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Perfluoro(7-methylbicyclo[4.3.0]nonane) Purification from Close-Boiling Impurities by Heteroazeotropic Distillation Method †

Andrei V. Polkovnichenko *, Egor V. Lupachev *, Alexey V. Kisel', Sergey Ya. Kvashnin and Nikolai N. Kulov

Kurnakov Institute of General and Inorganic Chemistry RAS, Moscow 119991, Russia;
email1@email.com (A.V.K.); email2@email.com (S.Y.K.); email2@email.com (N.N.K.)
* Correspondence: anzakhlevniy@rambler.ru (A.V.P.); egorlu91@gmail.com (E.V.L.)

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Abstract: The purification of perfluoro(7-methylbicyclo[4.3.0]nonane) industrial fractions with component content above 0.950 mass fraction is not effective and requires the use of special separation methods. According to experimental data, the separation factor of the initial mixture during distillation with no additional substances is close to 1. At the same time the acetone (Ac) adding makes it possible to significantly intensify the process. Ac allowed to obtain MBCN with purity higher than 0.998 mass fraction in one separation cycle, the degree of recovery was more than 0.85 by weight. The paper presents data on the distribution of components (target product, identified and unidentified impurities of electrochemical fluorination of decalin) between the distillate and bottom product fractions; separation factor; liquid-liquid phase equilibrium in the MBCN-Ac system and characteristics of the MBCN-Ac heteroazeotrope.

Keywords: perfluorocycloalkanes; perfluoro(7-methylbicyclo[4.3.0]nonane); perfluorodecalin; isomers separation; heteroazeotropic distillation

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1. Introduction

The perfluorodecalin (PFD) manufacturing in industry occurs in two stages [1]. First stage – "mild" fluorination which allows to protect the carbon chain. Second stage—the mixture is treated by molecular fluorine to get rid of the residual partially fluorinated molecules, the content of which is strictly regulated. At the same time, there is a partial destruction of the carbon chain in the molecules of the target component. As part of this process, a number of researches have been published on the structure and nature of impurity components [2–4] and properties of reaction mixture constituents [5–8]. However, the question of the mechanism of the side reactions and the structure of their products is still open, since the identification of the components required spectral analysis of the samples, which has not yet been obtained in pure form. That is, the reference samples are not available in practice, and data on the spectral and physicochemical properties are not available in the literature, which makes it deeply problematic to direct physical and chemical search for intensification methods of production and purification of these compounds.

Perfluoro(7-methylbicyclo[4.3.0]nonane) (MBCN) is one of the identified impurity of an industrial mixture of closely boiling configurational and structural isomeric reaction products of the electrochemical fluorination of decalin and naphthalene [9]. During the target component production, PFD, there is a partial destruction of the carbon chain followed by a partial radical cycle-closing reaction to form MBCN (Figure 1).

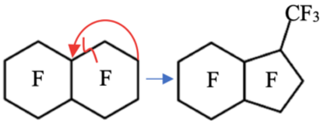


Figure 1. Mechanism of the side reaction of PFD carbon chain destruction and MBCN formation.

It should be noted that the side perfluorinated alicyclic impurities have their own commercial value. They are used as monomers in the production of lyophobic polymer films, tracers to assess leakage from the sequestration of CO_2 in a depleted oil reservoir, and optical elements including lenses where the focal length can be controlled using an electric field [10–13].

The purpose of this work is the process of distillation purification of the constituent of an industrial mixture of products of electrochemical fluorination of decalin and naphthalene—perfluoro(7-methylbicyclo[4.3.0]nonane).

2. Materials and Methods

As an investigation object, in the present work, the fraction of MBCN with main component content ranged from 0.950 to 0.975 mass fraction is considered. The mixture itself with initial content of target product about 0.80 mass fraction was taken directly from industry. Further, the mixture can be purified by distillation to 0.950÷0.975 mass fraction of MBCN. Subsequent separation of the resulting mixture by distillation does not lead to a change in fractions composition. The impurities content can be divided into the following subsections: identified—PFD (≈0.004 ÷ 0.025 mass fraction); not identified—main impurity (main imp. ≈ 0.012 ÷ 0.028 mass fraction) and sum of other impurities (∑ other imp. ≈ 0.0001 ÷ 0.008 mass fraction; up to 10 compounds).

The heteroazeotropic distillation was used to intensify the separation process. Acetone (Ac) (CAS No 67-64-1, ≥0.995 mass fraction) and dimethylformamide (DMFA) (CAS No 68-12-2, ≥0.990 mass fraction) were considered as heteroazeotrope-forming agents (SA). All distillation experiments were performed at atmospheric pressure (P) on a semi-commercial batch distillation column with an efficiency of 85 theoretical separation stages. The flow diagram of the unit and its structure are fully described in [14]. During the experiment, distillate was sampled every two hours, each 8 samples are a fraction of the distillate (Fr). Gas chromatography (GC) and nuclear magnetic resonance (NMR) methods were used for analytical determination of phase compositions. The initial mixture (F), the distillate fractions (Fr), the total distillate (∑D) and the bottom (W) were analyzed. In the case of heteroazeotropic distillation, the dissolved separating agent was removed from the samples by extraction with water.

Liquid-liquid equilibrium data were obtained by the cloud point method. The composition of each cloud point is determined gravimetrically. All quantities are weighted in analytical balance ($\pm 5 \times 10^{-4}$ g). Heteroazeotrope characteristic was determined by continuous distillate flow sampling at 0 reflux ratio value. The obtained fraction was thermostated in separating flask, after that the phases were separated and weighed. The composition of the phases was determined from the data on the liquid-liquid phase equilibrium. For the experiments was used fraction with a content of MBCN ≥0.998 mass fraction.

3. Experimental Results

Experimental data on MBCN distillation, including in the presence of heteroazeotrope-forming agents, are shown in Table 1. According to the Table 1 data were plotted the dependences (Figure 2) of: distillate fractions (Fr), total distillate (∑D) and bottom (W) compositions versus sampling ratio (Equation (1)):

$$Sampling\ ratio = \sum m_{Fr}/m_F, \quad (1)$$

where m_F—feed weight, g; $\sum m_{Fr}$—the total amount of sampled distillate, g.

Table 1. Experimental data on MBCN purification by distillation at atmospheric pressure.

	Fraction	Components Content X_i, Mass % (u(X) = 0.05 Mass %)				Sampling Ratio, Mass Fraction
		Identified		Not Identified		
		MBCN	PFD	Main Imp.	∑ Other Imp.	
P = 99.0 ± 3 kPa	Experiment No 1. Distillation without additional substances (I)					
	∑D	96.791	1.051	1.375	0.783	0.80
	F	95.359	2.493	1.305	0.843	-
	W	89.557	7.720	1.114	1.609	0.20
	Experiment No 2. Distillation without additional substances (II)					
	∑D	97.412	0.631	1.645	0.313	0.79
	F	96.925	1.058	1.659	0.358	-
	W	95.066	2.690	1.712	0.532	0.21
	Experiment No 3. Distillation without additional substances (III)					
	∑D	97.411	1.180	1.210	0.199	0.78
	F	97.512	0.990	1.311	0.187	-
	W	97.516	0.555	1.739	0.190	0.22
	Experiment No 4. Heteroazeotropic distillation in the presence of DMFA					
	∑D	97.835	0.583	1.249	0.333	0.89
	F	97.410	0.894	1.505	0.191	-
	W	92.616	3.353	3.306	0.725	0.11
	Experiment No 5. Heteroazeotropic distillation in the presence of Ac (I)					
	∑D	99.912	0	0	0.088	0.87
	F	96.400	0.689	2.846	0.066	-
	W	80.537	3.782	15.681	0	0.13
	Experiment No 6. Heteroazeotropic distillation in the presence of Ac (II)					
	∑D	99.835	0	0	0.165	0.87
	F	98.379	0.399	1.207	0.016	-
	W	87.344	2.167	10.489	0	0.13

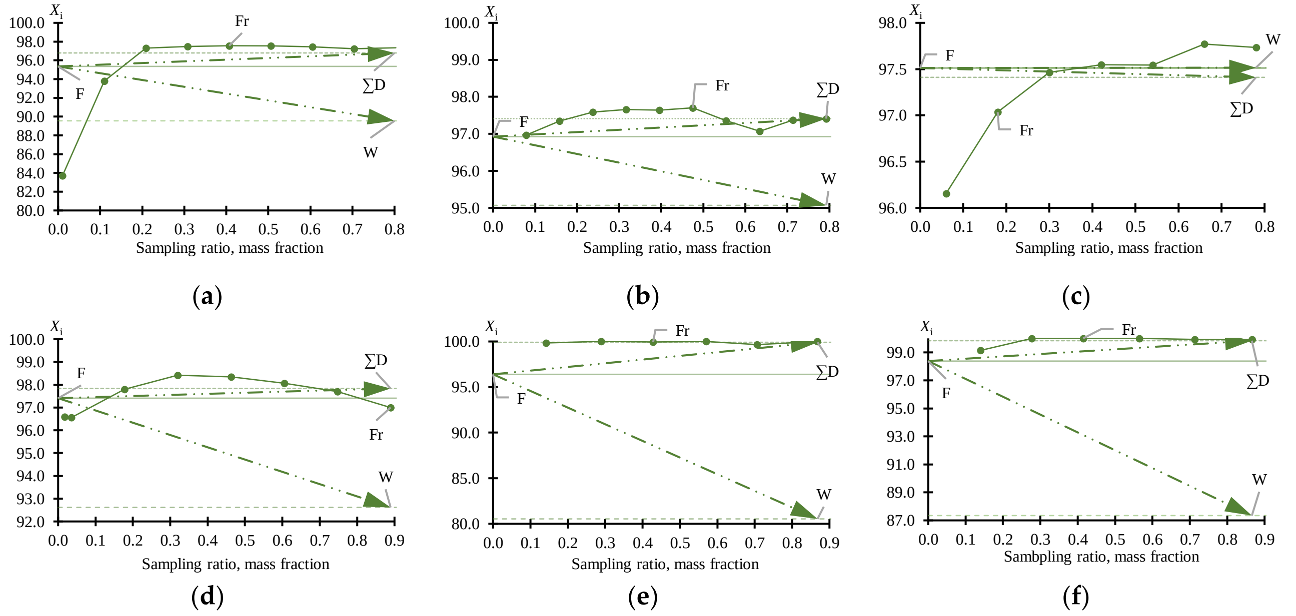


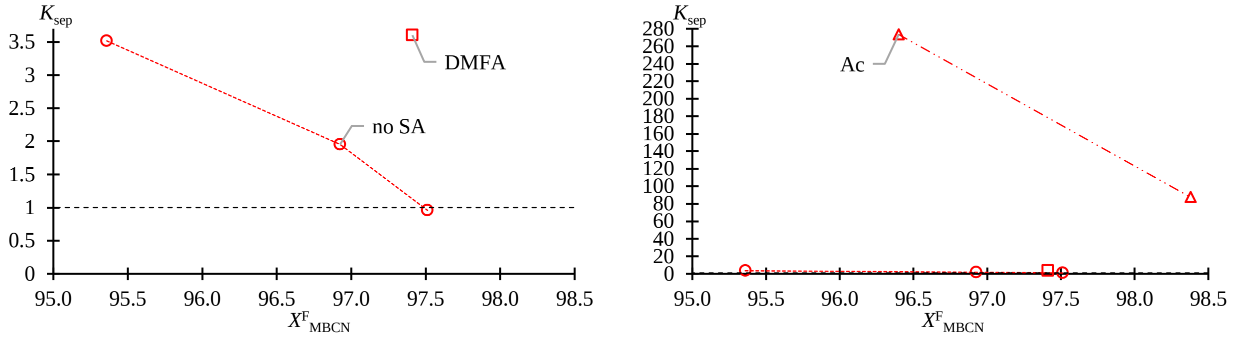
Figure 2. MBCN content (X, mass %) in samples versus sampling ratio according to the Table 1: (**a**) Experiment No 1; (**b**) Experiment No 2; (**c**) Experiment No 3; (**d**) Experiment No 4; (**e**) Experiment No 5; (**f**) Experiment No 6.

Dependences of separation ratio (K_{sep}) and ratio of enrichment (K_{enr}) of MBCN versus target component content in feed fraction are shown in Figure 3 and Figure 4, accordingly. The K_{sep} (Equation (2)) and K_{enr} (Equation (3)) are calculated according to Table 1:

$$K_{sep} = \frac{\left(x_{\sum D}^{MBCN}/\left(1-x_{\sum D}^{MBCN}\right)\right)}{\left(x_{W}^{MBCN}/\left(1-x_{W}^{MBCN}\right)\right)}, \tag{2}$$

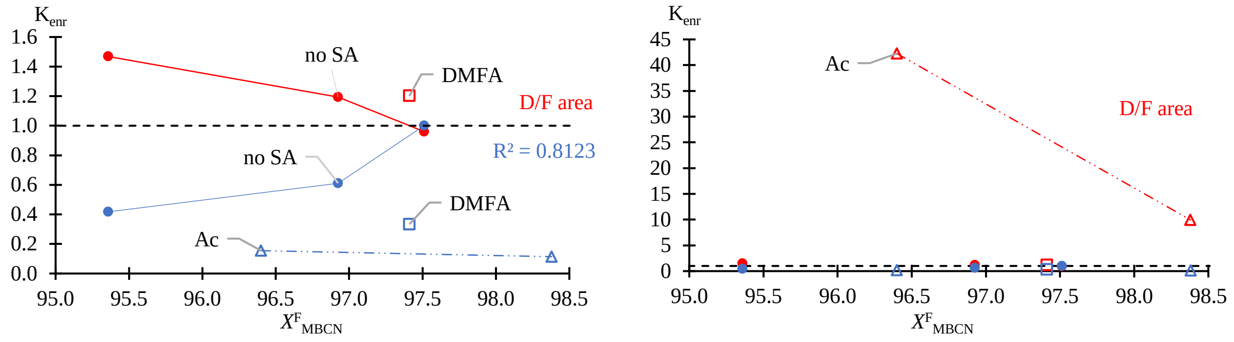
$$K_{enr}^{\sum D/F} = \frac{\left(x_{\sum D}^{MBCN}/\left(1-x_{\sum D}^{MBCN}\right)\right)}{\left(x_{F}^{MBCN}/\left(1-x_{F}^{MBCN}\right)\right)} \quad or \quad K_{enr}^{W/F} = \frac{\left(x_{W}^{MBCN}/\left(1-x_{W}^{MBCN}\right)\right)}{\left(x_{F}^{MBCN}/\left(1-x_{F}^{MBCN}\right)\right)} \tag{3}$$

where X_i^{MBCN}—MBCN content, mass %; F—feed; W—bottom; ∑D—total distillate.



(**a**) (**b**)

Figure 3. Separation ratio (K_{sep}) of MBCN versus target component content in feed fraction. (**a**) Zoomed in; (**b**) Normal view.



(**a**) (**b**)

Figure 4. Ratio of enrichment (K_{enr}) of MBCN versus target component content in feed fraction. (**a**) Zoomed W/F area ($K_{enr}^{W/F}$); (**b**) Diminishable D/F area ($K_{enr}^{\sum D/F}$).

Experimental data on liquid-liquid equilibrium in the MBCN-Ac system for the temperature range (T) from 25 to 50 °C are given in Table 2; the characteristics of the MBCN-Ac heteroazeotrope at atmospheric pressure are given in Table 3; a view of the MBCN-Ac mixture phase diagram according to Tables 2 and 3 are shown in Figure 5.

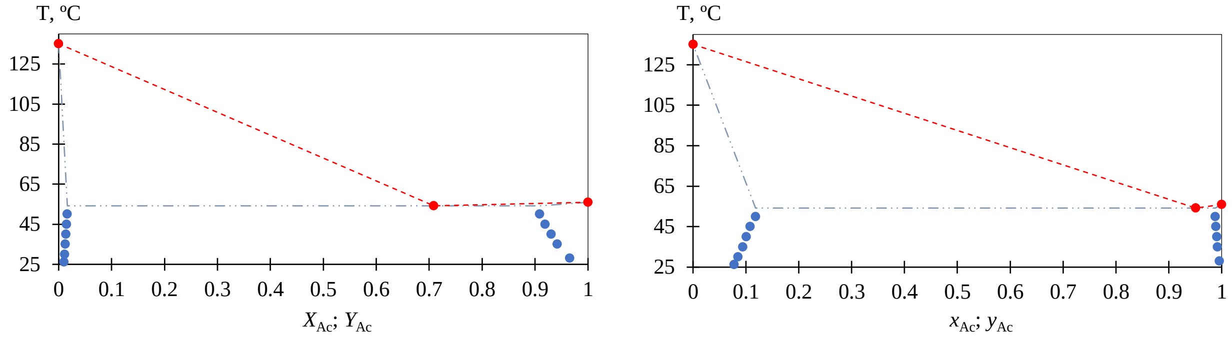
Table 2. Liquid-liquid equilibrium data in MBCN-Ac system at atmospheric pressure 100.0 kPa.

T		**Ac in MBCN**			**MBCN in Ac**	
°C	**Mass fr.**	**Mole fr.**	**Δ Mole fr.**	**Mass fr.**	**Mole fr.**	**Δ Mole fr.**
26.2 ± 0.1	0.0105	0.0778	±0.0028	-	-	-
28.0 ± 0.1	-	-	-	0.9659	0.9956	±0.0002
30.0 ± 0.1	0.0116	0.0852	±0.0008	-	-	-
35.0 ± 0.1	0.0129	0.0939	±0.0013	0.9419	0.9923	±0.0002
40.0 ± 0.1	0.0138	0.1004	±0.0006	0.9309	0.9908	±0.0002
45.0 ± 0.1	0.0150	0.1081	±0.0008	0.9193	0.9891	±0.0001

50.0 ± 0.1	0.0166	0.1183	±0.0006	0.9090	0.9876	±0.0002

Table 3. MBCN-Ac heteroazeotrope composition.

P	T	mass fr.		mole fr.		
kPa	°C	Ac	MBCN	Ac	MBCN	Δ mole fr.
99.7 ± 0.3	54.2 ± 0.5	0.7085	0.2915	0.9508	0.0492	±0.0003



(**a**) (**b**)

Figure 5. Experimental liquid-liquid-vapor equilibrium data in the MBCN-Ac system at atmospheric pressure. Points—experimental data (blue—Table 2; red—Table 3). (**a**)—mass fraction; (**b**)—mole fraction.

4. Discussion

The data given in Table 1 fully reflect the complex of thermodynamic constraints on the distillation process. The main problem is the withdrawal of PFD and the so-called "main impurity" (still not identified due to the difficulty of its concentration and purification). From the Table 1 and Figure 2a–c data, it follows that at relatively low MBCN concentrations in the feed solution, the distillation method allows the fractionation of the mixture and concentrate the target component in distillate. However, when getting close to 0.975 mass fraction of MBCN in the feed solution, this method becomes useless (K_{sep}→1; K_{enr}→1). DMFA adding allows a minor, but intensified separation process (Figure 2d): K_{sep}≈1→3.6 (Figure 3); $K_{enr}^{W/F}$≈1→0.33 and $K_{enr}^{\Sigma D/F}$≈1→1.2 (Figure 4).

Ac was more efficient not only when compared to DMFA (Figure 2f), but also when separating a mixture with a lower (0.964 mass fraction) concentration of the target component in the feed solution (Figure 2e). Thus, Ac adding makes it possible to obtain MBCN fraction with purity higher than 0.998 mass fraction, the degree of recovery is quite high ≥0.85 mass fraction in just one process cycle. At X_{MBCN}^{F} = 0.964÷0.984 mass fraction the separation process intensifies by an order of magnitude: K_{sep} ≈ 1→273.46 ÷ 87.55 (Figure 3); $K_{enr}^{W/F}$ ≈ 1→0.15 ÷ 0.11 and $K_{enr}^{\Sigma D/F}$ ≈ 1→42.26 ÷ 9.96 (Figure 4).

For MBCN-Ac system the liquid-liquid phase equilibrium data were also obtained in the temperature range from 25 to 50 °C (Table 2) and heteroazeotrope characteristics were determined (Table 3). The solubilities of Ac in MBCN (xAc = 0.0778 → 0.1183 mole fraction) and MBCN in Ac (xAc = 0.9956→0.9876 mole fraction) increase with increasing temperature from 25 to 50 °C; the heteroazeotrope composition at atmospheric pressure is greatly shifted toward Ac. The presented data (Figure 5) allow to estimate the loss of Ac in the distillate flow and calculate the amount of heteroazeotrope-forming agent required for the process, as well as being essential for the process flowsheet design.

5. Conclusions

This work presents only a part of a large data set on the purification of MBCN from close-boiling impurities and on the separation of the mixture of configurational and structural isomeric reaction products of the electrochemical fluorination of decalin and naphthalene. The major difficulties faced to intensify the process are the insufficient reference data on the composition of the mixture, the properties of the components present in it, and the topology of the phase diagram of the reaction system. Nevertheless, despite the absence of impurity nomenclature in the present work it was possible to significantly (by an order of magnitude) increase the efficiency of the MBCN purification process. The effect was achieved by adding a heteroazeotrope-forming agent, Ac. Experimental data on liquid-liquid phase equilibrium were also obtained for the MBCN-Ac binary mixture and the characteristics of the heteroazeotrope at atmospheric pressure were determined.

First of all, the new experimental data reported in the present work are reference data, technological solution and entry point for further research in terms of intensification of the process of production and purification of perfluorinated cycloalkanes.

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