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Pervaporative desulfurization of gasoline—separation of hydrocarbon/thiophene mixtures using polydimethylsiloxane (PDMS)-based membranes

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ABSTRACT

A series of vacuum pervaporation tests were carried out to investigate the performance of the commercial composite membrane with an active layer made of polydimethylsiloxane (PDMS). The effects of feed temperature, the sulfur content in the mixture, and feed composition on membrane performance were investigated. Toluene/thiophene and *n*-heptane/thiophene binary organic mixtures (thiophene concentration 0.8–1.6% by mass) simulating gasoline were separated at 30–50˚C, at laboratory scale. Studies have shown that the concentration of thiophene in the mixture and the temperature of the feed have a significant impact on the yield and selectivity of the desulfurization process. Experimental results indicated that higher feed temperature yielded higher total and partial fluxes and a lower sulfur enrichment factor. The total and partial fluxes increased as the sulfur content in the feed increased. The sulfur enrichment factor decreased with the amount of thiophene added in the gasoline. The experiments also showed that commercial PDMS membrane was more selective to thiophene in the case of *n*-haptane/thiophene mixture and it may be mainly due to higher affinity of toluene toward PDMS. The total fluxes for *n*-heptane/thiophene mixture and toluene/thiophene mixture were measured to be 7.4 and 9.4 kg/m^2 h at 40˚C, with the corresponding enrichment factor values of 1.7 and 1.4, respectively.

Keywords: Desulfurization; Vacuum pervaporation; FCC gasoline; Polymeric membranes

1. Introduction

Due to growing environmental awareness, reduction of the sulfur content in transportation fuels has been receiving more and more attention. That is why, new and more rigorous regulations on sulfur content in both, gasoline and diesel fuels, were adopted—the specification in European Union countries demands a reduction of the sulfur level to 10 ppm [1].

Toxicity of sulfur compounds, which by the combustion of motor fuel enters the atmosphere, are primarily associated with the formation of acid rain, which

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further contributes to the acidification of soil and surface water as well as the formation of photochemical smog. Moreover, the presence of sulfur oxides in exhaust gases from vehicles contributes to the larger emission of NO_x and VOC's caused by the reduction of low-temperature catalytic converters activity.

Nearly all of the sulfur (85–95%) in a typical refinery plant comes from fluid catalytic cracking (FCC) gasoline, and a small amount originates from the light straight run, reforming and isomerisation units. That is why, FCC gasoline is the natural place to focus on the sulfur reduction. The sulfur concentration of FCC gasoline depends on the sulfur type and its level in the FCC feedstock which contains 0.5–1.5 wt% of sulfur generally [2]. Although elemental sulfur, mercaptans, sulfides, disulfides, thiophene, and its homologes are all present in petroleum or in petroleum fractions, sulfur occurs mainly in the form of thiophene, sulfides, mercaptans, and disulfides [3].

A lot of effort is now being made to develop some novel and efficient hydrogen and non-hydrogen technologies such as selective extraction [4], selective oxidation [5], selective adsorption [6], biodesulfurization [7], electrochemically catalytic oxidation [8], and pervaporative desulfurization (PVDS). It should be noted that some of them, including PVDS technology, has already progressed beyond the lab-scale tests stage. In comparison with the traditional and other non-HDS separation processes, the membrane separation offers many advantages including lower energy consumption and operating cost, simple operation and control scheme, and easy scale up and adaptability to changes in process streams [9].

Pervaporation is a membrane technology utilizing a dense non-porous homogeneous polymeric film. The liquid solute selectively dissolves and diffuses in the membrane and is removed as vapor at the downstream side. The vacuum pervaporation is carried out by maintaining the downstream pressure, lower than the saturation pressure of the permeating liquid solute at that temperature [10].

Pervaporative separation is based on the affinity of a specific compound or a class of compounds to the membrane. The generally accepted mechanism explaining the mass transport across the dense membrane is solution–diffusion model. According to this model, pervaporation process can occur only when a certain amount of solvent is dissolved in the membrane material. The liquid feed solution is contacted with the membrane active surface at the upstream side, which is at atmospheric pressure. The components of a mixture are selectively dissolved and then diffuse or permeate through the membrane. The permeated compounds are then removed on the opposite side. The driving force for the separation process is maintained by constant withdrawal of the permeated compounds from the membrane [11].

Positive interaction between the polymeric membrane and preferably one of the components of the mixture is necessary for the appropriate separation. For satisfactory process performance, the material of active film needs to show high affinity toward the removed component. Hence, solubility parameter (defined as the square root of cohesive energy, E_{coh} (J/mol) per molar volume, V (cm^3/mol)) [12] and membrane polarity are the two main interested factors in the development of the novel membrane materials. The internal energy change, ΔE (kJ/mol), which gives some information about the interaction between the solvent and polymer, is defined as:

$$\nabla E = v_S v_P (\delta_S - \delta_P{}^2) = v_S v_P |\Delta\delta|^2 \tag{1}$$

where v is the volume fraction, and the subscripts S and P represent the solvent and polymer, respectively. As shown in Eq. (1), the more similar the solubility parameters of the polymer and solvent (i.e. lower ΔE), the more soluble solvent in the polymer [12].

As the solubility parameters of most membrane materials are more similar to the thiophene and its derivatives than to the hydrocarbon compounds, the membranes show larger affinities to sulfur species [13].

Polarity of membrane material also contributes to the separation performance. In order to remove a specific component from a mixture, the polarity of these components must be close to the polarity of the polymeric material of the active film [14].

The other way to determine the potential applicability of the membranes used in gasoline desulfurization is to investigate their swelling properties [13,14]. Swelling degree gives the information about membrane chemical resistance toward organic solvents. High swelling of the membrane induced by high concentrations of the permeating components results in the reduction of membrane selectivity.

Analysis of the sorption, diffusion, and permeation coefficients is another way of selecting preliminary membrane materials. By the comparison of dynamic sorption curves for the gasoline component, it is seen that the time required to reach sorption equilibrium is different for various compounds [13,14].

In most of the cases [13,14], polymeric membranes were used for the process. The main drawback of polymeric membranes is high swelling and, as a consequence, decrease in membrane selectivity during the organic–organic mixtures separation caused by high concentration of the permeating solvent. It can be seen that involved materials are hydrophobic polymers as well as hydrophilic ones. Hydrophilic properties of the polymer enhance the selectivity of sulfur compounds due to their higher polarity in comparison with the hydrocarbon species.

The experimental data presented in literature [15–19] demonstrated that the polydimethylsiloxane (PDMS)-based membranes could be effective for desulfurization by pervaporation. As can be seen, in spite of the active layer made of the same material, the examined membranes demonstrated quite varying performance. Different results, obtained by different researchers, might be due to either incorporating a particular additive in membrane, possible crosslinking, or the selected range of process parameters. Particularly interesting is the influence of the sulfur content. In the case of the sulfur concentration, there is no universal dependence as for the feed temperature or the downstream pressure. Moreover, it should be noted that none of the results presented in the literature apply to commercial membranes.

Therefore, the authors decided to carry out a series of PV tests to investigate the performance and separation properties of the commercial, publicly available composite membrane with an active layer made of PDMS. The aim of this work was to determine the efficiency of organic sulfur compound removal (thiophene) depending on its concentration. The temperature dependency of the flux and the enrichment factor were also investigated. Furthermore, the influence of feed composition on process indicators was examined.

2. Experimental

2.1. Materials

To prepare model binary hydrocarbon/thiophene mixtures simulating gasoline, thiophene (99.5%, extra pure, benzene free) obtained from Across Organics, *n*-heptane (99% purity) (99%) obtained from J.T. Baker and toluene (pure p.a.) obtained from Avantor Performance Materials Poland SA were used. PDMS membranes were obtained from PERVATECH, the Netherlands. These are composite membranes consisting of a porous support with a very thin, but dense separating layer on the top of it.

2.2. Feed and permeate samples analysis

The thiophene, *n*-heptane, and toluene concentrations in both, the feed and the permeate samples, were analyzed using a gas chromatograph (SRI Instruments, USA) equipped with a flame ionization detector (FID) and Restek RTX-5 (0.53 μm, 0.53 mm × 30 m) capillary column. Methanol (pure p. a.) obtained from Avantor Performance Materials Poland SA was used as GC solvent. Hydrogen was used as a carrier gas. Retention time for thiophene was 3.40 min, for *n*-heptane was 7.10 min, and for toluene was 10.20 min.

2.3. Pervaporation experiments

The experimental setup, designed by Sulzer Chemtech, was used for the pervaporation measurements (Fig. 1). The pervaporation test cell with a diameter of 15.9 cm was made of stainless steel. The membrane with an effective area of 187 cm^2 was kept on highly porous stainless steel support with a shiny polymeric layer facing the feed solution. Both feed tank and membrane cell were maintained at the constant temperature by a thermostat (Thermo Electron Co., Model Haake DC 30). The temperature was controlled by a PID controller device (Greisinger Electornics GTH 1100/2 DIF). The feed solution was circulated to the upstream side of the membrane using a recirculation pump (Speck Pumpen model PY-2071), while retentate was sent back to the flask. Sufficient feed flow rate

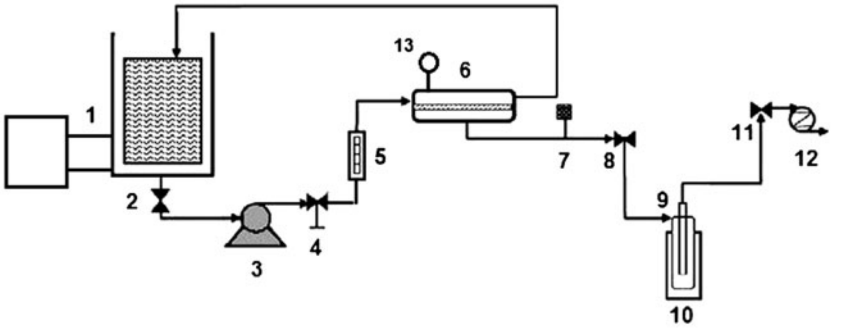

Fig. 1. Schematic diagram of the pervaporation system: (1) thermostat, (2) feed tank, (3) circulation pump, (4) pump regulator, (5) rotameter, (6) membrane module, (7) vacuum pressure gauge, (8) valve, (9) cold trap, (10) liquid nitrogen bath, (11) valve, and (12) vacuum pump.

was maintained using a circulation pump. The membrane upstream side was kept at atmospheric pressure. A vacuum pump (Alcatel, model Pascal 2015 SD) was used to create a pressure gradient across the membrane from the permeate side with the pressure at the downstream side equal to 100 Pa. The total downstream pressure was measured by an electronic vacuum gauge (Vacuubrand DRV 2). The permeated vapors were condensed and frozen by a cold trap cooled with liquid nitrogen. The frozen permeate was collected within a specified time interval. The cold traps were brought to room temperature prior to measurement of their weight using a balance (RadWag PS 210/C/2) in order to calculate the mass flux. Experiments were conducted for five thiophene concentrations—0.8, 1.0, 1.2, 1.4, and 1.6 wt% which correspond to sulfur concentrations of 0.30, 0.38, 0.46, 0.52, and 0.60 wt%, respectively. The feed temperature was ranged from 30 to 50˚C. Feed flow rate (75 L/h) and downstream pressure (100 hPa) were kept at the constant level.

Yield of the pervaporation process was evaluated on the basis of the mass permeation flux J_m, kg/m^2 h, Eq. (2) determined as total and partial one. Efficiency and selectivity of sulfur removal were evaluated basing on the dimensionless enrichment coefficient β Eq. (3).

$$J_m = \frac{m_p}{S_m \cdot t} \tag{2}$$

where m_p, pemreate weight, kg; S_m, membrane effective area, m^2; t, time of experiment, h

$$\beta = \frac{c'}{c} \tag{3}$$

where c, concentration of thiophene in feed sample, %; c', concentration of thiophene in permeate sample, %.

3. Results and discussion

3.1. Effect of feed temperature

Feed temperature is an important factor in the pervaporation process and affects all of the constituent steps of solute transport from feed solution to permeate side, as well as the driving force for mass transfer. Thus, feed temperature affects the feed/membrane characteristics and the driving force of the process.

Temperature dependence of the total permeate flux and partial fluxes of an individual compound for model mixtures are illustrated in Figs. 2–5. Experimental data indicated an increase in the total flux and partial fluxes with the rise of the feed temperature. This could be attributed to the increased mobility of the permeating molecules in the bulk feed solution, which results in higher partial vapor pressure and provides some greater driving force for the permeation of components. As temperature increases, frequency and amplitude of polymer jumping chains increase, resulting in an increase in free volume of the membrane and, as a result, diffusion of the compounds is enhanced by a higher flexibility of polymer chains.

On the other hand, during the pervaporation experiments, a trade-off phenomenon between the flux and selectivity was observed—as the feed temperature increased, the total flux increased but the sulfur enrichment factor showed a degressive trend. Increased swelling of the membranes active layer, caused by dissolution of feed components, additionally enhanced by the rise of feed temperature, decreased the selectivity toward thiophenes. In Fig. 5, enrichment factors decline with an increase in feed temperature for both hydrocarbon/thiophene mixtures.

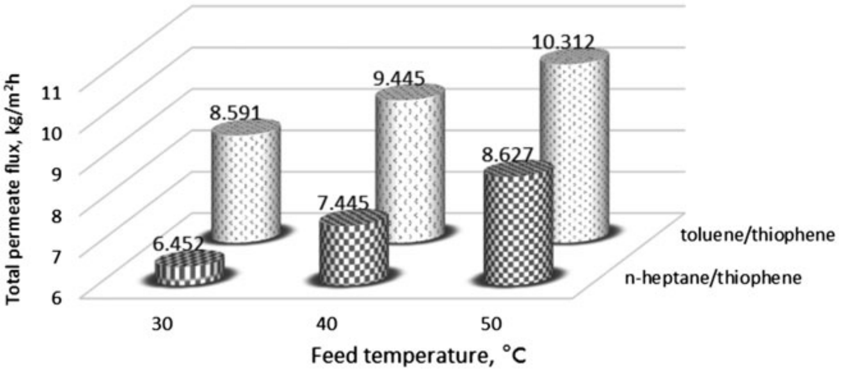

Fig. 2. Effect of feed temperature on the total permeate flux at thiophene concentration of 1 wt% and permeate pressure of 100 hPa.

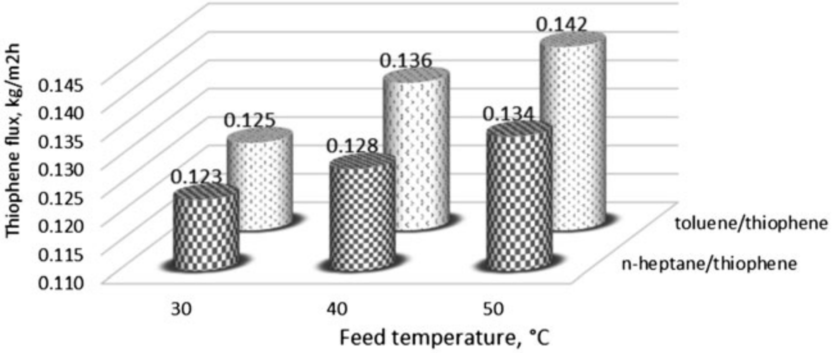

Fig. 3. Effect of feed temperature on the thiophene flux at thiophene concentration of 1 wt% and permeate pressure of 100 hPa.

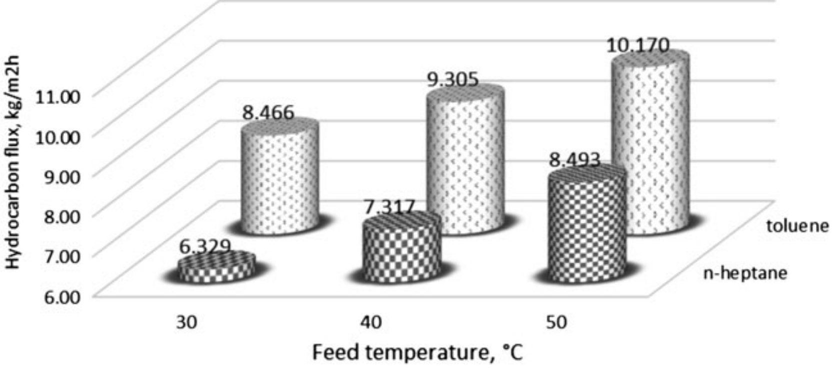

Fig. 4. Effect of feed temperature on the hydrocarbon flux at thiophene concentration of 1 wt% and permeate pressure of 100 hPa.

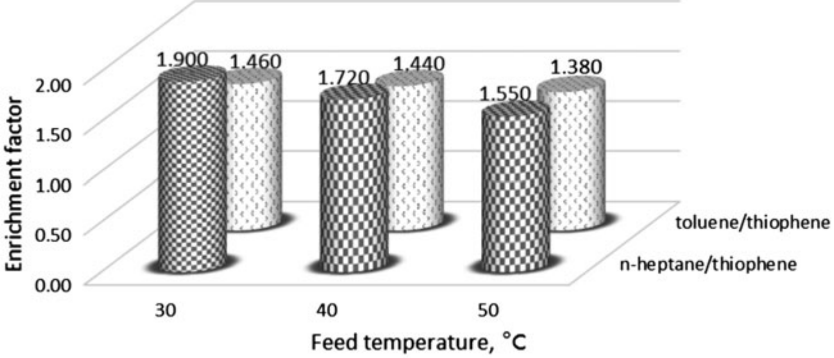

Fig. 5. Effect of feed temperature on the permeate enrichment factor at thiophene concentration of 1 wt% and permeate pressure of 100 hPa.

3.2. *Effect of feed concentration*

Taking into account the variable sulfur content in crude oil from different sources, it is very important to determine the effect of the concentration of this element in gasoline on selectivity of the membrane and the efficiency of the pervaporation process.

Research proved that an increase in the sulfur content of model *n*-heptane/thiophene and toluene/thiophene mixtures simulating gasoline caused a slight increase in the total permeate flux (Fig. 6) and both, thiophene (Fig. 7) and hydrocarbon fluxes (Fig. 8), while lowering the enrichment factor of the permeate (Fig. 9).

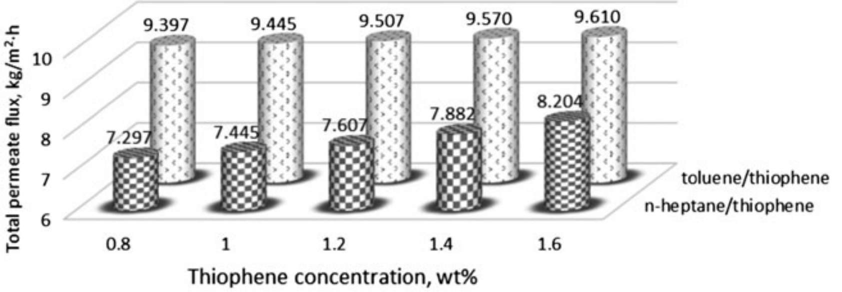

Fig. 6. Effect of sulfur content in the feed on the total permeate flux at feed temperature of 40˚C and permeate pressure of 100 hPa.

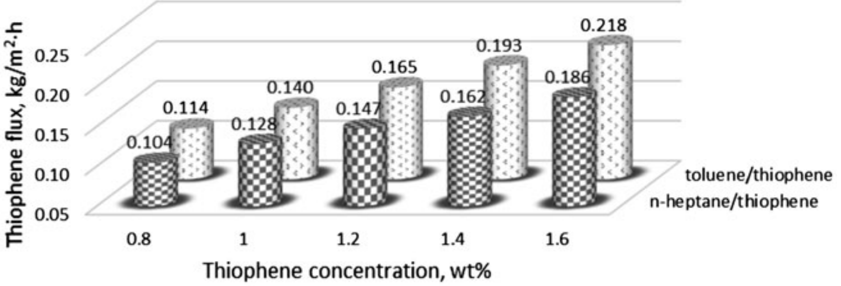

Fig. 7. Effect of sulfur content in the feed on thiophene flux at feed temperature of 40˚C and permeate pressure of 100 hPa.

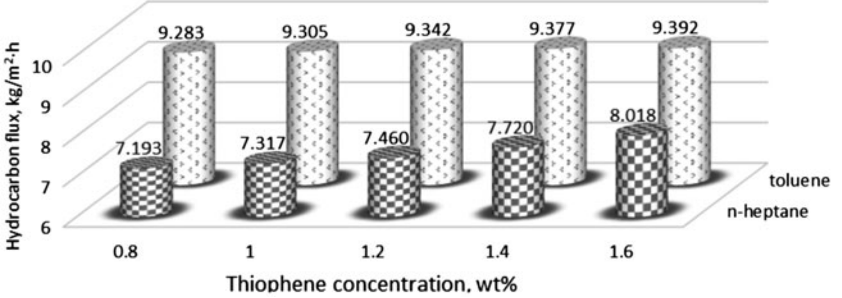

Fig. 8. Effect of sulfur content in the feed on hydrocarbons flux at feed temperature of 40˚C and permeate pressure of 100 hPa.

The authors chose to present the results obtained for 40˚C, since this temperature was considered to be the most optimal: the values of both total and partial fluxes for 30˚C were lower than those for 40˚C and the values of permeate enrichment factor for 40˚C were higher in comparison with those obtained for 50˚C.

Such dependency can be explained by the fact that with an increase in the concentration of thiophene, its activity increased, which in turn facilitated its dissolution in the active layer of the membrane. Accordingly, with an increase in thiophene concentration, some increase in thiophene flux and the total permeate flux for both mixtures was observed.

Furthermore, due to the high chemical affinity of thiophene to the poly(dimethylsiloxane), from which the membrane active layer was made (the solubility parameter for thiophene is $\delta = 20.0\ (\mathrm{J/cm^3})^{1/2}$ and for PDMS is $\delta = 21.1\ (\mathrm{J/cm^3})^{1/2}$), an increase in the content of thiophene in the model feed intensified the membrane swelling phenomenon.

As a result of the experiments, the total flux and both hydrocarbon's partial fluxes increased due to enhanced mobility of the polymer chains. This relationship is particularly noticeable in the case of *n*-heptane/thiophene system. Although *n*-heptane has a relatively low affinity toward PDMS (the solubility parameter for

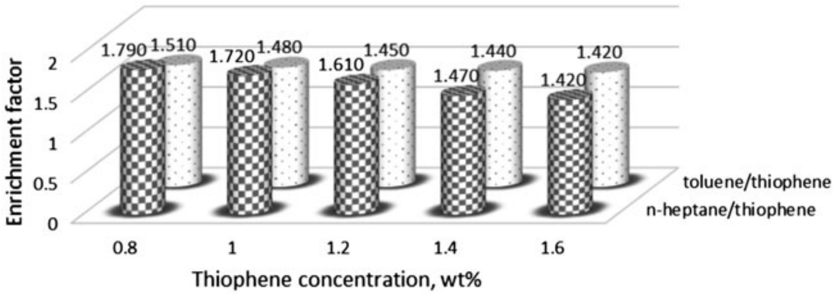

Fig. 9. Effect of sulfur content in the feed on the permeate enrichment factor at feed temperature of 40°C and permeate pressure of 100 hPa.

n-heptane is δ = 15.3 $(\mathrm{J/cm^3})^{1/2}$), and when compared with thiophene, it is more difficult to dissolve it in an unswollen membrane, the swelling enhanced its diffusion, which also had some influence on the total permeate flux. In the case of toluene/thiophene mixture, sulfur concentration had nearly negligible influence on partial hydrocarbon flux. This is probably related to a relatively high affinity of toluene toward PDMS and its facilitated solubility in this polymer [14].

Previously mentioned phenomenon also explains a decrease in the permeate enrichment factor β (Fig. 9) with an increase in thiophene concentration. As a result of the selective layer swelling and enhanced dissolution of *n*-heptane in the active layer material, a decline in the selectivity of the thiophene sorption process occurred.

3.3. Effect of feed composition

Since gasoline is a complex mixture composed of hundreds of compounds, in which five typical hydrocarbon groups are alkanes, isoalkanes, cycloalkanes, aromatics, and alkenes, deep understanding of the solution/diffusion gasoline molecules on/in the membrane is essential. The above hydrocarbon groups have different interactions with the membrane, which influences the membrane performance significantly. It has been proven [20,21] that transport of one component across the membrane during the separation of organic–organic mixtures is composition dependent. It means that transport of a compound is not only driven by its own chemical potential gradient, but also by the gradient of chemical potential of other molecules present in the feed. Thus, it is also very important to investigate the synergetic effect of gasoline components on pervaporation behavior of membranes.

As it can be seen in Fig. 6, the total permeation flux in the case of aromatic/thiophene mixture, with toluene as the representative aromatic hydrocarbon, was higher in comparison with that obtained for *n*-alkane/thiophene mixture. Furthermore, as it is shown in Fig. 7, the variation of hydrocarbon, which was the main feed components, had an impact on the transport of thiophene across PDMS membrane. In the presence of toluene, a partial flux of thiophene was higher compared to the thiophene flux obtained during the separation of *n*-heptane/thiophene mixture. This phenomenon can be explained by the Hansen solubility parameter theory—the affinity between toluene ($\delta = 18.2$ $(\mathrm{J/cm^3})^{1/2}$) and PDMS ($\delta = 21.1$ $(\mathrm{J/cm^3})^{1/2}$) is stronger than between *n*-heptane (δ ~15.3 $(\mathrm{J/cm^3})^{1/2}$) and the aforementioned membrane [13,14].

4. Conclusions

(1) Experiments have shown that the sulfur content in gasoline has a significant impact on the selectivity of the membrane, and hence—the efficiency of PV desulfurization process.
(2) With an increase in the sulfur content in the feed, some increase in the total permeate flux was observed. This is due to an increase in the swelling degree of the membrane as a result of dissolution of larger amounts of thiophene in the active layer material.
(3) Simultaneously, an increase in the total permeation flux resulted in the enrichment factor decrease, which was caused by an increase in the mobility of the polymer chains and a decrease in the selectivity of the active layer.
(4) Differences of chemical affinity of the hydrocarbons to poly(dimethylsiloxane) led to various selectivities thereof within PDMS membrane for both separated mixtures.
(5) Experimental results indicated that higher feed temperature yielded higher total flux and lower sulfur enrichment factor.

Acknowledgments

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