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Investigation of the Influence of Thiocarbamide in the Process of Carbamide Deparaffinization

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The influence of thiocarbamide in the process of carbamide dewaxing was investigated. The dependence of separated paraffins on the quantity of thiocarbamide was examined experimentally. It was determined that the separation of paraffins becomes equal to zero when moles of carbamide and thiocarbamide in water-isopropyl alcohol solution are equal. The low-temperature qualities (the temperature of dimness and freezing) of dewaxed fuels were also examined. By using infrared spectroscopy methods, the compound of received paraffins was investigated.

Key Words: carbamide deparaffinization, isopropyl alcohol-water solution, oil-products, thiocarbamide, hydrogen bonding, infrared spectroscopy

Introduction

The process of carbamide deparaffinization is divided into two groups according to the phase state of the carbamide applied [1]. In the first group of processes carbamide is used in the form of a solution; however, in the second group of processes carbamide is used in the solid form [2]. In this work, we investigated the process of carbamide deparaffinization, in which carbamide is applied in the form of isopropyl alcohol-water solution [3-4].

Analyses have shown that carbamide solution on the plants of deparaffinization of oil-products steadily is enriched due to thiocarbamide [5]. In our opinion this happens as a result of sulphureous compounds of oil penetrating into the zone of deparaffinization where the carbamide is transformed into thiocarbamide. Therefore, with this in mind, we carried out this study of influence of thiocarbamide present in carbamide solution in the process of deparaffinization.

Experimental Results

In order to investigate this process we used hydro-cleaned diesel oil. The deparaffinization of the diesel oil was carried out in the following conditions:

- The mass concentration of the mixture of carbamide and thiocarbamide in the alcohol-water solution 36%
- The mass concentration of alcohol in the water-isopropyl alcohol solution 70%
- The volume ratio of solution to diesel oil 2:1
- The temperature at the beginning of deparaffinization 55°C
- The temperature at the end of deparaffinization 40°C
- The duration of deparaffinization 15 min

Thiocarbamide was added to the content of carbamide in different ratios. The influence of the thiocarbamide present in the carbamide solution in the process of deparaffinization and the compounds of the received products were investigated. It was established that a small quantity of thiocarbamide had no significant effect on the process. The curve of dependence of the separated paraffins against the quantity of thiocarbamide can be divided conditionally into three parts (Figure 1):

I - In the first part, the separated paraffins do not change with the small variation in the quantity of thiocarbamide, i.e., the curve of dependence runs paralell to the axis of abscissa.
II - In the second part, the separated paraffins decrease to full disappearance.
III - In the third part, the separated paraffins increase again and the curve goes up.

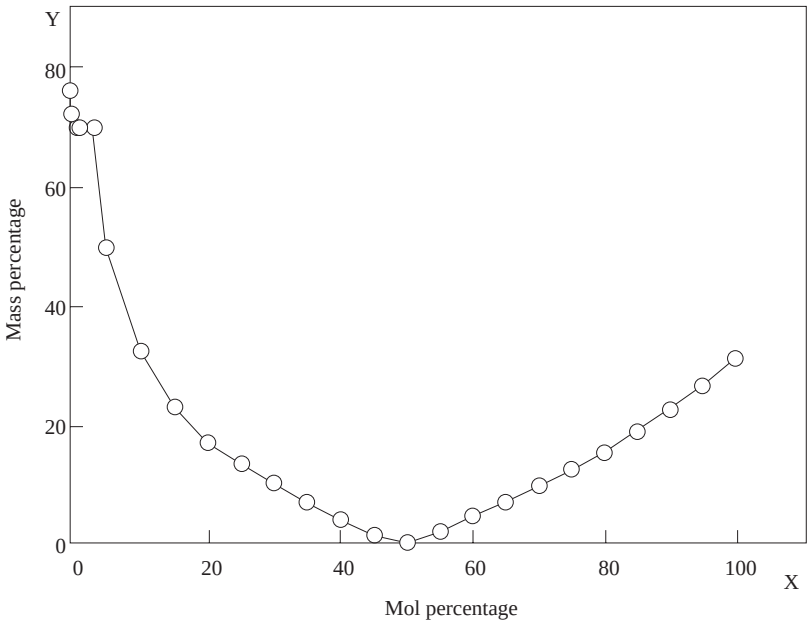

Figure 1. The dependence of the quantity of separated paraffins against the quantity of thiocarbamide. Here, x- mol percentage of thiocarbamide with respect to the mixture, y- the mass percentage of the separated paraffins according to the maximum obtainable quantity.

As can be seen, at equal moles of carbamide and thiocarbamide, the quantity of separated paraffins becomes zero, that is, deparaffinization has stopped. This is also confirmed by the fact that deparaffined diesel oil has low-temperature properties similar to diesel oil. It was also determined that the low-temperature qualities (the temperature of dimness and freezing) of deparaffined fuel diminished with increasing thiocarbamide in the alcohol-water solution (Figure 2).

It is known that in the deparaffinization of petrol products, the complex is formed in the results of

enveloping n-alkane molecules by carbamide molecules. In this case the carbamide molecules joining themselves by hydrogen bonding then form a spiral. The diameter of the spiral corresponds to the cross-section of n-alkanes. However, these properties of carbamide make it distinguishable for n-alkanes. Analogously to urea, the thiocarbamide molecules in the process of deparaffinization joining themselves by means of hydrogen bonding form a complex with isoalkanes and partially aromatic hydrocarbons [5].

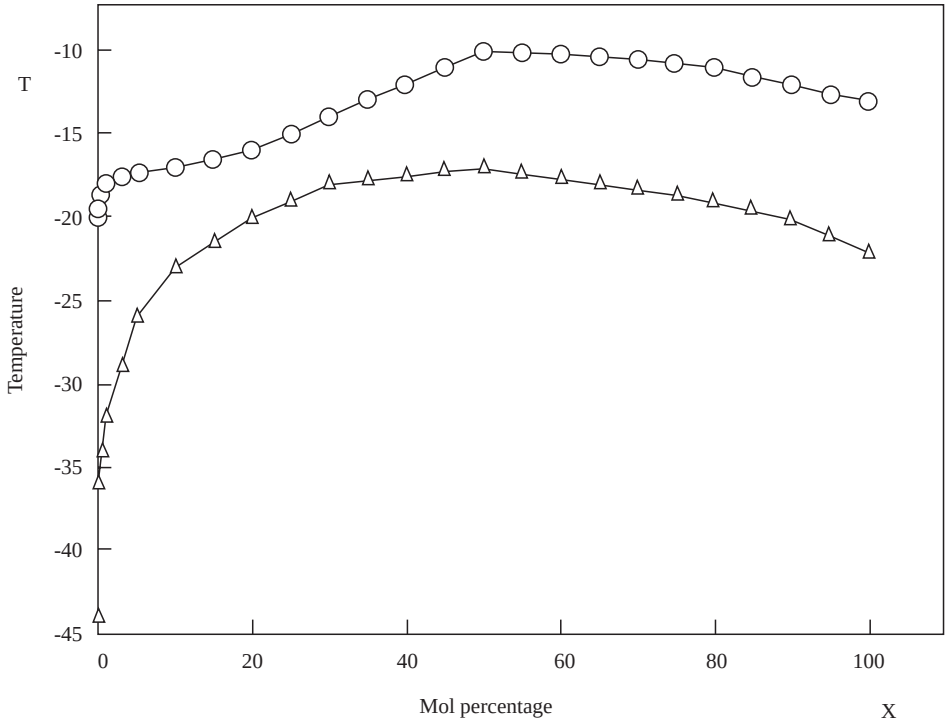

Figure 2. The curves I and II correspond to the temperature T of dimness and freezing respectively.

According to this, the mixture of carbamide and thiocarbamide at any ratio has to form a complex with paraffin hydrocarbons. However, experiments have shown that a mixture of carbamide and thiocarbamide in a mol ratio of 1:l is not capable of creating a complex either with n-alkanes or with isoalkanes with aromatic hydrocarbons.

In our opinion, in the process of deparaffinization, thiocarbamide molecules, in joining molecules of carbamide by means of hydrogen bonding, exclude them from the process of complex-creation. In this case the formation of the spiral is impossible because the diameters of the oxygen and sulphureous atoms (present in carbamide and thiocarbamide molecules respectively) are different. If such a spiral could be created, van der Waals forces between the spiral and alkan molecules would be much smaller, and the complex would be unstable.

The creation of the complex by further increasing the mol percentage of thiocarbamide in the mixture is explained by the fact that the extra quantity of thiocarbamide creates a complex with isoalkanes and aromatic hydrocarbons.

Infra-red spectroscopy analysis of the alkanes, which are separated in the process of deparaffinization at different ratios of carbamide and thiocarbamide, also confirms the explanation above.

As is shown in the spectrogram, the paraffins which are obtained in the process of deparaffinization of diesel oil, in which the quantity of carbamide is greater are mainly composed of n-alkanes (Figure 3) mixed

with an insignificant amount of isoalkanes.

Paraffins which are obtained with a mixture in which the quantity of thiocarbamide is greater mainly consist of isoalkanes and aromatic hydrocarbons.

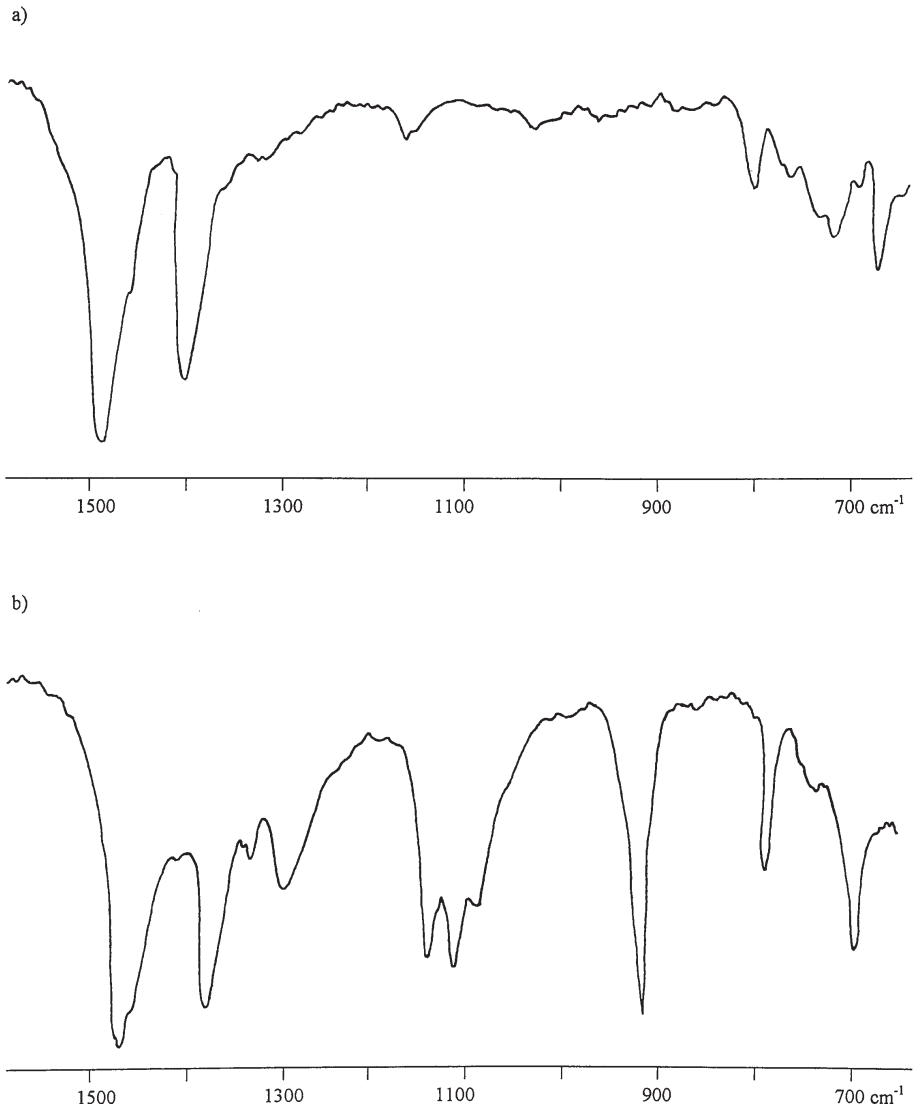

Figure 3. Infra-red spectrum of paraffins which are obtained in the process of deparaffinization of diesel oil with the isopropyl alcohol-water solution at mol percentages of thiocarbamide with respect to mixture of a) 20% and b) 80% respectively.

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