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COMPLEXATION OF INDOLE, METHYLINDOLES, AND CARBAZOLE WITH ORGANIC SOLVENTS (REVIEW)

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Data on the complexation of indole, its methyl derivatives, and carbazole with organic solvents in solutions are summarized. Examples of the use of these data for the isolation of the heterocycles from their mixtures with aromatic hydrocarbons are examined.

It is known that indole, methylindole, and carbazole accompany aromatic hydrocarbons (and naphthalene and methylnaphthalene, in particular), biphenyl in the absorption fraction, and anthracene and phenanthrene in the anthracene fraction, produced during the rectification of coal tar. In Russia (and in the SNG) these fractions are the only raw material source of the above-mentioned heterocycles, since methods for the synthesis of these compounds have not been introduced on an industrial scale in the countries of the SNG. The practical potential of the compounds is quite high. Thus, according to data in [1], the indole content of the coal tar processed in the east of Russia amounted to about 0.2%, while the carbazole content amounted to 2.2-2.6%. During the rectification of tar an absorption fraction (~10% of the amount of tar) is obtained, in which the indole content amounts to 2%. From this fraction an indole fraction, which contains 7-9% of indole, is isolated by rectification [2]. The anthracene fraction (≥17% of the weight of the tar), also obtained by rectification of the tar, contains 5.6% of carbazole.

Since the investigated condensed heterocycles accompany condensed aromatic hydrocarbons with similar physicochemical properties and indole and methylindole even form azeotropes with some of them, these mixtures can only be separated by nontraditional methods. They mainly include extractive and azeotropic rectification, liquid extraction, and extractive crystallization and are carried out with the use of selective solvents. All these methods are based on the differing interaction of the above-mentioned heterocycles and aromatic hydrocarbons with polar solvents, characterized by the formation of molecular complexes with various degrees of stability. Here, it is known that unsubstituted aromatic hydrocarbons, which are weak CH acids (e.g., for benzene $pK_a = 37.0$, for indene 21.0, for fluorene 25.0, etc. [3]), behave as π-electron donors in systems with polar solvents. Heterocyclic compounds of the pyrrole series (indole, methylindole, carbazole) are fairly strong NH acids (for indole $pK_a = -2.4$, for carbazole -1.0 [4]) and can clearly behave as donors of π-electrons and of the proton of the NH group, depending on the partner. It is this circumstance that explains the need to look for published data on the interaction of these heterocycles with various chemical types of organic compounds.

In view of the complex mechanism of intermolecular interaction that appears in the indicated systems it is of undoubted interest to know the values of the parameters characterizing the interaction of the heterocyclic components with the organic solvents in such systems and primarily the stability constants of the molecular complexes (K_c), the enthalpy and entropy of complexation (ΔH_k and ΔS_k respectively), and the specific solvation or complexation energy (ΔG_c). These thermodynamic parameters are related by the familiar equation:

$$\Delta G_c = -RT \ln K_c = \Delta H_K - T \cdot \Delta S_K$$

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TABLE 1. Parameters of Complexation in Indole–Polar Solvent Systems (1:1) [8]

Proton acceptors and their concentration limits, M	K_c, liter/mole		$-\Delta H_k$, kJ/mole
	20 °C	55 °C	
Acetonitrile, 0,1...0,5	1,85	1,41	6,15
Benzophenone, 0,075...0,4	3,04	2,12	8,25
Acetone, 0,05...0,5	2,84	1,75	11,10
1,4-Dioxane, 0,3...0,6	2,64	1,89	7,54
DMFA, 0,03...0,2	12,20	6,47	14,24
Pyridine, 0,15...0,35	$4{,}49^{15}$	$3{,}30^{30}$	14,86
Tetrahydrofuran, 0,1...0,5	2,03	1,50	6,82

TABLE 2. Effect of Neutral Solvents on the Complexation of Indole with DEAA and Ethyl Acetate (EA) (1:1) [10]

Inert solvent	Indole–DEAA		Indole–EA	
	K_c, liter/mole	$-\Delta G_k$, liter/mole	K_c, kJ/mole	$-\Delta G_k$, kJ/mole
Heptane	43,5	9,59	4,0	3,52
CCl_4	14,2	6,74	2,1	1,88
Benzene	3,8	3,39	0,7	-0,92

TABLE 3. Complexation of Indole with Some Proton Acceptors in a Nonpolar Solvent (1:1)

Proton acceptors	Temperature, °C	Medium	Constant K_c, liter/mole	Reference
Dioxane	18	Isooctane	1,57	[14]
Dioxane	25	"	1,45	[14]
Dioxane	32	"	1,34	[14]
Diethyl ether	25	"	1,23	[14]
Di-n-propyl ether†	20	Cyclohexane	2,40	[11]

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*In this system $-\Delta H_k = 8.1$ kJ/mole.

†For the 3-methylindole–di-n-propyl ether system (in cyclohexane) $K_c = 1.3 \pm 0.5$ liter/mole.

(where K_c is expressed in liter/mole, ΔH_k and ΔG_k in kJ/mole, and ΔS_k in J/K·mole) and can be determined by NMR, IR, and UV spectroscopy and calorimetry, which reliably establish the fact that complexation occurs and make it possible to obtain specific information on the nature of the intermolecular bond.

Beginning in the 1960s data on the complexation between indole and organic solvents, based on spectral investigations, appeared in the literature. Ioganseh [5] established a relation between the energies of the H bond and the intensity of the IR absorption for the case of the increase in the integral intensity of the band for the stretching vibrations (ν_{NH}). With coworkers he showed that indole is a weaker acid than phenol in H bonds but is somewhat stronger than unsubstituted aliphatic alcohols [6]. In addition, it was established that indole is a significantly stronger acid than amides and aliphatic amines. A spectral investigation of the H complexes of indole was carried out by Kurchki [7], who used the data in [8] to check the relation between the energy of the H bond and ν_{NH}.

The role of indole as donor of the NH proton was noted in a series of papers. Thus, the energy of the H bond was determined by IR spectroscopy in a system consisting of a proton donor (indole) and a proton acceptor, for which purpose substances of various chemical types were studied. The K_c values of the complexes (1:1) in solution (inert solvent carbon tetra-

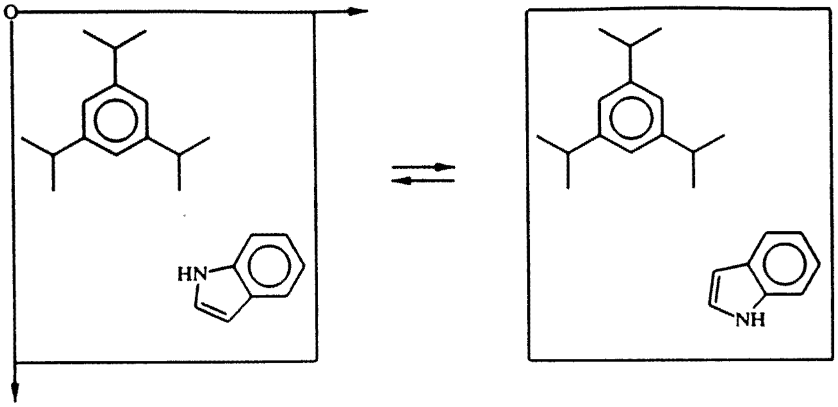

Fig. 1

chloride) and the ΔH_k values were calculated [8]. As seen from the data of this work, presented in Table 1, indole forms the most stable complexes with DMFA and pyridine. These results agree satisfactorily with the values obtained on the basis of calorimetric measurements [9] for the indole–DMFA ($-\Delta H_k$ = 17.38 kJ/mole) and indole–pyridine ($-\Delta H_k$ = 16.71 kJ/mole) systems in chloroform.

The interaction of indole as proton donor with such acceptors as diethylacetamide (DEAA) and ethyl acetate (EA) was studied by IR spectroscopy at 32°C in various neutral solvents [10]. n-Heptane, carbon tetrachloride, tetrachloroethylene, chloroform, carbon disulfide, benzene, dichloromethane, and trichlorotrifluoroethylene were used as solvents. (Data on some of them are given in Table 2 for comparison.) It was established that n-heptane has the smallest effect on the complexation of indole with the investigated proton acceptors. Thus, in the indole–DEAA system in heptane K_c = 43.5 liter/mole while $-\Delta G_k$ = 9.59 kJ/mole. In the indole–EA system under the same conditions K_c = 4.0 liter/mole, and $-\Delta G_k$ = 3.52 kJ/mole.

The formation of the H complexes of indole and its derivatives (3-methylindole and 5-methoxyindole) with di-n-propyl ether in cyclohexane was studied by UV spectroscopy. The authors in [11] observed an analogy in the structure of the H complexes of indole with the above-mentioned ether and with alcohols (methanol, ethanol, butanol) and also with propylene glycol. This fact was confirmed by the results in [12]. The formation of H complexes with the participation of 2,3-dimethylindole was also studied [13].

Quantitative data on the H complexes of indole with dioxane and ethers in isooctane and cyclohexane according to data in [11, 14] are given in Table 3. The ability of indole to act as proton donor was also noted in [15-17].

During investigation of the NMR spectra of solutions of indole in dimethyl sulfoxide, triethylamine, acetone, dioxane, and other solvents [16] it was established that these solvents give rise to a more appreciable downfield chemical shift of the signal for the proton of the NH group of indole ($\Delta\tau_{NH}$ = 4.11 ppm) than the chemical shift of the α- and β-protons of indole ($\Delta\tau_{\alpha H}$ = 0.76 ppm, $\Delta\tau_{\beta H}$ = 0.19 ppm). This fact confirms the idea that the NH group of indole is a proton donor during the formation of an intermolecular H bond with the investigated compounds. The formation of the most stable complexes is observed in the indole–DMSO system. (According to data in [17], in this system $-\Delta H_k$ = 16.87 kJ/mole, while in the indole–diphenyl sulfoxide system $-\Delta H_k$ = 14.8 kJ/mole.) According to the intensity of the interaction the proton acceptors investigated in [16] can be arranged in the order: DMSO > triethylamine > acetone > dioxane > carbon tetrachloride > carbon disulfide. The energy of complexation of indole with tetramethylurea $-\Delta G_k$ = 9.55 kJ/mole [18].

On the other hand, a series of papers are known in which it was shown that indole and its methyl-substituted derivatives act as π-electron donors. In particular, it was shown that indole and 3-methylindole (skatole) behave as π-electron donors during complexation (1:1) with 1,3,5-trinitrobenzene, as confirmed by the data from the PMR spectra [19, 20]. In the last paper the geometry of these complexes is examined. The authors propose, for example, possible equilibrium mutual steric orientations of the donor and acceptor, shown in Fig. 1.

There are other investigations that confirm that the π-electron system of indole and its methyl-substituted derivatives can serve as a proton acceptor [21, 22]. In [23] it was shown on the basis of UV spectroscopic investigations that whereas indole and 3-methylindole behave as proton donors during complexation with diethyl ether in systems with n-butanol the H bond is formed not only at the NH group of the heterocycle but also with the participation of its π-electronic system.

TABLE 4. Energy of Complexation of Indole with Polar Substances (1:1) (according to the UV spectra [25])

Polar substances	T, °C	Free energy of complexation, $-\Delta G_k$, kJ/mole	Medium
Monoethanolamine	25	18,17	Heptane
	50	17,69	"
DMFA	20	7,70*	Heptane
	60	7,12	"
N-Methylpyrrolidone	20	9,68 †	Heptane
	60	8,29	"
2-Pyrrolidone	20	8,96	Octane
	20	5,23	CCl_4
Piperidine	20	5,57	Heptane
Cyclohexanol	20	4,35	Heptane
Cyclohexanone	20	5,23	Heptane

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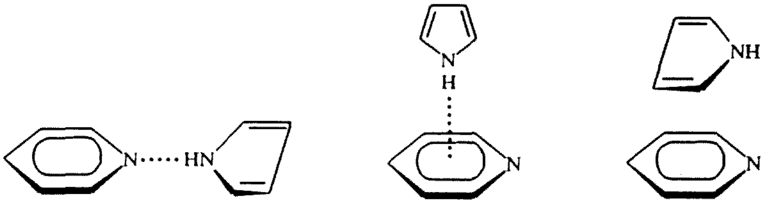
*In carbon tetrachloride $-\Delta G_k$ = 6.16 kJ/mole (see Table 1 and [8]).

†In heptane $-\Delta H_k$ = 21.2 kJ/mole, according to data in [27], in 1,1,1-trichloroethane $-\Delta H_k$ = 19.13 kJ/mole.



a) b) c)

Fig. 2

Of some interest in this connection are the results [24] from IR-spectroscopic study of the NH···π association in crystals of indole (ΔH_{ass} = 2.09 kJ/mole) and also of the intermolecular H bond during the complexation of indole with naphthalene (in carbon tetrachloride solution): $-\Delta H_k$ = 6.28 kJ/mole.

We also studied [25] the ability of the NH group of indole to act as proton donor during the formation of a bond with a series of polar substances of various chemical types. As the latter we studied bifunctional compounds (2-pyrrolidone and N-methylpyrrolidone), amides (DMFA) and monoethanolamine, and also model monofunctional substances (cyclohexanone, cyclohexanol, and piperidine). The UV spectra of binary mixtures in inert solvents (n-heptane, octane, and carbon tetrachloride) were recorded, where the concentration of indole amounted to $2 \cdot 10^{-4}$ M, while the concentration of the polar substances varied between $7 \cdot 10^{-3}$ and $8.2 \cdot 10^{-2}$ M. The results from calculation of the energy of complexation are given in Table 4.

As seen from the obtained data, the values of the free energy of complexation of indole with a series of polar substances in n-heptane (octane) are higher than in carbon tetrachloride. This agrees well with the familiar idea that the formation of complexes between an acid (indole) and carbon tetrachloride is possible in a weakly basic solvent with low dielectric constant (particularly in carbon tetrachloride), i.e., specific nucleophilic solvation occurs [26]. Thus, the inertness of n-heptane (octane) toward indole was confirmed.

Of the model substances piperidine forms the most stable H bond (the NH···OH bond), while cyclohexanone (the NH···O═C bond) forms less stable complexes. This made it possible to suppose that of all the substances investigated in [25] the proton of the NH_2 group of monoethanolamine is the strongest proton-accepting center during complexation with indole (Table 4). The last fact was also confirmed by the data from the IR spectra of mixtures of indole with monoethanolamine.

During the investigation of complexation an important role is played by the stereochemical structure of the complexes. It is known that as far back as the 1970s the dipole moment method [28, 29], including the electrooptical method of determining the Kerr effect employed later in [30, 31] on H complexes with the O−H···N bond, was proposed for the investigation of the structure of the H complexes.

TABLE 5. Thermodynamic Constants of the Complexes of Pyrrole, Indole, and Carbazole with Some Sulfones in Solution at 25°C (1:1) [35]

Proton acceptors	Proton donors	Thermodynamic constants			
		K_c, liter/mole	$-\Delta H_k$, kJ/mole	$-\Delta G_k$, kJ/mole	$-\Delta S_k$, J/mole·K
N,N-Dimethyl-methanesulfonamide	Pyrrole	4,65	7,94	3,81	13,8
	Indole	6,16	8,86	4,51	14,6
	Carbazole	9,19	12,70	5,49	24,2
N,N-Dimethyl-benzenesulfonamide	Pyrrole	4,18	7,36	3,53	11,5
	Indole	5,37	8,00	4,16	12,9
	Carbazole	6,78	10,40	4,75	18,8
Diphenyl sulfone	Pyrrole	4,44	7,49	3,69	12,7
	Indole	5,36	7,13	4,16	15,0
	Carbazole	6,60	10,80	4,79	20,2

TABLE 6. Thermodynamic Parameters of the Complexes of Heterocycles with Dibenzyl Sulfoxide (1:1) at 25°C [17]

Heterocyclic Carbazole	Thermodynamic parameters		
	$-\Delta H_k$, kJ/mole	$-\Delta G_k$, kJ/mole	$-\Delta S_k$, J/mole·K
Pyrrole	14,4	5,82	28,7
Indole	14,5	7,05	24,9
Carbazole	16,4	7,96	28,2

TABLE 7. Parameters of the Complexation of Heterocycles with N,N-Dimethyl-4-toluenesulfonamide and N,N-Dimethyl-4-toluenesulfonimide (1:1) at 25°C [38]

Heterocycles	Thermodynamic parameters					
	N,N-Dimethyl-4-toluenesulfonamide			N,N-Dimethyl-4-toluenesulfinamide		
	$-\Delta H_k$, kJ/mole	$-\Delta G_k$, kJ/mole	$-\Delta S_k$, J/mole·K	$-\Delta H_k$, kJ/mole	$-\Delta G_k$, kJ/mole	$-\Delta S_k$, J/mole·K
Pyrrole	7,85	3,83	13,5	12,2	5,04	24,0
Indole	9,77	4,45	17,8	13,7	6,03	25,7
Carbazole	11,30	5,26	20,3	15,5	7,01	28,4

TABLE 8. Parameters of the Complexes of Carbazole with a Series of Electron Acceptors (1:1) [40]

Electron acceptors	Thermodynamic parameters		
	K_c, liter/mole	$-\Delta H_k$, kJ/mole	$-\Delta G_k$, kJ/mole
I	28,1	8,4	21,4
II	2,5	2,7	12,1
III	13,7	6,7	13,0
IV	5,9	4,4	12,3

The above-mentioned method was used to investigate the stereochemical structure of the H complexes of indole and its uncondensed analog pyrrole with a series of N-containing bases (an H bond of the NH···N type) [32]. For the case of pyrrole and pyridine the three most probable stereochemical structures of 1:1 complexes were examined (Fig. 2). In the first structure (a) the H bond lies on the straight line connecting the symmetry axes lying in the planes of the pyridine and pyrrole rings, and in the second structure (b) the NH···π bond is perpendicular to the plane of the proton acceptor. The possibility of

TABLE 9. Enthalpy of Complexation of Carbazole with Some Solvents (1:1) [44]

Organic solvents	Enthalpy of complexation $(-\Delta H_k)$, kJ/mole
Tetrahydrofuran*	18,0 ± 1,7
DMFA	26,4 ± 2,1
Tributyl phosphate	28,5 ± 2,1
Hexamethylphosphorotriamide*	30,6 ± 1,7

*The data for these substances coincide with the results in [49], obtained when the absorption spectra of solutions in hexane were recorded.

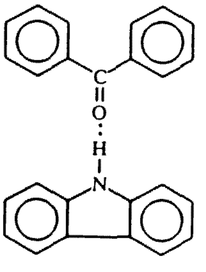


Fig. 3

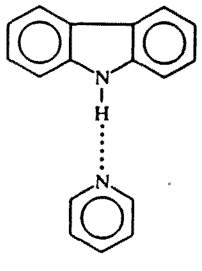


Fig. 4

a third structure (c), where the planes of the components of the complex are parallel, is noted. However, the second structure prevails, as previously proposed in [33]. From the cited papers it follows that the complexes resulting from two types of interaction can be present simultaneously in the solution: 1) interaction of the unshared electron pair of the nitrogen atom of the base with the NH group of the acid; 2) interaction of the NH group of the acid with the π system of the base. Here, the relative content of the second type of complexes increases with decrease in the pK_a value of the base and with increase in its π system. The latter was confirmed during investigation of the complexes of indole with derivatives of aniline [34].

A series of papers are known in which the complexation parameters of indole and carbazole (and sometimes pyrrole) with the same solvents are compared. Thus, IR spectroscopy was used to study the complexes (1:1) formed by pyrrole, indole, and carbazole with a series of sulfones (in solution in carbon tetrachloride at 15-45°C), and their thermodynamic characteristics (given in Table 5) were obtained [35]. As follows from these data, stronger interaction with the investigated sulfones appears in the carbazole systems (proton donor the NH group) than in the other members of the series. This effect was also observed by the authors in [36], in which the enthalpy of solution of indole and carbazole in a series of solvents was studied. It was emphasized that these compounds are characterized by the formation both of π-complexes (through the π electrons of the heterocycle) and of an H bond through the NH group. The authors point out that the enthalpy of interaction of carbazole with the series of polar solvents (acetonitrile, hexamethylphosphorotriamide, N-methylpyrrolidone, N,N-dimethylacetamide) exceeds the enthalpy of interaction of indole with the same solvents on account of the formation of more stable π-complexes. However, the enthalpy of interaction due to the formation of an H bond between these solvents and indole is 15-30% higher than with carbazole, and this bears witness to the stronger proton-donating capacity of indole compared with carbazole. This is confirmed by the results in [37], in which the interaction of indole and carbazole with tetrahydrofuran and benzene (in the form of dilute solutions in carbon tetrachloride) was studied by IR spectroscopy. In addition, it was established on the basis of data on the variation of the integral intensity that in systems with benzene or tetrahydrofuran indole exhibits stronger proton-donating capacity than carbazole.

It is necessary to mention two other papers, in which the complexation parameters of all three heterocycles are compared. Thus, the complexation of pyrrole, indole, and carbazole with dibenzyl sulfoxide was studied by IR spectroscopy (in carbon tetrachloride solution), and the thermodynamic parameters of the complexes were calculated on the basis of the change in the intensity of the bands for the OH or NH stretching vibrations in the IR spectra [17] (see Table 6). The same meth-

TABLE 10. Thermodynamic Parameters of the Complexes of Carbazole and Anthracene (1:1) with Some Acids [45]

Acids	Thermodynamic parameters			
	Carbazole		Anthracene	
	K_c, liter/mole	$-\Delta G_k$, kJ/mole	K_c, liter/mole	$-\Delta G_k$, kJ/mole
3,5-Dinitrobenzoic acid	2230	19,1	1160	17,5
2-Chloro-4-nitrobenzoic acid	325	14,3	2960	19,8
2-Chloro-5-nitrobenzoic acid	298	14,1	760	16,4
Picric acid*	635	15,6	955	16,6

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*The parameters of the complexes of indole with picric acid are: K_c = 1140 liter/mole, $-\Delta G_k$ = 17.0 kJ/ mole [45].

TABLE 11. Approximate Values of the Solubility of Carbazole and the Stability Constants of the Complexes with Some Solvents [47]

Organic solvents	Approximate solubility value X, mole fraction	Stability constant of complexes K_c, liter/ mole
Hexamethylphosphorotriamide	0,28	142,0
DMSO	0,14	22,0
DMFA	0,16	24,3
N-Methylpyrrolidone	0,16	16,3
Cyclohexanone	0,07	10,3
Methyl ethyl ketone	0,04	4,4
Tetrahydrofuran	0,07	2,3
Ethyl acetate	0,02	1,9
Acetophenone	0,04	3,6
1,4-Dioxane	0,04	2,9

od was used to study the complexation of the above-mentioned heterocycles with N,N-dimethyl-4-toluenesulfonamide and N,N-dimethyl-4-toluenesulfinamide [38]. Parameters of the complexes (1:1), calculated from the spectra, are given in Table 7.

As follows from the data in Tables 5-7, the thermodynamic characteristics of complexation of pyrrole, indole, and carbazole with various polar compounds vary in a similar way. The two previously mentioned types of intermolecular interaction (an H bond through the NH group and a π-complex through the π-electrons of the heterocycle) undoubtedly appear in these systems.

A series of investigations into the H-complexation of heterocycles with polar substances was devoted solely to carbazole. Thus, the complexation of carbazole with benzoquinone (1:1) at 77 K was studied in [39]. (The emission spectra of the complexes in hydrocarbon and in polar solvents were obtained.) The authors found that for this complexation (see Fig. 3) $-\Delta H_k = 12.14 \pm 2.1$ kJ/mole (in the methylcyclohexane – isopentane mixture of nonpolar solvents) and $-\Delta H_k = 9.17$ kJ/mole (in a mixture of alcohol and ether). The absorption spectra were investigated (in dichloroethane) for the complexes of carbazole with 2,3-dichloro-5,6-dicyanobenzoquinone (I), tetracyanoethylene (II), 9-dicyanomethylene-2,4,7-trinitrofluorenone (III), and 2,4,7-trinitrofluorenone (IV) [40]. The results of the calculation are given in Table 8.

The complexation of carbazole with pyridine (K_c = 12 liter/mole) and 2,6-dimethylpyridine (K_c = 13 liter/mole) in cyclohexane was investigated in [41] (see Fig. 4). On the basis of the data from the IR spectra an H bond (O···HN) was established in the carbazole systems with trinitrobenzene at 22°C [42]. The H-complexation (1:1) of carbazole with p-xylene ($-\Delta H_k = 6.28 \pm 2.1$ kJ/mole) and with 1,4-dioxane ($-\Delta H_k = 8.37 \pm 2.1$ kJ/mole) [43] was also studied.

The results from spectroscopic determination of the enthalpy of complexation (1:1) of carbazole with a series of familiar solvents were set out in [44] (Table 9). The ΔH_k values were calculated from data on the variation of K_c with temperature.

The results from spectrophotometric determination of K_c (in methyl ethyl ketone) for the complexes (1:1) of carbazole and anthracene with a series of acids (3,5-dinitrobenzoic, 2-chloro-4-nitrobenzoic, 2-chloro-5-nitrobenzoic, and picric) are presented in Table 10. In [45] it was noted that chloronitrobenzoic acids form complexes as a result of π,π interaction, while

TABLE 12. Stability Constants of the Complexes of Carbazole with Dibutyl Ether (1:1) in Various Hydrocarbons [51, 52]

Medium, hydrocarbon	K_c, liter/mole	Medium, hydrocarbon	K_c, liter/mole
n-Hexane	24	Cyclooctane	25
n-Heptane	22	Isooctane	30
n-Octane	25	n-Hexadecane	24
Cyclohexane	24	Squalane	23
Methylcyclohexane	26	*tert*-Butylcyclohexane	30

TABLE 13. Thermodynamic Parameters of the Complexes of Carbazole with Some Polar Substances (1:1) in Hexane* [53]

Polar substances	Parameters of complexes	
	K_c, liter/mole	$-\Delta G_k$, kJ/mole
Tetrahydrofuran	7,6	5,02
Ethyl alcohol	6,3	4,61
Methyl alcohol	5,2	3,98
Acetone	4,3	3,35

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*At concentrations up to 10^{-6} M.

dinitrobenzoic acids form them both through the π,π systems and through H bonds. The possibility of both types of intermolecular interaction is also mentioned in [46], in which the complexation of carbazole and 9-ethylcarbazole with toluene, acetone, DMFA, and other substances was studied.

It is necessary to mention the papers devoted to the study of the solubility of carbazole in polar solvents and the determination of the K_c values from these data. Thus, the solubility of carbazole in polar solvents was studied, and the nature of this interaction was determined by IR spectroscopy [47]. The K_c values calculated by an approximate equation are give in Table 11. The authors point out that the solubility of carbazole in proton-accepting solvents is mainly determined by the stability of the obtained H complexes. Therefore, the K_c values can be used to determine the solubility of carbazole in such solvents. In [48] the solubility of carbazole in binary mixtures of dibutyl ether with chlorooctane, chlorotetradecane, and chlorocyclohexane was determined over the whole range of concentrations. It was established that complexes were present in the solutions of carbazole with these compounds, and the stability constants of the complexes of carbazole with ether (K_c = 25-25 liter/mole) are an order of magnitude higher than the constants of the complexes of carbazole with chloroalkanes (K_c = 2.0-3.0 liter/mole) at 25°C.

The solubility of carbazole, anthracene, and phenanthrene in polar solvents of various chemical types was studied in [50]. The higher selectivity of trimethyl phosphate and N,N-dimethylacetamide toward carbazole was established, and the authors explained this by the considerable polarization of the P═O and C═O bonds in these compounds.

The stability constants of the complexes (1:1) were also calculated from the data on the solubility of carbazole in binary systems of dibutyl ether with various hydrocarbons [51, 52], and these are given in Table 12.

The solvation of carbazole in binary solvents was the subject of [53], in which the results from a spectroscopic investigation of the complexation of carbazole in binary mixtures of n-hexane with alcohols, acetone, and tetrahydrofuran — compounds having various polarities and various donor–acceptor characteristics — were examined. To reveal the differences between the H bond that forms and the dipole–dipole interactions under various conditions the authors also investigated N-methylcarbazole, which is not capable of H-complexation. The calculated data are given in Table 13.

Thus, as seen from the papers on complexation with carbazole (like indole), fairly extensive data covering various chemical types of polar substances can be found in the literature.

Analysis of the complexation of indole and its methyl derivatives with organic compounds in solutions shows that the most inert of the nonpolar substances to these heterocycles are the hydrocarbon solvents and n-heptane, in particular. Of the investigated polar substances monoethanolamine, DMSO, and 2-pyrrolidone are more selective toward indole.

For the selective extraction of indole from mixtures with aromatic hydrocarbons [54] we proposed a method of counterflow liquid extraction with two immiscible solvents — nonpolar (n-heptane) and polar. For the latter it was proposed to use monoethanolamine or 2-pyrrolidone, or DMSO, or their mixture with water. This method with the heptane–monoethanolamine system was successfully tested for the extraction of indole and methylindole from technological mixtures on continuous plant with a packed column extractor [55]. The yield of indole was ≥95%. The extraction of the indole and methylindole from the extractant with the production of high-purity indole (≥99%) was achieved by rectification [56]. This method was developed in more recent papers by Japanese authors, who repeated the results obtained in [54, 55], using analogous extraction systems and, in particular, petroleum ether–monoethanolamine, C_5-C_{10}-alkanes–sulfolane (with a water content of 20%), hexane–monoethanolamine, hexane–DMSO, and hexane–methyl alcohol or glycol (see the review [57]).

In [58] a binary polar solvent based on monoethanolamine and *tert*-allyl methyl ether in conjunction with a nonpolar hydrocarbon solvent was used for the extraction of indole from the 8-12% fraction.

Analysis of the data on the complexation of carbazole confirms that carbazole can be isolated from mixtures with anthracene (and phenanthrene) by liquid extraction methods with two solvents or by extractive crystallization.

A method is known for the extraction of an anthracene–carbazole mixture at 100°C in the white spirit–N,N-dimethylacetamide system containing 15-20% of water [59]. As a result 88% pure carbazole was obtained with a yield of 96%. Another method by the same authors [60] was based on the use of white spirit in conjunction with N-methylpyrrolidone, containing 10-15 vol.% of water. It was proposed to use these solvents with technical carbazole and white spirit in a weight ratio of 1:7-9 and N-methylpyrrolidone and technical carbazole in white spirit in a ratio of 3:1. Carbazole was obtained with a purity of up to 98% with allowance for subsequent recrystallization (yield 98.3%). The same authors [61] proposed an improved method, also based on the use of N,N-dimethylacetamide (containing 15-20% of water); 98% pure carbazole was obtained with ≥98% extraction allowing for recrystallization.

An extraction method is known for the separation of mixtures of carbazole with anthracene using other mixed solvents: DMSO–ε-caprolactam and N-methylpyrrolidone–ε-caprolactam–water. The extraction was again combined with recrystallization [62, 63]. The interaction of carbazole and anthracene with a series of selective solvents was examined in [64]. Another paper by these authors [65] demonstrated the fundamental possibility of separating mixtures of carbazole and anthracene by extractive crystallization with 1,3-dimethyl-2-imidazolidone, which in the opinion of the authors is more effective than N-methylpyrrolidone.

The presented examples demonstrate the practical possibility of using data on complexation in solutions to seek and choose selective solvents for the extraction of valuable heterocyclic raw material from industrial fractions.

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