

Citation:

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Chemistry. — “*Investigations on the Temperature-Coefficients of the free Molecular Surface-Energy of Liquids between -80° and 1650° C.*” **XII.** *The Surface-Energy of the Isotropic and Anisotropic Liquid Phases of some Aromatic Azoxy-Compounds and of Anisaldazine.* By Prof. F. M. JÄGGER and Dr. JUL. KAHN.

§ 1. With the purpose of elucidating better the significance of the temperature-coefficients of the free molecular surface-energy μ of liquids as a criterion for the degree to which these liquids are associated, we have now extended our measurements to some of these compounds which show more than one liquid phase and of which all, with the exception of the last, are optically anisotropic.

There can hardly be a doubt any longer that these anisotropic liquids should be considered really as quite *homogeneous* liquid phases of very peculiar molecular structure, while the mutual relations of these anisotropic phases to the isotropic phase on the one side and to the solid phase on the other, are quite analogous to those commonly observed in the cases of polymorphism.

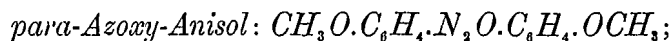
The successive anisotropic liquids, which reveal themselves in the case of some of these substances and which in the case of *enantiotropic* transformations can exist within a proper, sharply limited temperature-range, may be distinguished according to the explanation given by the most probable hypothesis yet suggested, by a motion of the molecules in “swarms”, which decrease in complexity after each higher transformation-temperature has been passed; these molecules themselves probably have moreover an atomistic structure, causing a general shape which is in one direction of space considerably more elongated than in the two directions perpendicular to the first.

By this hypothesis it thus becomes highly probable, that the *isotropic* liquid, which always appears at the *highest* transition-point, will possess a much less complex structure than the foregoing anisotropic liquids, — a supposition which will be found to agree entirely with our usual ideas about the progress of a dissociation occurring with increase of temperature.

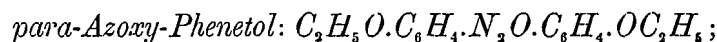
If the hypothesis accepted till now was right, that a smaller value of $\frac{\partial \mu}{\partial t}$ than the normal of **2,2** erg stated by Eotvós, indicates an association, but that a larger value than **2,2** Erg pro degree points to a dissociation of the liquid, — we may expect here that the

mean value of the coefficient $\frac{\partial \mu}{\partial t}$ at temperatures *below* the transition-point of the anisotropic liquid will appear to be *smaller* than that of the isotropic liquid *above* the transformationpoint. The following measurements were made to verify this conclusion by means of experiments.

§ 2. The substances investigated here are in the first place the following compounds often studied already, which have been purified here with the utmost care:

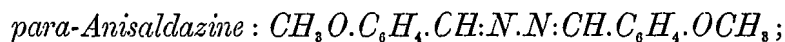


$$t_1 = 114^\circ C. \text{ and } t_2 = 138^\circ C.$$



$$t_1 = 138^\circ C \text{ and } t_2 = 168^\circ C.$$

and



$$t_1 = 169^\circ C \text{ and } t_2 = 180^\circ C.$$

The last mentioned substance was prepared from p-anisaldehyde and hydrazine-sulphate; it was purified by repeated crystallisation from boiling benzene.

Furthermore we choose: *Ethyl-para-Azoxybenzoate*: $C_2H_5O.CO.C_6H_4.N_2O.C_6H_4.CO.OC_2H_5$, which was purified by recrystallisation from a mixture of chloroform and benzene. The beautifully crystallized compound shows the transition-temperatures: $t_1 = 114^\circ C.$ and $t_2 = 121^\circ C.$ Finally we prepared, for other purposes also, a quantity of *Ethyl-para-Ethoxybenzalamino- α -Methylcinnamylate*: $C_2H_5O.C_6H_4.CH:N.C_6H_4.CH:\alpha(CH_3).CO.OC_2H_5$ for the transitiontemperatures we found: $t_1 = 95^\circ C.$ and $t_2 = 117,8^\circ C.$ which numbers do not agree with those given in the literature on this compound.

The purity of the three first-named substances is above all doubt; for the two last mentioned compounds the certainty is somewhat less, but it is very probable that the impurities possibly intermingled with them, are not of any considerable importance. Since the behaviour of the three first substances differs appreciably from that of the last two, the resp. μ - t -curves are placed in two different diagrams.

I.

para-Azoxy-Anisol: $C_3HO \cdot C_6H_4 \cdot N_2O \cdot C_6H_4 \cdot OCH_3$.					
Temperature in ° C.	Maximum Pressure H		Surface- tension λ in Erg pro cm ² .	Specific gravity d_{40}	Molecular Surface- energy ν in Erg pro cm ² .
	in mm. mer- cury of 0° C.	in Dynes			
115°	1.136	1515.2	40.1	1.171	1463.3
120	1.104	1472.3	39.0	1.166	1427.3
126	1.067	1422.8	37.7	1.159	1385.2
129.5	1.034	1378.5	36.4	1.156	1339.8
133.5	1.072	1429.1	37.8	1.152	1394.6
138.1	1.077	1435.8	37.9	1.142	1406.4
144.5	1.056	1407.7	37.2	1.136	1385.2
155.2	1.025	1366.0	36.0	1.126	1348.5
160.5	1.003	1338.8	35.5	1.124	1331.3
174.5	0.977	1302.0	34.2	1.112	1292.0
190	0.940	1253.2	33.0	1.100	1255.5
211	0.897	1195.7	31.4	1.080	1209.4

Molecular weight: **258.14.** Radius of the Capillary tube: 0.05425 cm.
Depth: 0.1 mm.

The compound was purified by repeated crystallisations. At 114° C. the solid phase begins to transform into an orange anisotropic liquid, which at 133.5 C. is almost, at 138° completely, clear and transparent.

The temperature-coefficient of ν is remarkably great for the anisotropic liquid: between 115° and 126° C. about 7.1 Erg per degree, between 126° and 133° even 12.2 Erg per degree. For the isotropic liquid however it decreases gradually from the transition-temperature from 3.45 Erg to 2.20 Erg at 190° C.

para-Azoxyphenetol: $C_2H_5O.C_6H_4N_2O.C_6H_4OC_2H_5$.					
Temperature in ° C.	Maximum Pressure H		Surface- tension α in Erg pro cm^2 .	Specific gravity d_{40}	Molecular Surface- energy μ in Erg pro cm^2 .
	in mm. mer- cury of 0° C.	in Dynes			
142.5	0.882	1198.0	31.6	1.094	1292.5
147.5	0.875	1165.9	30.7	1.089	1259.5
151.8	0.854	1138.5	30.0	1.084	1234.6
159	0.827	1102.2	29.0	1.076	1199.4
164	0.813	1085.0	28.3	1.072	1173.3
168.5	0.835	1113.2	29.3	1.068	1217.6
174.5	0.814	1087.4	28.6	1.053	1200.0
190	0.779	1038.5	27.3	1.039	1155.7
205	0.742	990.8	26.2	1.026	1118.5
219	0.722	962.6	25.2	1.014	1084.2

Molecular weight: 286.17. Radius of the Capillary tube: 0.05425 cm.
Depth: 0.1 mm.

This beautifully crystallised compound is transformed into an anisotropic liquid at 138° C., which becomes transparent at 168° C. With this compound thus once more the fact is proved that the temperature-coefficient of μ for the anisotropic liquid is abnormally high: it decreases gradually from 6.60 Erg. at 143° C. to 4.89 Erg. between 159° and 164°, and then increases suddenly under change of the algebraic sign, to 9.84 Erg. For the isotropic liquid it is nearly constant; its mean value is 2.6 Erg. per degree.

Molecular Surface-Energy
in Erg pro cm^2 .

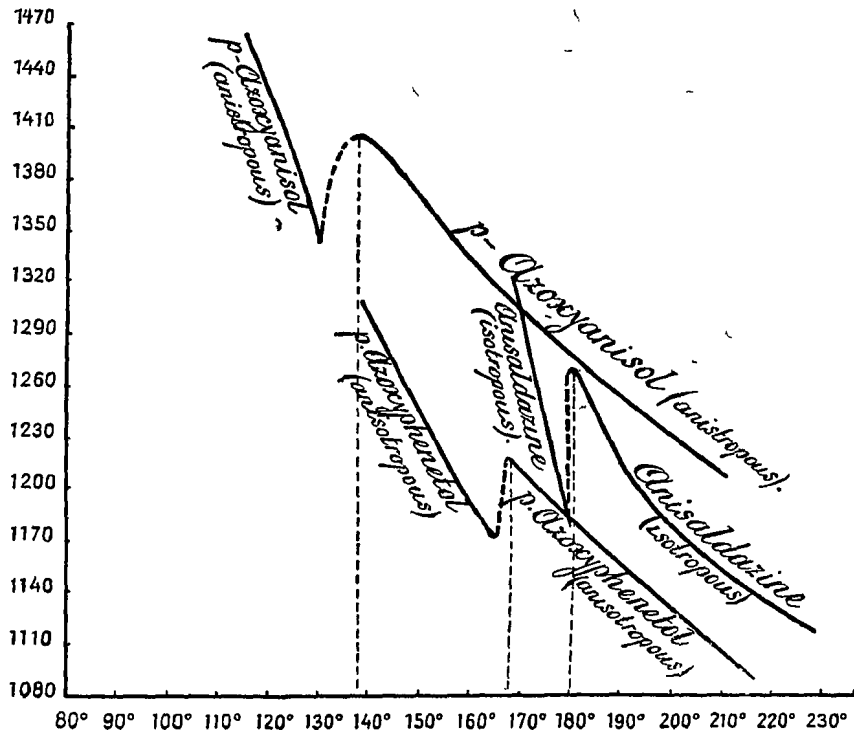


Fig. 1.

Temperature

Molecular Surface-Energy
 μ in Erg pro cm².

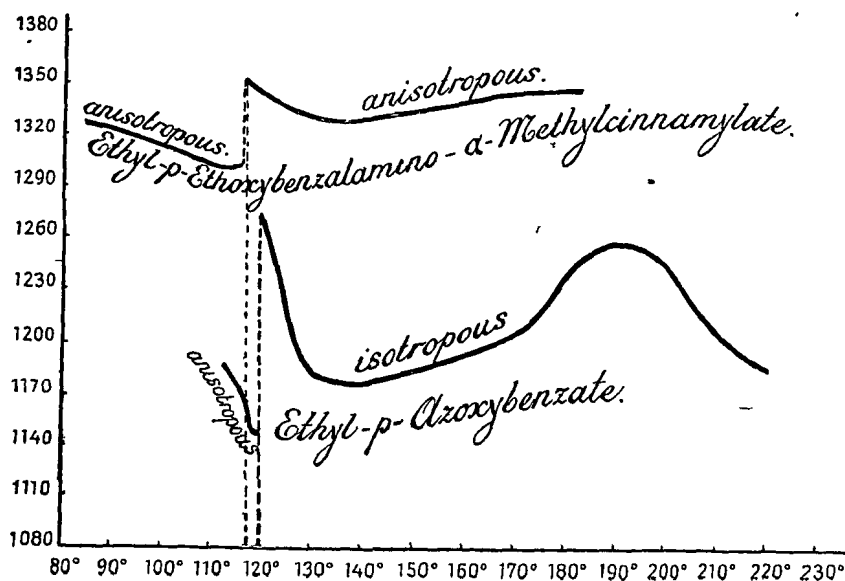


Fig. 2.

III.

Anisaldazine: $\text{CH}_3\text{O} \cdot \text{C}_6\text{H}_4\text{CH} : \text{N} : \text{N} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OCH}_3$.					
Temperature in ° C.	Maximum Pressure H		Surface- tension χ in Erg pro cm ² .	Specific gravity d_{40}	Molecular Surface- energy μ in Erg pro cm ² .
	in mm. mer- cury of 0° C.	in Dynes			
171°	0.932	1242.5	32.1	1.051	1291.2
173.5	0.911	1214.0	31.4	1.049	1264.7
174.5	0.902	1203.5	31.1	1.048	1253.4
176.5	0.886	1181.2	30.5	1.046	1230.8
178	0.865	1154.8	29.9	1.044	1208.0
179	0.845	1128.4	29.4	1.043	1188.7
180.5	0.908	1210.5	31.2	1.035	1267.9
185	0.886	1181.2	30.4	1.031	1238.6
195	0.851	1134.5	29.2	1.023	1195.9
204.5	0.822	1096.4	28.3	1.015	1165.1
219	0.800	1067.1	27.4	1.002	1137.8
230.5	0.789	1044.7	26.8	0.993	1119.6

Molecular weight: 268.14. Radius of the Capillary tube: 0.05301 cm.
 Depth: 0.1 mm.

The compound was prepared from anisaldehyde and hydrazinesulphate in cold-aqueous solution, and repeatedly crystallized from boiling benzene. The beautiful yellow crystals are at 169° C. transformed into an isotropous liquid, which at 180° C. gets clear and isotropous. The density of the isotropous liquid was: 1.0313 at 185° C.; at 205° C: 1.0150; at 225° C.: 0.9977. At t° C. in general: $d_{40} = 1.0355 - 0.0007775(t - 180) - 0.00000125(t - 180)^2$. For the anisotropous liquid the density at 173° C. was: 1.0486; at 180° C.: 1.0416; at t° C: $d_{40} = 1.0516 - 0.001(t - 170)$. In this case also the temperature-coefficient of μ is for the anisotropous liquid exceptionally great: between 171° and 176° about: 11.0 Erg, afterwards 15.2 and even 19.3 Erg per degree. For the isotropous liquid it rapidly decreases with rise of temperature: At the transitionpoint: 6.5 Erg, then 4.27; 3.25; and finally 1.88 and 1.53 Erg per degree.

IV.

Ethyl-para-Azoxybenzoate: $C_2H_5O.CO.C_6H_4.N_2O.C_6H_4.CO.OC_2H_5$.					
Temperature in ° C.	Maximum Pressure H		Surface- tension α in Erg pro cm^2 .	Specific gravity d_{40}	Molecular Surface- energy ν in Erg pro cm^2 .
	in mm. mer- cury of 0° C.	in Dynes			
114°	0.789	1052.6	27.0	1.176	1185.6
116	0.788	1049.4	26.9	1.174	1182.5
118	0.776	1034.6	26.5	1.172	1166.3
119	0.764	1018.3	26.1	1.170	1150.0
120	0.762	1014.3	26.0	1.168	1146.9
121	0.832	1109.2	28.5	1.148	1271.7
124	0.809	1079.0	27.7	1.145	1238.1
125	0.779	1038.4	26.7	1.144	1194.2
130	0.774	1030.3	26.5	1.141	1187.3
140	0.768	1023.9	26.2	1.135	1178.0
150	0.770	1027.1	26.3	1.128	1187.4
160	0.771	1030.0	26.3	1.121	1192.3
170	0.770	1027.1	26.3	1.114	1197.3
180	0.799	1065.2	27.3	1.108	1247.3
190	0.804	1072.2	27.5	1.102	1261.0
200	0.793	1057.2	27.1	1.096	1247.2
210	0.762	1011.0	26.1	1.090	1205.6
220	0.757	1005.1	25.7	1.084	1191.2
230	0.741	987.9	25.3	1.079	1176.5

Molecular weight: **342.18**. Radius of the Capillary tube: 0.05301 cm.
Depth: 0.1 mm.

The beautiful orange coloured crystals are at 114° C. transformed into the anisotropic liquid, which at 121° C. is changed into the clear, amorphous one. All measurements were repeated after crystallisations of the substance used in mixtures of chloroform and benzene; as the peculiarities were observed again every time, they must be considered as essential features of the substance.

In this case also the temperature-coefficient of ν is abnormally high: irregularly oscillating, but with a mean value of about 7.2 Erg. per degree. Then ν increases suddenly with rise of temperature, and afterwards falls rapidly and irregularly in the isotropous liquid; then it increases again slowly to a maximum at about 190° C., to decrease afterwards slowly, and reach a final gradient of about 1.45 Erg. per degree. Very complicated reactions seem indeed to take place in this liquid.

Ethyl-para-Ethoxybenzalamino- α -Methylcinnamate: $C_2H_5O \cdot C_6H_4 \cdot CH : N \cdot C_6H_4 \cdot CH : C(CH_3)C \cdot OOC_2H_5$.					
Temperature in $^{\circ}C$.	Maximum Pressure H		Surface- tension γ in Erg pro cm^2 .	Specific gravity d_{40}	Molecular Surface- energy μ in Erg pro cm^2 .
	in mm. mer- cury of $0^{\circ}C$.	in Dynes			
85 $^{\circ}$	0.843	1123.7	28.7	1.075	1324.7
94.5	0.837	1112.9	28.5	1.068	1321.2
99	0.831	1108.0	28.3	1.064	1315.2
105.5	0.829	1104.7	28.1	1.058	1310.9
111	0.822	1095.8	27.9	1.053	1305.7
115.3	0.819	1090.9	27.8	1.049	1304.3
117.6	0.843	1123.7	28.7	1.045	1350.0
123.7	0.831	1107.8	28.3	1.040	1335.4
130.5	0.828	1101.9	28.1	1.034	1331.1
139	0.825	1099.9	28.0	1.027	1332.4
149	0.822	1095.8	27.9	1.018	1335.4
159	0.819	1091.9	27.8	1.010	1337.6
168.5	0.818	1089.8	27.8	1.002	1344.8
179	0.816	1085.8	27.7	0.993	1348.0

Molecular weight: 337.11. Radius of the Capillary tube: 0.05265.
Depth: 0.1 mm.

The compound was prepared by the method described by W. KASTEN (Dissertation, HALLE, 1909 p. 41), and purified by repeated crystallisations. Contrary to the data given there, we found the transition-points to be: $95^{\circ}C$. into the anisotropic, greenish opalescent liquid, and $117^{\circ}.8C$. into the amorphous liquid. If every crystallisation-germ is excluded, the liquid can be undercooled to about 79° ; it remains then only slightly viscous, and has a yellow colour. In this case also the temperature-coefficient of the surface-energy is extremely small; nor does the break in the curve at the transition-temperature seem to be of any considerable magnitude.

The density at $95^{\circ}C$. was: 1.0673; at $115^{\circ}C$. 1.0491. For the anisotropic liquid the density may thus be calculated from $d_{40} = 1.0809 - 0.000905(t - 80)$.

For the isotropic liquid at 120° was found: 1.0428; at $140^{\circ}C$.: 1.0257; at $160^{\circ}C$.: 1.0086. In general at $t^{\circ}C$.: $d_{40} = 1.0599 - 0.000855(t - 100)$. (Only to be used for temperatures from 117° upwards).

With the exception of the sudden increase of μ in the neighbourhood of $117^{\circ}C$., the temperature-coefficient of μ is here exceptionally small; for the isotropic liquid moreover it *increases* gradually with rise of temperature, and with a gradient of about 0.33 Erg per degree. The entire behaviour is very strange and enigmatic.

§ 3. If now we review in the first instance the results obtained with the three first-mentioned compounds, it will immediately attract attention that the corresponding μ - t -curves have all a *completely analogous* shape: this shows *two* branches, of which the first has regard to the anisotropic, the second to the isotropic liquid

phase, and in all cases *without exception the first branch falls with increase of temperature more rapidly than the second*. The result is thus just opposite to what we should expect if we founded our opinion on the mentioned hypotheses about the molecular state of the two liquid phases; and with regard to the great probability of the correctness of these views, the fact observed may be considered as a rather strong argument *against* the opinion, that it is right to consider the smaller or greater values of $\frac{\partial \mu}{\partial t}$ as a somewhat sure criterion for the judgment of the degree of an occurring dissociation in the liquids.

It will be remarked further that the mutual position of the two branches of the curve always indicates *a sudden increase* of the value of μ at the transformation from the anisotropic-liquid into the isotropic-liquid condition. This discontinuity does not set in precisely at the transition-temperature: from the observations it seems rather probable, that it occurs in a *continuous* way, and already starts at temperatures below the transition-temperature.

In that case the two branches could perhaps be linked together in the way indicated in the diagrams by dotted lines (fig. 1).

Now although in the cases of both ethers *two* branches were also present in the μ - t -curves (fig. 2), and here too μ seems to increase suddenly at the transformation into the isotropic-liquid state, another remarkable peculiarity reveals itself here in so far, as the values of μ for the isotropic-liquid phase fall in the beginning with increase of temperature and then increase again to a flatter or steeper maximum in the curve. It can hardly be doubted that these phenomena are *real* ones; in these isotropic liquids we were therefore forced to see the first instances of liquids, whose free surface-energy increases with a rise of temperature. The explanation of such an abnormal phenomenon must be found in the algebraic sign of the heat-effect which accompanies the eventually isothermical enlargement of the surface-layer of the liquid. What peculiarities of the molecular structure of these isotropic liquids could be the cause of such abnormal heat-effect, is for the moment incomprehensible and very difficult to imagine. In any case the said phenomena indicate the presence of molecular conditions in these liquids, differing of course very much from those, which are intrinsic for most of the common isotropic liquids.

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