UDC 543.45 + 547.7

FORMATION OF CHARGE-TRANSFER COMPLEXES IN SYSTEMS CONTAINING SUBSTITUTED AROMATIC HYDROCARBONS AND ELECTRON-DONATING ORGANIC COMPOUNDS

IV. Refractometric Studies of Binary Systems Containing Furan, Thiophene, Pyridine, Tetrahydrofuran, and Piperidine and Certain Monosubstituted Benzene Derivatives*

M. G. Voronkov, A. Ya. Deich, and E. V. Akatova

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 2, No. 1, pp. 8-13, 1966

Binary systems of monosubstituted benzene derivatives of type C_6H_5X (X = CN, NO_2, COMe, F, Cl, Br, I) and furan, pyrrole, thiophene, pyridine, tetrahydrofuran, and piperidine are analyzed physicochemically by a refractometric method.

From deviations from additivity of n(V) isotherms for systems containing furan plus C_6H_5CN, $C_6H_5NO_2$, or C_6H_5COMe, conclusions can be drawn about interactions of components leading to formation of charge-transfer complexes (CTC) of 2:1 composition.

With pyrrole possible intermolecular interaction must be confirmed by other methods of physicochemical analysis.

Almost all of the systems containing tetrahydrofuran investigated, differ by showing more marked interaction between the components, giving CTC of 1:1 composition.

n(V) isotherms for systems containing pyridine and $C_6H_5NO_2$ are slightly concave to the composition axis.

At the same time piperidine clearly reacts with C_6H_5CN and $C_6H_5NO_2$, giving a 2:1 complex with the former, and a colored mixture with the latter, (formation of a complex in this case requires confirmation by other methods).

All the thiophene binary systems investigated are characterized by linear refractive index isotherms, i.e., they are refractometrically ideal.

The electron-donor properties of the heterocyclic compounds investigated vis a vis the aromatic ring with a lowered π-electron density lie in the order tetrahydrofuran > furan > piperidine > pyrrole > thiophene.

We previously showed [1-7] that in solution charge-transfer molecular complexes (CTC) are formed between highly polar monosubstituted benzene of the type C_6H_5X (where X is an electron-withdrawing substituent) and electron-donating organic compounds containing a hetero atom with a lone pair of electrons (O, N, Cl, etc).

In such complexes the C_6H_5X molecule, where the electron density in the aromatic ring is decreased by substituent X, acts as an electron acceptor (Lewis acid).

It was of interest to study the possibility of formation of such complexes due to manifestation of electron-donor properties by a hetero atom of the simplest heterocyclic rings (furan, pyrrole, thiophene, pyridine, tetrahydrofuran, pyridine). It is of interest if only because, for example, it has not been fully demonstrated that furan can behave as a Lewis base [8].

Investigation of electron-donor properties of furan, pyrrole, thiophene, pyridine, tetrahydrofuran and piperidine towards the aromatic ring can be based on physicochemical study of binary systems containing monosubstituted benzene derivatives C_6H_5X. In the latter, the ring has varying electron affinity depending on the nature of the substituent X. The systems studied included compounds of the C_6H_5X type in which the substituents are of type I and II (X = CN, NO_2, COMe, F, Cl, Br, I).

The methods of purifying the substances, the preparation of the mixtures, making the measurements, and the calculations were similar to those previously described [9].

The experimental results (Tables 1 and 2) show that all the aromatic compounds investigated form mixtures with thiophene, whose isotherms n(V) are linear in nature. Most of the heterocyclic compounds investigated give compounds of the same type with monosubstituents of benzene containing a type I (F, Cl, Br, I) substituent. Tetrahydrofuran, forming 1:1 complexes with C_6H_5Br and C_6H_5I, is an exception (formation of CTC with this composition in systems containing C_6H_5F and C_6H_5Cl stands in need of confirmation by other methods), and so is the C_6H_5F-pyrrole system, whose refractive index isotherm is slightly convex to the composition axis ($\Delta n(V) \cdot 10^4 = 23$).

Table 1 gives systems which are almost ideal refractometrically. The coefficients a and b of the interpolation formula $n_D^{20} = a + bV^{20}$ enable the refractive index of any particular system to be calculated.

---

*For Part III see [6].

Table 1

Values of the Coefficients a and b in the Interpolation Formula $n_D^{20} = a + bV^{20}$, Calculated by the Method of Least Squares from the Found Values of n_D^{20} and V^{20}, Compared with Values of $(n_1 - n_2)$ from the Equation $n_a = n_2\ (n_1 - n_2)\ V$ for Binary Systems Containing C_6H_5X and Furan, Pyrrole, Thiophene, or Piperidine, n(V) Isotherms Linear.

Heterocyclic compound (μ, D)		X (μ, D)		a	n_1	$(n_1-n_2) \cdot 10^2$	$b \cdot 10^2$	Mean slope from the linear relationship $(n_{exp}-n_a) \cdot 10^4$
Furan	(0.67)	F	(1.48)	1.4650	1.4214	−4.36	−4.30	±3
"		Cl	(1.58)	1.5237	1.4214	−10.23	−10.20	±3
"		Br	(1.56)	1.5601	1.4214	−13.87	−13.80	±4
"		I	(1.38)	1.6191	1.4214	−19.77	−19.80	±2
Pyrrole	(1.87)	Cl		1.5237	1.5088	−1.49	−1.50	±1
"		Br		1.5601	1.5088	−5.13	−5.13	±2
"		I		1.6191	1.5088	−11.03	−10.99	±2
Thiophene	(0.4)	CN	(4.02)	1.5290	1.5287	−0.03	−0.03	±1
"		NO_2	(4.00)	1.5526	1.5287	−2.39	−2.39	±4
"		$COCH_3$	(2.07)	1.5335	1.5287	−0.48	−0.52	±3
"		F		1.4650	1.5287	+6.37	+6.30	±2
"		Cl		1.5237	1.5287	+0.50	+0.40	±1
"		Br		1.5601	1.5287	−3.14	−3.20	±3
"		I		1.6191	1.5287	−9.04	−9.10	±3
Piperidine	(1.17)	NO_2*		1.5526	1.4530	−9.96	−9.96	±2
"		Cl		1.5240	1.4530	−7.10	−7.10	±3

---

*System colored.

Table 2 gives results obtained by investigating systems with nonlinear n(V) isotherms. They indicate that interaction of the components, with formation of complexes of composition 2:1 and 1:1 is found refractometrically $(\Delta n(V) \cdot 10^4 \geq 0.004)$ mainly in systems containing tetrahydrofuran and furan, partly in those containing piperidine, along with monosubstituted benzene derivatives C_6H_5X containing a type II substituent (CN, NO_2, COMe).

Systems containing pyrrole and C_6H_5CN, $C_6H_5NO_2$, or C_6H_5COMe have $\Delta n(V) \cdot 10^4 = 17$-$29$, so that it is not possible to speak with certainty of complex formation in them. However, coloring of the pyrrole-nitrobenzene system indicates that this may occur, giving reason to think that it may occur too in the other pyrrole systems. Also in favor of this hypothesis is the fact that pyrrole systems show the maximum deviation of refractive index from additivity at a definite mole ratio of components (1:1). As the assumed complexes must be quite labile, and exist in minute concentrations, other methods of physicochemical analysis must be used to uncover them.

In the systems containing pyridine and C_6H_5CN or $C_6H_5NO_2$, the n(V) isotherms are concave to the composition axis $(\Delta n(V) \cdot 10^4 = -0.001$ to $-0.0015)$. The possibility of complex formation taking place in them requires further study using other physicochemical methods of analysis.

According to the refractometric data, the indicated intensity of interaction between components in systems containing monosubstituted benzenes C_6H_5X (X being meta-orientating), as a function of the nature of the heterocyclic compound, forms a series tetrahydrofuran > furan > piperidine > pyrrole > pyridine > thiophene. It is of interest that the order of this series depends but little on the nature of the substituent X or on the dipole moment of the molecule C_6H_5X (Table 2). This is evidence in favor of the view that the interaction between components in the systems investigated is not dipole interaction.

Comparison of deviation of $\Delta n(V)$ as a function of the type of substituent X, shows that the n(V) isotherms depart more considerably from linearity in the case of systems containing monosubstituted benzene derivatives C_6H_5X when X is meta-orientating. This is evidence in favor of the correctness of the view that the aromatic ring functions as an electron acceptor.

Comparison of $\Delta n(V)$ for like binary systems containing monosubstituted benzene derivatives and furan of tetrahydrofuran (Table 2) simply indicates the inconsiderably large tendency of the latter to complex formation despite its considerably greater basicity. For systems of these two oxygen-containing heterocyclic compounds with $C_6H_5NO_2$ and C_6H_5COMe, the $\Delta n(V)$ values occupy about the same position in the series, and a considerably greater interaction for tetrahydrofuran is observed only in systems containing benzonitrile. Evidently this can be connected with the delocalization of the lone electron pair of the oxygen atom in the furan ring due to p_π-p_π-interaction with the double bonds of the heterocyclic ring, leading to lowering of the ionization potential of the molecule (for example the ionization potential of the furan molecule is 10% lower than that of its saturated analog, tetrahydrofuran).

Judging by data for the departure of refractive index from additivity, with pyrrole, pyridine, and thiophene, delocalization of the hetero-atom lone electron pair does not result in appreciable increase in their tendency to complex formation. Still, in pyrrole-$C_6H_5NO_2$ systems the deviations of refractive index from additivity are greater than for a similar system containing nitrobenzene and a much stronger base, e.g. piperidine. However, the reverse obtains for corresponding systems containing benzonitrile.

The refractometric results make it possible to speak of the occurence of electron donor properties with respect to an aromatic ring with decreased π-electron density in the cases of furan, tetrahydrofuran, and piperidine, and of their evident absence with thiophene.

As will be shown in subsequent papers, this conclusion is supported by other methods of physicochemical analysis.

REFERENCES

1. M. G. Voronkov and A. Ya. Deich, Izv. An LatvSSR, ser. khim., 499, 1963.
2. M. G. Voronkov and A. Ya. Deich, ZhSKh, 5, 482, 1964.
3. M. G. Voronkov and A. Ya. Deich, Izv. AN LatvSSR, ser. khim., 145, 1964.
4. M. G. Voronkov and A. Ya. Deich, Izv. AN LatvSSR, ser. khim., 52, 1965.
5. M. G. Voronkov and A. Ya. Deich, Izv. AN LatvSSR, ser. khim., 432, 1965.
6. M. G. Voronkov and A. Ya. Deich, Izv. AN LatvSSR, ser. khim., no. 6, 1965.
7. A. Ya. Deich and M. G. Voronkov, Trudy RIIGA, 48, 3, 1964.
8. Z. N. Nazarova and V. N. Novikov, ZhOKh, 34, 767, 1964.
9. M. G. Voronkov and A. Ya. Deich, Izv. AN LatvSSR, ser. khim., 417, 1964.

11 November 1964

Institute of Organic Synthesis AS Latvian SSR, Riga