig. 4, hydrogen atoms in PX are surrounded by red, which indicates that the hydrogen atom is easy to obtain electrons; the blue around the oxygen atom in the DMSO/EGME/NFM indicates that this atom is easy to lose electrons. This result can also explain that all three solvents have extraction ability in extractive distillation.

4. Design of the Process

4.1. Economic optimization

There are many operation parameters in distillation system, and the optimization of operation parameters is indispensable in the distillation process. It is of great significance to obtain the optimal operation conditions for improving the distillation column efficiency and maximizing the industrial production benefits. Based on minimum TAC, sequential iterative optimization method is used to optimize the extractive distillation process to determine the optimal operating conditions. In this work, a unified economic evaluation formula is adopted for all systems, and 3 years is selected as the service life of the equipment [39]. In addition, the operation time of distillation system is set at 8000 hours per year. Table S9 gives the economic calculation formula, size relationship and parameters of distillation system based on Douglas cost calculation model [40]. The equation is as follow:

$$TAC = \text{steam costs} + \text{colling water cosys} + \frac{\text{capital costs}}{3} \quad (10)$$

Fig. 5 shows the effect of parameters on TAC in basic extractive distillation (BED) by sequential iterative optimization. It should be noted that when the RR_1 setting is less than 0.85, the product purity is less than 99.9% (mol). Hence, the optimized RR_1 is 0.85. Number of theoretical plates of column 1 (NT1), number of theoretical

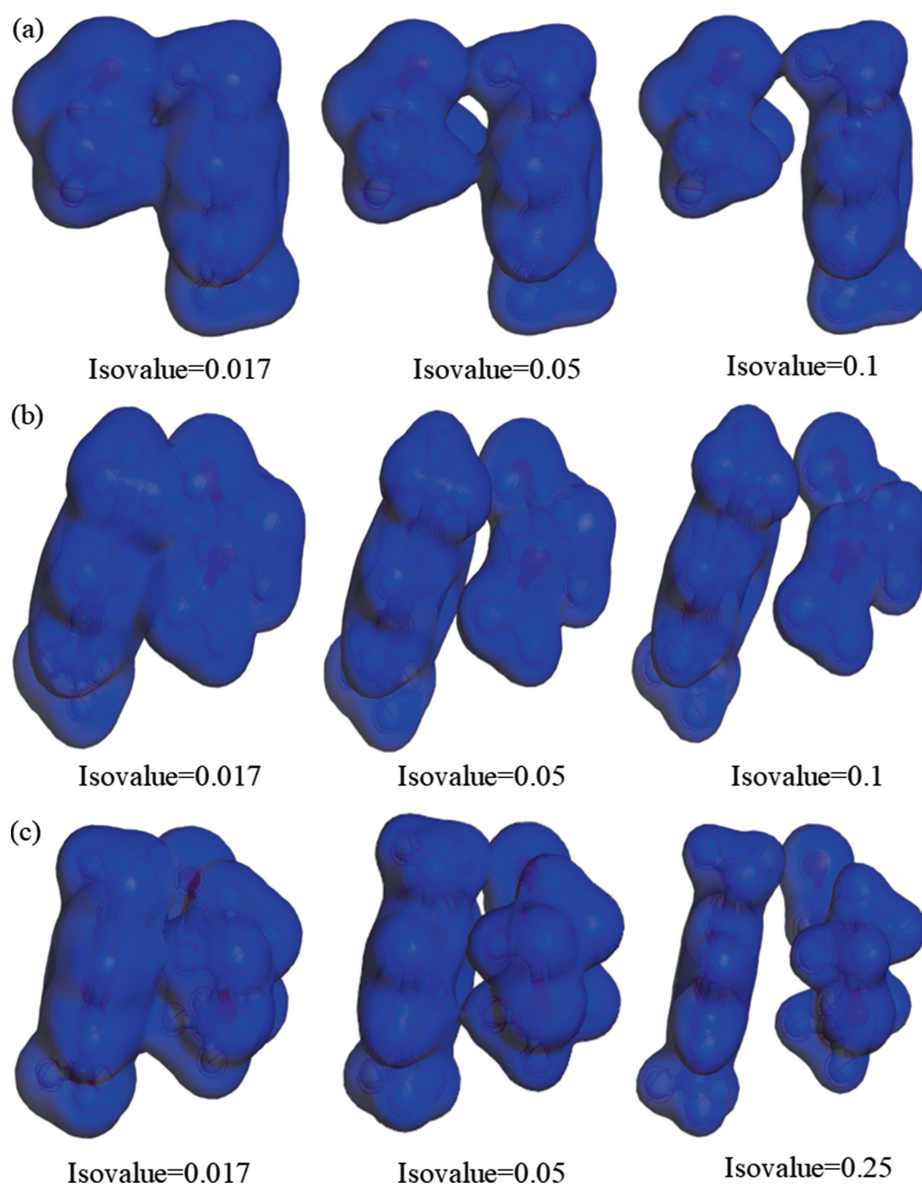


Fig. 3. Total charge density maps of different Isovalues for DMSO, EGME and NFM (a) PX-DMSO, (b) PX-EGEM, (c) PX-NFM.

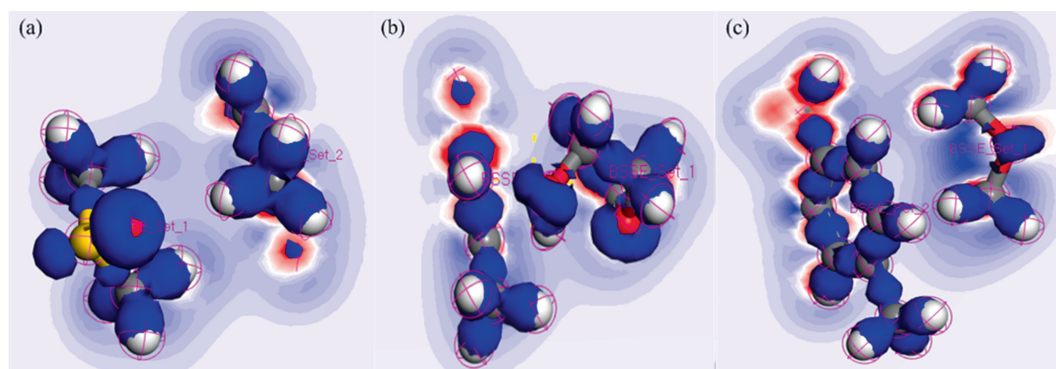


Fig. 4. Deformation charge density maps of DMSO, EGME and NFM (a) PX-DMSO, (b) PX-EGEM, (c) PX-NFM.

plates of column 2 (NT2), feed location of column 1 (NF1), NREC and feed location of column 2 (NF2) were also optimized to achieve minimum TAC (Fig. 5). If the TAC is not the minimum when optimizing a parameter, the upper parameter needs to be adjusted. After optimizing all parameters, the minimum TAC will be obtained.

4.2. Basic extractive distillation

These steady-state simulations use experimental data calculate to obtain Aspen NRTL model parameters [41]. The solvent selected in this work is NFM with boiling point of 513.15 K. Fig. 6 shows the flow chart of the basics process. Feed flow rate is $100 \text{ kmol} \cdot \text{h}^{-1}$, the molar content of PX and octane are same. Some parameters of the feed conditions (flow rate, temperature and composition) and the column structure (column level, operating pressure and flow composition) are determined by the sequential iterative method. The tray number of extractive distillation column (EDT) is 37, feed plate number is 33, extractor feed plate number is 7, the reflux ratio (RR) is 0.85, the tray number of solvent recovery column (SRT) is 15, the number of feed plates is 10, the reflux ratio is 2. The pressure of EDT is 15 kPa, which is determined by product purity and energy consumption of reboiler, as shown in Fig. S5.

4.3. Vapor recompression-assisted extraction distillation

The vapor recompression-assisted process can be divided into two types: one is to pass all the steam flow on the top of SRT through the compressor, the other is to pass part of the steam flow on the top of SRT through the compressor to increase the heat demand of reboiler. When all the steam flow from the top of SRT passes through the compressor, the heat required by the reboiler may be exceeded. Compressing the excess steam will lead to the increase of expensive power and economic loss. This uneconomical behavior could be improved through splitting the overhead stream flowrate (only a portion of the overhead stream is compressed to provide the heat requirement in reboiler) and the major costs in compressor are further decreased.

If the heat flow of the SRT can preheat the feed flow, the heat loss of the heat flow can be greatly reduced, and the heat load of the distillation column can be greatly reduced. Therefore, the feed preheating process is first used to reduce the energy consumption of extractive distillation. The bubble point feeding is generally used in industry, which is beneficial to energy saving and process stability. Therefore, the feed preheating process preheats the feed flow of the two columns to the bubble point temperature, reducing the loss of power and entropy [42,43]. Observed from the feed preheat-

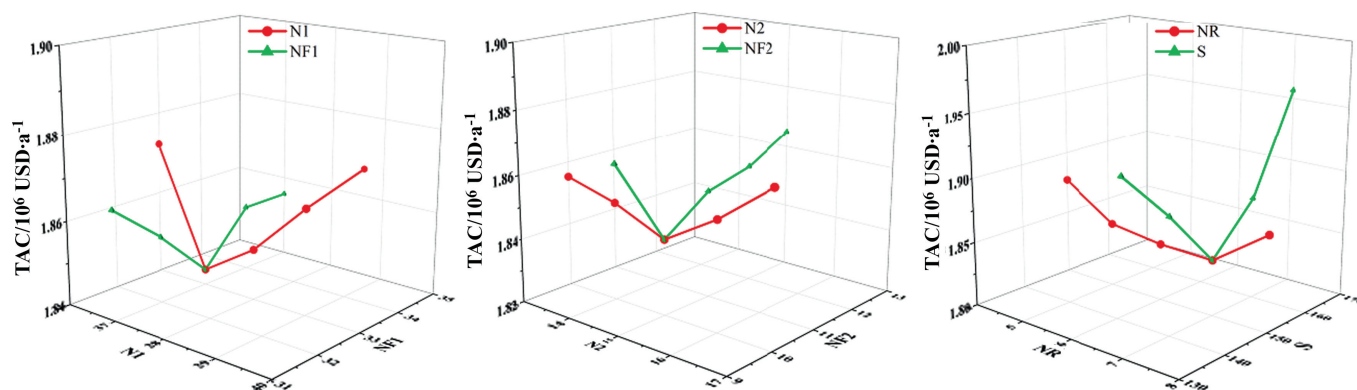


Fig. 5. The effect of the parameters on TAC under the sequential iterative optimization procedure.

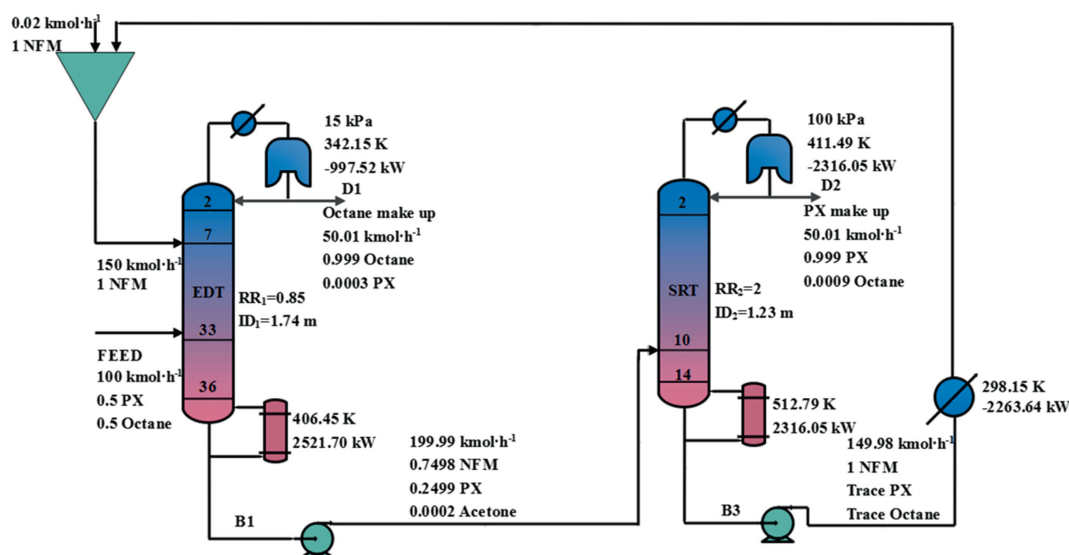


Fig. 6. Process flow chart of PX/octane separation by basic extractive distillation.

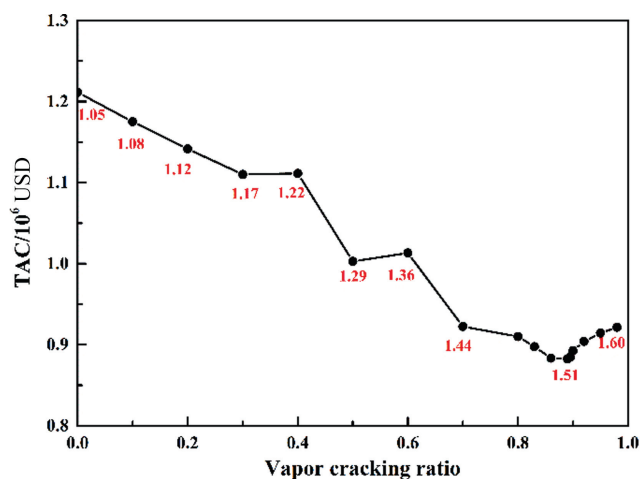


Fig. 7. The effect of operating parameters on TAC for vapor recompression-assisted process.

ing process, the latent heat released by the top steam flow (1763.3 kW) is larger than the heat demand of the reboiler (1606.8 kW). The energy grade of top steam flow through compressor is increased by use of a split device, and this process is called enhanced vapor recompression-assisted extraction distillation (SRAED). The steam flow of the SRT top is divided into two strands, one of which improves its energy quality through the compressor to meet the energy consumption of the reboiler, the other bypasses the two kinds of energy dissipation equipment and drops to the distillation temperature through the cooler. Performance of this vapor recompression-assisted process is further improved by using heat of part of the SRT top steam flow. For this split arrangement, three decisive variables that of TAC, compression ratio and steam cracking ratio need to be optimized. There is a design trade-off between the three decisive variables. Therefore, it is necessary to discuss the feasibility and economy of SRAED process. It must be pointed out that the compression ratio is determined by the coefficient of performances (COPs) [44]. The compression ratio is deter-

mined by the COPs value, and the corresponding compression ratio when the COPs value is slightly greater than 10 is selected.

The red values in Fig. 7 represent the best compression ratio at different steam cracking rates. The TAC optimum is 0.8824×10^6 USD when the optimum compression ratio (critical value) is 1.51 and the steam cracking ratio is 0.895, as shown in Fig. 7. The SRT condenser load of vapor recompression-assisted process is reducing from 1273.6 kW to 512.8 kW, and the cooling requirement of SRT top distillate is reduce from 1506.1 kW to 297.154 kW. The energy saving performance of the newly designed split arrangement process is higher than that of the basics distillation, because the heat utilization rate and process economy can be improved by the energy reuse in the system.

As shown in Fig. 8, the high temperature flow at the bottom of the SRT is first used to preheat the feed flow of the SRT, and the heat exchanger with the high temperature outlet flow is used to preheat feed flow of EDT. After economic optimization, the plate number of EDT is 37, the plate number of feed is 33, the plate number of solvent feed is 26, the reflux ratio is 0.75, the plate number of SRT is 11, the plate number of feed is 8, and the reflux ratio of SRT is 2. And some low temperature and low pressure steam at the SRT top is compressed and heated, and the steam that reaches the required temperature and pressure becomes the high quality heat source of the EDT reboiler. After heat exchange, the pressure is reduced and the temperature is reduced by throttle valve, part of the column as top products, part of the reflux to the column.

4.4. Results comparison and analysis

The operating cost of the BED process is 1.166×10^6 USD·a⁻¹ and the capital cost is 1.162×10^6 USD. And the steam cost is as high as 1.123×10^6 USD·a⁻¹, accounting for 96.27% of the operating cost. Hence, reducing the amount of steam in extractive distillation can effectively reduce TAC. The SRAED process is optimized by sequential iterative optimization. Adding feed preheating process and heat pump process can save fresh hot steam of two columns reboiler. At the same time, the cooling water used for condensing top steam of SRT can also be reduced. Capital cost reduced to 1.123×10^6 USD·a⁻¹, 3.36% lower than the capital cost

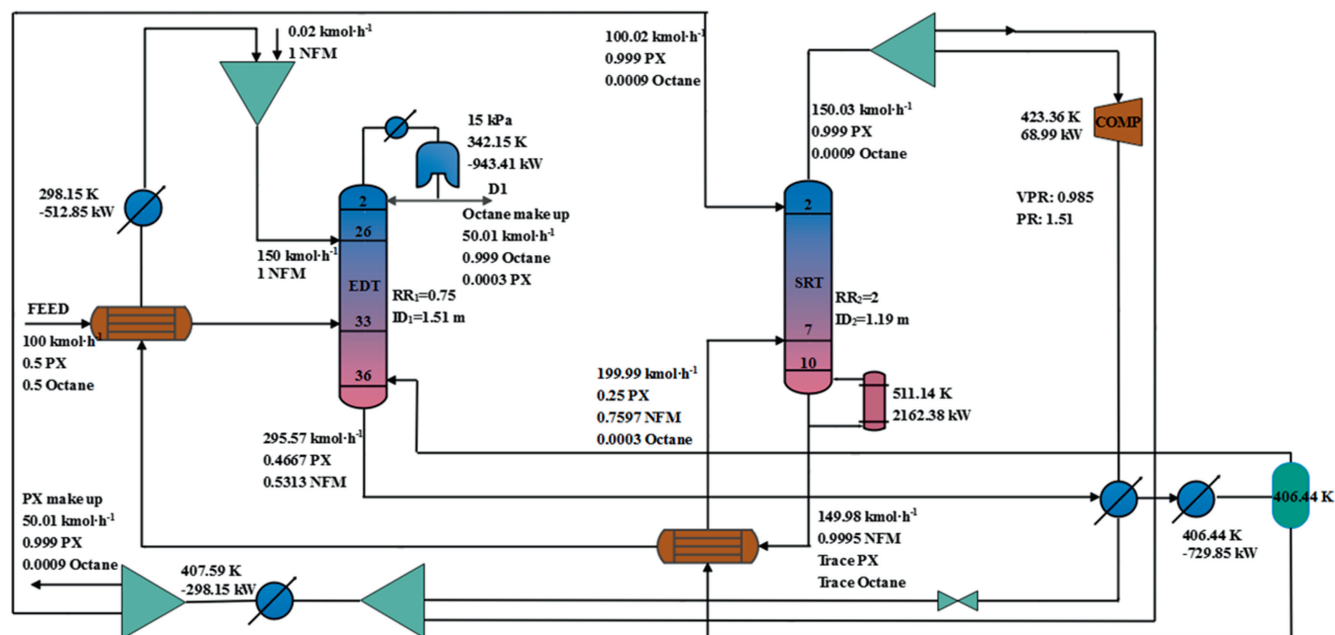


Fig. 8. Optimal flowsheet of PX/octane separation by vapor recompression-assisted extraction distillation.

of traditional extractive distillation processes. Operation cost is reduced to 5.304×10^5 USD·a⁻¹, which saved 54.5% compared with the BED process, and 43.2% reduction in total cost.

5. Conclusions

In this work, the VLE properties and extraction separation mechanism of solvents in difficult systems are studied by experimental and quantum chemical methods, respectively. Taking octane-PX as the research system, aiming at the lack of VLE data between solvent and azeotrope system, combining quantum chemistry method, an effective and complete solvent screening process from phase equilibrium experiment to quantum chemistry calculation is proposed. The binary interaction parameters are regressed from the experimental data and used to calculate the relative volatility accurately. The bond length, interaction energy and charge density distribution between solvent and PX are calculated by quantum chemistry method. The selectivity of solvent for octane-PX system is NFM > DMSO > EGME > cyclohexanol > butyl butyrate, which is consistent with the calculation of relative volatility. In addition, octane-PX are separated by feed preheating and vapor recompression-assisted process, feed preheating process preheats feed flow to its bubble point, vapor recompression-assisted process further improves process performance and heat recovery rate. The feasibility and effectiveness of the SRAED are further discussed. Compression ratio of 1.51 and steam splitting ratio of 0.895 are the most suitable according to TAC evaluation index. Compared with basic process, TAC can be reduced by 43.2%.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2021.06.010>.

Nomenclature

E_{AB}	the intermolecular interaction energy of A and B
E_A	the intermolecular interaction energy of A
E_B	the intermolecular interaction energy of B
p_A^0	the saturated vapor pressure of pure component A, kPa
p_B^0	the saturated vapor pressure of pure component B, kPa
x	liquid phase mole fraction
y	vapor phase mole fraction
α	relative volatilization, $\alpha = y_A x_B / y_B x_A$
γ_A	the activity coefficients of components A
γ_B	the activity coefficients of components B

References

- [1] M.A. Rodriguez, J. Ancheyta, Detailed description of kinetic and reactor modeling for naphtha catalytic reforming, *Fuel* 90 (2011) 3492–3508.

- [2] J. Liu, X. Xiao, Extractive distillation technology and its industrial application, *Modern Chem. Ind.* 6 (2004) 14–17.
- [3] X. Gao, X. Geng, Application of the chemical-looping concept for azeotrope separation, *Engineering* 7 (2021) 84–93.
- [4] S. Sun, L. Lü, A. Yang, S. Wei, W. Shen, Extractive distillation: Advances in conceptual design, solvent selection, and separation strategies, *Chin. J. Chem. Eng.* 27 (2019) 1247–1256.
- [5] X. You, T. Ma, T. Qiu, Design and optimization of sustainable pressure swing distillation for minimum-boiling azeotrope separation, *Ind. Eng. Chem. Res.* 58 (2019) 21659–21670.
- [6] J. Chen, Q. Ye, T. Liu, H. Xia, X. Feng, Design and control of heterogeneous azeotropic distillation for separating 2-methylpyridine/water, *Chem. Eng. Technol.* 41 (2018) 2024–2033.
- [7] L. Zhao, X. Lyu, X. Wang, Comparison of heterogeneous azeotropic distillation and extractive distillation methods for ternary azeotrope ethanol/toluene/water separation, *Comput. Chem. Eng.* 100 (2017) 27–37.
- [8] W.L. Luyben, Comparison of extractive distillation and pressure-swing distillation for acetone-ethanol separation, *Comput. Chem. Eng.* 50 (2013) 1–7.
- [9] O.A. Deorukhkar, T.B. Rahangdale, Y.S. Mahajan, Entrainer selection approach for distillation column, *Int. J. Chem. Eng. Res.* 8 (2016) 29–38.
- [10] H. Li, P. Zhou, J. Zhang, D. Li, X. Li, X. Gao, A theoretical guide for screening ionic liquid extractants applied in the separation of a binary alcohol-ester azeotrope through a DFT method, *J. Mol. Liq.* 251 (2018) 51–60.
- [11] O. Felipe, R. Gonzalo, Q. Angelica, R. Julio, P. Jaime, O. Claudia, Q. Esteban, Theoretical prediction of selectivity in solvent extraction of La(III) and Ce(III) from aqueous solutions using β -diketones as extractants and kerosene and two imidazolium-based ionic liquids as diluents via quantum chemistry and COSMO-RS calculations, *J. Mol. Liq.* 325 (2021) 114655.
- [12] H. Li, G. Sun, D. Li, L. Xi, P. Zhou, X. Li, J. Zhang, X. Gao, Molecular interaction mechanism in the separation of a binary azeotropic system by extractive distillation with ionic liquid, *Green Energy Environ.* (2020).
- [13] L. Li, L. Guo, Y. Tu, N. Yu, L. Sun, L. Tian, Q. Li, Comparison of different extractive distillation processes for 2-methoxyethanol/toluene separation: Design and control, *Comput. Chem. Eng.* 99 (2017) 117–134.
- [14] X. You, J. Gu, C. Peng, I. Rodriguez-Donis, H. Liu, Optimal design of extractive distillation for acetic acid dehydration with *N*-methyl acetamide, *Chem. Eng. Process.* 120 (2017) 301–316.
- [15] L. Sun, X. Chang, T. Tan, Application of thermal coupling technology in azeotropic distillation system, *Progr. Chem. Ind.* 29 (2010) 2228–2233.
- [16] H. Cao, H. Wang, C. Li, Heat integrated extractive distillation of methyl acetate/methanol water, *Progr. Chem. Ind.* 4 (2017) 148–151.
- [17] D.M. Van de Bor, C.A.I. Infante Ferreira, Quick selection of industrial heat pump types including the impact of thermodynamic losses, *Energy* 53 (2013) 312–322.
- [18] G. Modla, P. Lang, Comparison of extractive and pressure-swing batch distillation for acetone-methanol separation, *Comput. Aided Chem. Eng.* 29 (2011) 382–386.
- [19] A.K. Jana, Heat integrated distillation operation, *Appl. Energ.* 87 (2010) 1477–1494.
- [20] T. Shi, W. Chun, A. Yang, S. Jin, W. Shen, J. Ren, J. Gu, The process control of the triple-column pressure-swing extractive distillation with partial heat integration, *Sep. Purif. Technol.* 1238 (2020) 116416.
- [21] S. Sun, A. Yang, I. Chien, W. Shen, S. Wei, J. Ren, X. Zhang, Intensification and performance assessment for synthesis of 2-methoxy-2-methyl-heptane through the combined use of different pressure thermally coupled reactive distillation and heat integration technique, *Chem. Eng. Process.* 142 (2019) 107561.
- [22] H. Luo, C.S. Bildea, A.A. Kiss, Novel heat-pump-assisted extractive distillation for bioethanol purification, *Ind. Eng. Chem. Res.* 54 (2015) 2208–2213.
- [23] K.A. Kobe, Elements of fractional distillation, *J. Chem. Educ.* 28 (1951) 231–232.
- [24] C. Zheng, S. Song, Y. Mu, Research Progress on application forms of heat pump distillation, *Modern Chem. Ind.* 28 (2008) 114–117.
- [25] P. Shi, Q. Zhang, A. Zeng, Y. Ma, X. Yuan, Eco-efficient vapor recompression-assisted pressure-swing distillation process for the separation of a maximum-boiling azeotrope, *Energy* 196 (2020) 117095.
- [26] L. Zhao, X. Lyu, W. Wang, J. Shan, T. Qiu, Comparison of heterogeneous azeotropic distillation and extractive distillation methods for ternary azeotrope ethanol/toluene/water separation, *Comput. Chem. Eng.* 100 (2017) 27–37.
- [27] M. Li, Y. Cui, X. Shi, Z. Zhang, X. Zhao, X. Zhu, J. Gao, Simulated annealing-based optimal design of energy efficient ternary extractive dividing wall distillation process for separating benzene-isopropanol-water mixtures, *Chin. J. Chem. Eng.* 5 (2021) 203–210.
- [28] Z. Xing, Y. Gao, H. Ding, X. Wang, L. Li, H. Zhou, Isobaric vapor-liquid equilibrium for ternary system of ethanol, ethyl propionate and para-xylene at 101.3 kPa, *Chin. J. Chem. Eng.* 26 (2018) 560–565.
- [29] H. Jia, H. Wang, K. Ma, M. Yu, Z. Zhu, Y. Wang, Effect of thermodynamic parameters on prediction of phase behavior and process design of extractive distillation, *Chin. J. Chem. Eng.* 26 (2018) 993–1002.
- [30] H.C. Van Ness, S.M. Byer, R.E. Gibbs, Vapor-Liquid equilibrium: Part I. An appraisal of data reduction methods, *AIChE J.* 19 (1973) 238–244.
- [31] H. Renon, J.M. Prausnitz, Local compositions in thermodynamic excess functions for liquid mixtures, *AIChE J.* 14 (1968) 135–144.

- [32] Y. Liu, Y. Wang, W.F. Cai, Salting effect of sodium hydroxide and sodium formate on the liquid-liquid equilibrium of polyoxymethylene dimethyl ethers in aqueous solution, *J. Chem. Eng. Data* 64 (2019) 2578–2592.
- [33] X. Li, X. Zhang, L. Meng, S. Zheng, Y. Zeng, Quantum chemistry study on the interaction between serine and water, *J. Hebei Normal Univ. (Natural Sci. Ed.)* 34 (2010) 696–701.
- [34] Y. Shen, Z. Chen, H. Qi, Z. Ma, Y. Dai, Q. Zhao, Z. Zhu, Y. Ma, Y. Wang, Mechanism analysis of extractive distillation for separation of acetic acid and water based on quantum chemical calculation and molecular dynamics simulation, *J. Mol. Liq.* 332 (2021) 115866.
- [35] M.J.G. Revision Frisch, G.W. Trucks, H.B. Schlegel, Gaussian, Inc., Wallingford CT, 2004.
- [36] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, B. Barone Mennucci, Gaussian 09, Inc., Wallingford CT, 2009.
- [37] H. Zhang, Y. Liu, X. Yu, X. Qiu, Y. Shen, J. Yang, P. Cui, Y. Wang, J. Gao, Application of green solvent to separate the minimum boiling point azeotrope based on molecular structure prediction and experimental verification, *Sep. Purif. Technol.* 240 (2020) 1383–5866.
- [38] Y. Xu, D. Meng, H. Li, X. Yu, Z. Zhu, Y. Wang, Y. Ma, J. Gao, Mechanism analysis for separation of cyclohexane and tert-Butanol system via ionic liquids as extractants and process optimization, *ACS Sustain Chem. Eng.* 7 (2019) 19984–19992.
- [39] A. Yang, H. Zou, I. Chien, D. Wang, S. Wei, J. Ren, Z. Ren, W. Shen, Optimal design and effective control of triple-column extractive distillation for separating ethyl acetate/ethanol/water with multiazeotrope, *Ind. Eng. Chem. Res.* 58 (2019) 7265–7283.
- [40] J.M. Douglas, *Conceptual Design of Chemical Processes*, McGraw-Hill, New York, 1988.
- [41] X. Huang, S. Xia, P. Ma, S. Song, B. Ma, Vapor-Liquid Equilibrium of *N*-formylmorpholine with toluene and xylene at 101.33 kPa, *J. Chem. Eng. Data*, 53 (2008) 252–255.
- [42] Q. Zhang, M. Liu, C. Li, A. Zeng, Heat-integrated pressure-swing distillation process for separation of the maximum-boiling azeotrope diethylamine and methanol, *J. Taiwan Inst. Chem. E* 93 (2018) 644–659.
- [43] Q. Zhang, M. Liu, C. Li, A. Zeng, Design and control of extractive distillation process for separation of the minimum-boiling azeotrope ethyl-acetate and ethanol, *Chem. Eng. Res. Des.* 136 (2018) 57–70.
- [44] V. Plesu, A.E.B. Ruiz, J. Bonet, J. Llorens, Simple equation for suitability of heat pump use in distillation, *Comput. Aided Chem. Eng.* 33 (2014) 1327–1332.