

OPTICAL EVIDENCE FOR MOLECULAR CLUSTERING IN FLUIDS.

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1. Introduction.

IN order to explain certain peculiar diffraction haloes (Plotnikow Effect) observed by him when a strong beam of light passes through a column of liquid, Plotnikow¹ postulated the existence in fluids of large molecular aggregates of size comparable with the wave-length of light. *Prima facie*, it is difficult to accept Plotnikow's suggestion that in ordinary liquids such large molecular aggregates exist, and in a recent paper,² the present author has shown that the Plotnikow effect is not a true molecular phenomenon but is due to the presence of dust. Certain lines of evidence, however, suggest that temporary molecular groupings of relatively small size, may occur in liquids and liquid mixtures. This is the postulate of G. W. Stewart to which he has given the name "Cybotaxis", on which he bases an explanation of X-ray diffraction patterns in fluids. Ornstein and Zernike³ have postulated that in liquids at the critical temperature and in liquid mixtures at the critical solution temperature, large molecular clusters exist in order to account for the special opalescence proportional to λ^{-2} observed under these conditions. Placzek⁴ supports the same view. The object of the present investigation was to examine this question more thoroughly by specially delicate optical methods.

2. Two Possible Optical Methods.

Two methods, both based on the phenomena of light scattering, are available for examining the question whether molecular clusters exist in liquids. Theoretically as well as experimentally Mie⁵ and Rayleigh⁶ have shown that when the scattering particle ceases to be small in size in comparison with the wave-length of light, a definite asymmetry of scattering is

¹ J. Plotnikow and Nishigishi, *Phys. Zeits.*, 1931, **32**, 434.

² R. S. Krishnan, *Proc. Ind. Acad. of Sci.*, 1934, **1**, 44.

³ Ornstein and Zernike, *Proc. Amsterdam*, 1914, **17**, 793; 1916, **18**, 1520.

⁴ Placzek, *Physik. Zeits.*, 1930, **31**, 1052.

⁵ G. Mie, *Ann. d. Physik.*, 1908, **35**, 377.

⁶ Lord Rayleigh, *Scientific Papers*, **5**, 547.

observed, the scattering being more intense in the forward direction than in the backward direction. So far it has generally been assumed that in the case of dust-free liquids, except possibly in the immediate vicinity of the critical temperature, no such asymmetry is observed. But a very careful investigation may possibly show an appreciable difference in intensities even under ordinary conditions. This point is reserved for future study. The second method which is actually used in the present investigation, is based on a study of the depolarisation of the transversely scattered light. According to the theory of Rayleigh and Mie, a spherical particle of finite size gives a definite depolarisation only when the incident beam is unpolarised: when the incident beam is polarised with its vibrations vertical or horizontal, the light scattered transversely in the horizontal direction is also polarised, according to the scheme shown in Table I.

TABLE I.

Case	Nature of particle	Incident light unpolarised	Incident light polarised with Electric vector vertical	Incidental light polarised with Electric vector horizontal
1	Small spherical particles	$\rho_u=0$	$\rho_v=0$	$\rho_h \sim$
2	Spherical particles of finite size	$\rho_u < 1$	$\rho_v=0$	$\rho_h = \infty$
3	Small ellipsoidal particles.	$\rho_u = \frac{2\rho_v}{\rho_v+1} < 1$	$\rho_v < 1$	$\rho_h = 1$
4	Ellipsoidal particles of finite size	$\rho_u < 1$	$\rho_v < 1$	$\rho_h > 1$

Table I gives an analysis of the depolarisation of the scattered light for particles of varying size and shape. The depolarisation ρ is understood as the ratio of the intensity of the horizontal component to that of the vertical component of the transversely scattered light, the incident beam and the scattered beam both being assumed to lie in a horizontal plane. ρ_u signifies the depolarisation observed with incident unpolarised light, ρ_v and ρ_h , the depolarisations observed with incident light polarised with vibrations vertical and horizontal respectively. For spherical particles of finite size ρ_u becomes equal to zero and ρ_h becomes infinite. On the other hand, when the scattering particles are small in size but are ellipsoidal in shape, ρ_u and ρ_v are both less than unity, whereas ρ_h is equal to one, *i.e.*, the horizontal and the vertical components of the transversely scattered light are of equal

intensity for this case. But when the particles are ellipsoidal in shape and of finite size, the resultant of the two effects 1 and 2 is obtained. The most important point is that ρ_h becomes larger than unity in this case, *i.e.*, the horizontal component is more intense than the vertical component of the transversely scattered beam. A value of ρ_h greater than unity is termed as anomalous depolarisation and its magnitude affords an estimate of the approximate size of the scattering particles. The phenomena cited under case 2 are very easily observed with sulphur suspensions, whereas those described under case 4 are easily observed with starch and protein solutions.

3. Negative Results with Ordinary Liquids.

Pure dust-free acetic acid was transferred into a wide cylindrical tube with flat ends by slow vacuum distillation by the usual method of Martin. The cylindrical portion of the tube was blackened excepting for a small window for observation of the scattered light. The light entered the cell through the flat end. The cell was kept immersed in an outer rectangular glass cell containing water. A narrow parallel beam of light of square section was passed through the liquid, the incident light being polarised by a nicol. The light scattered transversely in the horizontal direction was observed through a double image prism. The direction of the incident electric vector was adjusted to be exactly horizontal. The two images appeared to be of equal intensity. Rotation of the plane of polarisation of the incident light did not produce any reversal of polarisation; ρ was always ≤ 1 .

The visual observations were confirmed by the photographic method. A series of photographs of the scattered light was taken from different directions of the incident electric vector about the mean horizontal position. The comparison of the intensities of the two images in each case was made with the aid of a microphotometer set up temporarily by using a vacuum Thermocouple and a Zernike galvanometer. For any position of the incident polarising nicol, the depolarisation was always found to be ≤ 1 . This case was thus found to be analogous to the case 3 of Table I.

The failure to detect any trace of anomalous depolarisation clearly shows that molecular clusters of size comparable with the wave-length of light may not be present at all in ordinary fluids, or, even if they exist, the size may not be large enough to give a detectable effect with the experimental arrangement used. The same negative result was obtained with methyl alcohol, acetone, chlorobenzene, normal heptane and allyl alcohol, observations being made at the room temperature.

4. *Positive Results with Binary Liquid Mixtures.*

A mixture of pure dust-free carbon disulphide and methyl alcohol in the ratio (3:1) was transferred into a small thick bulb by repeated slow vacuum distillation. The bulb containing the dust-free mixture was evacuated and sealed off at the neck. It was blackened on the outside excepting for three windows. The mixture was slowly heated up by immersing the bulb in a water-bath contained in a copper vessel provided with three glass windows for incident and scattered beams, the water being heated electrically.

The water in the bath was maintained at $40^{\circ}\cdot5\text{C}$. at which the two liquids mixed together completely to form a homogeneous fluid. The transversely scattered light was studied photographically and the amount of depolarisation was measured for incident polarised as well as unpolarised light, the observations being repeated for temperatures above the critical solution temperature T_c° . The depolarisation values are tabulated as shown below.

TABLE II.

Temperature of Mixture	ρ_u	ρ_v	ρ_h
$40^{\circ}\cdot5\text{C}$.	0.026	0.013	4.90
$46^{\circ}\cdot0\text{C}$.	0.030	0.015	1.60
$51^{\circ}\cdot0\text{C}$.	0.041	0.020	1.40
$56^{\circ}\cdot0\text{C}$.	0.060	0.028	1.28
$61^{\circ}\cdot5\text{C}$.	0.080	0.038	1.00

The photographs are reproduced in the plate. In the plate given, each set corresponds to a particular temperature of the mixture; (a) corresponds to the temperature of $40^{\circ}\cdot5\text{C}$., *i.e.*, the critical solution temperature T_c° ; (b) to 46°C .; (c) to 51°C . and (d) to 56°C . Each set consists of three pairs of images of the scattered light, the upper pair corresponding to incident unpolarised light, the middle and the lower ones correspond to incident light polarised with vibrations vertical and horizontal, the incident and the scattered beams both lying in a horizontal plane. In each pair the upper image represents the intensity of the vertical component of the scattered light, and the lower image represents the intensity of the horizontal component. In each case the upper image or the vertical component is more

intense than the horizontal component. But when the incident beam is polarised with vibrations horizontal, the horizontal component is distinctly more intense than the vertical component as is seen from the last pair in each set. The anomalous depolarisation is found to be maximum at $40^{\circ}\cdot5\text{C}$., *i.e.*, at the critical solution temperature. Anomalous depolarisation gets progressively diminished as temperature is raised above T_c° . Even for a considerable range of temperature say for 15°C . above the critical point, the anomalous depolarisation is detectable. However, at $61^{\circ}\cdot5\text{C}$. it ceases to be observable, the two components of the scattered light being of equal intensity when the light is polarised with vibrations horizontal.

Observations by Ornstein, Zernike,⁷ Andant⁸ and others have shown that very near the critical temperature the ordinary laws of scattering break down and the light is scattered with intensity varying as λ^2 and not as λ^4 . This has been explained by Zernike and others by postulating the presence of molecular clusters in the immediate vicinity of the critical solution temperature. The interesting point about the present experiment is that the method used is so delicate that it has made it possible to detect the anomalous depolarisation even far remote from the critical solution temperature which is an indication that molecular clusters are present not only in the immediate vicinity of T_c° but also at temperatures far remote from it.

5. Conclusion.

The above experimental observations give a definite positive evidence for the formation of large molecular clusters of size comparable with the wave-length of light far remote from the critical solution temperature. According to the theory of Raman and Ramanathan⁹ on the scattering of light by fluid mixtures, the scattering arises from (1) the spontaneous local fluctuations in the composition of the mixture, (2) to the local fluctuations in density, and (3) the varying orientations of the molecules. But in the neighbourhood of the critical solution temperature the composition scattering becomes enormous and consequently the depolarisation ρ_u should be negligible. On the other hand, a definite value for the depolarisation ρ_u say, to the extent of 3%, has been observed by Kameswara Rav¹⁰ and others. In all probability this arises from the fact that molecular clusters are formed near T_c° and the scattering due to finite size also influences the depolarisation ρ_u . Since the anomalous depolarisation is

⁷ Ornstein and Zernike, *loc. cit.*

⁸ M. A. Andant, *Ann. d. Physique*, 1924, **1**, 346.

⁹ Raman and Ramanathan, *Phil. Mag.*, 1923, **45**, 213.

¹⁰ Kameswara Rav, *Proc. Indian Assoc. Cultivation of Science*, 1925-26, **9**, 19.

maximum at T_c° , the clusters attain their maximum size at that temperature and above T_c° , they still exist over a considerable range of temperature, though the size gets progressively smaller.

The definite depolarisation observed by Ramachandra Rao,¹¹ in the case of simple liquids in the neighbourhood of the critical temperature may in all probability be a direct consequence of the formation of molecular clusters of finite size in fluids in the immediate vicinity of T_c° .

A more detailed study of the phenomenon involving also the measurement of the intensity of the scattered light is in progress. The experimental investigations will soon be extended to the case of other binary mixtures, emulsions, and protein solutions under various pH values.

The author takes this opportunity to express his grateful thanks to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for suggesting the problem and for rendering valuable help and guidance during the progress of this investigation.

6. Summary.

It is pointed out that the presence of molecular clusters in fluids of size comparable with the wave-length of light should be capable of detection by two optical methods, one based on the asymmetry of scattering, and the second based on the anomalous depolarisation of scattered light. In this investigation the second method is developed. Ordinary liquids did not give any positive evidence for the existence of large molecular aggregates at room temperatures. A mixture of carbon disulphide and methyl alcohol when examined gave definite evidence for the formation of molecular clusters in the mixture by the observation of the anomalous depolarisation. This method is so delicate that it has made it possible to detect the presence of molecular clusters in the mixtures even at temperatures considerably removed from the critical solution temperature.

¹¹ Ramachandra Rao, *Ind. J. Phys.*, 1927, 2, 7 & 179.

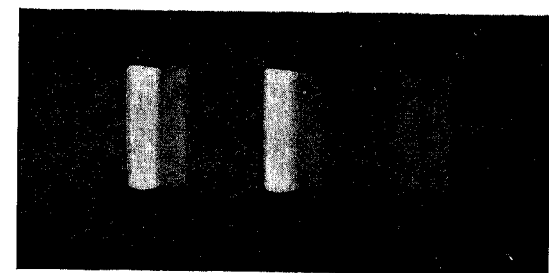


FIG. 4.

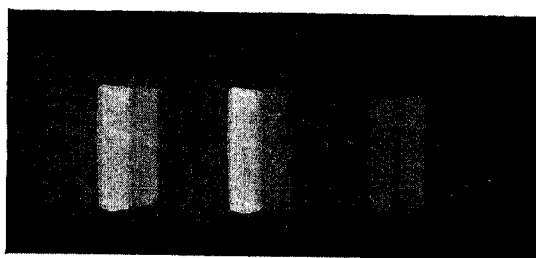


FIG. 3.

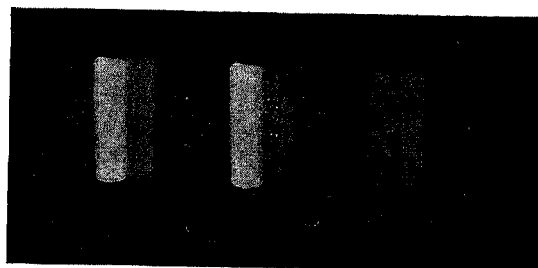


FIG. 2.

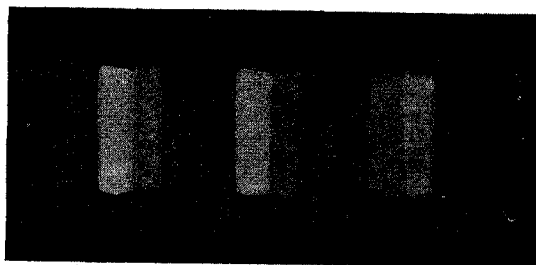


FIG. 1.

$\rho_u \leftarrow$

$\rho_v \leftarrow$

$\rho_h \leftarrow$