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INVESTIGATION OF THE REACTION OF QUINOLINE WITH BROMINE IN NITROBENZENE

E. Ya. Gorenbein, N. O. Labkovskaya, and I. L. Abarbarchuk

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The reaction of quinoline with bromine in nitrobenzene solvent is investigated using the properties of isomolar series. These properties, viscosity, conductivity, density, depression of the freezing point, are determined using a constant molar concentration of $C_9H_7N + Br_2$, 0.05 per mole of $C_6H_5NO_2$. It is shown that the nitrobenzene solution of quinoline forms with bromine a complex with the composition $C_9H_7N \cdot Br_2$. The molecular conductivity of this complex in nitrobenzene solvent increases with dilution.

According to the literature, bromine and quinoline form crystalline compounds of the compositions $C_9H_7N \cdot Br_2$ [1] and $C_9H_7N \cdot 2Br_2$ [2]. It was shown in paper [3] that bromine solutions of quinoline conduct an electric current rather well, but the system is unstable, and the conductivity decreases with time. Evidently the appearance of conductivity on mixing the two nonelectrolytes Br_2 and C_9H_7N is due to formation in solution of a current-conducting complex of undetermined composition.

Table 1

Viscosity (η), Density (d), Specific Electrical Conductivity (k) and Freezing Point Depression (Δt) of the System C_9H_7N-Br_2-$C_6H_5NO_2$ for Isomolar Concentrations of $C_9H_7N + Br_2$ of 0.05, per 1 Mole $C_6H_5NO_2$, Temperature 18° C

Quinoline mole %	d_4	$\eta \times 10^2$ poises	$k \times 10^4$ $ohm^{-1} \cdot cm^{-1}$	$\Delta t°$
0.0	1.2380	2.020	0	2.78*
12.20	1.2372	2.120	3.84	2.44
27.37	1.2360	2.226	5.51	2.08
35.75	1.2350	2.325	6.32	1.90
43.29	1.2344	2.345	6.46	—
52.32	1.2270	2.350	6.89	1.56
65.28	1.2189	2.333	5.91	1.88
79.01	1.2111	2.261	4.00	2.20
100	1.1980	2.210	0	2.78*

*Theoretical calculated values.

Table 2

Specific (k) and Molar (μ) Electrical Conductivities of $C_9H_7N \cdot Br_2$ Solutions in Nitrobenzene at 18° C

Concentration $C_9H_7N \cdot Br_2$, %	$k \times 10^4$ $ohm^{-1} \cdot cm^{-1}$	φ	μ	Concentration $C_9H_7N \cdot Br_2$, %	$k \times 10^4$ $ohm^{-1} \cdot cm^{-1}$	φ	μ
0.65	0.895	36850	3.30	4.49	4.59	5330	2.44
1.24	1.47	19200	2.82	6.03	6.31	3860	2.43
1.91	2.25	12400	2.79	9.34	8.70	2485	2.16
2.55	3.11	9165	2.85	29.16	28.15	744	2.09
3.18	3.53	7580	2.63	34.37	31.42	623	1.96
3.81	4.01	6200	2.48	—	—	—	—

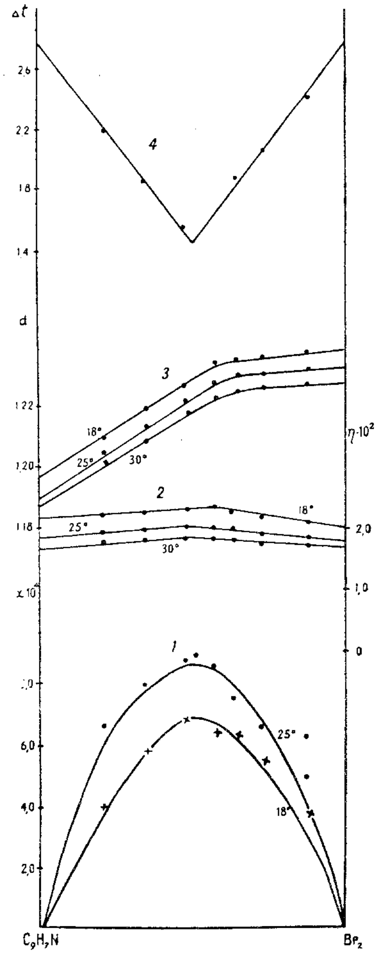
According to our investigations, pyridine and bromine in nitrobenzene solvent form a complex of composition $C_5H_5N \cdot 2Br_2$ [4]. Naturally for comparison it was of interest to study the reaction of quinoline with bromine in the same solvent. This study is further important because the conductivities of bromine solutions of quinoline and pyridine are not inferior to the conductivities of aqueous solutions of some typical electrolytes, though the dielectric constant of bromine is 3.18, while that of water is 80. In this connection, a study has now been made of the reaction of quinoline with bromine in nitrobenzene solvent, using the properties of isomolar series: conductivity, viscosity, density, and depression of the freezing point of solutions for a constant molecular concentration of $C_9H_7N + Br_2$ per 1 mole of nitrobenzene, viz. 0.05.

The nitrobenzene was purified as described in [5], and dried over P_2O_5. Material which distilled at constant temperature was stored in sealed ampuls. Quinoline was dried over potassium hydroxide, distilled, and stored in the same way as the nitrobenzene. Bromine was purified as described in [6], dried over P_2O_5, and distilled over BaO and $CaBr_2$. It was collected in drawn-out test tubes which were sealed immediately they were full.

The solutions were prepared as in [4]. It is characteristic that on passing from the concentration of bromine being higher to the quinoline concentration being greater, the color changed from orange to straw yellow. Viscosity and density were determined as described in [7], while conductivity was measured as in [8].

The measurements were made at three temperatures, 18° C, 25° C, and 30° C. The electrical conductivity changes with time, especially with increase in temperature, e.g., at quinoline concentration 52.32 mole % and bromine 47.68%, at 30° C, after an hour the electrical conductivity changed from 8.6×10^{-4} to 9.8×10^{-4}, after 20 hr it reached 10.7×10^{-4} $ohm^{-1} \cdot cm^{-1}$. The electrical conductivity was investigated only at 18° C and 25° C. As bromine reacts with platinum black, the measurements were made in an Arrhenius cell with unplatinized platinum electrodes.

The cryoscopic measurements were made with a Beckmann apparatus using the same isomolar concentrations. The solution was stirred with a platinum stirrer [4]. The results of the measurements are shown graphically, and given in Table 1 for one of the temperatures.



Relationship between (1) specific electrical conductivity, (2) viscosity, (3) density, (4) freezing point depression and the ratio of the components C_9H_7N and Br_2 in the system C_9H_7N-Br_2-$C_6H_5NO_2$.

Plots 1 and 4 (figure) show that maximum conductivity and minimum freezing point depression for the solutions occur at the same ratio of components in the system. The slight viscosity maximum (plot 2) and bend on the density plots (3) correspond to about the same ratio of components. These results confirm that using nitrobenzene as a solvent, bromine and quinoline give a complex of composition $C_9H_7N \cdot Br_2$. It is characteristic that quinoline and ICl also form an equimolecular complex [9]. In the same solvent pyridine and bromine give a complex $C_5H_5N \cdot 2Br_2$ [4].

To determine the effect of dilution on the molar electrical conductivity of the complex established in benzene, the way in which that property varied with dilution at 18° C was investigated.

First, some nitrobenzene was poured into the Arrhenius cell, bromine was added, followed by an amount of quinoline calculated to correspond to a complex composition of $C_9H_7N \cdot Br_2$. The substances were weighed out. After making the first conductivity measurement, a definite amount of nitrobenzene was added, and another measurement made, 3-4 dilutions being used in all. Then another solution was made up using a different concentration of complex, and measurements made as before, at a number of dilutions, and so on. It must be mentioned that the electrical conductivity is somewhat time-dependent, causing the points on the plot to be scattered. The data obtained are shown in Table 2.

To calculate molar conductivities, densities of some solutions of different concentrations were measured at 18° C:

$C_9H_7N \cdot Br_2$, %	0.65	1.24	2.55	3.81	6.03	9.34	29.16	34.37
d_4	1.2075	1.2107	1.2167	1.2278	1.2415	1.2519	1.3340	1.3580

A graph was plotted from these results, and densities required for the calculations obtained from it by interpolation.

The results in Table 2 show that the specific electrical conductivity increases with increase in concentration of $C_9H_7N \cdot Br_2$, while the molar electrical conductivity increases with increased dilution, i.e., for the particular concentration region the ordinary relationship between molar electrical conductivity and dilution is found.

The plots for the systems studied do not show special points corresponding to Lyubavin and Crimaux's complexes. Apparently such complexes do not exist in dilute nitrobenzene solutions of quinoline plus bromine.

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Ukrainian Agricultural Academy, Kiev