Separation and Purification of Methyl Isobutyl Ketone from Acetone + Isopropanol + Water + Methyl Isobutyl Ketone + Methyl Isobutyl Carbinol + Diisobutyl Ketone Mixture

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ABSTRACT: The paper presents the results of the study of phase equilibrium in the system containing acetone, isopropanol, water, methyl isobutyl ketone, methyl isobutyl carbinol, and diisobutyl ketone. Mathematical modeling in AspenPlus V.10.0 was chosen as a method of studying. Thermodynamic-topological analysis was used to analyze the structure of the VLE diagram. The technique of studying the full composition diagram based only on a two-dimensional scan (determining the presence of a three-dimensional separatric manifold and distillation regions) was presented and demonstrated on the example of five components constituent of the mixture. It is shown that, in some cases, it is sufficient to study the two-dimensional scan of the phase diagram to predict its internal structure. Two separation flowsheets based on the use of direct and sharp distillation were considered, and the operating column parameters corresponding to minimum energy consumption were determined. The sharp distillation was proved to be less energy-intensive.

1. INTRODUCTION

Methyl isobutyl ketone (MIBK) is an important solvent in the chemical industry (cellulose treatment, paint production, solvent in extraction, and dewaxing processes).1-7 There are several ways to obtain this compound: one-step method (liquid-phase or gas-phase process),8-10 two-step method,11 and three-step method,12 differing in the use of raw materials (acetone/hydrogen8-12 or isopropanol11-13), catalysts, process conditions (reactor pressure and temperature), and a set of by-products. Chemical processes are characterized by various parameters: conversion of reagents, selectivity, etc. (depending on the listed factors that determine the reaction unit operation). Thus, a mixture differing in qualitative and quantitative compositions can be obtained at the exit from the reaction block. The next step is to separate MIBK of commercial quality and reagents that should be recycled to the chemical reaction stage. The multicomponent mixture contains MIBK (a target product), acetone (A), isopropanol (IP), water (W), methyl isobutyl carbinol (MIBC), diisobutyl ketone (DIBK), and diacetone alcohol, mesityl oxide, and mesitylene (depending on the method used). The literature analysis shows that the most promising method of separation is distillation. The proposed separation flowsheets12 are based on the use of a direct sequence in the first distillation column (acetone is taken overhead as a distillate final product). The bottom flow is sent to decanter to separate most of water in an aqueous phase (water forms azeotropes with the other components). The remaining water along with isopropanol is removed in the second column. Commercial MIBK is obtained in the third column, the bottom of which contains heavy-boiling by-products. The disadvantage of such flowsheets is the difficulty of acetone separation (a large number of theoretical stages and a high reflux ratio) as well as the loss of MIBK (in the distillate of the second column) due to the presence of the W + MIBK azeotrope. The latter problem was solved in ref 12 by using extractive distillation with ethylene glycol. Other separation variants are not considered in the literature.

Up to 70% of energy consumption is accounted for by the separation unit in the technology of basic organic synthesis since distillation is an energy-intensive process.19 Therefore, the development of an energy-efficient flowsheet for MIBK separation is an important task.

To propose a separation flowsheet, it is necessary to investigate the phase behavior of the system. One of the most effective methods is thermodynamic-topological analysis.20-22 This area of knowledge is constantly expanding and improving: methods for studying phase diagrams of multicomponent mixtures, internal azeotrope prediction, features of the mutual arrangement of separatric manifolds, and simplices of splitting have been developed. The more azeotropes in a system, the
The study of the phase diagram allows identifying the presence of separatric hypersurfaces of the \((n-2)\) dimension, which divides the composition space into several distillation regions. Table 4 lists the types of all the singular points and their Poincaré indexes. Checking the diagram by the azeotropy rule\(^{22-24}\) showed that the latter is constructed correctly (the sum of Poincaré indexes is equal to 2):

\[
2(N_{\text{S}} + S_i^+ - S_i^-) + \sum_{i=2}^{4} (N_{\text{S}} + S_i^+ - S_i^-) + N_{\text{S}} = 2
\]

where \(N\) is the number of singular points of the node type, \(S\) is the number of singular points of the saddle type, \(+/-\) is the sign of the Poincaré index, and \(i\) is the boundary singular point. The stable and unstable nodes have a Poincaré index \(+1\) or \(-1\) in five-component systems; for this reason, the sign \(+\) or \(-\) near a point of type \(N\) is not specified. In addition, this equation does not include singular points with a zero index (for example, saddles that are located on the border of the composition simplex constituents glued and characterized by a zero Poincaré index).

In Table 1, the singular points MIBK, IP + W, and W + MIBK are zero-index saddles in the composition pentatope because their type is a saddle node in the two-dimensional scan; azeotrope W + DIBK is a singular point of the saddle (of the first order) type. This point will generate a separatric surface of the third dimension inside the phase diagram.

The pentatope scan contains one-dimensional separatrices (S1). Figure 1a shows that they form a closed line (highlighted in red). S1 is one-dimensional traces of a three-dimensional separatric manifold (S3) (the toned area in Figure 1b). The composition pentatope is divided by S3 into two distillation regions (the two-dimensional borders of the distillation regions are highlighted in white and gray in the Figure 1a). Acetone is a common unstable node for both regions. Water and DIBK are stable nodes that are separated from each other by red borders of S1 on the distillation regions (the two-dimensional borders of the distillation regions are highlighted in white and gray in the Figure 1a).

Determining the types of singular points (azeotropes and pure components) allows identifying the presence of the saddles of the first or \((n-2)\) order in the system (the order of the saddle is determined by the number of negative roots of the linearized system of differential equations describing the distillation process\(^{20,21}\)). The presence of such a point indicates that the system will contain a separatric hypersurface of the \((n-2)\) dimension, which divides the composition space into several distillation regions. The presence of such a point indicates that the system will contain a separatric hypersurface of the \((n-2)\) dimension, which divides the composition space into several distillation regions. The presence of such a point indicates that the system will contain a separatric hypersurface of the \((n-2)\) dimension, which divides the composition space into several distillation regions.
demonstrates that, in some cases, it is sufficient to use a two-dimensional scan to analyze the complete phase diagram.

If we return to the analysis of the diagram of the six-component system, we should add two more singular points to the data in Table 1: the pure MIBC (saddle node with an index of zero) and the azeotrope W + MIBC (saddle node with an index of zero). The index of the singular point corresponding to acetone will change the sign to the opposite (⟨⟨−1⟩⟩: the space of an odd dimension). The azeotropy rule is being executed (the sum of the indices of singular points is zero).

The azeotrope W + DIBK will remain a first-order saddle, and the composition hexatope will be divided by a separatric surface of dimension 4 into two distillation regions.

The initial mixture (100 kmol/h) to be separated contains acetone of 0.4934, isopropanol of 0.1717, water of 0.0847, MIBK of 0.1927, MIBC of 0.0015, and DIBK of 0.0575 mole fractions. This composition belongs to the distillation region with DIBK as a stable node. Theoretically three different types of distillation (direct, indirect, and sharp) can be used for the development of separation flowsheets (it is desirable that there is no component(s) distributed between the bottom and distillate flows). Restrictions on the use of one of the separation modes may be due to the presence of azeotropes or a separatric hypersurface. The direct distillation implies separation of acetone at the column’s top (there are no restrictions here since acetone does not form azeotropes with other components); the bottom flow will contain an IP + W + MIBK + MIBC + DIBK mixture. Sharp distillation leads to the separation of the ternary mixture A + IP + W in a distillate flow, the other components will be presented in the bottom flow (limitation: the column’s material balance line cannot cross S4). Indirect distillation implies separation of DIBK in the bottom of the column (the distillate flow will contain an A + IP + W + MIBK + MIBC + DIBK mixture). The disadvantage of the latter case is the presence of a recycling flow in the separation flowsheet, which will negatively affect energy consumption (it is not possible to separate DIBK completely, and, therefore, an additional column will be required to separate the remaining DIBK, which will lead to an increase in capital and operating costs). The separation flowsheets based on the use of direct and sharp distillation are given in Figure 2.

To find the columns’ operating parameters, sensitivity analysis was used. The requirement for the purity of the target product is at least 0.998. Tables 2 and 3 present the parameters of column work, energy consumption, and the compositions of distillate and bottom flows. All the parameters correspond to the minimum energy consumption allowing minimizing impurities in the distillate and bottom flows. The efficiency of the column was chosen based on plotting the energy consumption dependence on the number of stages in the column. The reduced pressure in some columns is explained by the difficulty of separating acetone from water (these components form a tangential azeotrope) and methyl isobutyl ketone from methyl isobutyl carbinol (the relative volatility of components is close to 1).

3. CONCLUSIONS

Knowing the structure of the vapor–liquid equilibrium diagram allows predicting possible sets of products in the distillation process. The phase diagram of an n-component system can be divided into distillation regions by a separatric manifold of an (n − 2) dimension (S_{n−1}). If there are no S_{n−1}’s in the system, there are no restrictions on using direct, indirect, or sharp distillation in the first column. If the phase diagram contains S_{n−1}, then, depending on the number of stable and unstable nodes, it is possible to recommend one or another mode.

The possibility of using a boundary space of the second dimension for a complete analysis of the phase diagram (information about the number of distillation regions about the presence of a separatric manifold of the (n − 2) dimension) was shown on the example of five- and six-component systems.

Based on the thermodynamic-topological analysis of the phase diagram, two separation flowsheets based on the direct and sharp distillation were considered (indirect distillation was not recommended). It is more difficult to separate pure acetone from the initial mixture than the ternary mixture acetone + isopropanol + water (the higher reflux ratio is needed). This is due to the presence of a tangential azeotrope in the binary constituent acetone–water (water and acetone have similar volatilities near the singular point of pure acetone despite the large difference in boiling points). The volatility of acetone relative to water is higher in the ternary system acetone + isopropanol + water mixture compared to the binary one.

The separation flowsheet based on the use of sharp separation can compete with the flowsheet previously proposed in the literature.
4. COMPUTATIONAL METHODS

Thermodynamic modeling of phase equilibrium of the systems was based on the NRTL \[\text{equation}\] using Aspen Plus.

\[
\ln y_i = \sum x_i r_i G_i + \sum_j x_j G_j \left( r_j = \frac{\sum_m x_m G_{mj}}{\sum_k x_k G_{kj}} \right)
\]

where \(G_j = \exp \left( -\alpha_j \tau_{ij} \right)\), \(r_j = a_{ij} + \frac{b_j}{T} + c_j \ln T + f_j T\), \(\alpha = c_i d_{ij} \left( T - 273.15 \text{ K} \right)\); \(\tau_{ii} = 0\), \(G_{ii} = 1\); and \(\tau_{ij} = a_{ij} + \frac{b_i}{T} + c_i \ln T + f_i T\).

The parameters of the NRTL model were taken from the AspenPlus V.10.0 database for systems A + IP, A + W, A + MIBK, IP + W, W + MIBK, and W + DIBK and were regressed using experimental data or a UNIFAC model for systems IP + MIBK, A + DIBK, IP + DIBK, and MIBK+DIBK (Table 4).

The comparison between the evaluated and experimental parameters, boiling temperature of pure components, azeotrope characteristics (composition and boiling temperature) (Table 5), and compositions of liquid phases corresponding to liquid–liquid equilibrium (LLE) (Table 6), was made. If the relative standard uncertainty \((u_r)\) of the description of VLE and LLE was less than 0.05, the set of parameters was used for further calculations (phase equilibrium studies and simulation of the distillation process):

\[
u_a = \frac{u_a}{a_{exp}} = \frac{|a^{exp} - a^{cal}|}{a^{exp}}
\]

where \(a\) can be presented as the temperature \((T)\) or concentration \((X)\).

Table 2. Column Operating Parameters of Separation Flowsheet Presented in Figure 2a

| Column (pressure, kPa) | Stage number | Feed stage | Reflux ratio | Comp. | Distillate composition (mole frac) | Bottom composition (mole frac) | Energy consumption (kW) |
|------------------------|--------------|------------|--------------|-------|-----------------------------------|-------------------------------|------------------------|
| 1 (81.06)              | 38           | 33         | 3.5          | A     | 0.9951                            | 0.0048                        | 2117.4                 |
|                        |              |            |              | IP    | 0.0000                            | 0.3389                        |                        |
|                        |              |            |              | W     | 0.0049                            | 0.1624                        |                        |
|                        |              |            |              | MIBK  | 0.0000                            | 0.3804                        |                        |
|                        |              |            |              | MIBC  | 0.0000                            | 0.0030                        |                        |
|                        |              |            |              | DIBK  | 0.0000                            | 0.1105                        |                        |
| 2 (101.32)             | 37           | 31         | 2.7          | A     | 0.0092                            | 0.0000                        | 1245.3                 |
|                        |              |            |              | IP    | 0.6768                            | 0.0000                        |                        |
|                        |              |            |              | W     | 0.3208                            | 0.0000                        |                        |
|                        |              |            |              | MIBK  | 0.0027                            | 0.7595                        |                        |
|                        |              |            |              | MIBC  | 0.0000                            | 0.0060                        |                        |
|                        |              |            |              | DIBK  | 0.0000                            | 0.2245                        |                        |
| 3 (70.93)              | 32           | 10         | 0.9          | A     | 0.0000                            | 0.0000                        | 362.8                  |
|                        |              |            |              | IP    | 0.0000                            | 0.0000                        |                        |
|                        |              |            |              | W     | 0.0000                            | 0.0000                        |                        |
|                        |              |            |              | MIBK  | 0.9983                            | 0.0058                        |                        |
|                        |              |            |              | MIBC  | 0.0016                            | 0.0207                        |                        |
|                        |              |            |              | DIBK  | 0.0001                            | 0.9735                        |                        |

\(\Sigma = 3725.5\)

Table 3. Column Operating Parameters of Separation Flowsheets Presented in Figure 2b

| Column (pressure, kPa) | Stage number | Feed stage | Reflux ratio | Comp. | Distillate composition (mole frac) | Bottom composition (mole frac) | Energy consumption (kW) |
|------------------------|--------------|------------|--------------|-------|-----------------------------------|-------------------------------|------------------------|
| 1 (101.32)             | 35           | 30         | 1.3          | A     | 0.6580                            | 0.0000                        | 1902.4                 |
|                        |              |            |              | IP    | 0.2290                            | 0.0000                        |                        |
|                        |              |            |              | W     | 0.1130                            | 0.0000                        |                        |
|                        |              |            |              | MIBK  | 0.0000                            | 0.7701                        |                        |
|                        |              |            |              | MIBC  | 0.0000                            | 0.0060                        |                        |
|                        |              |            |              | DIBK  | 0.0000                            | 0.2239                        |                        |
| 2 (70.93)              | 36           | 31         | 2.1          | A     | 0.9950                            | 0.0096                        | 1277.4                 |
|                        |              |            |              | IP    | 0.0001                            | 0.6695                        |                        |
|                        |              |            |              | W     | 0.0049                            | 0.3208                        |                        |
|                        |              |            |              | MIBK  | 0.0000                            | 0.0001                        |                        |
|                        |              |            |              | MIBC  | 0.0000                            | 0.0000                        |                        |
|                        |              |            |              | DIBK  | 0.0000                            | 0.0000                        |                        |
| 3 (70.93)              | 32           | 10         | 0.9          | A     | 0.0000                            | 0.0000                        | 353.8                  |
|                        |              |            |              | IP    | 0.0000                            | 0.0000                        |                        |
|                        |              |            |              | W     | 0.0000                            | 0.0000                        |                        |
|                        |              |            |              | MIBK  | 0.9983                            | 0.0060                        |                        |
|                        |              |            |              | MIBC  | 0.0016                            | 0.0208                        |                        |
|                        |              |            |              | DIBK  | 0.0001                            | 0.9732                        |                        |

\(\Sigma = 3533.6\)

\(\Sigma = 3725.5\)
Table 4. NRTL Parameters for Binary Systems

| binary system | $a_{ij}$ | $b_{ij}$ | $c_{ij}$ |
|---------------|----------|----------|---------|
| A + IP        | −2.4106  | 2.4494   | 822.489 | −583.345 | 0.3     |
| A + W         | 6.3981   | 0.0544   | −1808.99| 419.972  | 0.3     |
| A + MIBK      | −5.4452  | 5.3013   | 1833.52 | −1735.91 | 0.3     |
| A + MIBC      | 0        | 0        | 222.198 | 7.94313  | 0.3     |
| IP + W        | −1.3115  | 6.8284   | 426.398 | −1483.46 | 0.3     |
| IP + MIBK     | 0        | 0        | 160.644 | 28.1164  | 0.3     |
| IP + MIBC     | 0        | 0        | 159.305 | −122.935 | 0.3     |
| W + MIBK      | 9.16294  | −3.23048 | −1248.74| 1208.88  | 0.2     |
| W + DIBK      | 11.6082  | −0.3283  | −969.938| 730.523  | 0.2     |
| W + MIBC      | 7.18523  | −1.15534 | −547.79 | 496.857  | 0.264   |
| A + DIBK      | 0        | 0        | 335.049 | −164.928 | 0.3     |
| IP + DIBK     | 0        | 0        | 263.227 | 125.6    | 0.3     |
| MIBK + MIBC   | −15.2238 | 9.49025  | 6102.93 | −3717.53 | 3.3     |
| W + DIBK      | 0        | 0        | 172.857 | 89.2098  | 0.3     |
| MIBK + DIBK   | 0        | 0        | 123.919 | −77.498  | 0.3     |

Table 5. Boiling Temperatures ($T$) of Pure Components and Azeotropic Data ($X_1$ and $T$) (Experimental$^{31-35}$ and Calculated) for the System A + IP + W + MIBK + MIBC + DIBK at 101.3 kPa

| pure component/azeotrope | $X_1^{exp}$ (mole frac.) | $X_1^{exp}$ (mole frac.) | $u_1$ (mole frac.) | $T_{cal}$ (K) | $T_{exp}$ (K) | $u_1$ (K) | $u_2$ (K) |
|--------------------------|--------------------------|--------------------------|-------------------|---------------|---------------|-----------|-----------|
| A                        | 1.0000                   | 1.0000                   | 0.0000            | 329.29        | 329.35        | 0.06      | 0.0002    |
| IP                       | 1.0000                   | 1.0000                   | 0.0000            | 355.20        | 354.75        | 0.45      | 0.0013    |
| W                        | 1.0000                   | 1.0000                   | 0.0000            | 373.17        | 373.15        | 0.02      | 0.0001    |
| MIBK                     | 1.0000                   | 1.0000                   | 0.0000            | 389.29        | 389.15        | 0.14      | 0.0004    |
| MIBC                     | 1.0000                   | 1.0000                   | 0.0000            | 404.83        | 404.95        | 0.12      | 0.0003    |
| DIBK                     | 1.0000                   | 1.0000                   | 0.0000            | 410.44        | 412.55        | 1.45      | 0.0033    |
| IP + W                   | 0.6728                   | 0.6816                   | 0.0088            | 353.33        | 353.25        | 0.08      | 0.0002    |
| W + MIBK                 | 0.6489                   | 0.6420                   | 0.0069            | 361.54        | 361.00        | 0.54      | 0.0015    |
| W + MIBC                 | 0.8105                   | 0.805                    | 0.0055            | 367.44        | 367.50        | 0.06      | 0.0002    |
| W + DIBK                 | 0.9036                   | 0.8641                   | 0.0395            | 370.35        | 370.15        | 0.20      | 0.0005    |

Table 6. Experimental$^{36-38}$ and Calculated LLE Data ($X_1′$ and $X_2′$) for Systems W + MIBK, W + MIBC, and W + DIBK at 101.3 kPa and 298.15 K (303.15 K for W + MIBC)

| binary system | $X_1′$ (cal) (mole frac.) | $X_2′$ (calc) (mole frac.) | $X_1′$ (exp) (mole frac.) | $X_2′$ (exp) (mole frac.) | $u_1$ (mole frac.) | $u_2$ (mole frac.) | $u_1$ (K) | $u_2$ (K) |
|---------------|--------------------------|---------------------------|--------------------------|--------------------------|-------------------|-------------------|-----------|-----------|
| W + MIBK      | 0.9059                   | 0.9965                    | 0.9505                   | 0.9984                   | 0.0009            | 0.0010            | 0.0019    | 0.0019    |
| W + MIBC      | 0.7427                   | 0.9973                    | 0.7342                   | 0.9973                   | 0.0085            | 0.0115            | 0.0000    | 0.0000    |
| W + DIBK      | 0.9693                   | 0.9999                    | 0.9937                   | 0.9997                   | 0.0244            | 0.0246            | 0.0002    | 0.0002    |

The relative standard uncertainty of description of phase equilibrium is less than 0.05. Thus, the conclusion can be drawn that the VLE and LLE data can be properly correlated by the NRTL model.

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Notes

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