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The Process of Isolation by Crystallization of Cis- and Trans-Isomers of Perfluorodecalines from Industrial Mixture of Electrochemical Fluorination of Napthaline †

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Abstract The process of crystallization separation of an industrial mixture of perfluorinated cycloalkanes is considered. The content of target products, cis- and trans- isomers of perfluorodecalin (PFD), in all initial fractions of the investigated samples of the reaction mixture was at least 70 wt.%. Based on the experimental data, the dependences of the crystallization (partition) coefficients between the solid and mother liquor ($D^{s/l}$), the enrichment factor (η^s) and the separation factor (F^s) on: the ratio of trans-PFD to cis -PFD; ratio of mother liquor to solid; crystallization temperature in the range −50÷−15 °C were obtained. It is shown that the values $D^{s/l}$ and η^s depend significantly on the concentration of trans-PFD in the initial solution, and the value of F^s decreases as the process temperature rises.

Keywords: perfluorocycloalkanes; perfluorodecalin; cis-/trans- isomers; crystallization; separation; purification

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1. Введение

Perfluorodecalin (PFD) is used in medicine, in particular, as a component of blood substitutes [1,2], as a perfusion fluid to transfer substances across the cell membrane, in bioengineering to modify biomolecules [3], and also provide handles for purification, mass spectrometry, and ^{19}F NMR studies in complex environments [4], which leads to stringent requirements for the purity of the final product. The main method for PFD manufacturing is the electrochemical fluorination of naphthalene or decalin [5,6], which results in the formation of two optical isomers of PFD: cis-PFD and trans-PFD. This process is also associated with the partial destruction of C–C chemical bonds in the PFD molecule and the formation of various impurities, including perfluoro(butylcyclohexane) (BCH) [7,8].

The industrial methods for separating the products of the reaction of electrochemical fluorination of decalin include: the distillation process [9], which is characterized by low relative volatility values, and crystallization [10,11]. The latter shows high efficiency in the final PFD purification from impurities, is characterized by higher values of the partition coefficient and allows to obtain individual PFD isomers of high purity. At the same time, the crystallization process is understudied, requires solid-liquid phase equilibrium data of the investigated systems and the dependences of process indicators on various technological parameters.

The purpose of this work is to study the process of separation of an industrial PFD mixture by the crystallization method.

2. Materials and methods

The initial mixture of PFD was taken directly from industrial plant. The content of the target products—cis- and trans-PFD in all initial fractions of the studied samples of the reaction mixture was at least 70 wt. %.

To carry out the crystallization process, the initial fraction with known composition (f_i) and weight was placed in a chest freezer and kept at a constant temperature (T_{sep}) for at least 24 h. Next, the mother liquor was separated from the solid by decanting for three hours in a chest freezer at T_{sep}. The fractions obtained were weighed and their compositions were determined.

Gas chromatography (GC) was used for analytical determination of phase compositions. All quantities are weighted in analytical balance ($\pm 5 \bullet 10^{-4}$ g).

3. Results and Discussion

The analysis of the initial fraction composition showed that in addition to PFD isomers various impurities are presented in the mixture. The nomenclature of the latter includes about 8 components, most of which have not been identified due to the lack of relevant researches and the complexity of their self-concentration to identify their structure. The main impurity (up to 30 wt. %) was BCH.

The array of experimental data, obtained during crystallization (Figure 1), was processed in order to calculate the process indicators of the process, which are presented below in graphical form.

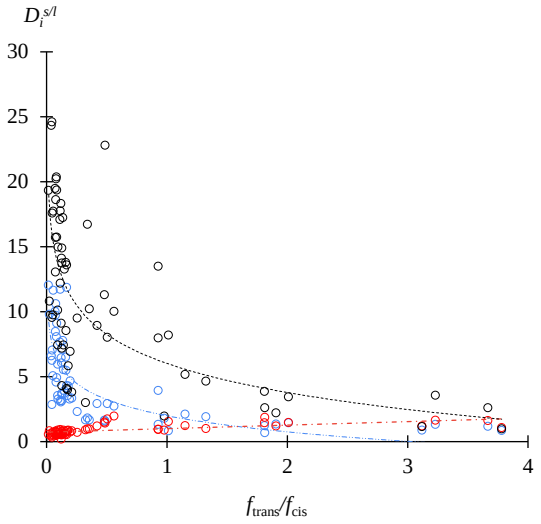

Figure 1. The dependence of the partition coefficient between the solid and mother liquor $D_i^{s/l}$ on the ratio of trans-PFD/cis-PFD in the initial fraction (f_{trans}/f_{cis}). Red—trans-PFD; blue—cis-PFD; black—∑PFD.

3.1. Crystallization coefficient

The dependence of the crystallization (partition) coefficient between the solid and mother liquor ($D^{s/l}$—Equation (1)) on the ratio of components in the initial fraction (f_i/f_j) is shown in Figure 2.

$$D_i^{s/l} = \left(\frac{x_i/(1-x_i)}{y_i/(1-y_i)}\right), \quad (1)$$

where x_i and y_i are the concentrations of the mixture component i in the crystalline and mother liquor, respectively.

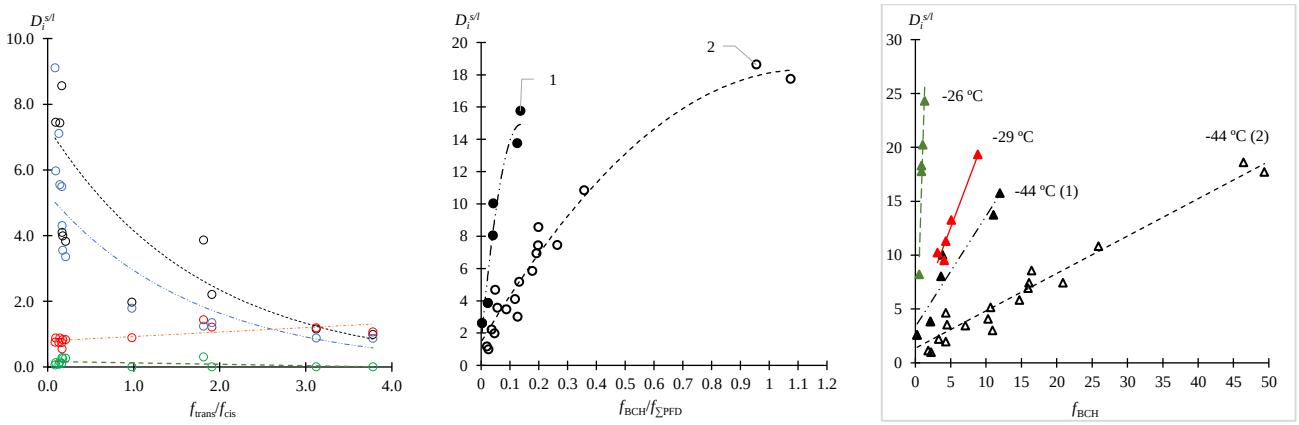

Figure 2. The dependence of the partition coefficient between the solid and mother liquor ($D^{s/l}$): (**a**) on the ratio of trans-PFD/cis-PFD in the initial fraction (f_i/f_j) for components of the mixture at T_{sep} = −44 °C; (**b**) on the ratio of BCH/∑PFD in the initial fraction (f_i/f_j) for ∑PFD at different nomenclature and quantity of unidentified impurities at T_{sep} = −44 °C; (**c**) on concentration of BCH in the initial fraction (f_{BCH}) for ΣPFD at different T_{sep}. Dots: red—trans-PFD; blue—cis-PFD; black—∑PFD; green—BCH.

According to the experimental data (Figure 2a), the $D^{s/l}$ value significantly depends on the presence of trans-PFD in the initial solution. Thus, with an increase in the ratio of trans-PFD/cis-PFD: the $D^{s/l}$ value for the low-melting BCH tends to 0—BCH is completely absent in the solid phase; the majority of unidentified impurities are concentrated in the mother liquor ($D^{s/l} < 1$); the $D_{trans}^{s/l}$ value has a linear dependence with the point of inversion ($D_{trans}^{s/l} \gtrless 1$ at the ratio of trans-PFD/cis-PFD ≷ 1); $D_{cis}^{s/l} \geq 1$ for almost all trans-PFD/cis-PFD ratios and $D_{cis}^{s/l} \gg 1$ at trans-PFD/cis-PFD < 1. Thus, according to the experimental data the crystallization of the fractions with high trans-PFD content is less effective than that with high cis-PFD content. In addition, the $D^{s/l}$ value depends on the nomenclature and concentration of impurities in the initial fraction (Figure 2b,c—curve 1 and curve 2). The latter is very interesting given that the melting point (T_m) of cis-PFD is lower than that of trans-PFD (Table 1). There are also clear dependences of the partition coefficient on T_{sep} (Figure 2c).

Table 1. Crystallization temperatures of pure trans- and cis-PFD and BCH.

Substance	T_m, °C
Trans-PFD	21.46 [12]
Cis-PFD	−6.45 [12]
BCH	−49.37 [9]

3.2. Enrichment factor

The dependence of PFD enrichment factor into the solid (η^s—Equation (2) [13]) on the ratio of trans-PFD/cis-PFD in the initial fraction (f_{trans}/f_{cis}) at different ratios of mother liquor to solid (L/S) is shown in Figure 3.

$$\eta_i^s = \left(\frac{S \cdot x_i}{F \cdot f_i}\right), \quad (2)$$

where f_i is the concentration of the component in the initial fraction, F and S are the masses of the initial and crystalline fractions, respectively.

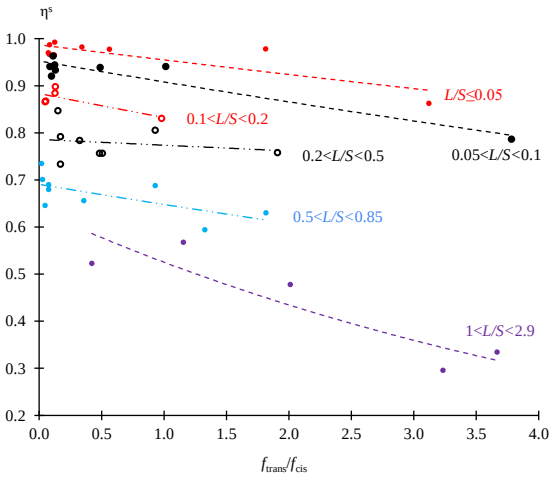

Figure 3. The dependence of the enrichment factor of PFD into solid $\eta^s_{\sum PFD}$ on the ratio of trans-PFD/cis-PFD in the initial fraction (ftrans/fcis) at different ratios of mother liquor to solid (L/S).

From Figure 3 it follows that $\eta^s_{\sum PFD}$ decreases insignificantly with an increase in the ratio f_{trans}/f_{cis} (horizontally) at all values of *L*/*S*. In addition, for f_{trans}/f_{cis} = const an increase in the proportion of the mother liquor in relation to the solid leads to a decrease (vertically) in the value of the PFD enrichment factor from the mixture $\eta^s_{\sum PFD}$.

3.3. Separation factor

The dependence of the separation factor of cis-PFD on the solid (F^s_{cis}—Equation (3) [13]) on the ratio BCH/ΣPFD in the initial fraction (f_{BCH}/f_{PFD}) at different temperatures of the crystallization process T_{sep} is shown in Figure 4.

$$F_i^s = \left(\frac{1-x_i}{1-f_i}\right). \quad (3)$$

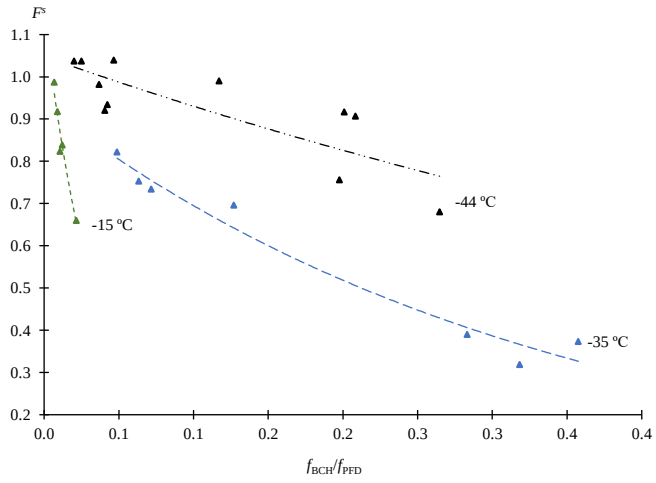

Figure 4. The dependence of the separation factor of cis-PFD F^s on the ratio f_{BCH}/f_{PFD} at different T_{sep} values.

It follows from Figure 4 that an increase in the BCH concentration in the initial fraction leads to a decrease in the F^s_{cis} value at all T_{sep}. The effect of the BCH relative concentration on the F^s_{cis} value increases significantly with T_{sep} increasing. It should be noted that at T_{sep} = −44 °C, which is close to the BCH crystallization temperature, the value of F^s_{cis} is close to 1, enrichment of the solid phase of cis-PPD practically does not take place. However, BCH entrains other law-melting impurities into the mother liquor.

4. Conclusions

The paper considers the separation by crystallization of an industrial mixture of PFD and its impurities. BCH acts as the main impurity. During the crystallization process, in addition to the separation of PFD and impurities, a partial separation of PFD isomers takes place. Despite the higher melting point of trans-PFD, it's partition coefficient is less than that of cis-PFD ($D_{trans}^{s/l} < D_{cis}^{s/l}$). This phenomenon can presumably be associated with the presence of a significant amount of BCH in the investigated samples, which affects the solid-liquid phase equilibrium. It should be noted that despite all the difficulties in processing the array of experimental data associated with the multicomponent nature of the mixture and the mutual, possibly multidirectional influence of variables affecting the indicators of the crystallization process, a number of explicit temperature and concentration dependences are observed for the mixture.

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