KINETICS OF UREA ADDUCT FORMATION IN THE PRESENCE OF AROMATIC HYDROCARBONS

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In connection with the need for expanding the production of liquid paraffins, it is extremely important to investigate the effects of inhibitors on the dewaxing or deparaffinization process. It is known that certain types of resins or tars will suppress the reaction of urea adduct formation with n-alkanes [1-3]. Certain aromatic hydrocarbons that are present in diesel fuel cuts are adsorbed on the crystals of urea and the complex [4, 5], probably resulting in lower yields of n-alkanes.

Here, we are reporting on studies of the influence of aromatic hydrocarbons on adduct formation, with a view toward establishing the relationship between their adsorption interaction and their inhibiting properties. In forming the adducts we used n-heptadecane as the starting material; the urea was crystalline material in "ch.d.a" ["pure, for analysis"] grade; the solvent was reference-grade isooctane; the activator was methanol. As inhibitors we used α-methylnaphthalene and tetralin, as the most representative of the aromatic hydrocarbons that are present in diesel fuel cuts from a number of prospective crude oils and are distinguished by the ability to be adsorbed on urea crystals [5]. In our experiments, the following conditions were maintained: volume ratio of n-heptadecane to solvent 1 : 9; mass ratio of feedstock to crystalline urea $\omega : 1$; mass ratio of feedstock to activator 1 : 0.04; temperature 25°C; stirring rate 900 rpm.

The studies were carried out in a laboratory unit (Fig. 1), using a thermographic analytical technique. The n-heptadecane was premixed with the solvent; then the mixture was charged to the 500-ml thermostated flask 6. Through the transformer 8, the electric motor 4 was turned on, driving the stirrer 5. At the same time, the electronic section 2 was switched on, as well as the electronic potentiometer 1. A weighed sample of urea was added slowly, in small portions, to the flask 6, so as to ensure uniform mixing of the two phases. After stabilizing the temperature conditions of the two-phase system, the activator was introduced into the reaction system. The amount of heat released as a result of the adduct formation was registered by means of the resistance thermometer 7. The signal was stabilized, amplified in the section 2, and recorded in the form of a continuous curve on the strip chart of the potentiometer 1, showing the concentration as a function of time.

These experiments have yielded the first data on the relationship between the amount of n-heptadecane that has entered into the action and the concentration of aromatic hydrocarbons, as described by the empirical formula

$$y = ae^{be^{ct}}$$

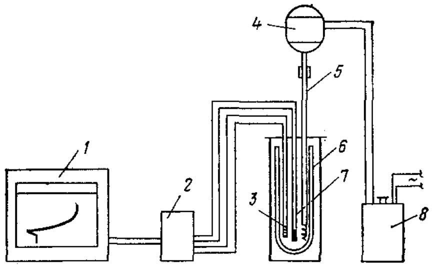

Fig. 1. Diagram of unit for determination of adduct formation rate by a thermographic method: 1) electronic potentiometer; 2) electronic section; 3) heater; 4) electric motor; 5) stirrer; 6) thermostated flask; 7) resistance thermometer; 8) transformer.

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TABLE 1. Form of Relationships with Different Concentrations of Aromatic Hydrocarbon

Concn. of aromatic hydrocarbon, mass % relative to urea	Empirical formula	Absolute standard error
	Tetralin	
0,00	$y_1 = 92{,}660\, e^{-5{,}531\, e^{0{,}0107t}}$	1,3137
4,85	$y_2 = 72{,}581\, e^{-4{,}109\, e^{-0{,}00898t}}$	0,6239
9,70	$y_3 = 65{,}335\, e^{-3{,}138\, e^{-0{,}00631t}}$	0,8232
14,55	$y_4 = 55{,}886\, e^{-3{,}595\, e^{-0{,}00748t}}$	0,3505
21,60	$y_5 = 55{,}779\, e^{-3{,}255\, e^{-0{,}00606t}}$	0,4557
	α-Methylnaphthalene	
0,00	$y_1 = 92{,}660\, e^{-5{,}531\, e^{0{,}0107t}}$	1,3137
10,20	$y_2 = 79{,}160\, e^{-4{,}973\, e^{-0{,}00916t}}$	1,0297
15,35	$y_3 = 69{,}821\, e^{-3{,}603\, e^{-0{,}00845t}}$	1,8815
21,58	$y_4 = 65{,}415\, e^{-5{,}353\, e^{-0{,}00969t}}$	1,0718
43,25	$y_5 = 59{,}006\, e^{-5{,}905\, e^{-0{,}0103t}}$	1,0856

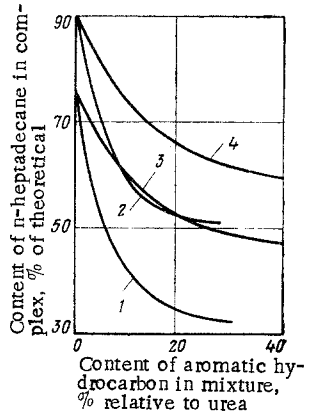

Fig. 2. Effect of aromatic hydrocarbons on adduct formation reaction: 1) with added tetralin (5-min reaction); 2) same (10-min reaction); 3) with added α-methylnaphthalene (5-min reaction); 4) same (10-min reaction).

where y is the quantity of n-heptadecane that has entered into the adduct, % of theoretical; a, b, and c are constants that depend on the concentration of aromatic hydrocarbon in the mixture and on its physicochemical properties; t is the reaction time, sec.

The equation relating the quantity of n-heptadecane that has entered into the adduct and the length of the reaction period, with different concentrations of aromatic hydrocarbon, are shown in Table 1.

For a comparison of the inhibiting effects of tetralin and α-methylnaphthalene on the adduct formation reaction, curves were plotted for the quantity of n-heptadecane entered into the adduct after 5 and 10 min from the start of the reaction, as a function of the concentration of aromatic hydrocarbon in the reaction mixture (Fig. 2). These plots show that tetralin inhibits the reaction of adduct formation to a greater degree than does α-methylnaphthalene. For a given concentration of aromatic hydrocarbon in the mixture and for a given reaction period, the amount of n-heptadecane entering into the adduct is considerably less when tetralin is present than when α-methylnaphthalene is present. The relationship between the amount of n-heptadecane entering into the adduct and the concentration of aromatic hydrocarbon, with a reaction time of 5 min, is described by the equation

$$y = a + \frac{x-1}{-b-cx}$$

where y is the quantity of n-heptadecane that has entered into the adduct, % of theoretical; a, b, and c are constants; x is the concentration of aromatic hydrocarbon, mass % relative to urea.

For tetralin, the constants a, b, and c in this equation are respectively 68.152, 0.119, and 0.0221; the absolute standard error in this relationship is 0.2665. For α-methylnaphthalene, the respective values are 73.608, 3.507, and 0.0273; the absolute standard error is 0.4828.

With a reaction time of 10 min, the relationship is expressed by the equation

$$y = a + bx + cx^2$$

where for tetralin a = 90.142, b = 4.123, and c = 0.107; for α-methylnaphthalene, the respective values are 89.227, 1.588, and 0.0205. The absolute standard error is 0.8427 for tetralin and 1.1407 for α-methylnaphthalene.

Thus we see that the kinetic curves for urea adduct formation with an n-alkane in the presence of aromatic hydrocarbons are logarithmic. The relationships between the content of n-heptadecane in the adduct and the content of tetralin of α-methylnaphthalene in the reaction mixture are nonlinear. Tetralin inhibits the adduct formation process to a greater degree than does α-methylnaphthalene. For these two aromatic hydrocarbons, we find that the stronger inhibition of complex formation is associated with more strongly manifested adsorption bonding to the urea crystals.

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