

**The study of relaxational processes thermodynamic parameters by light scattering method
in some organic compounds of aromatic row and its solutions.**

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It is known that dipole relaxation process of molecules represents the orientational shakes about some temporary equilibrium states and next quick uneven reorientations which are able to accompanied by transference of molecules in new equilibrium state and by the molecules changes in positions and in number of surrounding. Reorientation of molecules has the character of activated jumps over potential barrier. Therefore by consideration processes of dielectric relaxation one can profit by the notions of absolute reaction rates theory [1,2]. According to this theory the change of activation free energy ΔF_τ at transition of molecules to activated state may be connected with dielectric relaxation time τ_d by following expression

$$\tau_d = (h/kT) \exp(\Delta F_\tau/RT) \quad (1)$$

taking into consideration the connection between dipole and anisotropy τ relaxation times [3] the formula (1) may be rewritten as:

$$\tau_d = (h/3kT) \exp(\Delta F_\tau/RT) \quad (2)$$

where K is Boltzman's constant, h is Planc's constant, T - temperature, R - universal gas constant. It is known that the change of free activation energy ΔF_τ was connected with change of activation enthalpy ΔH_τ and change of activation entropy ΔS_τ :

$$\Delta F_\tau = \Delta H_\tau + \Delta S_\tau \quad (3)$$

as follow from these expressions defining experimental anisotropy relaxation time τ one can determine of ΔF_τ , ΔH_τ and ΔS_τ values. The methods of such determinations was described in work [4].

In our experiments as excited light source was He-Ne laser and recorder device was diffrational photoelectric spectrometer. For determination of ΔF_τ , ΔH_τ and ΔS_τ we used the experimental determined values of τ , listed in work [5]. Obtained results of ΔF_τ , ΔH_τ , ΔS_τ for studied liquids were displayed in Table 1.

Substance	$\Delta F_{\tau}, KJ _{moll}$			$\Delta H_{\tau}, KJ _{moll}$
	293K	373K	473K	
Benzene	13,06	13,20	14,3	8,78
Toluene	13,40	13,70	14,7	6,10
Chlorobenzene	13,04	14,53	16,00	7,60
Brombenzene	14,00	14,53	16,46	6,30
Iodinebenzene	10,71	11,32	14,22	7,90
Fluorobenzene	10,70	11,34	14,28	5,25

From this Table one can see that with increase the temperature ΔF_{τ} for all liquids is slightly increased. Knowing the dependence $\lg(\tau \cdot T)$ from $\frac{1}{T}$ one can define ΔH_{τ} . In conformity with work [6], we find this dependence has straight – forward shape. Obtained results for ΔH_{τ} displayed on last column Table 1.

Values of ΔS_{τ} determined according to equation (3) are displayed on table 2.

Substance	$\Delta S_{\tau}, KJ _{moll}$		
	293K	373K	473K
Benzene	-20	-21	-22
Toluene	-27	-22	-23
Chlorobenzene	-22	-24	-25
Brombenzene	-26	-29	-
Iodinebenzene	-19	-20	-21
Fluorobenzene	-20	-21	-22

One can see from Table 2 that value of ΔS_{τ} for aggregated by hydrogen bond liquids (benzyl alcohol, phenol) is less than those for nonaggregated liquids. This indicate that actived state of nonaggregated liquids more ordered than those of aggregated liquids, and negative values of ΔS_{τ} for studied liquids indicate that the actived states always more ordered than normal state of liquids.

The change of activation free energy – may be defined also from viscous flow process from formula

$$\eta = (\eta^{N/V}) \exp(\frac{\Delta F_{\eta}}{RT}) \quad (4)$$

For determinational – we used with references data for ΔF_{η} , which is listed in work [7]. Values of η calculated by

$$\Delta F_{\eta} = \Delta H_{\eta} + \Delta S_{\eta} \quad (5)$$

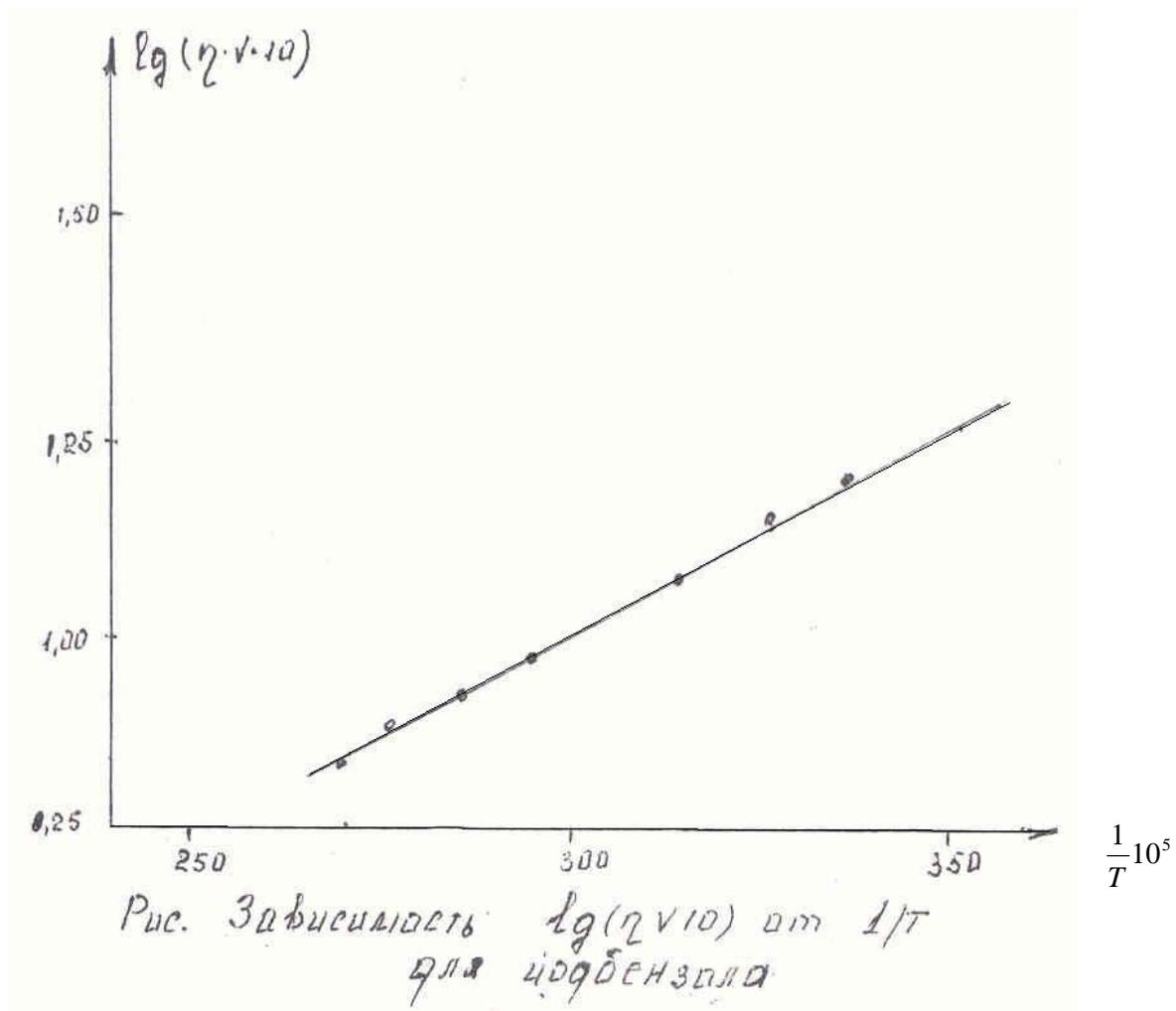


Fig 1.

our results indicate that the dependence $\lg(\eta \cdot V)$ from $\frac{1}{T}$ for studied substances is straight line.

Such dependence for iodine benzene is displayed on Fig 1.

Therefore in according with formula (4), the change viscous flow activation enthalpy we defined by formula

$$\Delta H_{\eta} = \frac{[\lg(\eta_1 V_1) - \lg(\eta_2 V_2)] \cdot R}{(\frac{1}{T_1} - \frac{1}{T_2}) \lg e} \quad (6)$$

obtained results for ΔF_{η} , ΔH_{η} and ΔS_{η} are displayed on Table 3.

Substance	$\Delta F_{\eta}, KJ _{moll}$			$\Delta H_{\eta}, KJ _{moll}$
	293K	373K	473K	
Benzene	13,06	13,20	14,28	8,8
Toluene	12,39	13,69	14,5	6,1
Chlorobenzene	13,10	14,53	16,00	7,60
Brombenzene	14,00	15,7	16,04	7,9
Iodinebenzene	15,37	16,72	17,6	9,3
Fluorobenzene	12,3	14,15	15,12	7,7

From Table 3 one can see that for all studied liquids $\Delta F_{\eta} > \Delta F_{\tau}$ and ΔF_{η} under increasing of temperature is slightly increased also. Results for ΔS_{η} are displayed on table 4.

Substance	$\Delta S_{\eta}, J _{moll \cdot K}$		
	293K	373K	473K
Benzene	-14	-11	-11
Toluene	-21	-21	-
Chlorobenzene	-18	-18	-19
Brombenzene	-16	-21	-
Iodinebenzene	-18	-22	-20
Fluorobenzene	-17	-19	-18

In viscous flow process as show the results for ΔS_{η} (see Table 4), the activated state of studied substances are more ordered also than its normal state.

The results of determination ΔF_{τ} at T =293K in different solutions for some studied liquid are displayed in Table 5 (volume concentration 15%).

Table 5.

Substance	$\Delta F_{\tau}, KJ _{moll}$			
	Pure substance	acetone	gexsane	geptane
Benzene	10,37	9,45	10,8	-
Hylbenzene	10,88	9,66	10,5	10,92
Iodinebenzene	12,85	10,5	10,92	12,05
Petrol spirit	13,48	12,18	12,6	-
Phenoll	13,65	11,17	12,6	12,6

In case of solutions ΔF_τ slightly depends from nature of solvent. Calculations show that for solutions the values of ΔS_τ have negative values also. For solutions of toluene and ethylbenzene the value of ΔS_τ for pure liquid is less than those solutions for some mono substituted derivatives of benzene [8].

Conclusion:

1. ΔF_τ is increased with increase of molecular volume and weight.
2. In spite of a proximity of molecule volume and weight of benzene to those for phenol ΔF_τ for phenol is more than for benzene.
3. For all studied liquids $\Delta F_\tau > \Delta H_\tau$ and with increasing of temperature slightly ΔF_τ grows and ΔS_τ has negative value.
4. ΔH_τ is for less for benzene than for other substances. The most values ΔH_τ correspond aggregated by hydrogen bond liquids (aniline, phenol, benzene, alcohol)
5. The experiments indicate that ΔH_τ depends from temperature dependence of τ . The quickly is increased ΔS_τ with temperature, the more is value ΔH_τ .
6. For solutions of weak viscous substances the value of ΔS_τ for pure liquid is less than those for solutions.

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