

On the Applicability of Fresnel's Law in Deducing Evidence in Favour of Surface Structure from Surface Reflectivity.

BY S. S. BHATNAGAR, D. L. SHRIVASTAVA AND N. G. MITRA.

Fresnel, from considerations of the electro-magnetic theory of light, worked out an equation for calculating the energy in the reflected ray, when the incident light is unpolarised.

The equation is :

$$I = \frac{1}{2} a^2 \left[\frac{\sin^2(i-r)}{\sin^2(i+r)} + \frac{\tan^2(i-r)}{\tan^2(i+r)} \right]$$

where I = the intensity of the reflected ray;

a = amplitude of incident vibration ;

i and r = the angles of incidence and refraction respectively.

This equation, however, postulates a sudden change in physical properties in passing from one medium to another and a similar uniform arrangement of molecules throughout the bulk as also on the surface of the liquid. But from the work of Langmuir, *J. Amer. Chem. Soc.*, 1917, 39, 1848; *Chem. and Met. Eng.*, 1916, 15, 468; Harkins, *J. Amer. Chem. Soc.*, 1917, 39, 541; Adams, *Proc. Roy. Soc.*, 1921, 99A, 336; 1922, 101A, 452, 516) and others on the orientation of surface molecules in a liquid, it is clear that the arrangement of molecules at the surface is quite different from what it is in the bulk. The polar groups like OH, COOH, NH₂, etc., are supposed to be pointing downwards towards the bulk of the liquid, leaving the non-polar groups floating on the surface. If this be so it would be interesting to find out if some deviations from the Fresnel's equation would be observed in the case of reflection from liquid surfaces which are known to have a definite surface orientation. It was with this view that the present investigation was undertaken to explore the limits of applicability of the Fresnel's equation in the case of liquids, on the assumption that the first reflection from the liquid surface takes place from the molecules in the surface layer.

EXPERIMENTAL.

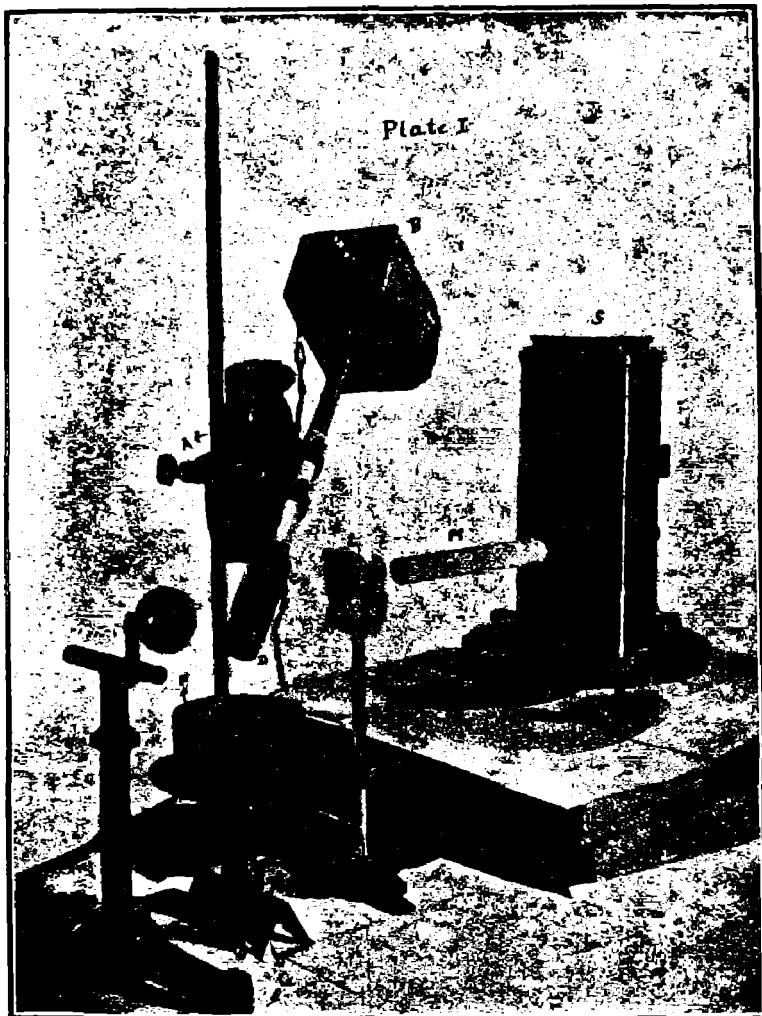
The intensity of the reflected ray of light was measured by the Boys' radiomicrometer manufactured by Cambridge Instrument Co. The arrangements made for the experiments are shown in Plate I. They consisted of devices—

- (1) to take the incident beam of light ;
- (2) to put the liquid, whose surface-reflectivity was to be examined in a suitable manner in a non-reflecting vessel ;
- (3) to focus the reflected ray on the receiving plate of the Boys' radiomicrometer.

(1) *To take the incident beam of light.*

The arrangement for the incident beam of light was such that the light could be arranged to fall on the liquid surface at any desired angle to the normal. For this purpose a theodolite scale was used. It was graduated into 360 divisions, each division representing a degree. A tangent screw with a graduated head was also attached to the scale which had to be released for moving the scale independent of it. One full turn of the screw head rotated the scale through one degree and graduations on it were such that readings could be taken with an accuracy of about 1'. At the centre of the scale was carefully fixed a metallic tube of 1.5 cm. diameter in such a way that when it was vertical as seen by the spirit levels fixed on the surface of the scale, the reading on it as well as on the graduated head of the tangent screw was zero. After this the tangent screw was moved until the tube became horizontal as shown by the spirit levels, when the angle reading was found to be 90°. This confirmed the initial setting of the tube. Later on adjustments of angles were made by the tangent screw only.

On one end of the tube was soldered a metallic disc which had a circular hole of 3 mm. diameter bored into it. This end of the tube carried a small wooden box, in which was fixed a small 12 volt, 21 c.p. bulb in such a way that the light from a small portion of the filament only could pass through the small hole in the disc, attached to the tube. The other end of the tube carried a brass head soldered to it. Into this head was fitted another metallic tube which could smoothly slide into it. The outer end of the sliding tube was closed by means of a metallic disc which had a circular hole of 4 mm. diameter accurately bored into its centre. This tube carried a lens



- A = Theodolite scale for measuring the angles of incidence.
B = A wooden box containing a 12 volt 21 c. p. half-watt bulb.
C = A brass head.
D = A brass tube sliding into C.
E = Watch glass on which the liquid is placed.
F = Wooden block on which a groove is cut to fit the watch glass.
G = Adjustable table.
H = Plane mirror capable of moving both on its horizontal and vertical axes.
L = Lens to focus the reflected ray to the thermopile.
M = Tube containing several diaphragms.
S = Boys' radiomicrometer.

in it to give a parallel beam of incident light. The sliding tube was pushed in or out until the distance between the source of light and the lens was equal to the focal length (36 cm.) of the latter. The parallelism of the emergent beam was tested by means of a telescope focussed for infinity.

All the tubes and the box containing the bulb were coated on the inner surfaces with a dull black paint to avoid all reflections from surfaces. The scale with all the arrangements described above carried a clamping device so that the whole thing could be raised or lowered or rotated as desired. The stand carrying it was rigidly fixed on a wooden base board which was placed on a stone table, so that the liquid surface was not disturbed by any external vibration.

(2) *The arrangement for placing the liquid whose surface reflectivity was to be examined in a suitable vessel.*

The liquid was put on a shallow watch glass which was finely ground both on its inner and outer surfaces. The outer surface was coated with a dull black paint to reduce the reflection from the liquid glass interface to a minimum, and thus only the first reflection from the liquid surface was examined. In order that the watch glass may be put in the same position in all the experiments, a groove was carefully cut in a block of wood in which the watch glass fitted exactly. The latter rested on a metallic support that could be adjusted at any height. This was also rigidly fixed to the base board.

(3) *To focus the reflected ray on the receiving plate of the Boys' radiomicrometer.*

The ray of light after being reflected from the liquid surface was made to fall on a plane mirror of small aperture, which was capable of movement both on the horizontal and vertical axes. The mirror was clamped in a stand which could be adjusted laterally as also vertically and was thus rendered capable of all sorts of motions, helping thereby in adjustment to throw the reflected ray horizontally on to the receiving plate of the radiomicrometer. After the second reflection from the mirror the ray was focussed on the receiving plate by means of a lens whose focal length was equal to the distance between the lens and the receiving plate.

To get rid of other external radiations a tube carrying four or five diaphragms of gradually decreasing diameters was fitted into the

radiomicrometer The range of these diameters varied from 8 cms. at the outer end to 5 mms. at the inner one, which in this way allowed only a horizontal ray to pass through it and fall on the thermopile. Proper adjustments of the reflecting mirror were made to give a perfectly horizontal beam, which after passing through all these diaphragms could be seen as a bright circular patch of light with the shadow of the receiving plate at the centre, on a ground glass plate placed at the opening provided in the instrument for observations, opposite to the one carrying the tube. The next step was to focus the circular patch on the plate by the lens and the patch thus obtained was just big enough to cover the receiving plate. No portion of the light was allowed to fall outside of it. The deflections obtained were noted on a scale put at a distance of a metre from the radiomicrometer. These deflections were taken to be proportional to the intensity of the reflected ray of light.

The liquids used in the investigation were either Kahlbaum's or Merck's extra pure chemicals. Some of them had to be specially purified for this work by repeated distillations or crystallisation. They were all freshly distilled just before use and the refractive index of the liquid for the light used in our experiment was determined by the Abbe refractometer. This was necessary to determine the Brewsterian angle for the liquid and served as an evidence of the purity of the substance. The experiments were carried on in a constant temperature room.

Before examining the reflected ray from a liquid surface at any particular angle, the reflected ray at that angle from the water surface was first examined. This reading was taken as the standard in terms of which the deflections of the new liquid was expressed. Thus if at an angle θ , I_1 and I_2 be the intensities of the reflected rays in the case of a liquid and water respectively, and d_1 and d_2 be the corresponding deflections, then

$$I_1 = K \cdot d_1$$

$$\text{and } I_2 = K \cdot d_2,$$

$$\therefore \frac{I_1}{I_2} = \frac{d_1}{d_2}.$$

(where K the constant will remain the same in both the cases).

To note the deflection due to the reflected ray from the water surface, it was freshly distilled every time before use. Some of it was poured on the clean dry watch glass and the surface was made

to overflow after which the liquid was thrown away. This was done to ensure the absence of any dust particles sticking on the watch glass and also to guard against lens formation. The watch glass was next put into the groove on the block of wood and 2 c.c. of water were accurately measured into it. All the necessary adjustments described above were made as soon as possible and deflections were observed. No readings were considered unless they could be repeated at least five times.

To get the deflection from a liquid surface the watch glass was removed from the groove and dried by blowing a current of hot air over it. It was then cooled, rinsed with a few drops of freshly distilled liquid to be examined, and replaced in the groove, when 2 c. c. of the liquid were measured out in it and the deflections noted. The different angles at which the liquids were examined were 30°, 45°, 60°, 70° and also their respective Brewsterian angles. Angles below 30° could not be examined owing to the feeble intensity of the reflected ray and above 70°, the deflections were found to be very large. The results are enumerated in the following tables. Table I gives a few readings at random to show the range of variations in the deflections observed in any particular case.

TABLE I.

Liquid.	Angle of incidence.	Deflections observed (in cms).					
		(1)	(2)	(3)	(4)	(5)	Mean.
Water ...	70°	29·75	29·75	29·70	29·75	29·70	29·73
Methyl acetate ...	65°	20·35	20·35	20·35	20·35	20·35	20·35
Ethyl alcohol ...	60°	12·85	12·85	12·85	12·85	12·85	12·85
Toluene ...	45°	9·00	9·00	9·00	9·00	9·00	9·00
Dimethyl aniline ...	30°	8·60	8·60	8·60	8·60	8·60	8·60

In Table II are given the deflections observed in the case of various liquid surfaces at their respective Brewsterian angles.

TABLE II.

Liquids.	Brewsterian angle.	Deflection in cms.	Ratio of the deflection observed in the case of liquid to the corresponding water deflection.
Water ...	53°5'	7·75	1·000
Ethyl alcohol ...	53°42'	9·20	1·125
<i>n</i> -Propyl alcohol	54°6'	9·46	1·245
<i>iso</i> -Propyl ..	53°57'	9·00	1·200
<i>n</i> -Butyl ..	54°22'	9·90	1·269
<i>iso</i> -Butyl ..	54°17'	9·82	1·271
<i>n</i> -Amyl ..	54°32'	10·15	1·269
Dimethyl ethyl carbinol ...	54°30'	10·45	1·259
Acetic acid ...	53°55'	9·28	1·167
Propionic acid ...	54°10'	9·90	1·222
<i>n</i> -Butyric acid ...	54°38'	10·55	1·302
<i>iso</i> -Butyric acid	54°19'	10·20	1·241
Benzene ...	56°16'	13·95	1·550
Toluene ...	56°9	14·40	1·532
<i>m</i> -Xylene ...	56°4'	14·25	1·524
Methyl acetate ...	53°33'	8·85	1·141
Ethyl acetate ...	53°50'	9·17	1·183
Propyl acetate ...	54°5'	9·90	1·214
<i>iso</i> -Butyl acetate	54°12'	10·13	1·213
Ethylene chloride	55°13'	12·60	1·403
Aniline ...	57°40'	18·06	1·750
Ethyl aniline ...	57°10'	17·20	1·685
Dimethyl aniline	57°13'	16·70	1·704
Diethyl aniline ...	56°57'	16·5	1·659
Toluidine ...	57°27'	17·2	1·720
Dimethyl toluidine. ...	56°41'	15·55	1·637
Copper ferrocyanide sol.	53°5'	7·75	1·000
Gelatine sol	53°5'	7·75	1·000

Tables III-VII give the value of the ratio between the deflection noted in the case of the liquid to that in the case of the water at the same angle for different groups of substances. Side by side with the experimental values are given the values of the ratio as calculated from the Fresnel's formula.

If I_1 be the intensity of the reflected ray from a liquid surface at an angle of incidence i and I_2 be that in the case of water at the same angle and if r_1, r_2 be the respective angles of refraction, we have

$$I_1 = \frac{1}{2} a^2 \left[\frac{\sin^2(i-r_1)}{\sin^2(i+r_1)} + \frac{\tan^2(i-r_1)}{\tan^2(i+r_1)} \right]$$

$$\text{and } I_2 = \frac{1}{2} a^2 \left[\frac{\sin^2(i-r_2)}{\sin^2(i+r_2)} + \frac{\tan^2(i-r_2)}{\tan^2(i+r_2)} \right].$$

(a will be the same in both the cases because the source of light is the same).

$$\therefore \frac{I_1}{I_2} = \frac{\frac{\sin^2(i-r_1)}{\sin^2(i+r_1)} + \frac{\tan^2(i-r_1)}{\tan^2(i+r_1)}}{\frac{\sin^2(i-r_2)}{\sin^2(i+r_2)} + \frac{\tan^2(i-r_2)}{\tan^2(i+r_2)}}$$

Now, intensity of the light can be taken proportional to the deflections observed.

$$\therefore \frac{I_1}{I_2} = \frac{d_1}{d_2} = \frac{\frac{\sin^2(i-r_1)}{\sin^2(i+r_1)} + \frac{\tan^2(i-r_1)}{\tan^2(i+r_1)}}{\frac{\sin^2(i-r_2)}{\sin^2(i+r_2)} + \frac{\tan^2(i-r_2)}{\tan^2(i+r_2)}}$$

From this it is clear that if Fresnel's formula holds in the case of liquids examined, we should have the ratio of the deflections observed in the case of a liquid to that in the case of water under similar conditions, equal to the ratio of the intensities in the two cases as calculated from the formula.

In the following tables are given the results obtained with alcohols, saturated carboxylic acids, esters, aromatic hydrocarbons and aromatic amines.

TABLE III.

Alcohols.

Alcohols.	Angle 70°			Angle 65°			Angle 60°		
	Obs.	Calc.	Per- centage differ- ence.	Obs.	Calc.	Per- centage differ- ence.	Obs.	Calc.	Per- centage differ- ence.
	$\frac{d_1}{d_2}$	$\frac{I_1}{I_2}$		$\frac{d_1}{d_2}$	$\frac{I_1}{I_2}$		$\frac{d_1}{d_2}$	$\frac{I_1}{I_2}$	
Ethyl alcohol ...	1'088	1'056	+3'03	1'096	1'072	+2'24	1'106	1'091	+1'28
Propyl alcohol ...	1'105	1'095	+0'91	1'185	1'121	+5'71	1'191	1'163	+3'295
<i>iso</i> -Propyl alcohol	1'104	1'081	+2'13	1'120	1'106	+1'27	1'157	1'132	+2'21
Butyl alcohol ..	1'138	1'119	+1'698	1'165	1'155	+0'87	1'214	1'168	+3'94
<i>iso</i> -Butyl alcohol	1'112	1'112	0'000	1'162	1'147	+2'18	1'213	1'182	+2'62
Amyl alcohol ...	1'148	1'134	+1'23	1'193	1'176	+1'45	1'236	1'221	+1'23
Dimethyl ethyl carbinol ...	1'120	1'132	-1'06	1'174	1'172	+0'17	1'221	1'216	+0'37

TABLE III (Continued).

Alcohols.

Alcohols.	Angle 45°			Angle 30°		
	Obs.	Calc.	Per- centage differ- ence.	Obs.	Calc.	Per- centage differ- ence.
	$\frac{d_1}{d_2}$	$\frac{I_1}{I_2}$		$\frac{d_1}{d_2}$	$\frac{I_1}{I_2}$	
Ethyl alcohol ...	1'163	1'131	+2'74	1'184	1'152	+2'78
Propyl alcohol. ...	1'296	1'227	+5'62	1'318	1'256	+5'095
<i>iso</i> -Propyl alcohol ...	1'261	1'196	+5'43	1'294	1'217	+6'33
Butyl alcohol ...	1'382	1'296	+6'63	1'429	1'336	+6'96
<i>iso</i> -Butyl alcohol ...	1'378	1'244	+2'73	1'445	1'313	+10'43
Amyl alcohol ...	1'387	1'336	+3'82	1'460	1'382	+5'64
Dimethyl ethyl car- binol ...	1'350	1'325	+1'89	1'408	1'371	+2'699

TABLE IV.

Acids.

Acids.	Angle 70°			Angle 65°			Angle 60°		
	Obs.	Calc.	Per- centage differ- ence.	Obs.	Calc.	Per- centage differ- ence.	Obs.	Calc.	Per- centage differ- ence.
	$\frac{d_1}{d_2}$	$\frac{I_1}{I_2}$		$\frac{d_1}{d_2}$	$\frac{I_1}{I_2}$		$\frac{d_1}{d_2}$	$\frac{I_1}{I_2}$	
Acetic acid ...	1'076	1'077	-0'093	1'104	1'099	+0'46	1'152	1'124	+2'49
Propionic acid	1'109	1'102	+0'64	1'144	1'132	+1'06	1'170	1'165	+0'49
<i>n</i> -Butyric acid	1'160	1'142	+1'58	1'189	1'188	+0'08	1'250	1'236	+1'13
<i>iso</i> -Butyric acid	1'119	1'114	+0'45	1'153	1'148	+0'44	1'189	1'185	+0'34

TABLE IV (Continued).

Acids.	Angle 45°			Angle 30°		
	Obs.	Calc.	Percentage difference.	Obs.	Calc.	Percentage difference.
	$\frac{d_1}{d_2}$	$\frac{I_1}{I_2}$		$\frac{d_1}{d_2}$	$\frac{I_1}{I_2}$	
Acetic acid ...	1'177	1'183	-0'42	1'216	1'205	+0'91
Propionic acid ...	1'295	1'247	+3'85	1'320	1'278	+3'26
n-Butyric acid ...	1'411	1'359	+3'83	1'732	1'414	+22'49
iso-Butyric acid ...	1'312	1'279	+2'53	1'320	1'319	+0'08

TABLE V.

Name.	Angle 70°			Angle 65°			Angle 60°		
	Obs.	Calc.	Percentage difference.	Obs.	Calc.	Percentage difference.	Obs.	Calc.	Percentage difference.
	$\frac{d_1}{d_2}$	$\frac{I_1}{I_2}$		$\frac{d_1}{d_2}$	$\frac{I_1}{I_2}$		$\frac{d_1}{d_2}$	$\frac{I_1}{I_2}$	
Methyl acetate	1'071	1'053	+1'81	1'083	1'067	+1'41	1'113	1'089	+2'37
Ethyl acetate	1'079	1'070	+0'84	1'114	1'091	+2'11	1'131	1'112	+1'71
Propyl acetate	1'101	1'095	+0'55	1'143	1'121	+1'96	1'166	1'153	+1'13
iso-Butyl acetate	1'107	1'106	+0'09	1'152	1'137	+1'32	1'186	1'172	+1'19

TABLE V (Continued).

Esters.	Angle 45°			Angle 30°		
	Obs.	Calc.	Percentage difference.	Obs.	Calc.	Percentage difference.
	$\frac{d_1}{d_2}$	$\frac{I_1}{I_2}$		$\frac{d_1}{d_2}$	$\frac{I_1}{I_2}$	
Methyl acetate ...	1'155	1'119	+3'22	1'216	1'136	+7'04
Ethyl acetate ...	1'215	1'164	+4'38	1'233	1'184	+4'14
Propyl acetate ...	1'258	1'227	+2'53	1'289	1'256	+2'63
iso-Butyl acetate...	1'295	1'256	+3'11	1'329	1'290	+3'02

TABLE VI.

Aromatic Hydrocarbons.

Aromatic Hydrocarbon.	Angle 70°			Angle 65°			Angle 60°		
	Obs.	Calc.	Percentage difference.	Obs.	Calc.	Percentage difference.	Obs.	Calc.	Percentage difference.
	$\frac{d_1}{d_2}$	$\frac{I_1}{I_2}$		$\frac{d_1}{d_2}$	$\frac{I_1}{I_2}$		$\frac{d_1}{d_2}$	$\frac{I_1}{I_2}$	
Benzene ...	1.251	1.281	-2.34	1.345	1.385	-2.89	1.453	1.494	-2.74
Toluene ...	1.248	1.272	-1.89	1.341	1.369	-2.05	1.442	1.476	-2.30
Xylene ...	1.227	1.265	-3.00	1.316	1.358	-3.09	1.429	1.463	-2.32

TABLE VI (continued).

Aromatic Hydrocarbons.

Aromatic Hydrocarbon.	Angle 45°			Angle 30°		
	Obs.	Calc.	Percentage difference.	Obs.	Calc.	Percentage difference.
	$\frac{d_1}{d_2}$	$\frac{I_1}{I_2}$		$\frac{d_1}{d_2}$	$\frac{I_1}{I_2}$	
Benzene ...	1.760	1.800	-1.11	1.933	1.933	-0.05
Toluene ...	1.740	1.763	-1.30	1.890	1.889	+0.05
Xylene ...	1.726	1.739	-0.75	1.890	1.861	+1.56

TABLE VII.

Aromatic Amines.

Aromatic amines.	Angle 70°			Angle 65°			Angle 60°		
	Obs.	Calc.	Percentage difference.	Obs.	Calc.	Percentage difference.	Obs.	Calc.	Percentage difference.
	$\frac{d_1}{d_2}$	$\frac{I_1}{I_2}$		$\frac{d_1}{d_2}$	$\frac{I_1}{I_2}$		$\frac{d_1}{d_2}$	$\frac{I_1}{I_2}$	
Aniline ...	1.331	1.388	-4.83	1.478	1.541	-4.09	1.647	1.714	-3.91
Ethyl aniline ...	1.310	1.351	-3.03	1.445	1.479	-2.30	1.580	1.636	-3.42
Dimethyl aniline	1.313	1.354	-3.03	1.442	1.490	-3.22	1.603	1.644	-2.49
Diethyl aniline ...	1.292	1.329	-2.78	1.418	1.461	-2.94	1.566	1.601	-2.19
Toluidine ...	1.326	1.373	-3.42	1.478	1.518	-2.64	1.640	1.682	-2.50
Dimethyl toluidine	1.278	1.313	-2.67	1.406	1.429	-1.61	1.536	1.557	-1.35

TABLE VII (continued).

Aromatic Amines.

Aromatic amines.	Angle 45°			Angle 30°		
	Obs. $\frac{d_1}{d_2}$	Calc. $\frac{I_1}{I_2}$	Percentage difference.	Cbs. $\frac{d_1}{d_2}$	Calc. $\frac{I_1}{I_2}$	Percentage difference.
Aniline ...	2'180	2'215	-1'58	2'453	2'439	+0'57
Ethyl Aniline ...	2'066	2'062	+0'19	2'273	2'266	+0'05
Dimethyl aniline	2'088	2'073	+0'72	2'294	2'274	+0'88
Diethyl aniline ...	2'018	1'995	+1'15	2'195	2'175	+0'92
Toluidine ...	2'153	2'153	+0'00	2'400	2'369	+1'31
Dimethyl toluidine	1'942	1'913	+1'52	2'174	2'072	+4'92

Summary and Discussion of Results.

From the tables it is clear that the calculated ratio of intensities I / I_2 is not equal to d_1 / d_2 in all cases. This can be due to two possible causes:

1. To an error in the value of the angle observed.
2. To a variation in the refractive index of the liquid due to temperature or other causes.

The observed difference cannot be ascribed to the cause (1), as it can be seen that an error of at least more than 2° should be assumed to have occurred to account for this difference. Such a large error in measuring the angle is not likely in the apparatus. The error of setting does not exceed 10' and it is readily seen that this small difference will not appreciably change the calculated ratio. This will be clear from the following calculations for propyl alcohol:—

Angles.	Ratio (I_1 / I_2).
60°6'	1'153
60°	1'153
59°52'	1'152

Any error in the refractive index can only take place in either of the following ways:

1. The temperature not being constant in the course of the experiment.
2. The values of the refractive indices used may not be for the effective wave-lengths.
3. Presence of impurities in the substance.

As we have mentioned above the experiments were all carried out in a double walled underground room whose temperature variation was negligible during the interval of the experiments and further the refractive indices of the liquids were determined immediately before use at room temperature by the Abbe refractometer, whose temperature was kept constant by means of a water circulating arrangement; hence we think that no error due to this factor was possible.

As the liquids used in this investigation were extra pure chemicals of Kahlbaum or Merck, and in several cases special cares were taken to purify them, no error due to (3) is also present.

The source of light used was the same throughout and the battery maintained a constant voltage all along. Prof. Raman, in a private letter, has kindly drawn our attention to the advisability of taking for the refractive index the value for the infra-red region, as the radiomicrometer has a maximum sensitivity for those rays. We give below the calculated values for ethyl and propyl alcohols and also for benzene using the refractive index for $\lambda=1\cdot028$ and $0\cdot997 \mu$.

TABLE VIII.

Name.	μ^{λ}	Angle 70°			Angle 65°			Angle 60°		
		Obs.	Calc.	Percentage difference.	Obs.	Calc.	Percentage difference.	Obs.	Calc.	Percentage difference.
Ethyl alcohol	25°									
	$1\cdot028\mu$ $=1\cdot3521$	1\cdot088	1\cdot057	+2\cdot93	1\cdot096	1\cdot074	+2\cdot05	1\cdot105	1\cdot092	+1\cdot19
Propyl alcohol	$19^{\circ}\cdot5$									
	$1\cdot028\mu$ $=1\cdot3782$	1\cdot105	1\cdot106	-0\cdot09	1\cdot185	1\cdot139	+4\cdot04	1\cdot191	1\cdot172	+1\cdot62
Benzene	25°									
	$0\cdot997 \mu$ $=1\cdot4823$	1\cdot261	1\cdot279	-2\cdot19	1\cdot345	1\cdot378	-2\cdot40	1\cdot453	1\cdot488	-2\cdot35

TABLE VIII (continued).

Name.	Angle 45°			Angle 30°		
	Obs. $\frac{d_1}{d_2}$	Calc. $\frac{I_1}{I_2}$	Percentage differ- ence.	Obs. $\frac{d_1}{d_2}$	Calc. $\frac{I_1}{I_2}$	Percentage differ- ence.
Ethyl alcohol ...	1.162	1.132	+2.65	1.184	1.182	+0.17
Propyl alcohol ...	1.296	1.256	+3.18	1.318	1.326	-0.60
Benzene ...	1.780	1.783	-0.17	1.932	1.967	-1.78

Fresnel's Law seems to hold for reflections from liquid surfaces within limits of reasonable accuracy. There are, however, several points of interest.

It is evident from Table VIII that the substitution of the values of refractive indices for larger wave-lengths changes the values of I_1/I_2 calculated on the Fresnel's Law in a manner that the agreement between these values and those experimentally deduced becomes much closer. The differences in some cases, however, are larger than can be ascribed to experimental error even after the correct value of μ in the infra-red region is taken into account and although the authors are not definite, they consider it possible that these differences may have a physical meaning. Their reasons for suspecting this are the following:

I. It is seen that the compounds having polar groups behave differently from those having no polar groups in the following respects:—

- (a) In aliphatic compounds with polar groups the differences between the calculated and the observed values are always positive, *i.e.*, the observed value is greater than the calculated value.
- (b) In compounds with no polar groups in them the calculated values are always greater than the observed values.

II. It is seen that the differences observed in the case of aliphatic compounds and aromatic amines, (*i.e.*, those substances which have got polar groups in them) are always greater than those of aromatic hydrocarbons, which contain no polar group.

III. In the two aromatic series examined, namely, the aromatic hydrocarbons and the amines, the values of I_1/I_2 observed are always

less than the calculated ones at higher angles of incidence. At smaller angles of incidence, the aromatic amines exhibit a positive difference which may be due to the presence of at least one orientating radical in them. In the aliphatic compounds the observed values are always greater than the calculated values.

IV. When comparing the mean deviation from the calculated values in the case of aromatic hydrocarbons and aromatic amines, the latter (which have a chance of assuming orientation) show always the greater deviation. If these small differences were due to error in experimentation they should have very little chance of exhibiting the regularities shown above.

Further work on the subject is in progress and an apparatus is being devised for using a bright monochromatic light in these investigations.

Investigations on the reflectivity of light from the surface of a colloidal solution are already under way and we hope to throw further light in the near future on the subject by trying various monochromatic lights from the ultra-violet to the infra-red region.

UNIVERSITY CHEMICAL LABORATORIES,
UNIVERSITY OF THE PUNJAB,
LAHORE.

Received April 5, 1928.