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Study of the Structure of the Surface of a Liquid by the Method of Reflection of Light

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Measurements were carried out on the elliptical polarization of light reflected from the surface of a liquid with incidence at Brewster's angle, for 60 liquids. The dependence of the effect on temperature was studied and its relation to the characteristics of a near-oriented arrangement is shown. A modification in the structure of the surface in the neighborhood of the freezing point was revealed, also a connection of this phenomenon with supercooling.

THE works[1-4] have demonstrated the possibility of studying the surface structure of a liquid by means of the effect which arises upon reflection of light by this surface--elliptical polarization of the reflected beam when the incident beam is linearly polarized. The results obtained are of great interest for the theory of a liquid; however, for their complete theoretical interpretation, an increase is necessary of the experimental material which is entirely insufficient up to now. In the present work, the results of investigations carried out along this line are reported.

1. THE EXPOSED SURFACE OF A NONABSORBING LIQUID

A description of the method, apparatus and experimental procedure is given in reference 1.

The results of our measurements are presented in Tables I-IV; for comparison, some data from earlier works are included. The characteristics of the optical anisotropy are taken from references 5 and 6 without recalculation, and some improvements in the precision are made according to references 7 and 8.

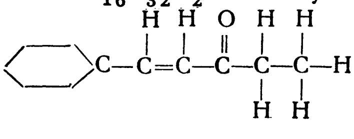
The measurements were performed at 15-18° C, unless another temperature is indicated. The values marked with the sign $\sim$ are given tentatively (see below). The limits of variation of the quantity (everywhere in the text the values given are for $\rho' = \rho \times 10^5$) are from 220 to 30; for the overwhelming majority of liquids, the values lie within narrower limits--from $\sim$ 180 to 80.

We made measurements of the coefficient of ellipticity ρ for 60 liquids; from earlier works data can be obtained for about another 30. On the basis of such material, it is already possible to look for relations of the effect with various parameters of the liquids investigated.

Let us consider Table I. Here there is a clearly expressed regularity--ρ increases with increase in the number of carbon atoms. The growth at the beginning of the series is very rapid, slowing down further along, and ρ tends to a definite limit. For the acids and the alcohols, this course is seen distinctly; for the ethers, the limit is apparently not yet completely attained. The limits for the acids and the alcohols are practically the same; the values of the limits for the ketones and the ethers are close.

The observed dependence does not permit one to relate ρ directly to the length of the molecular chain, which is known to increase linearly, nor with the anisotropy which is essentially different, for instance, for acids and alcohols. On analyzing the data for the various substituents (Tables II and III, likewise Table IV), one is forced to note that no direct correlation can be seen between ρ and the parameters that have been introduced; in particular, large ρ's do not at all tally with a large anisotropy.

Relations with the size and shape of molecules are apparently eliminated, for instance, for CCl_4, palmitic acid ($C_{16}H_{32}O_2$) and ethyl cinnamate



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[1] V. A. Kizel', J. Exper. Theoret. Phys. USSR 26, 228 (1954).

[2] C. Bouhet, Ann. de Phys. 15, 5 (1931).

[3] C. V. Raman and L. A. Ramdas, Phil. Mag. 3, 220 (1927).

[4] D. V. Sivukhin, J. Exper. Theoret. Phys. USSR 21, 76 (1951).

[5] J. Cabannes, *La Diffusion Moleculaire de la Lumiere*, Paris, 1929.

[6] Bhagavantam, *Scattering of Light*, Calcutta, 1940.

[7] H. Stuart, in Landolt-Bornstein's Phys. Chem Tab., 1951.

[8] M. F. Vuks, J. Exper. Theoret. Phys. USSR 24, 351 (1953); M. F. Vuks and I. I. Bilenko, J. Exper. Theoret. Phys. USSR 23, 105 (1952)

TABLE I

Homologous Series

Liquid	Coefficient of Ellipticity $\rho \times 10^5$	Optical Anisotropy $\delta^2 \times 10^3$		Surface Tension σ 18°	Thermal Coefficient of Free Energy k
		Vapor	Liquid		
	Hydrocarbons				
Pentane	70	11.0	3.1		
Hexane	~ 62	12.7	2.8		
n. Octane	92	12.5	2.2	27.2	
Isooctane	90	10.1	1.8		
	Alcohols				
Methyl	46	17.5	3.5	22.7	0.67
Ethyl	~ 95	7.6	2.6	22.6	0.94
n. Propyl	90	10.1	1.9	22.6	1.11
Isopropyl	99	11.0	1.1	21.0	1.05
n. Butyl	103	14.5	1.6	24.4	1.36
n. Amyl	102	11.0	1.5	25.7	1.35
Isoamyl	100	9.3	—	24.4	1.35
Octyl[2]	102	—	—	27.7	—
	Acids				
Formic	34	35.9	47.0	37.8	0.57
Acetic	91	24.1	25.1	28.0	1.3
Propionic[2]	96	23.2	20.1	26.7	1.53
Butyric	~ 90	17.1	16.5	27.1	1.63
Caproic	~ 108	—	—	—	—
Pelargonic[2]	102	—	—	—	—
Palmitic (110°)	~ 106	—	—	—	—
	Ketones				
Methylmethylketone[2]	81	14.3	11.3	23.3	1.57
Methylethylketone	130	28.8		24	1.89
Methylpropylketone	122	17.1		24.3	1.73
	Ethers				
Diethyl (0°)	108	22	3.7	19.2	1.9
Dibutyl	125			23.4	
Diisoamyl	140				

TABLE II

Substitutions for Methane and Ethane

Liquid	Substitute	Coefficient of Ellipticity $\rho \times 10^5$	Optical Anisotropy $\delta^2 \times 10^3$		Surface Tension σ_{18°	Thermal Coefficient of Free Energy k
			Vapor	Liquid		
Formic Acid	O, OH	34	35.9	47	37.8	0.57
Nitromethane	NO_2	35	—	—	37.7	1.14
Methyl Alcohol	OH	46	17.5	3.5	22.7	0.67
Carbon Tetrachloride . . .	Cl, Cl, Cl, Cl	107	0 – 1.7	1.6	26.3	1.95,
Chloroform	Cl, Cl, Cl	129	11.0	9.4	27.5	2.06
Bromoform	Br, Br, Br	130	25.0	9.5	51 (20°)	
Methyl Iodide	I	137				
Dibromomethane	Br, Br	200				
Diiodomethane	I, I	221				
Ethylene Glycol	OH, OH	79			46.0	1.04
Acetic Acid	O, OH	91	24.1	25.1	28.0	1.30
Ethyl Alcohol	OH	95	7.6	2.6	22.6	0.94
Ethyl Acetate	O, OC_2H_5	99	18.8	7.4	24.0	2.23
Tetrabromoethane	Br, Br, Br, Br	103			49.0	2.51
Ethyl Bromide	Br	123	19.7	13.9		
Ethyl Iodide	I	129			28.4	1.65
Dibromoethane	Br, Br	159	32.2	29.5	38.0	2.14
Dichloroethane	Cl, Cl	178	29.5	14 - 18	32.0	2.17
Ethylenediamine	NH_2, NH_2	180				

ρ's were obtained equal to 107, 102 and 114, respectively[2]. The influence of double bonds is likewise imperceptible. Thus, for propyl (C_3H_7OH) and allyl (C_3H_5OH) alcohol we have values for ρ' of 90 and 110, respectively[3]; the values for pentane and amylene, for oleic acid and the saturated acids are close. Evidently, there is no effect of the compactness of the molecular structure, as well.

With respect to the effect of various functional groups, one can make discrete observations; thus, for example, the substitution of H by CH_3 produces almost no change in ρ. Substitution of one halide by another usually changes ρ a little; apparently, introduction of NO_2 reduces ρ while NH_2 increases it; however, all of these observations are qualitative. There is also no connection with the magnitude of the dipole moment, as comparison has shown. No direct correlation between the values of ρ and of δ^2_{liq} can be recorded. One can say the same about the relation with the crystal structure of a given substance. Thus, for cyclohexanol, which crystallizes in the isotropic cubic system, and for water, which has an isotropic tetrahedral coordination of molecules, the values of ρ' are 132 and 40, respectively, while for paradichlorobenzene and napthalene, which are highly anisotropic in crystal form (monoclinic system), the values of ρ' are 105 and 110, respectively.

Theory indicates that the effect of ellipticity is determined not by the individual properties of the molecules and not by the properties of the liquid, as such, but by the fact of a difference of the surface layers from the deeper lying material, and the magnitude of the effect, schematically speaking, depends on the degree of the difference. If one proceeds from the concept of a surface (which is prevalent in the literature) as a layer (with a more or less well-ordered orientation) of molecules strictly on the surface of the liquid, with a coated layer of mobile, freely rotating adsorbed molecules of vapor (of the more recent works, cf. reference 9), then one can suppose that both of these layers contribute their share in the creation of the ellipticity. With such a model, the value of ρ must naturally depend on many parameters. For homologous series, where all the parameters vary regularly from one term to another, the value of ρ

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[9] A. Wyllie, Proc. Roy. Soc. (London) 197, 383 (1949).

TABLE III

Substitutions for Benzene

Liquid	Substitute	Coefficient of Ellipticity $\rho \times 10^5$	Optical Anisotropy $\delta^2 \times 10^3$		Surface Tension σ_{18°	Thermal Coefficient of Free Energy k	Total Surface Energy U *
			Vapor	Liquid			
Benzene		135	37.5	18.0	29.1	2.73	70.26
Phenol (100°)	OH	~ 80	30.4	18.5	36.5	1.70	
Benzaldehyde	CHO	87			38.8	2.17	
Para-Dichlorobenzene (100°)	Cl, Cl	~ 90	67.8		-----	-----	71.45
Para-Dibromobenzene (120°)	Br, Br	~ 92		55.8	-----	-----	-----
Nitrobenzene	NO_2	101	54.7		42.9	2.23	81.70
Ortho-Nitrotoluene	CH_3NO_2	109	46.1				
Toluene	CH_3	114	37.7	20.4	28.5	2.13	65.53
Benzyl Chloride	CH_2Cl	114	41.4				
Ortho-Nitrochlorobenzene	Cl, NO_2	~116					
Anisole[2]	OCH_3	118		14.5	35.2	2.0	
Bromobenzene	Br	120	42.3	31.7	37.5	2.33	71.48
Benzyl Alcohol	CH_2OH	122					
Mesitylene	CH_3, CH_3, CH_3	134			28.5	2.40	
Ortho-Xylene	CH_3, CH_3	137	44	21.6	30.5	2.20	
Chlorobenzene	Cl	138	43.3	30.6	33.7	2.79	71.01
Aniline	NH_2	186	54.7	21.6	43.4	1.57	82.40

* S. Sugden, Trans.Farad. Soc. **22**, 486 (1926)

also changes regularly; for the substituents, where the changes of the various parameters can proceed sometimes in the same direction and sometimes in opposite directions for different substances, the dependencies are masked.

The complex dependence of ρ on temperature established below, which is essentially different for different liquids, confirms these deliberations.

2. MEASUREMENTS FOR THE SURFACE OF A LIQUID IN VACUUM

Spherical, thin-walled (~ 0.4 — 0.6 mm) glass ampoules, 80 mm in diameter, were filled with the investigated liquids by distillation under vacuum. After the filling, the ampoules were disconnected from the distillation apparatus and the pumping was continued for some time while the liquids boiled; then the ampoules were also disconnected from the pump. The level of the liquid in the disconnected ampoule passed through its center. The measurements were carried out on the earlier setup ; the point of reflection was fixed in the center of the surface.and in this way the beams went through the glass normally (the aperture of the beam was 12′). Such an arrangement led to a minimum of error arising from reflections from the glass. The glass of the ampoules was examined initially, for freedom of double refraction in the interval 0° — 220° C. The quality of the glass of the ampoules was likewise checked according to the quality of the image of a cross-hairs given by transmitted beams; ampoules in which a somewhat distorted image was obtained were rejected.

Control experiments were carried out with separated ampoules which had contained a little liquid, to determine the effect of a layer of vapor molecules adsorbed on the glass; such an effect was not detected.

The outside surface of the ampoule was very carefully cleaned immediately before a measurement. Brewster's angle was determined for a given temperature *in situ* by phase difference (the principal angle determined practically[1] coinciding with Brewster's angle). In this way, difficulties in the measurement of the index of refraction at various temperatures and pressures were avoided, and also errors which can be caused by a slight nonparallelism of the walls of the ampoules and the like. After each series of 10 twofold measurements, Brewster's angles was determined anew; for each liquid, 3 — 5 such series were made.

The results of several measurements are given

TABLE IV

Liquid	Coefficient of Ellipticity $\rho \times 10^5$	Optical Anisotropy $\delta^2 \times 10^3$		Surface Tension $\sigma_{18°}$	Thermal Coefficient of Free Energy k
		Vapor	Liquid		
Heterocyclic Compounds					
Pyridine	177	42.4		35.8	2.30
Quinoline[2]	125	72.5		44.8	1.92
Dioxane	107	9.4		35.7	2.31
Furfuryl Alcohol	71				
Other Compounds					
Stannic Chloride	$\sim$ 125	0			
Napthalene (100°)	$\sim$ 110	72.5	55	30.3	2.29
α-Chloronapthalene	128				
α-Bromonapthalene	139			44.6	
Cyclohexanol (30°)	$\sim$ 132	12	2.5		
Benzyl Ether	102				2.63

in Table V. As is seen, for all liquids the values of ρ are somewhat less than with an exposed surface. This can be explained by the influence of several factors (most likely operating together). It is known that the least impurity strongly increases the value of ρ. Such impurities even arise on an ideally pre-cleaned surface after its contact with the atmosphere; the latter was demonstrated both by the investigations of ellipticity and by the methods of luminescent analysis (see, for instance, the review in reference 10). There is no doubt that with the procedure described, the surface is cleaner than an exposed surface periodically cleaned by scraping off the top adulterated layer, which is the method used by all authors, including ourselves. This also reduces the values of ρ.

On the other hand, the character of the adjoining medium is far from indifferent to the condition of the surface, which can vary with a change in the total pressure and in the partial pressure of the vapor of the investigated substance.

It should be mentioned that in a layer of the order of 0.1 — 0.5 mm in depth from the exposed surface of a liquid, there exists a temperature jump of the order of 1 — 4°. This circumstance, shown, for example, in reference 11, was established also for our specific conditions---of an exposed surface---by measurements carried out in our laboratory by A. F. Stepanov*. All such type measurements were carried out with thermocouples 0.03 — 0.05 mm in diameter, which averaged the temperature over a relatively thick layer; the true jump in the surface layers might be even larger. Inasmuch as the true temperature of the surface layer is lower when it is exposed than when it is in equilibrium with the vapor, the value of ρ is correspondingly larger, since it increases with cooling (see below).

Leaving asided these considerations, we emphasize the chief result---the overwhelming part of the effect survives even under vacuum. This demonstrates without a doubt that its origin lies not in contaminations of the surface or in chemical processes on it, but in its structure.

3. DEPENDENCE OF THE COEFFICIENT OF ELLIPTICITY ON TEMPERATURE

The ampoules described in Sec. 2 were placed in an oil thermostat (Fig. 1). To eliminate the infiltration of cold air into the thermostat, a stream of hot air could be produced along the outer walls by means of the coils C_1 and C_2 with adjustable heating. Fluctuations of the temperature of the liquid did not exceed ±0.1°. The inside of the thermostat was charged with fine blackened

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[10] V. A. Kizel' and M. N. Rakhmatov, Uch. Zap. Tomsk State Univ. 1, 4 (1954).

[11] W. Prüger, Z. Physik 115, 202 (1940).

* Ready for press.

TABLE V

Liquid	$\rho_{\text{vac}} \times 10^5$	$\frac{\rho_{\text{vac}}}{\rho_{\text{atm}}}$
Dichloroethane	147	0.83
Dibromoethane	135	0.85
Pyridine	151	0.85
Acetic Acid	81	0.88
Chlorobenzene	123	0.89
Cyclohexanol (28°)	138	0.89
Dibromomethane	180	0.90
Bromoform	120	0.92
Benzene	127	0.94
Nitrobenzene	97	0.96
CCl_4	105	0.98
$SnCl_4$	123	-----
Average		0.91

aluminum filings into which the ampoule was sunk; this assured uniform heating up and completely eliminated convection currents (in the presence of which measurements are impossible). The thermostat was provided with adjusting screws and shock absorbers.

Before measurements, the liquid was held at the assigned temperature for ½ — 1 hour. For each temperature, 3 — 5 series of 10 double measurements were made; Brewster's angle was determined as described above. The results of the measurements are given in Figs. 2 and 3.

It is evident that the described method gives the variation of $\rho = \rho(p, T)$. It is difficult to doubt that the chief cause of the variation of ρ is the variation in temperature and that the effect of pressure is small. The vapor pressure for the majority of the liquids, even at the maximum temperatures, lies within the range of ~ 1 atm, and in this way the variation of ρ lies within a 10% range (Sec. 2). The pressure reaches large values only for CCl_4 (~ 5 atm), benzene and dichlorethane (~ 2 atm); however, no noticeable peculiarities are seen in the course of these curves. If, on the basis of the considerations of Sec. 2, one supposes that a decrease in pressure reduces ρ, then one might assume that an increase in p raises it. Then the curves $\rho = \rho(T)$ should fall somewhat more steeply, i.e., the dependence on T should become sharper.

The method employed eliminates errors introduced by the procedure of cleaning the surface. Let us consider the feasibility of some others.

1. The determination of Brewster's angle was carried out to a precision of $0.5'$; even over this interval ρ changes somewhat, as we showed in reference 1; probably this is the chief source of random errors. The presence of the surfaces of glass can increase the scattered light somewhat and reduce the contrast range of the stripes of the compensator; this does not give systematic errors, however.

2. The variation with pressure and temperature of the properties of the layer of vapors adsorbed on the inner walls of the ampoule can hardly be

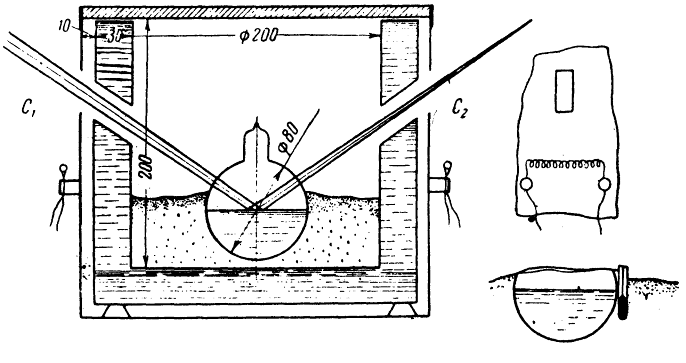

FIG. 1. Diagram of the Thermostat.

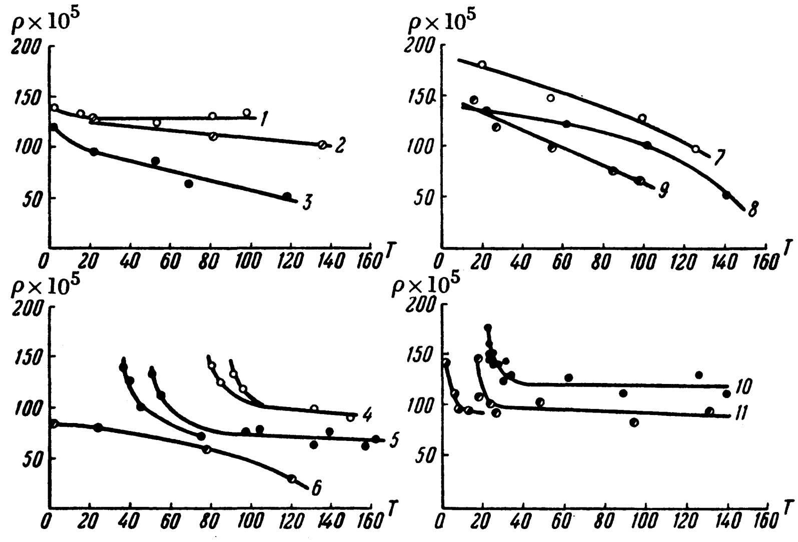

FIG. 2. Temperature dependence of ellipticity. *1*-benzene, *2*-chlorobenzene, *3*-nitrobenzene, *4*-napthalene, *5*-phenol, *6*-acetic acid, *7*-dibromomethane, *8*-dibromoethane, *9*-dichloroethane, *10*-cyclohexanol, *11*-benzophenone.

noticed, for the rays pass normally, and the effects of the thin layers act on the polarization only in the vicinity (±20′ – 30′) of Brewster's angle[1]

3. One cannot categorically maintain that the advent of double-refraction in the glass of the ampoules at large pressures (~ 5 atm) is not possible, but this could be somewhat marked only for CCl_4, where it is difficult to infer this effect, judging by the course of the curve.

What has been stated permits us to believe that the chief errors of the method are random, not systematic, and that the trend of the phenomenon is accurately shown. However, as is seen from Figs. 2 and 3, the error in the course of the curves can amount to 5 — 6% on the average.

From the data obtained it is possible to make a series of very substantial deductions. The chief of these is that, without a doubt, a significant dependence of the effect on temperature was established.

In the majority of liquids, the freezing point of which lies in the interval studied, a sudden drop is clearly visible in the vicinity of the freezing point and a considerably more sloped course beyond it*.

We discuss the phenomena in the neighborhood of the freezing point in Sec. 4; here we consider the shape of the curves somewhat removed from the freezing point.

The liquids studied can be divided into three groups. In the first, the dependence on temperature in the range under consideration is absent. (cyclohexanol, CCl_4, bromoform); in the second it is hardly noticeable or weak (benzene, paradichlorobenzene, bensophenone, orthochloronitrobenzene, chlorobenzene, napthalene, phenol). Finally, the third is characterized by a sudden drop (nitrobenzene, acetic acid, dibromoethane, dichloroethane, dibromomethane, pyridine). The first group

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* We note here that those rough data which are entered in Tables III and IV were calculated by means of this curve. For $SnCl_4$ it was assumed that on going over to an exposed surface, ρ changes in the same manner as for CCl_4; for the remaining substances, values of ρ were taken in the sloping part of the curves (evidently, more appropriate for comparison with the other liquids) and it was assumed that for an exposed surface, the values are larger by 10%, according to Table V.

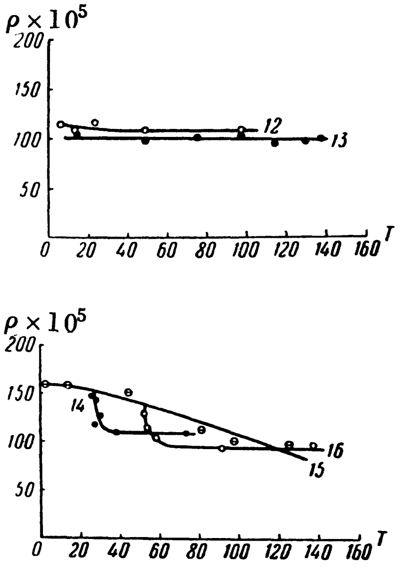

FIG. 3. Temperature Dependence of Ellipticity.
12 - bromoform, *13* - CCl_4, *14* - orthochloronitrobenzene, *15* - pyridine, *16* - paradichlorobenzene.

TABLE VI

Curve No. in Figs. 2 & 3	Liquid	Crystal		$\gamma_{eff} = f(T)$	γ^2_{eff}/γ^2
		System	Optical Anisotropy		
	1st Group				
10	Cyclohexanol	Cubic	Weak		0.2
12	Bromoform	Hexagonal	"	slowly rising	0.38
13	CCl_4	Cubic	"		0.27^5
	2nd Group				
1	Benzene		"	Rising	0.61
5	Phenol		"	"	0.61
4	Napthalene	Monoclinic	Strong	No Change	0.76
16	Para-Dichlorobenzene . .	"	"	"	0.77
2	Chlorobenzene			Slowly rising	0.84
	3rd Group				
9	Dichloroethane				0.62 - 1.06*
8	Dibromoethane				0.92
6	Acetic Acid		"	Decreasing	1.24
3	Nitrobenzene		"	rapidly falling	1.54
15	Pyridine				

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* Measured in our laboratory.

can be characterized rather clearly: these are substances with small effective anisotropy of the liquid, and have crystals weakly optically anisotropic. In the second group are substances with values of effective anisotropy of the liquid ranging from large (napthalene, benzophenone) to moderate (benzene). The anisotropy of the crystals is likewise varied---from large (napthalene, paradichlorobenzene) to moderate (benzene, phenol). For nitrobenzene and acetic acid of the third group, both large values of δ^2_{liq} and considerable crystal anisotropy are characteristic[8,12]. A comparison with the course of the temperature dependence of the effective anisotropy of the liquids permits one to delineate the second and third groups. From Table VI, in which the 5th and 6th columns are derived from reference 8 ($\gamma^2 = \delta^2 9 \alpha^2$, where α is the mean polarizability), it is seen that for substances of the second group there is an increase or an invariance of the effective anisotropy, but for those of the third, a drop in it.

Especially characteristic is the ratio $\gamma^2_{\mathrm{eff}}/\gamma^2 = \delta^2_{\mathrm{liq}}/\delta^2$; it is very small for the first group, for the second group it is less than 1 and for the third > 1 or very near to it. For chlorobenzene this ratio is somewhat larger than for the rest of the substances of the second group, and the drop of the curve is a bit steeper. Data on the anisotropy of cyclohexanol is lacking, but if one proceeds from analogies with the aliphatic alcohols, on the one hand, and with the small change of anisotropy on going from benzene to phenol, on the other, and takes into account that for cyclohexanol and cyclohexane Δ_{liq} is 0.12 and 0.08, respectively, one can assume values for it, tentatively, a little larger than for cyclohexane (for which $\gamma^2_{\mathrm{eff}}/\gamma^2 = 0.16$, cf. reference 8); this was also done in Tables IV and VI. For pyridine there are no values of γ, and the ratio $\Delta_{\mathrm{liq}}/\Delta_{\mathrm{vap}}$, measured by us, equals 13.6, i.e., the anisotropy of the liquid is large (in benzene this ratio if 9), and the drop of the curve is rapid.

Recently, a series of weighty arguments have been put forward in favor of the idea that the difference of the anisotropy of the molecules from the effective anisotropy of the liquid is a result of the existence of a near-oriented arrangement in the latter[12]; the effective anisotropy is regarded as a guage of the anisotropy of near order in the liquid, and the ratio $\gamma^2_{\mathrm{eff}}/\gamma$ as a measure of the character and extent of the near-oriented arrangement[8]. In the work of reference 13 this ratio is related to the "correlating parameter" of Ansel'm[12].

As is seen, this ratio also determines the thermal course of ρ in the region considered. On the basis of what has been said, one can suppose that the presence of ellipticity is brought about by two factors. One of these is undoubtedly connected with differences in the oriented arrangement on the surface of the liquid, and in its thickness. Its effect increases with an increase in $\gamma^2_{\mathrm{eff}}/\gamma^2$; for liquids with large values of this ratio and with large anisotropy of near order, the chief role is played by just this factor, since at higher temperatures where the oriented arrangement is broken up, ρ falls off to very small values in these liquids. The other factor is not connected with the temperature or with an oriented arrangement (cf. Sec. 4); for certain liquids with small anisotropy of near order it evidently plays the main role. For most of the liquids, both of these factors probably act together.

4. PROCESSES NEAR THE FREEZING POINT

The sharp deflection of the curves, in approaching the freezing point is very interesting. In greater or lesser degree it is observable in all liquids which have their freezing point within the temperature interval studied.

Benzene and nitrobenzene were supercooled to ~ -4 or -5°, acetic acid to -10°. Our method did not permit measurements to be made for $T \leqslant 2°$ C, but for the first two liquids the beginning of the rise of the curves is nevertheless seen. Only in bromoform was the rise not detected; probably, this is explained by the fact that the curve is very steep for it, and our preparations scarcely allowed supercooling. Instead, they crystallized at approximately 6° with the least variation of temperature, so that the rise could not be detected.

That the phenomenon is functionally related to changes of structure during "preparations" for solidification, is shown especially clearly by effects which arise during supercooling. It is known that the process of supercooling depends on the previous history of a liquid; this is reflected in our curves. Thus, for example, our preparation of benzophenone melted in open air at ~ 40°. After melting it in an evacuated ampoule, measurements were performed; it was cooled to ~ 17.2°, when it began to crystallize, and then heated to

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[12] M. F. Vuks, Uspekhi Fiz. Nauk 61, 393 (1953); A. I. Ansel'm, J. Exper. Theoret. Phys. USSR 17, 489 (1947).

[13] V. I. Elfimov, Dissertation, Leningrad State Univ., 1954.

140° (right-hand curve). Further measurements were carried out during cooling and the left-hand curve was obtained (at 0° the liquid still had not solidified).

An analogous procedure was carried out for napthalene and phenol; the latter was melted in the thermostat heated to 55°, and measurements were conducted during heating (curve on right). Measurement during cooling gave the left-hand curve. In all cases, the sloping parts of the curves agree within the limits of our accuracy. From these examples it is seen that the bend of the curves comes right after the freezing point.

Cyclohexanol permitted only an insignificant supercooling, orthochloronitrobenzene likewise; therefore, the curves were reduced to a few "settings" with intermediate heating, and the described phenomena left a mark only in the scatter of the points.

In the curves in the region considered, within the limits of our accuracy of measurement and with the available material, it is hard to notice the difference between substances with different effective anisotropy of the liquid or with different crystal lattices, and also differences in the behavior of the three groups noted. The difference in the curves for liquids disposed to strong supercooling (for example, benzophenone) and indisposed (for example, orthochloronitrobenzene)[14], apparently reduces only to a different slope of the curve (which also depends on the previous history).

The facts we stated lead to the idea that in the immediate vicinity of the freezing point the changes in the structure of the surface and stratum of the liquid accelerate sharply. The mechanism of this process, as far as can be judged, is not exactly like that which prevails away from the freezing point.

Other facts can be pointed out which illustrate the likelihood of such differences (cf. also reference 15). Thus, it is noted in reference 8 that the approach to the melting point and supercooling have no special effect with respect to the intensity and depolarization of light scattered in the volume. On the other hand, for the surface layers of liquids (of the saturated acids) the appearance of anisotropy over an interval of 1-4° from the melting point was found[16] (though also not for a free surface, but for a boundary with glass, which can introduce an orienting effect[17]). Thus the hypothesis seems possible that the observed phenomena are brought about by changes in the structure, namely, in the surface. To detail the mechanism of these changes is difficult at present.

It should be kept in mind that the presence in a liquid of the slightest impurities (which are difficult to determine chemically) can, generally speaking, act on its structure (which was shown already in Stuart's early works). It is likely that this applies to the structure of the surface in even greater degree. A special synthesis of the compounds is desirable here, although the good agreement of some of our data from Tables I-III with reference 2 also indicates the reproducibility of the data with the use of the usual compounds with proper purification.

In conclusion, it can be said that the present work, being in many respects still exploratory, demonstrates with certainty the great complexity of processes on the surface of a liquid, and also indicates the possibility of obtaining information about them which yields to interpretation by means of our method.

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