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Optimal temperature for the absorption of C₂-C₅ mercaptans by sodium hydroxide solutions from isooctane

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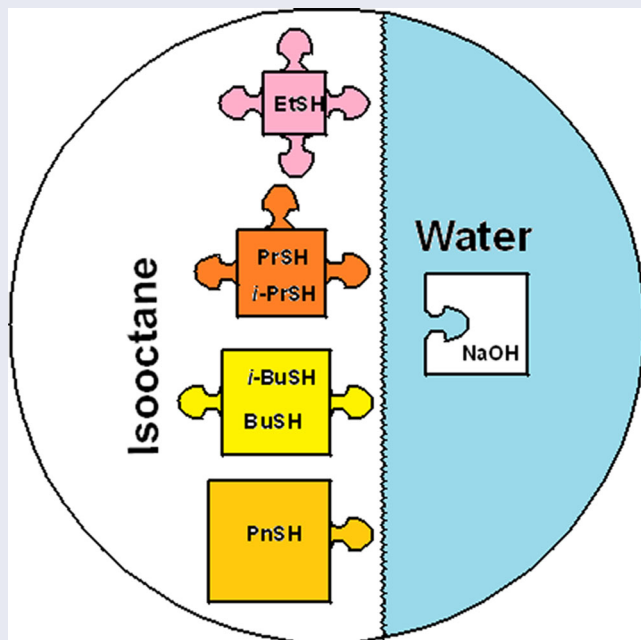
ABSTRACT


This work is the first to assess the effect of the nature of the alkyl substituent of mercaptans, the concentration of the absorbent and the temperature on the chemisorption processes from isooctane. The temperature range of the experiment was from 30 to 70°C. The most effective absorption was observed at an alkali concentration of 1.91 to 9.3 mol/l and at 30 ÷ 70°C. Low molecular weight ethyl mercaptan is effectively sorbed by 9.3 mol/l alkali, propyl mercaptan and butyl mercaptan - by 3.85 mol/l alkali, and branched isopropyl and isobutyl mercaptans by 3.85 mol/l alkali. Experiment times were 5 minutes.


KEYWORDS

mercaptans; thiols; isooctane; sulfur; chemisorption; X-ray-fluorescence analyzer; sulfur pickup parameter

GRAPHICAL ABSTRACT



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1. Introduction

Purification of hydrocarbon raw materials from sulfur-containing components, in particular from mercaptans, is a necessary task to obtain high-quality fuels and lubricants with the required characteristics (Akhmadullina A.G et al., 2012). A number of environmental and economic concerns drives the trend toward low-sulfur fuels.

Among the huge amount of methods for mercaptan removal of hydrocarbons, the most accessible, simple and easily implemented method is the absorption (extraction) of mercaptans with an aqueous-alkaline solution (Akhmadullina A.G et al., 2008). In addition, a large variety of methods for removing mercaptans from a hydrocarbon mixture by aqueous-alcoholic amine solutions (Charry Prada Orcid I.D. et al, 2017), amine solutions (Andreev B.V. et al, 2020) and oxidative methods (Motahari K. et al, 2020) are known.

All known methods operate in various ranges of concentrations and temperatures, which does not give a clear understanding of the effect of the nature of the alkyl substituents of mercaptans, the concentration of an aqueous-alkaline solution, and the effect of temperature on the degree of extraction of thiols from hydrocarbons. During chemisorption, the absorbed components - thiols - enter into a chemical reaction with the absorbent substance - an aqueous-alkaline solution. Then, due to the separation of liquid phases of hydrocarbons and water that are immiscible in each other, the absorbed mercaptans removed from the purified raw material. The entire absorption process takes place between the interfaces between the aqueous phase and the adsorbate (mercaptans). It is the effect of the concentration of the absorbent (alkali) on the surface, diffusion and thermal processes that should have a definite influence on the sorption of mercaptans. The rate and kinetics of absorption can depend on many factors, in particular temperature, pressure, interaction time, concentration, viscosity, mass transfer, nature of the interacting substances, etc. In particular, a study was carried out on three parameters - temperature, absorbent concentration and the nature of mercaptans.

In previous works, some patterns of extracting mercaptans from oil fractions were revealed, and these obtained facts highly coincide with our studies (Yabroff D.L., 1940):

1. Easy removal of mercaptans from the oil phase with aqueous alkaline solution is highly dependent on molecular weight of mercaptans and, to a lesser extent, according to its configuration. Straight chain and lighter mercaptans recovered more easily than heavier ones and branched chain members.

2. Increase of sodium hydroxide concentration improves the extraction of mercaptans, but not proportionally. Increasing concentration of hydroxide above to specified range (2 to 3 N sodium hydroxide) lead to actually poorer extraction.
3. Reduction of extraction temperature increases degree of removal of mercaptans from the oil phase.

Most mercaptans, interacting with alkaline solutions of sodium hydroxide, convert to mercaptides, and this reaction is reversible due to hydrolysis. The hydrolysis of mercaptides can be reduce by increasing the concentration of the alkali solution and decreasing the temperature. With an increase in the molecular weight of mercaptans, their solubility in an alkali solution decreases, which can also be associated with the acidity of the mercaptans themselves. For example, the degree of recovery of n-butyl mercaptan is 35% less than for ethyl mercaptan (Bondarenko B.I., 1983).

In addition, the degree of extraction of mercaptans depends on the polarity and acidity of the medium. The use of an aqueous, aqueous-alcoholic or ionic medium as an absorbent differs sharply, which is associated with the ionic strength of the solution and the ionization constant of mercaptans. The use of various organic salts and alcohols as "solutizers" increases several times the degree of extraction of thiols from hydrocarbons, which is possibly also associated with their different dissociation constants in an alcoholic and ionic medium (Yabroff & White, 1940; Li J. et al, 2017).

The influence of pressure and temperature on the absorption of mercaptans is closely related to the temperature of the extracted phase (Samadi Afshar A. et al., 2013). In addition, the formation of water-thiol clathrates depends on the molecular weight and structure of thiols. The standard hydration energies of thiols in water are given in a research paper (Kelly C.P. et al, 2006; Mirzaei S. et al, 2019).

Caustic removes lighter mercaptans more effectively than heavier mercaptans due to their greater solubility in water; water free N-methyl diethanolamine removes heavier mercaptans more effectively than lighter mercaptans due to salting-in effects and solvating properties (Jones C.E. et al, 2013). In addition, mercaptans have weaker intermolecular forces. They show little association by hydrogen bonding with water molecules or among themselves. Mercaptans have lower boiling points and are less soluble in water and other polar solvents than alcohols of similar molecular weight. Therefore, mercaptans will have a higher equilibrium vapor pressure and will be more soluble in hydrocarbon phases. That is methylmercaptan is gaseous at ambient conditions in comparison to it O₂ analogues, due to its lower boiling point.

2. Chemicals and materials

In experiments, all reagents were purchased from commercial sources and used as received unless otherwise indicated. They are as follows: NaOH (Russia, GOST 4328–77, reagent grade), ethyl mercaptan C_2H_6S (USA, Sigma-Aldrich, CAS 75-18-3, $\geq 97\%$), propyl mercaptan C_3H_8S (USA, Sigma-Aldrich, CAS 107-03-9, $\geq 97\%$), isopropyl mercaptan C_3H_8S (USA, Sigma-Aldrich, CAS 75-33-2, $\geq 98\%$), butyl mercaptan C_4H_9S (USA, Sigma-Aldrich, CAS 109-79-5, 99%), isobutyl mercaptan C_4H_9S (USA, Sigma-Aldrich, CAS 513-44-0, $\geq 95\%$), pentyl mercaptan $C_5H_{11}S$ (USA, Sigma-Aldrich, CAS 110-66-7, $\geq 98\%$), isooctane (Russia, CAS 540-84-1, reagent grade), distilled water H_2O (Russia, GOST 6709–72), technical gaseous nitrogen in cylinders (Russia, GOST 9293–74, 99,9%)

3. Experimental

All experiments were carried out in a flat-bottom flask with a reflux condenser by stirring on a magnetic stirrer and in nitrogen gas atmosphere. Solutions of mercaptans in isooctane with a concentration of 1000 ppm were prepared in advance. 25 ml of this solution was taken and placed in a 50 ml flat-bottomed flask. Then, with stirring and thermostating in a water bath, 2.5; 5 and 10% by volume with respect to the isooctane solution of an alkaline solution of a certain concentration (1, 2, 4, 8, 16, 24, 32 and 40%) was added. The resulting mixture was stirred for 5 minutes at a certain temperature. Next, a sample of isooctane solution analyzed on an X-ray fluorescence analyzer. The scheme of the experiment is shown in [Figure 1](#).

Alkali solutions with proper concentrations were prepared by the gravimetric method. The calculated amount of caustic soda dissolved in about half the amount of water, after cooling the solution was transferred to a volumetric flask and brought to the mark. The concentration was clarified by titration. The concentration of mercaptan was obtained by the volumetric method: the required volume of mercaptan proportional to the mass and density was taken with a measuring pipette and added to the corresponding mass of isooctane. The concentration was checked on the device.

X-ray fluorescence analysis on sulfur quantity performed on a Sulfur Meter Tanaka Scientific RX-360SH (ASTM D4294-03, ISO 8754, JIS K 2541-4). Radiation source X-ray tube, 7 kV, 0.15 mA, radiation leakage max 0.6 micro Zv/hour.

4. Result and discussion

The aim of this work is to find optimal conditions for the most efficient chemisorption of C_2 - C_5 mercaptans in aqueous-alkaline solutions.

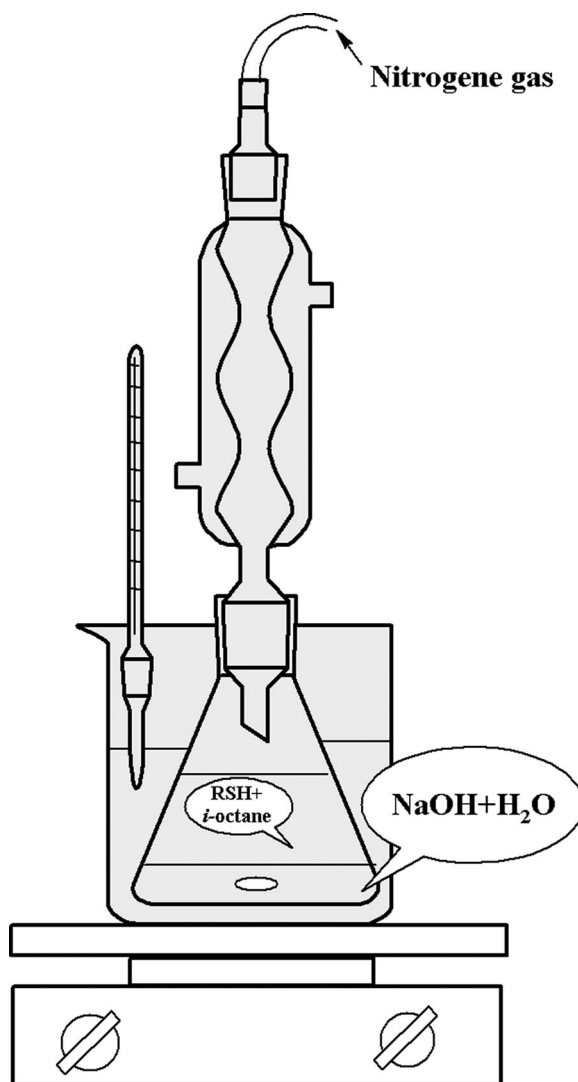


Figure 1. Scheme of the experiment.

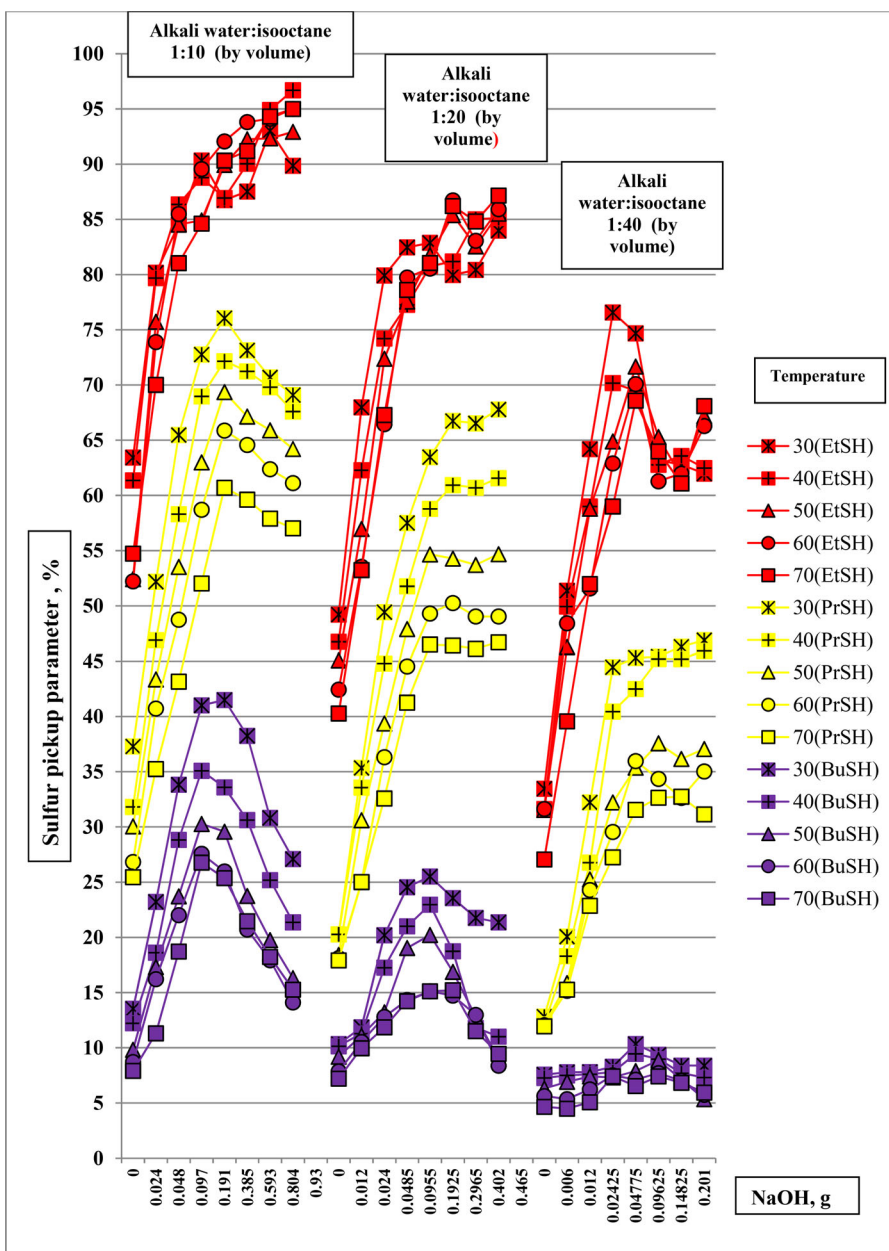
Table 1. Boiling point temperature and solubility of mercaptans.

Mercaptans	EtSH	PrSH	BuSH	i-PrSH	i-BuSH
Boiling point	35 °C	67 ÷ 68 °C	98.2 °C	52.5 °C	85.15 °C
Solubility in water (20 °C)	1.5 g/100g (20 °C)	0.19 g/100g (25 °C)	0.0597g/100g (20 °C)	hardly soluble	hardly soluble

From the analysis of the data in [Table 1](#) and [Table 2](#), it can be seen that the absorption of alkyl mercaptans has a low dependency on temperature of the process and for all derivatives, absorption proceeds best at 30 °C and a large volume of alkali, however, the concentration of alkali affects the absorption ambiguously, which is associated with solubilization processes. It is noteworthy that ethyl mercaptan dissolves in water best of all the

Table 2. Physical and chemical properties, molal quantities and mass weights of C₂-C₅ mercaptans (Dalman et al. 1961).

Mercaptans	EtSH	PrSH	BuSH	i-PrSH	i-BuSH	PnSH
pK, extraction methods	10.60	10.65	10.65	10.86	11.05	10.70
Density, g/ml, 20 °C	0.8617	0.8400	0.8337	0.8130	0.8357	0.8410
Molar mass, g/mol	62.13	76.15	90.187	76.15	90.187	104.21
Molal quantity, mmol	0.2768	0.2259	0.1907	0.2259	0.1907	0.1651

**Figure 2.** RSH (C₂-C₄ normal mercaptans) absorption with 0.24; 0.48; 0.97; 1.91; 3.85; 5.93; 8.04 and 9.3 mol/l. NaOH water solutions.

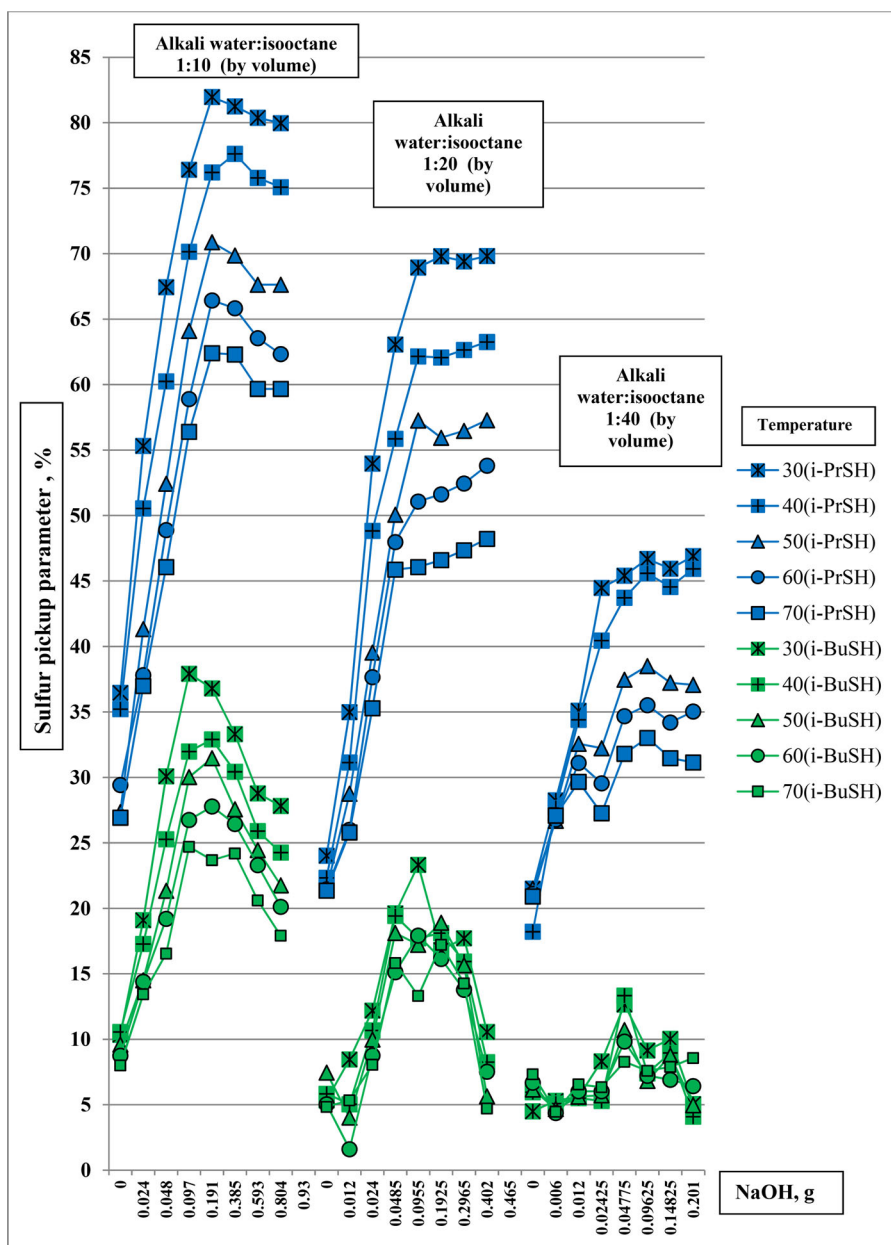


Figure 3. RSH (*iso*-propyl and *iso*-butyl mercaptans) absorption with 0.24; 0.48; 0.97; 1.91;3.85;5.93; 8.04 and 9.3 mol/l. NaOH water solutions.

presented series of thiols; moreover, it has the lowest boiling point and higher acidity, which allows it to be better distributed in an aqueous-alkaline medium, and, so, to diffuse into an aqueous medium (Table 2).

The process of chemisorption of mercaptans in an aqueous-alkaline medium mainly depends on the temperature of the medium and the concentration of alkali, as well as on the acidity of the mercaptans themselves.

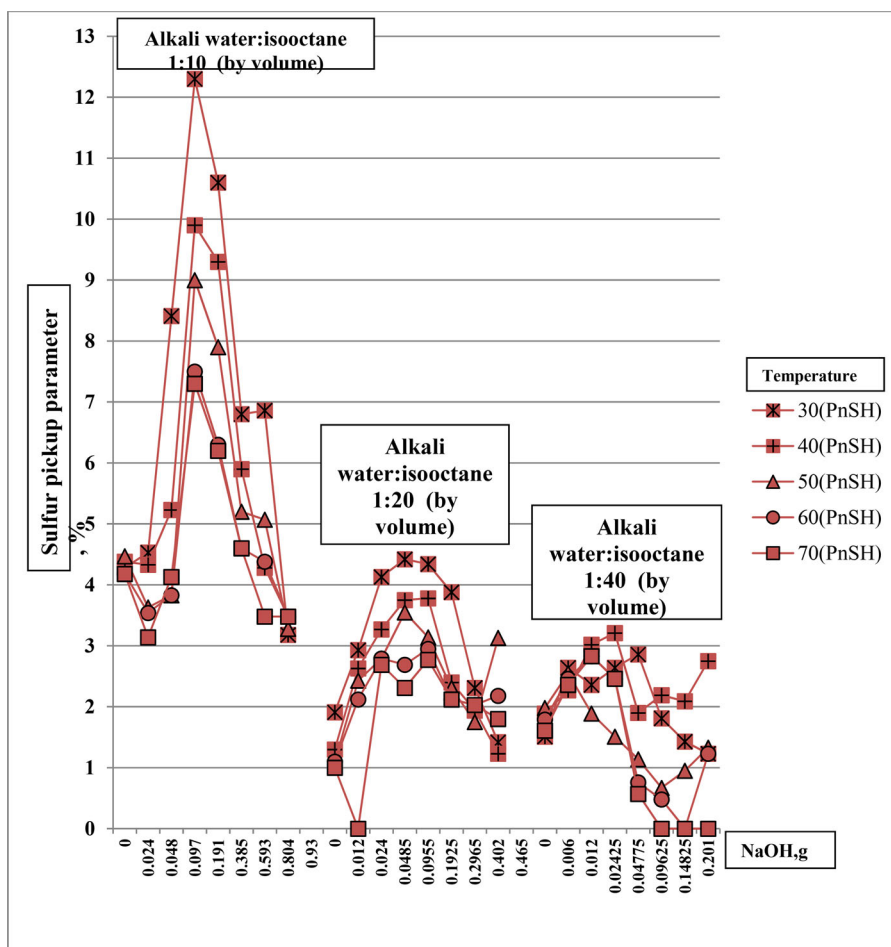


Figure 4. PnSH absorption with 0.24; 0.48; 0.97; 1.91;3.85;5.93; 8.04 and 9.3 mol/l. NaOH water solutions.

The content of mercaptan sulfur in the isooctane solution was 1000 ppm. Alternatively, its relative mass content $0.001 * (0.688 \text{ g/ml} * 25 \text{ ml}) = 0.0172 \text{ g}$ (0.688 g/ml isooctane density).

According to the data presented in Figure 2, with an increase in the concentration of NaOH from the equivalent quantities (e.q.) to 9-fold more to the respect of normal mercaptans, the absorption values data change in direct proportion to the temperature dependence. Further, these values become constant and practically do not change. This dependence related to the acidity constant and the solubility of ethyl and propyl mercaptans, which is also confirmed by the ratio of the amount of water and alkali. The greater the amount of water at constant values of the amounts of alkali, the more likely the processes of dissociation and hydrolysis of sodium mercaptides occur. With an increase in the molecular weight of mercaptan (butyl), the tendency to hydrolysis becomes higher, which observed when

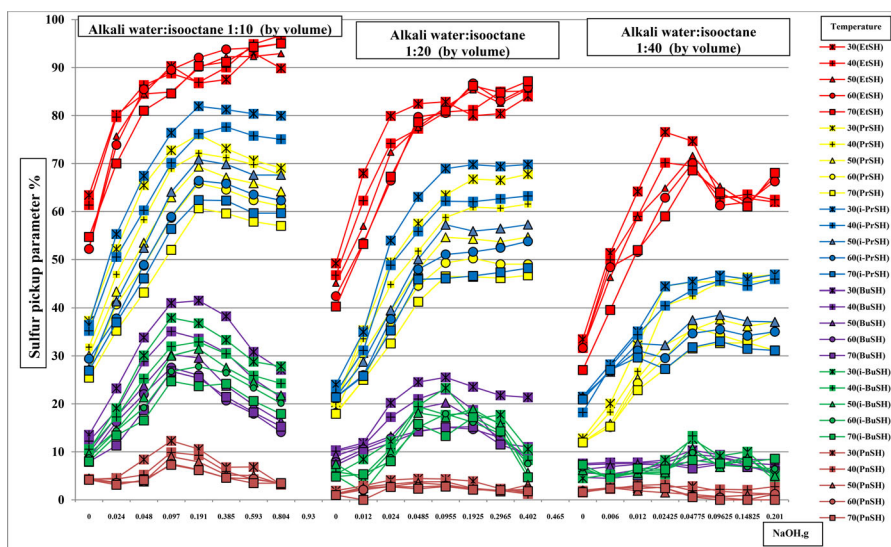


Figure 5. RSH (Ethyl, propyl, *iso*-propyl, butyl, *iso*-butyl, pentyl mercaptans) absorption with 0.24; 0.48; 0.97; 1.91;3.85;5.93; 8.04 and 9.3 mol/l. NaOH water solutions.

comparing the data for ethyl, propyl and butyl mercaptans. With an increase in the total amount of an aqueous solution of alkali, the processes of hydrolysis and dissociation become more intense and already change significantly with temperature.

The molecular structure of mercaptans practically does not affect the processes of chemisorption and hydrolysis of mercaptides. This fact is contrary with obtained earlier [6]. The data obtained for propyl and isopropyl thiols are practically comparable, but isopropyl mercaptides have better thermal stability to hydrolysis and better chemisorption at higher temperatures (Figure 2, 3 and 5).

With an increase in the molecular weight of thiols, the temperature dependence on chemisorption processes becomes more significant. The most effective chemisorption observed at 30 °C and decreases with increasing temperature. Dissociation and hydrolysis processes become even more intense and differ significantly at different temperatures (Figure 2, 3 and 5).

For the branched butyl mercaptan isomer, the chemisorption process acquires a random character, which is associated with the low solubility in water and the acidity of *iso*-butyl mercaptan. A similar tendency to the processes of chemisorption and hydrolysis of sodium mercaptide observed for pentylthiol (Figure 2, 3, 4).

The absorption of high molecular mercaptans decreases by increasing the concentration of alkali more than 3.85 mol/l highly and depends with alkali water viscosity and hence low mass transfer coefficients. The chemisorption equilibrium shifts toward the minimum amount of water in alkali solutions.

Table 3. Optimal conditions for mercaptan absorption.

Maximal Sulfur pickup parameter, degree of chemisorption of mercaptans %						
Mercaptans	Ethyl	Propyl	iso-propyl	Butyl	iso-butyl	Pentyl
30 °C	93,03 (32%NaOH, Alkali water:isooctane 1:10 (by volume), ×72,6 equimolar quantity)	76,05 (16%NaOH, Alkali water:isooctane 1:10, ×42,6 equimolar quantity)	81,96 (16%NaOH, Alkali water:isooctane 1:10, ×42,6 equimolar quantity)	41,51 (16%NaOH, Alkali water:isooctane 1:10, ×50,5 equimolar quantity)	37,92 (8%NaOH, Alkali water:isooctane 1:10, ×25 equimolar quantity)	93,03 (32%NaOH, Alkali water:isooctane 1:10, ×121,7 equimolar quantity)
40 °C	96,70 (40%NaOH, Alkali water:isooctane 1:10, ×84 equimolar quantity)	72,16 (16%NaOH, Alkali water:isooctane 1:10, ×42,6 equimolar quantity)	77,62 (24%NaOH, Alkali water:isooctane 1:10, ×65,6 equimolar quantity)	33,59 (16%NaOH, Alkali water:isooctane 1:10, ×50,5 equimolar quantity)	32,9 (16%NaOH, Alkali water:isooctane 1:10, ×50,5 equimolar quantity)	96,7 (40%NaOH, Alkali water:isooctane 1:10, ×140,8 equimolar quantity)
50 °C	92,93 (40%NaOH, Alkali water:isooctane 1:10, ×84 equimolar quantity)	69,37 (16%NaOH, Alkali water:isooctane 1:10, ×42,6 equimolar quantity)	70,87 (16%NaOH, Alkali water:isooctane 1:10, ×42,6 equimolar quantity)	29,58 (16%NaOH, Alkali water:isooctane 1:10, ×50,5 equimolar quantity)	31,47 (16%NaOH, Alkali water:isooctane 1:10, ×50,5 equimolar quantity)	92,93 (40%NaOH, Alkali water:isooctane 1:10, ×140,8 equimolar quantity)
60 °C	95,01 (40%NaOH, Alkali water:isooctane 1:10, ×84 equimolar quantity)	65,88 (16%NaOH, Alkali water:isooctane 1:10, ×42,6 equimolar quantity)	66,43 (16%NaOH, Alkali water:isooctane 1:10, ×42,6 equimolar quantity)	25,97 (16%NaOH, Alkali water:isooctane 1:10, ×50,5 equimolar quantity)	27,78 (16%NaOH, Alkali water:isooctane 1:10, ×50,5 equimolar quantity)	95,01 (8%NaOH, Alkali water:isooctane 1:10, ×140,8 equimolar quantity)
70 °C	95,01 (40%NaOH, Alkali water:isooctane 1:10, ×84 equimolar quantity)	60,7 (16%NaOH, Alkali water:isooctane 1:10, ×42,6 equimolar quantity)	62,4 (16%NaOH, Alkali water:isooctane 1:10, ×42,6 equimolar quantity)	25,37 (16%NaOH, Alkali water:isooctane 1:10, ×50,5 equimolar quantity)	24,7 (8%NaOH, Alkali water:isooctane 1:10, ×25 equimolar quantity)	95,01 (40%NaOH, Alkali water:isooctane 1:10, ×140,8 equimolar quantity)
Optimal conditions: NaOH concentration, isooctane(hydrocarbon): mass ratio for water: NaOH and temperature						
		16%NaOH 5.2:44.7:1; 30 °C	16%NaOH 5.2:44.7:1; 30 °C	16%NaOH 5.2:44.7:1; 30 °C	16%NaOH; 5.2:44.7:1; 40 °C	40%NaOH 1.5:18.5:1; 40 °C

The optimal conditions for the absorption of all used mercaptans revealed from the maximum extremes of the sulfur pickup parameter of aqueous-alkaline solutions of various concentrations (Table 3).

5. Conclusion

Based on the obtained data, the following conclusions were drawn:

1. With an increase in the molecular weight of mercaptans, chemisorption processes acquire a random order. In this case, the structure of the thiol molecule insignificantly affects the processes of their extraction from isooctane.
2. An increase in the concentration of alkali affects the chemisorption of ethyl- and propyl-mercaptans to a certain concentration, after which the process becomes constant and does not change with temperature. For C₄ and C₅ thiols, an increase in the alkali concentration above 25 times the equimolar mass value leads to a decrease in chemisorption processes and an increase in mercaptide dissociation processes.
3. Chemisorption of ethyl mercaptan is practically independent in the temperature range 30-70 °C. With an increase in the molecular weight of thiols, the chemisorption process proceeds better at low temperatures (30-40 °C).
4. The ratio of the concentration of alkali, water, and isooctane, as well as the process temperature, play a significant role in the establishment of chemical equilibrium in the hydrolysis of mercaptides, which makes it possible to select the optimal conditions for effective chemisorption. Largely, these conditions also depend on the acidity of the thiols.
5. Chemisorption equilibrium of mercaptans is shifting toward minimum water concentration alkali solutions.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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Abbreviations

- e.q. equivalent (equimolar) quantities
PnSH pentyl mercaptans