

# STUDIES ON LIGHT-SCATTERING IN EMULSIONS.

## Part I. Dilute Simple Emulsions.

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### 1. *Introduction.*

It is well known that by suitable treatment of two pure immiscible liquids, e.g., oil and water, fairly stable emulsions of oil in water are obtained. Such emulsions are usually termed as dilute simple emulsions since the concentration of oil is small and there is no stabilising agent present in the system. Such dilute emulsions which closely correspond to colloidal suspensions, are often called as oil hydrosols. The oil globules in these emulsions have diameters of the order of  $10^{-5}$  cm. It is believed that the emulsified droplets of one liquid in another are spherical in shape and isotropic in structure. Ultramicroscopic investigations which do not reveal any scintillations, however, support this view. Among the methods available the most delicate and useful method for the determination of the size, shape and structure of the emulsified particles is that based on the study of the depolarisation of the light scattered by these solutions. The intensive study of the state of polarisation of the scattered light with the incident light in different states of polarisation, namely, (1) unpolarised, (2) polarised with vibrations perpendicular to the plane containing the incident and scattered beams and (3) polarised with vibrations parallel to this plane, and its dependence on the wave-length of the incident light in a large number of colloidal solutions has resulted in great advances in our knowledge of the size, shape and structure of particles contained in them (Krishnan, 1937). A similar intensive study of the scattered light in dilute simple emulsions may well be expected to advance notably our knowledge of the size and shape of the droplets contained in these emulsions. Very little work has been done up till now in this direction. Some preliminary measurements of the depolarisation factors  $\rho_u$ ,  $\rho_v$  and  $\rho_h$  have been made by D. S. Subbaramaiya (1935) for castor-oil emulsions in water. His observations indicate that the emulsified particles have a definite optical anisotropy which seems to be too great to be accounted for by the Brownian oscillations in shape of the

particles. Droplets sticking together forming irregularly shaped groups may give rise to some anisotropy. But it is hard to believe the existence of such irregularly shaped groups especially in emulsions in which the oil content is small and no stabilising agent is present. The surface forces will always try to make the drops spherical. The present investigation was therefore undertaken in order to obtain sufficient data concerning the depolarisation factors  $\rho_u$ ,  $\rho_v$  and  $\rho_h$  in a large number of typical dilute simple emulsions, which would throw some light on the shape and structure of these emulsified droplets.

## 2. Experimental Details.

Two methods were employed for the preparation of the emulsions. The first method consists in boiling a large quantity of double distilled water into which one or two drops of the oil were added, in a flask fitted with a reflux condenser. After a day, the system was allowed to cool and the emulsion was transferred to a bottle with the aid of a separating funnel which removed the separate oil layer from the emulsion.

TABLE I.

Oil	Method of preparation	Filter used if any	$\rho_v$ %	$\rho_h$ %	$\rho_u$ %
Castor oil	1	Red filter	0.42	1.97	19.8
		Orange filter	0.36	1.73	21.7
		Blue filter	0.3	1.1	28.1
	2	Red filter	0.9	14.7	6.7
		Orange filter	0.77	8.8	7.2
		Blue filter	0.7	5.8	10.6
Paraffin oil	1	White light	0.45	0.8	42
	2	„ „	0.48	9.3	6.2
Bergmont oil	1	White light	0.7	2.1	39
	2	„ „	0.9	3.1	25.6
Lavender oil	1	White light	0.5	2.2	26.9
	2	„ „	1.1	3.1	38.3
Lemon oil	1	White light	0.62	1.4	43.3
	2	„ „	1.1	2.1	55.2

The second method consisted in dissolving a drop of the oil in about 5 c.c. of alcohol. 1 c.c. of the resulting alcohol solution was poured into a large quantity of double distilled water contained in a clean bottle. An emulsion resulted at once. Thus emulsions of the following oils were prepared: (1) castor oil, (2) paraffin oil, (3) bergmont oil, (4) lavender oil and (5) lemon oil.

The depolarisation measurements were made by the usual Cornu method. In some cases the measurements of  $\rho_v$  and  $\rho_h$  were very difficult because of the feeble intensity of the weaker components. Only in the case of castor oil it was possible to measure the depolarisation factors with coloured filters in the path of the incident beam. The values of  $\rho_u$ ,  $\rho_v$  and  $\rho_h$  are given in Table I.

### 3. Discussion of Results.

The values of  $\rho_v$  and  $\rho_h$  are very small in the emulsions studied showing thereby that the anisotropy of structure or the anisometry of shape of the droplets is very small. According to Mie's theory, if the droplets are spherical in shape and isotropic in structure  $\rho_v$  and  $\rho_h$  will be equal to zero. A finite though very small value of  $\rho_v$  has been observed. A comparative study of the values of  $\rho_u$ ,  $\rho_v$  and  $\rho_h$  shows that the droplets in the emulsions prepared by the first method, *i.e.*, by boiling, are bigger in size than those in the emulsions prepared by the second method. It has been noticed that for the same concentration of oil the emulsion prepared by the second method is more opalescent than the emulsion prepared by the first method. This is because in the second method the droplets are formed by the aggregation of oil molecules which are dispersed in the alcoholic solution. In the first method, on the other hand, the oil is dispersed by boiling and as such the disintegration cannot be extended to the limit. The emulsion prepared by this method will naturally contain a smaller number of bigger droplets. The size of the droplets can be calculated approximately from Mie's theory taking into consideration the relative refractive index of the oil with respect to that of water. The diameters of the particles vary from  $1 \times 10^{-5}$  to  $5 \times 10^{-5}$  cm.

The depolarisation factors exhibit appreciable dispersion. The type of dispersion observed in these emulsions is different from that observed in liquid mixtures very near the critical solution temperatures and in sols of platinum, selenium, tellurium, stearic acid, vanadium pentoxide, ferric hydroxide, etc. (Krishnan, 1937). In the latter case  $\rho_u$  and  $\rho_v$  increase with diminution in wave-length and  $\rho_h$  decreases. In the case of emulsions, on the other hand,  $\rho_u$  increases and  $\rho_v$  and  $\rho_h$  diminish with diminution in wave-length. If the value of  $\rho_u$  observed in these emulsions is really due to the

genuine optical anisotropy of the droplets,  $\rho_v$  should have the same type of dispersion as in the case of the ordinary sols mentioned above. The fact that the dispersion of  $\rho_v$  is in the opposite direction indicates that the finite value of  $\rho_v$  is not due to lack of spherical symmetry of shape or structure of the droplets. The finite value of  $\rho_v$  can be attributed to the following :—  
 (1) the presence of depolarised scattering of the surrounding medium, *i.e.*, water, (2) the anisotropy arising from the Brownian oscillation in shape of the droplets and (3) the presence of depolarised secondary scattering.

1. *Depolarised scattering of water.*—The depolarisation factor  $\rho_u$  of water is 9 per cent. and hence  $\rho_v$  will be equal to 4.7 per cent. Let us suppose that the light scattered by the droplets is completely polarised when the incident beam is polarised with vibrations vertical, *i.e.*,  $V_v$ \* is finite and  $H_v$  is zero. If the component  $V_v$  for the droplets is nine times more intense than the component  $V_v$  for water, *i.e.*, the total intensity of light scattered by the particles is about ten times that of the light scattered by water, the value of  $\rho_v$  for the emulsion will be equal to 0.5 per cent. Observations with the naked eye, however, indicate that the scattering power of water is very much feebler. Moreover, if the finite value of  $\rho_v$  can be explained on the basis of the depolarised scattering due to water, with diminution in wave-length the relative scattering power of water should increase more rapidly than that of the droplets and consequently the values of  $\rho_v$  and  $\rho_h$  should show a corresponding increase in the region of shorter wave-lengths. This is not actually the case. It follows therefore that the scattering of water does not influence the depolarisation factors to any appreciable extent.

2. *Brownian oscillation in shape of the droplets.*—It is well known that suspensions of fine particles, fine grained emulsions and colloidal solutions, all show under the ultramicroscope that the particles of the dispersed phase are in continuous zigzag motion, called the Brownian motion. As the size of the particles decreases the Brownian movements become very rapid. The droplets of oil in emulsions, in the course of the Brownian movements, collide against one another and in consequence they are deformed. The extent of deformation depends on the size of the droplets and also on the surface tension of oil in relation to water. After the collision the deformed droplets begin to execute a series of oscillations about the spherical shape. In the deformed state the droplets become optically anisotropic and they depolarise the light scattered by them. The anisotropy arising from the deformation can be calculated from a knowledge of the surface tension, the

\*  $V_v$  and  $H_v$  have the same significance as in the paper (R. S. Krishnan, *Proc. Ind. Acad. Sci.*, (A), 1938, 7, 21).

radius of the original droplet in the equilibrium position and the temperature of the emulsion. The energy of oscillation of each droplet is equal to  $\frac{1}{2} kT$ . As a first approximation we can consider the shape of the deformed droplets as a prolate spheroid of axial ratio B/A. Table II gives the

TABLE II.

Radius of the droplet in the equilibrium position in Å.U.	B/A, the axial ratio of the prolate spheroid	Optical anisotropy of the prolate spheroid	$\rho_v$ for the light scattered by the prolate spheroid
10	0.76	$9.09 \times 10^{-3}$	0.5%
50	0.957	$2.18 \times 10^{-4}$	0.013
100	0.98	$4.56 \times 10^{-5}$	0.003
250	0.99	$1.11 \times 10^{-5}$	0.0006
500	0.996	$1.77 \times 10^{-6}$	<0.0001
1000	0.998	$4.4 \times 10^{-7}$	<0.0001

values of the optical anisotropy in the deformed state for droplets of various sizes. It is seen from the above table that for droplets having diameters of the order of 1000 Å.U. the optical anisotropy is extremely small and the value of  $\rho_v$  arising therefrom is almost nothing. Hence it is obvious that Brownian oscillation in shape of the droplets by itself cannot explain the finite values of  $\rho_v$  and  $\rho_h$  observed in emulsions.

3. *Depolarised secondary scattering.*—The principle underlying the theory of secondary scattering is that when a beam of linearly polarised light is incident on the droplets each individual droplet becomes a luminous source and sends out radiations, called the primary scattering. This, in turn, forms a source of exciting radiation. Each individual droplet under the influence of the primary scattering by all the other droplets, becomes a secondary luminous source and sends out radiations which can be called as secondary scattering. Since the intensity of the primary scattering increases as the size and number of droplets increases, the intensity of the secondary scattering also increases and influences the observed depolarisation values. In the case of simple dipole oscillators the intensity of the secondary scattering and the depolarisation arising therefrom can be calculated by applying Rousset's theory (Rousset, 1934). But in the case of droplets of size

not small compared with the wave-length, the calculations are rather complicated since under the influence of the primary incident wave each droplet becomes a complex oscillator. *Prima facie*, it is evident that effect of the secondary scattering is to depolarise the light scattered in the transverse horizontal direction when the incident beam is linearly polarised, *i.e.*, to increase the values of  $\rho_v$  and  $\rho_h$ .

The effect of the secondary scattering on  $\rho_v$  and  $\rho_h$  was tested out in the following way: By pouring an alcoholic solution in water emulsions of different turbidity can be obtained. It was found that when the turbidity was maximum the factors  $\rho_v$  and  $\rho_h$  were also maximum. On diluting the turbid solution with water,  $\rho_v$  and  $\rho_h$  were found to fall down in value. Beyond a certain dilution the measurements of  $\rho_v$  and  $\rho_h$  became extremely difficult. It can, therefore, be inferred that the finite values of  $\rho_v$  and  $\rho_h$  observed in the various emulsions studied, are due to the presence of depolarised secondary scattering. This explains why in the emulsions prepared by the second method the values of  $\rho_v$  and  $\rho_h$  are comparatively higher.

In conclusion, the author takes this opportunity to express his respectful thanks to Professor Sir C. V. Raman for his kind interest in the work.

#### 4. Summary.

Measurements of the depolarisation factors  $\rho_u$ ,  $\rho_v$  and  $\rho_h$  have been made in some typical dilute simple emulsions. Two methods have been employed for the preparation of these emulsions: (1) by boiling a mixture of water and a few drops of the oil and (2) by pouring an alcoholic solution of the oil into a large quantity of water. The values of  $\rho_v$  and  $\rho_h$  are of the order of 0.5 per cent. and 2 per cent. respectively for most of the emulsions. Depolarisation measurements indicate that the droplets in the emulsions prepared by the first method are bigger in size than those in the emulsions prepared by the second method. The depolarisation factors exhibit appreciable dispersion. It is shown that the droplets in dilute simple emulsions are spherical in shape and that the observed finite values of  $\rho_v$  and  $\rho_h$  are due to the existence of depolarised secondary scattering.

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