

MOLECULAR CLUSTERING IN LIQUID FATTY ACIDS.

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1. Introduction.

It is well known that the light scattered transversely by a liquid is not in general perfectly polarised, but shows a defect of polarisation which is characteristic of each liquid. This partial depolarisation arises from the fact that in general, we are dealing with two types of scattering in an ordinary liquid, one type called the density scattering arising from the molecular disarray in the medium and consequent local fluctuations in its optical density, and the other type called the orientation scattering arising from the varying orientations of the molecules which are anisotropic. The density scattering is completely polarised, while the orientation scattering is depolarised to the extent of $6/7$. Due to the combined effect, the light scattered transversely is depolarised to some extent depending upon the proportion in which the two types of scattering exist. The above idea is based on the supposition that the scattering in a liquid is completely molecular in origin, *i.e.*, the ultimate scattering particles are the molecules of size small compared with the wave-length of light. Using incident unpolarised light, as also light polarised with electric vector respectively vertical and horizontal, different measures of the state of polarisation of the transversely scattered light are obtained, namely, ρ_u , ρ_v and ρ_h corresponding to the three cases. For any liquid where the scattering is really molecular in origin

$$\rho_h = 1 \text{ and } \rho_u = 2\rho_v/(1 + \rho_v) \dots \dots \dots \quad (1)$$

and consequently it is not necessary to measure all the three quantities separately. But once the above condition is not fulfilled, *i.e.*, when the particles in the medium can no longer be identified with the individual molecules but only with molecular clusters or aggregates, ρ_h does not have its limiting value unity, but is definitely less than 1 and the simple relation (1) between ρ_u and ρ_v given above will no longer be satisfied. Consequently it will be quite insufficient to measure ρ_u alone. In such a case it has already been shown by the author¹ that there is a simple general relation connecting

¹ R. S. Krishnan, *Proc. Ind. Acad. Sci. (A)*, 1935, 1, 782.

the three quantities ρ_u , ρ_v and ρ_h , namely,

$$\rho_u = (1 + 1/\rho_h)/(1 + 1/\rho_v) \quad \dots \quad \dots \quad \dots \quad (2)$$

Relation (1) is a special case of this very general relation. In any scattering experiment, therefore, it is highly necessary to make comparative studies of the intensity and state of polarisation of the scattered light with the incident light in the three different states of polarisation, in order to get a correct idea of the state of dispersion of the scattering particles in the medium. Any departure of the value of ρ_h from unity will at once indicate an appreciable size of the scattering particles.

The above method has been successfully employed by the author in the case of liquid mixtures in the neighbourhood of the critical solution temperature.² The observations furnished for the first time positive evidence for the existence of large clusters in liquid mixtures not only at the critical solution temperature but also at temperatures considerably above that temperature. It was, therefore, considered desirable to extend this sensitive method to the case of highly associated liquids in order to know more about the state of dispersion of the molecules in them. In the present investigation, a detailed study of the scattering of light in the first four members of the fatty acids, namely, formic acid, acetic acid, propionic acid and normal butyric acid, at different temperatures with the incident light in the three different states of polarisation. The experimental results have obviously an important bearing on some of the anomalies observed in these acids by the earlier investigators on light scattering.

2. Experimental Details.

Merck's extra pure sample of formic acid was further purified by re-distillation over pure anhydrous boric oxide (free from silicon) in an all-glass distillation apparatus. Extra pure glacial acetic acid (Merck's) was used as such without further chemical purification, whereas propionic acid and butyric acid were also purified by distillation over phosphorus pentoxide. The pure liquids were contained in small sealed bulbs about 2" in diameter of clear and homogeneous glass. They were rendered dust-free by repeated slow distillation *in vacuo* in the usual way before they were sealed off. Particular care was taken to see that the liquids were absolutely free from dust. The bulb containing the liquid to be examined was kept immersed in distilled water contained in a rectangular brass vessel provided with three glass windows for the incident and the scattered beams. The bath was heated electrically. The source of light and the optical arrangement were

² R. S. Krishnan, *Proc. Ind. Acad. Sci.*, (A), 1935, 1, 915; 1935, 2, 221.

the same as those employed in the earlier investigations of the author. Extraneous light, if any, coming out in the direction of observation was cut off by suitably blackening the bulb and the vessel and making observations at a distance of about 10" from the cell.

On inserting a double-image prism in the track of the incident beam and one in the track of the scattered beam (both of them oriented in such a way that the upper image as seen through them corresponded to vertical vibrations), it was found that in the case of acetic and formic acids the lowest image out of the four images observed was distinctly brighter than either of the middle two. The depolarisation factors ρ_u , ρ_v and ρ_h of the transversely scattered light were measured as usual with a double-image prism and a nicol using respectively incident unpolarised light, incident light polarised with vibrations vertical and horizontal. The value of ρ_h was found to be unusually less than its limiting value of 100 %. The observations were repeated with the four fatty acids at various temperatures. The relative intensity of scattering in these liquids at different temperatures was determined by using a photo cell in conjunction with a valve bridge amplifier, in the manner described in the author's earlier paper.³ The results are tabulated below.

The value of ρ_h is found to be less than 100 % in the case of the first two members at lower temperatures. This raises the question whether the observed value of ρ_h is genuine or is due to some errors in the experiment. Dust particles, if any, in the liquid would vitiate the results very much. But in the present experiment this question does not arise at all since the liquids used were completely free from dust. Another source of error is fluorescence. It was found that none of the liquids studied was sensibly fluorescent.

TABLE I.

Liquid	Nature of the container	ρ_h %	ρ_v %	ρ_u %
Acetic acid	Pyrex cross temp. = 25° C.	90	30.5	49.5
	Spherical bulb temp. = 25° C.	91	30	50
Formic acid	Pyrex cross temp. = 25° C.	88	31	51
	Spherical bulb temp. = 25° C.	87	30.5	49

³ R. S. Krishnan, *Proc. Ind. Acad. Sci.*, (A), 1935, 2, 221.

TABLE II.

(a) Formic acid (Bulb as container).

Tem- perature $t^{\circ}\text{C.}$	ρ_h (Observed) %	ρ_v (Observed) %	ρ_u (Observed) %	ρ_u Calculated from eqn. (1) %	ρ_u Calculated from eqn. (2) %	Relative intensity of scattering
25	87	30.5	49	47	50	1.2
41	90	27	47	43	45	1.1
55	91	24	40	39	40.5	1.05
70	93	21.5	36	35	37	1.0 (assumed)
90	100	18.5	30	32	32	1.2

TABLE III.

(b) Acetic acid (M.P. = 15°C.) (Bulb as container).

Temperature $t^{\circ}\text{C.}$	ρ_h (Observed) %	ρ_v (Observed) %	ρ_u (Observed) %	ρ_u Calculated from eqn. (1) %	ρ_u Calculated from eqn. (2) %	Relative intensity of scattering
20	91	33	52.5	50	52	1.3
25	91	31	50	47	50	1.3
45	93	23.5	40.5	38	40	1.25
60	95	22	38	36	37.5	1.2
80	96.5	19.5	33	32.5	33.5	1.0 (assumed)
93	100	18	29	30	30	1.0

TABLE IV. (c) Propionic acid (Bulb as container).

Temperature t° C.	ρ_h (Observed) %	ρ_v (Observed) %	ρ_u (Observed) %	ρ_u Calculated from eqn. (2) %	Relative intensity of scattering
25	100	27	42.0	42.5	1.00 (assumed)
42	100	23.5	37	38	1.05
60	100	19.5	33	33	1.11
75	100	17	28.5	29	1.25
85	100	16	27	27	1.33

TABLE V. (d) Normal Butyric acid (Bulb as container).

Temperature t° C.	ρ_h (Observed) %	ρ_v (Observed) %	ρ_u (Observed) %	ρ_u Calculated from eqn. (2) %	Relative intensity of scattering
25	100	20	34.5	33	1.08
45	100	19	32.5	32	1.00 (assumed)
60	100	16	27.5	27.5	1.00
74	100	13.5	24	24	1.08
88	100	11	18	20.5	1.19

where ρ_u and ρ_v are defined as the ratio of the intensity of the horizontal component to that of the vertical component of the scattered light and ρ_h is defined as the ratio of the intensity of the vertical component to that of the horizontal component. Column 5 in Tables II and III gives the values of ρ_u calculated from the observed values of ρ_v using the simplified relation (1). The column 6 in these tables gives the values of ρ_u calculated from the observed values of ρ_v and ρ_h using relation (2). It is seen that these calculated values of ρ_u are decidedly in better agreement with the observed values showing thereby that equation (1) is no longer true for these two acids.

Moreover, fluorescence, if any, would never have the effect of lowering the value of ρ_h . Another possible source of error in the measurement of depolarisation is the convergence of the incident beam. In the present case the diameter of the long focus lens employed for focussing the light emerging out of the square aperture was 4 cms. The light was brought to a focus at a distance of about 52 cms. from the lens. Consequently the angle of convergence is equal to 1/13th of a radian. This angle was further reduced to 3/52 radian inside the medium by the liquid in the rectangular cell. According to Gans⁴ and Ananthakrishnan⁵ the convergence correction for ρ_u is $\omega^2/8$, where ω is the angle of convergence, and for a convergence angle of 3/52 radian, the correction would be 0.0004. This is negligibly small compared with the high depolarisation of the fatty acids and consequently it can be neglected. The corrections for ρ_v and ρ_h are also likewise negligibly small.

In order to be sure that the observed values of the depolarisation were not vitiated by any irregularity in the walls of the container, a pyrex cross was made. Each of its arms was 3" long and 1½" in diameter. Strain free pyrex plates were fused on to the ends. This cross was connected to a flask. Acetic and formic acids were distilled dust-free into the cross from the flask, one after the other. The measurements of depolarisation were repeated at the room temperature with the cross as container. The readings taken with the bulb and the cross as containers are given in Table I. The two corresponding readings are quite in agreement within the limits of experimental error.

3. Discussion of Results.

The most striking characteristic of acetic and formic acids is that ρ_h is only about 90% at 25° C., showing thereby that the scattering in these liquids is no longer purely molecular in origin, but should be attributed to the presence of molecular clusters. The average size of these aggregates is not small compared with the wave-length of light. This fact is also evidenced from the accuracy with which the data satisfy the theoretical relation (2). As the temperature is increased, the value of ρ_h increases steadily and finally attains its limiting value of 100%. From this it naturally follows that the degree of association and the size of the molecular aggregates formed depend very much on temperature. The lower the temperature, the greater is the association and larger is the size of the clusters. In the case of propionic and butyric acids ρ_h is found to be always equal to 100%.

⁴ R. Gans, *Phys. Zeits.*, 1927, **28**, 661.

⁵ R. Ananthakrishnan, *Proc. Ind. Acad. Sci. (A)*, 1935, **2**, 133.

These two acids may also be associated to some extent ; but the degree of association is not so great as to be detected by the present experimental technique. In spite of the high value of ρ_u for formic acid, the value of ρ_h is least for this. From this it directly follows that of all the fatty acids, formic acid is the most highly associated one and the degree of association diminishes as the number of carbon atoms increases.

The intensity of scattering in acetic and formic acids shows some anomalies. On the basis of molecular theory, the orientation scattering in a liquid which depends on the number of molecules per unit volume, does not vary appreciably with rise of temperature ; whereas, the density scattering which is directly proportional to the absolute temperature T and the compressibility β increases with rise in temperature. Therefore, the total intensity of scattering in a liquid where the scattering is truly molecular, should rise with temperature. This fact is well illustrated in the case of propionic and butyric acids. On the other hand in the case of the first two members of the fatty acid series, the intensity of scattering diminishes at first with rise in temperature up to about $80^\circ C.$ and above this temperature it begins to increase. This also shows that at the ordinary temperatures the scattering in these two liquids is not in accordance with the molecular theory, but is influenced by the presence of large molecular aggregates.

In this connection it would be interesting to mention the anomalies observed by the earlier investigators on light scattering in these fatty acids. I. Ramakrishna Rao⁶ has determined the depolarisation of the transversely scattered light and the optical anisotropy of a large number of organic vapours, and in almost all the cases he finds that the molecular anisotropy in the liquid state is definitely less than that in the vapour state. The significant exceptions are formic acid and acetic acid where the anisotropy in the liquid state is greater than that in the vapour state. He has calculated the anisotropy from the observed value of the depolarisation using the modified formula of Ramanathan.⁷ The values of the anisotropy δ for these four fatty acids are given in the accompanying Table VI.

S. Ramachandra Rao⁸ has studied the variations of intensity and depolarisation factor of the transversely scattered light in the case of a large number of liquids. He finds that in almost all liquids the optical anisotropy as calculated from the depolarisation values using Ramanathan's modified formula, increases with rise in temperature. But in the case of acetic acid

⁶ I. Ramakrishna Rao, *Ind. Journ. Phys.*, 1927, 2, 61.

⁷ K. R. Ramanathan, *Ind. Journ. Phys.*, 1926-7, 1, 401.

⁸ S. Ramachandra Rao, *Ind. Journ. Phys.*, 1928, 3, 1.

TABLE VI.

No.	Liquid	δ in the vapour state	δ in the liquid state
1	Formic acid ..	33.3×10^{-3}	47×10^{-3}
2	Acetic acid ..	25.9×10^{-3}	36.2×10^{-3}
3	Propionic acid ..	23.5×10^{-3}	20.1×10^{-3}
4	Butyric acid ..	15×10^{-3}	16.5×10^{-3}

it is found that the optical anisotropy decreases from a value of 34×10^{-3} at 30°C . to 19×10^{-3} at 120°C . and above that temperature it increases steadily in the normal way. Formic acid was not included in his investigation as the values of its compressibility at different temperatures were not available. On the basis of molecular association this anomalous behaviour could be easily accounted for. The depolarisation factor arises not only from the actual anisotropy of the individual scattering particles, but also from their finite size. Consequently the anisotropy as calculated from the observed values of ρ_u without applying correction for the finite size of the molecular aggregates, is bound to give a higher value. Besides, the aggregates formed may also possess a higher effective anisotropy than the individual molecules themselves and consequently the anisotropy in the liquid state at the ordinary temperatures which is an aggregate of molecular clusters may be higher than that in the vapour state. This increase in the effective anisotropy will itself give rise to a higher value for the depolarisation factor ρ_u and also for the total intensity of scattering. As the liquid is heated up, the degree of association diminishes and the anisotropy decreases tending to attain its normal in the state of no association.

The present investigation furnishes for the first time definite experimental evidence for the existence of molecular clusters, of size not small compared with the wave-length of light in highly associated fatty acids. Further experimental work with other highly associated liquids and also with supercooled liquids is in progress.

In conclusion the author takes this opportunity to express his grateful thanks to Prof. Sir C. V. Raman, Kt., F.R.S., N.I., for his continued interest and guidance during the progress of this investigation.

5. Summary.

The variations in intensity and depolarisation factor of the transversely scattered light have been studied in detail in the case of the first four fatty

acids, namely, formic acid, acetic acid, propionic acid and normal butyric acid, with the incident light in the three different states of polarisation, namely, unpolarised, horizontally polarised and vertically polarised. In the case of formic and acetic acids at the room temperature the depolarisation factor ρ_h was found to be about 90% when the incident light is polarised with vibrations horizontal. This observation furnishes for the first time definite experimental evidence for the existence of large molecular aggregates in these highly associated liquids, of size not small compared with the wave-length of light.

ρ_h increases with rise in temperature and at about 90° C. it attains its limiting value of 100% in these two acids. The intensity of scattering also at first diminishes with rise in temperature in these two cases, contrary to the molecular theory of light scattering. It is shown that molecular association is distinctly the cause for the extraordinary behaviour of formic and acetic acids in the initial stages. Propionic and normal butyric acids do not show such anomalies.