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# COMPOUNDS OF THE THIOPHENE SERIES, ACCOMPANYING AROMATIC HYDROCARBONS IN TECHNICAL MIXTURES: COMPLEXES WITH ORGANIC SOLVENTS. A REVIEW

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*The data available in the literature on the complex formation of thiophene, its homologs, and benzannelated thiophenes with organic solvents have been reviewed.*

It is known that heterocyclic compounds accompany aromatic hydrocarbons in the products of heat treatment of solid fuels (coal, shale) and petroleum. In particular, thiophene was discovered in 1882 by W. Meyer in benzene from coal. It was shown later by the same researcher and his coworkers that thiophene can be considered as the heterocyclic analog of benzene, in which the vinylene group is replaced by a sulfur atom [1]. This is corroborated by the similar boiling points of benzene and thiophene, which make their separation by the usual rectification difficult [2].

In the following years the analogy of the physical and chemical properties of thiophene and its homologs with the corresponding compounds of the benzene series was established, for instance of the 2- and 3-methylthiophenes with toluene, etc. This analogy applies also to condensed systems, such as benzothiophene and naphthalene, dibenzothiophene and anthracene. It must be pointed out that, although the aromatic $\pi$-electron structures are preserved in the annelated thiopenes, the differences from their carbocyclic analogs also appear, caused by different electron densities and by different geometries of these systems, and by the specific orientation effect of the heteroatom. This is documented in a large number of studies, dealing with the quantum-chemical calculation of the electron structure and with spectral investigations of thiophene, methyl- and ethylthiophenes, benzothiophene, and dibenzothiophene, which were carried out in the 1960s and 1970s [3-12].

In view of what has been stated above, the data on the formation of complexes of compounds of the thiophene series with polar solvents must be compared with the results obtained in the study of the complex formation of benzene and its derivatives with the same solvents. Such a comparison makes it possible to choose selective solvents for the separation of aromatic and heterocyclic structures, or suitable solvents for chemical conversions of these compounds.

In the intermolecular interactions of the discussed substances in solutions with polar solvents the specific interaction is of predominant importance; we must therefore estimate the energy of specific solvation or complex formation ($\Delta G_k$). The latter is obtained from the equation:

$$\Delta G_k = -RT\ln K_c = \Delta H_k - T\Delta S_k,$$

where $K_c$ is the stability constant of the complexes, liter/mole; $\Delta H_k$ is the enthalpy of complex formation, kJ/mole; and $\Delta S_k$ is the entropy of complex formation, J/K mole.

In the early 1960s $^1$H NMR spectroscopy started to be used successfully for the study of complex formation in solutions; the method made it possible to detect very weak interactions in systems of aromatic hydrocarbons with polar substances. Subsequently, the complexation in solutions has been studied with the use of IR and UV spectroscopy as well as with other physicochemical methods, such as GLC and calorimetry.

The reaction of aromatic hydrocarbons, first of all of benzene, with aprotic polar solvents has been studied in detail in the review [13]. In later studies [14, 15] the formation of complexes of benzene and toluene with DMFA was observed by $^1$H NMR spectroscopy; it was established that the aromatic hydrocarbons acted as electron donors. It was assumed that the

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TABLE 1. Stability Constants of Complexes (1:1) of Benzene, Toluene, and Thiophene with DMFA at Different Temperatures

| Molecular complexes | *T*, °C | Stability constant, $K_c$ | Literature |
|---|---|---|---|
| Benzene–DMFA | 24 | 0,65 | [19] |
| | | 1,00 | [20] |
| | | 1,54 | [15] |
| Toluene–DMFA | 24 | 0,67 | [19] |
| | | 1,20 | [20] |
| | | 1,65 | [15] |
| | 35 | 0,63 | [19] |
| | | 1,00 | [20] |
| | 55 | 0,60 | [19] |
| | | 0,90 | [20] |
| Thiophene–DMFA | 25 | 0,70 | [21] |

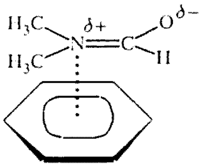

Fig. 1

components of the complexes were located in parallel planes. The electrophilic center of the DMFA molecule (the positively charged nitrogen atom) is located above the aromatic ring around the region of high π-electron density, while the negatively charged oxygen atom of the carbonyl group is located at the maximum distance from the ring (Fig. 1).

This geometry of the complexes between the molecules of the aromatic hydrocarbon and the discussed polar substance has been confirmed in [16, 17].

$^1$H NMR spectroscopy has been used in several studies to calculate the stability constants of complexes formed in the interaction of benzene, toluene and thiophene with DMFA [15, 18-21]. It was confirmed in these investigations that DMFA acts as an electron acceptor in the formation of the π-complexes. The $K_c$ values calculated at different temperatures for complexes with the molar composition 1:1 are presented in Table 1.

It must be pointed out that the discrepancies between the stability constants, in particular for the systems benzene (toluene)–DMFA are caused evidently by the fact that in [19-21] data based on NMR spectra are presented, while the data in [15] were calculated by a graphical method. However, even the data obtained from the NMR spectra are contradictory (data from [19] and [20]). Consequently, the data in Table 1 cannot be used to assess whether the $K_c$ values for benzene and thiophene can be compared.

Since the thiophene molecule is planar [22], we can assume that the geometry of complexation of thiophene with DMFA is analogous to the system benzene–DMFA (Fig. 2).

Based on these concepts we have compared by means of PMR spectroscopy the stability of complexes of benzene and thiophene with polar solvents, such as DMFA and N-methylpyrrolidone, as well as with monoethanolamine and diethylene glycol [23].

It is known that the complex formation equilibrium in solutions depends to a significant degree on the temperature and composition of the solution. The influence of these factors has been studied in particular, whereby the stability of the complexes was estimated from the change in the chemical shift of the donor protons ($\Delta_x^t$), since these values are proportional to the relative content of the molecules, forming the complexes in solution.

TABLE 2. Stability Constants (1:1) of Benzene, Toluene, Thiophene, and Methylthiophenes with Benzoyl- and Phenylacetylene (25°C)

| Electron donors | Stability constants, $K_c$, (liters/mole) | |
|---|---|---|
| | benzoylacetylene | phenylacetylene |
| Benzene | 1,02 ± 0,04 | 0,55 ± 0,04 |
| Toluene | 0,90 ± 0,02 | 0,45 ± 0,01 |
| Thiophene | 0,49 ± 0,01 | 0,51 ± 0,03 |
| 2-Methylthiophene | 0,93 ± 0,02 | 0,83 ± 0,04 |
| 2,5-Dimethylthiophene | 1,03 ± 0,02 | 0,30 ± 0,01 |

TABLE 3. Stability Constants of Complexes (1:1) of Thiophene and Some of Its Homologs[*] with Tetracyanoethylene at 20°C

| Heterocyclic compounds (electron donors) | Stability constant of the complexes, $K_c$, (liters/mole) |
|---|---|
| Thiophene | 1,00 |
| 2-Methylthiophene | 1,60 |
| 3-Methylthiophene | 1,72 |
| 2-Ethylthiophene | 1,50 |
| 2,5-Dimethylthiophene | 2,50 |

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[*] For dibenzothiophene $K_c$ = 4.76 liters/mole.

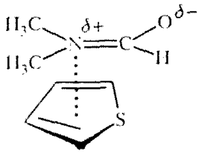

Fig. 2

The comparison of the chemical shifts for the α-proton of thiophene and for the aromatic proton of benzene showed that the complexes of all investigated polar substances with thiophene were more stable than with benzene. At T = const the difference between the stabilities of benzene and thiophene complexes increases more noticeably with the increasing concentration of the polar substance ($C_i$), particularly in the systems with monoethanolamine (from 85 to 95 mole %). When $C_i$ = const, in particular in systems with DMFA and N-pyrrolidone, the difference in the stability of the complexes decreases noticeably with increasing temperature (from 20 to 100°C). These rules have been confirmed later by data on the liquid–vapor phase equilibria in these systems [24].

In [25] the results are presented of the investigation of the complex formation of benzene, toluene, thiophene, and methylthiophenes with polar substances, such as benzoyl- and phenylacetylene; the results were based on the PMR spectra of binary solutions of these substances in cyclohexane as a neutral solvent (Table 2).

In the same study the change in $K_c$ was investigated as function of the temperature in the interval 10-60°C in systems of toluene and 2-methylthiophene with benzoylacetylene. The enthalpy of complex formation $-\Delta H_k$ is equal to 7.96 and 8.37 kJ/mole respectively. A comparison of the values of $K_c$ and $\Delta H_k$ shows that the stability of the complex of toluene and 2-methylthiophene with benzoylacetylene is virtually the same. On the other hand the stability of the thiophene and benzene complexes with the same electron acceptor differs considerably (see Table 2).

The complexation of thiophene and its homologs as well as of benzene with tetracyanoethylene has been studied most broadly [26-30]. Thus, the values of $K_c$ are presented in [26], calculated from the electron spectra of solutions of thiophene and its homologs with tetracyanoethylene in $CCl_4$ and $CH_2Cl_2$ at 20°C (Table 3).

TABLE 4. Energy of Interaction of Benzene, Thiophene, and Its Homologs with Dibutyltetrachlorophthalate (based on GLC data)

| Electron donors | Stability constant $K_c$ (liters/mole) | | | $\Delta G_k$ at 80°C, kJ/mole | $-\Delta H_k$, kJ/mole | $-\Delta S_k$, J/K mole |
|---|---|---|---|---|---|---|
| | 60 °C | 80 °C | 100 °C | | | |
| Thiophene | 0,93 | 0,80 | 0,69 | 0,067 | 7,49 | 23,11 |
| 2-Methylthiophene | 0,87 | 0,71 | 0,60 | 0,100 | 9,59 | 29,90 |
| 3-Methylthiophene | 0,84 | 0,70 | 0,59 | 1,046 | 9,21 | 29,00 |
| 2,5-Dimethylthiophene | 0,88 | 0,72 | 0,60 | 0,096 | 10,13 | 30,98 |
| 2-Ethylthiophene | 0,66 | 0,58 | 0,52 | 1,590 | 6,49 | 22,90 |
| Benzene | 0,82 | 0,68 | 0,58 | 1,130 | 9,04 | 28,81 |

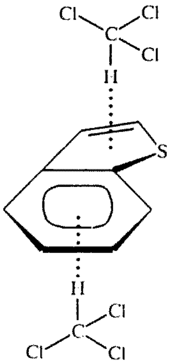

Fig. 3

A quantum-chemical calculation of the different geometrical isomers of the donor-acceptor complexes of thiophene and benzene with tetracyanoethylene has been carried out in [27]. It is shown that for the most stable geometry of the complexes, the stabilization energy for benzene and thiophene is equal to 31.4 and 79.4 kJ/mole respectively.

The influence of substituents on the electron structure and the $\pi$-donor properties of benzene and thiophene derivatives in the complex formation with tetracyanoethylene has been discussed in [28]. It was noticed that the derivatives of benzene and thiophene act as $\pi$-donors, by forming with the acceptor weak $\pi - \pi$ complexes with a small charge transfer.

Based on the UV spectra, the molecular (1:1) complexes of thiophene, methylthiophenes, and dibenzothiophene in solutions of hexane, $CH_2Cl_2$, $CHCl_3$, and $CCl_4$ have also been discussed in [29, 30]. Besides tetracyanoethylene, chloranil and 2,3-dichloro-5,6-dicyano-p-benzoquinone were also used as acceptors. The results of the thermodynamic investigation of the complex formation of thiophene and its homologs, and of benzene with dibutyltetrachlorophthalate at 60-100°C are presented in [31], based on GLC. Some data from this study are shown in Table 4.

The data show that thiophene, in distinction from benzene, forms more stable complexes with the discussed acceptor. It must also be pointed out that, according to PMR, benzene, thiophene, and its homologs form molecular complexes with acetonitrile [32]. Besides this, it was established that thiophene forms charge transfer complexes also with maleic anhydride, trinitrobenzene, tetranitromethane, and tetracyanoquinodimethane [33].

Thus, as a rule, the complexes of benzene, thiophene, and also of some of their homologs with polar solvents possess different stabilities with the same solvents. In the further text we shall discuss the condensed heterocyclic compounds and aromatic hydrocarbons, in particular benzothiophene and naphthalene.

A study of the $^{13}C$ NMR spectra revealed a planar structure of the benzothiophene molecule [9]; in analogy with the formation of a benzene complex with $CHCl_3$ at a molar ratio of 1:1 [12], it is assumed that benzothiophene and chloroform form complexes with the composition 1:2 [34] (see Fig. 3). It should be mentioned that the causes for the formation of complexes with such a composition are the hydrogen bonds and dipole-induced dipole interactions.

TABLE 5. Thermodynamic Parameters of (1:1) Complexes of Benzene, Benzothiophene, and Benzodithiophene with TCQDM

| Molecular complexes | Thermodynamic parameters | | |
|---|---|---|---|
| | $K_c$, (liters/mole) | $\Delta H_k$, kJ/mole | $\Delta S_k$, J/K mole |
| Benzene – TCQDM | 0,15 (-8,2 °C) | -2,0 ± 0,8 | -23,5 ± 3,2 |
| Benzothiophene – TCQDM | 0,55 (-8,8 °C) | -5,7 ± 0,5 | -26,7 ± 2,0 |
| Benzodithiophene – TCQDM | 2,90 (-4,0 °C) | 11,2 ± 0,2 | 33,1 ± 0,6 |

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*The error in the determination of $K_c$ is 4.5%.

TABLE 6. Stability Constants of (1:1) Complexes of Benzothiophene and Naphthalene with Some Polar Solvents at 20°C

| Polar solvents | $K_c$, (liters/mole) | |
|---|---|---|
| | benzothiophene | naphthalene |
| Hexamethylphosphorotriamide (hexametapol) | 8,6 | 2,3 |
| N-Methylpyrrolidone | 1,9 | — |
| DMFA | 1,3 | 0,5 |
| Pyrrolidone-2 | 2,0[40] | 0,5[40] |
| Monoethanolamine | 0,5[40] | 0,940 |
| Diethylene glycol | 5,3 | 4,6 |

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*The standard errors in the calculation of $K_c$ do not exceed 3%.

In [35] NMR spectroscopy has been used to investigate the complexation of binary mixtures in $C_2D_2Cl_2$ at low temperatures in the order benzene, benzothiophene, benzodithiophene, etc., with a strong electron acceptor: 7,7,8,8-tetracyanoquinodimethane (TCQDM); the thermodynamic parameters were also determined (Table 5). It must be pointed out that the $K_c$ values obtained in this study are in good agreement with the first ionization potentials ($I_1$): $I_1$ = 9.24 eV for benzene and 7.86 eV for benzothiophene.

In some studies the results obtained by NMR are compared with the calculated electron structures of naphthalene and benzothiophene [36, 37]; the equivalence of the system of $\pi$-electrons of benzothiophene and naphthalene, as well as of dibenzothiophene and fluorene, is demonstrated.

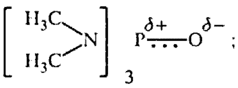
The charge transfer complexes which have a bond of the type ($\pi - \pi$) between naphthalene, benzothiophene, and 1,3,5-trinitrobenzene (a strong $\pi$-electron acceptor) have been studied by PMR in [38]. It has been found that the components of the 1:1 complex are located in parallel planes, with their centers arranged one above the other. This is in good agreement with Mulliken's data [39, 40] on the complex formation of aromatic electron donors and acceptors, and with the results obtained in investigating the interaction of naphthalene with chlorobenzene [41].

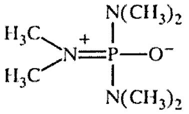
We have compared the $^1H$ NMR spectra of binary solutions of naphthalene and benzothiophene with polar compounds of different chemical classes in $CCl_4$ [42]. The values of $K_c$, calculated from these data, are presented in Table 6.

When considering the mechanism of complex formation of benzothiophene and naphthalene with the polar substances shown in Table 6, one can assume that DMFA and N-methylpyrrolidone behave in the same way as in the systems with benzene and thiophene, i.e., the center of complex formation is the nitrogen atom, interacting with the system of $\pi$-electrons of the donors, whereby the components of the complexes are located in parallel planes.

In solutions consisting of benzothiophene or naphthalene with monoethanolamine, the complexes are formed by the hydrogen bond of the OH group (or the $NH_2$ group of monoethanolamine, and the system of $\pi$-electrons of the donors. For pyrrolidone-2 one can assume formation of the complexes on account of the H-bond of the NH group, as well as due to a partial positive charge on the nitrogen atom.

Table 6 shows that the strongest interaction of benzothiophene and naphthalene occurs in solutions with hexametapol. Two variants can be proposed for the distribution of charges in the molecule [43]:

a 

b 

Since the positively charged phosphorus atom is strongly screened, one can assume that only the nitrogen atom acts as the center of acceptor activity in the formation of $\pi$-complexes with benzothiophene and naphthalene. The size and the pyramidal form of the hexametapol molecule creates steric hindrances to coordination; this leads to the formation of complexes with an unusual stereochemistry [44].

An analysis of the complex formation of condensed aromatic systems and S-heterocycles with polar solvents, as well as of thiophene and benzene, shows that in many instances the complexes of benzothiophene and naphthalene possess a different stability with the same polar compounds.

By summarizing the reviewed material on the complex formation of S-heterocycles in solutions with polar compounds it must be pointed out that particularly the above-mentioned fact can be used, having achieved the separation of mixtures of aromatic hydrocarbons and S-heterocycles, accompanying them in technical mixtures by extraction or extractive rectification methods, which are based on the use of selective organic solvents.

Thus, based on the investigation of complex formation of benzene and thiophene with different polar substances, we have chosen DMFA and N-methylpyrrolidone as the most promising solvents. Further physicochemical investigations have confirmed that these substances can be utilized for the selective separation of technical mixtures of benzene and thiophene by extractive rectification [5]. In the rectification on a column in the presence of one of these solvents, thiophene is retained much more strongly than benzene in the bottom section of the column and in the still, because it forms more stable complexes with the solvent; the concentration of thiophene in this section of the column is 80-85%, while the benzene, from which the thiophene has been removed, is withdrawn as the distillate from the top of the column [46]. We have also demonstrated that DMFA and N-methylpyrrolidone can be used in the same way for the separation of mixtures of toluene with 2- and 3-methylthiophenes [47].

For the separation of technical mixtures of naphthalene and benzothiophene we have investigated the possibility of using two methods of separation: liquid–liquid extraction in a system of two virtually immiscible solvents (or solvents with limited mutual solubility) and extractive rectification.

For the separation of naphthalene and benzothiophene by liquid–liquid extraction a system can be used, consisting of a nonpolar solvent (heptane, octane) and a polar solvent (hexametapol, DMFA, or diethylene glycol) (see Table 6). In such a two-phase system at 20-25°C benzothiophene forms the most stable complexes with the polar solvent, which leads to enrichment of the latter in the extract (polar solvent layer, while naphthalene is accumulated in the nonpolar solvent layer. However, the use of DMFA and hexametapol was found to be ineffective, due to significant mutual solubility with the nonpolar solvent; in particular, the solubility of DMFA in octane $\leq$ 4 mass %, of octane in DMFA $\leq$ 10 mass %. The use of diethylene glycol was therefore found to be best suited [48].

In the separation of technical mixtures of benzothiophene and naphthalene by extractive rectification it is expedient to use pyrrolidone-2 or hexametapol as the selective solvent (see Table 6). Their boiling points are higher than those of the components to be separated. In the liquid vapor system in the presence of one of these solvents the vapor phase is enriched to a much larger degree in naphthalene, while benzothiophene is predominantly retained in the lower section of the rectification column and in the still, because it forms more stable complexes with the solvent, in particular with pyrrolidone-2, the concentration of which in the bottom section of the column reaches 85-90% [49, 50].

Thus, the above examples illustrate the possibility of applying the data on the formation of complexes in solution to the search for and selection of effective extractants for the separation and purification of the discussed compounds. Organic solvents can be found on the same basis to carry out chemical conversions of the above-mentioned heterocyclic compounds.

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