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EFFECT OF CONVERGENCE ON DEPOLARISATION MEASUREMENTS IN COLLOID SCATTERING

BY K. VIJAYARAGHAVAN* AND R. S. KRISHNAN

. (Department of Physics, Indian Institute of Science, Bangalore-3)

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Abstract

The effect of convergence on the three depolarisation factors ρ_u , ρ_v and ρ_h has been investigated in the case of five different colloidal solutions. It is observed that while the values of ρ_u and ρ_v increase with the angle of convergence irrespective of the nature of the colloid, the value of ρ_h decreases with the angle of convergence in those cases where the particle size is very small compared with the wavelength of light, *i.e.*, corresponding nearly to the case of molecular scattering. For a scattering medium consisting of particles of bigger size, the value of ρ_h is found to increase with the angle of convergence. The convergence errors of ρ_u , ρ_v and ρ_h for a colloid are found to be much larger than those given by Ananthakrishnan's formulæ for molecular scattering. The actual values of the errors depend not only on the angle of convergence but also on the nature of the colloidal medium under investigation.

I. INTRODUCTION

It is well known that when a parallel beam of light traverses a liquid medium, the scattered light in the transverse direction is depolarised. The ratio of the weaker to the stronger of the two mutually perpendicular components of the scattered light is defined as the depolarisation factor. The theoretical

^{- *} Lecturer in Physics in the Annamalai University.

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investigations and the interpretation of experimental results in light scattering are based on the assumption that the incident light is strictly parallel and the direction of observation is truly at right angles to the incident beam. In practice, it is difficult to secure a parallel beam of light with requisite intensity for scattering experiments. Usage of a condensing lens while furnishing increased intensity at the focus involves convergent rays and it is only the axial ray that is transverse to the direction of observation. As the ideal conditions specified in the theory are not realised in practice, the observed values of the depolarisation factors have to be corrected for. The difference between the depolarisation factor measured with incident convergent light and that with parallel light is referred to as the convergence error. The magnitude of this correction becomes appreciable in the case of scattering media having low depolarisation factors, such as gases.

The effect of convergence on depolarisation measurements was theoretically investigated by Cabannes (1921), Ramanathan and Srinivasan (1926), Gans (1927), Rao (1927) and Ananthakrishnan (1935). Their investigations, however, were restricted to the case of molecular scattering, *i.e.*, where the particles in the scattering medium were very small compared with the wavelength of light. Gans and Ananthakrishnan independently obtained $\theta^2/2$ as the correction to be applied to the depolarisation factor for incident unpolarised light, where θ was the semi-angle of convergence.

The case of large particles of any shape and structure, such as are met

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with in colloids, does not lend itself easily to theoretical treatment. So, it was thought desirable to experimentally investigate the magnitude of the convergence error in the case of a representative selection of colloids. The three depolarisation factors, ρ_u , ρ_v and ρ_h and the corresponding corrections for the different colloids for various angles of convergence are reported in this paper. (ρ_h is defined here as the ratio of the intensity of the vertical to that of the horizontal component of the scattered light, when the incident light is polarised with vibrations horizontal.)

2. EXPERIMENTAL DETAILS

Measurements were carried out inside a dark cabin into which was let in a horizontal beam of sun light reflected by a single mirror Foucault heliostat kept outside. The beam of light was condensed by means of a large aperture lens of 15 cm. focal-length on to a glass cell containing the colloidal solution. The usual precautions were taken to eliminate parasitic illuminations. The state of polarisation of the scattered track in the transverse horizontal direction was measured by the Cornu method using a doubleimage prism and a nicol. The observations were restricted to the focal plane. A nicol of suitable aperture was placed in the path of the incident beam. In order to vary the angle of convergence of the incident beam, eight circular apertures of different diameters were used as stops for the condensing lens. The angle of convergence varied from about 31° to about 1°. Due to refraction, the effective convergence inside the colloid would be different from that outside. This was corrected for by taking the refractive index of the solvent, water, as 4/3.

For each colloidal solution the depolarisation factors ρ_u , ρ_v and ρ_h were first measured using incident parallel light. Subsequently, the measurements were repeated for convergent light, the angle of convergence being varied. Measurements of ρ_u , ρ_v and ρ_h were also made using vertical and horizontal slits covering the condensing lens. These slits were of the same length as the diameter of the lens, but their widths were of the order of 4 mm. Similar measurements were also made for dust-free ether and for a rectangular block of methyl methacrylate glass.

3. RESULTS

The values of the depolarisation factors corresponding to the different angles of convergence for seven different scattering media have been given in Tables I to VII. Columns 5, 6 and 7 of Tables I to V give the values of $\Delta \rho_u$, $\Delta \rho_v$ and $\Delta \rho_h$ respectively. $\Delta \rho$ is defined as the difference between the observed values of ρ for any angle of convergence and ρ_0 , *i.e.*, the value of ρ for parallel light. In the last column of the same tables are entered the values of $2\Delta \rho_v/(1 + \Delta \rho_v)$. Columns 5 and 7 of Tables VI and VII give the values of $\Delta \rho_u$ and $\Delta \rho_v$ for these two cases, while columns 6 and 8 give the theoretical convergence corrections for ρ_u and ρ_v , *i.e.*, $\theta^2/2$ and $\theta^2/4$ respectively. These are the correction factors given by Ananthakrishnan (1935) for molecular scattering. Table VIII gives the values of ρ_u , ρ_v and ρ_h for the seven different scattering media for parallel light and for $2\theta = 24\frac{1}{2}^\circ$.

4. DISCUSSION

A perusal of the values given in Tables I to VIII shows that irrespective of the nature of the colloid, the observed values of ρ_u and ρ_v progressively increase with increase in the angle of convergence. But the value of ρ_h , on the other hand, increases with the angle of convergence only in the case of those colloids for which ρ_h for parallel light is very much less than 100%, *i.e.*, the particles are not small compared with the wavelength of light. This

Angle of Conver- gence in radians 2θ	Р и %	ρ, %	Δρ1 %	Δρ. %	Δρ. %	Δρ. %	$\frac{2\Delta\rho_{o}}{1+\Delta\rho_{o}}\%$
. 0	32.0	6.2	20.8				
-014	32.0	6.2	20.8				·
·021	32.0	6.2	20.8				
-051	34.7	7.9	23.8	2.7	1.7	3.0	3.4
-102	43.8	12.2	33.3	11.8	6.0	12.5	11.3
·149	49·0	14.7	42.9	17.0	8.5	22.1	15.7
·207	54.8	19.8	49.0	22.8	13.6	28.2	23.9
·243	63.3	23.8	56.8	31.3	17.6	36.0	29.9
-428	70.4	29.5	61 • 0	38.4	23.3	40.2	37.8
Vertical Slit	70.4	29.5	61.0				
Horizontal Slit	32.0	6.2	21.3				

TABLE I Graphite Sol with Orange Filter

TABLE II

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Angle of Conver- gence in radians	ρ. %	P. %	Рж %	Δρ. %	Δρ. %	Δρ. %	$\frac{2\Delta\rho_{o}}{1+\Delta\rho_{o}}\%$
0	11.9	3.1	32.0				
·014	11.9	3.1	32.0				
-021	11.9	3.1	32.0			L	
·051	12.5	3.6	34.7	0.6	0.5	2.7	1.0
·102	17.2	6.7	40.6	5.3	3.6	8.6	6.9
·149	28.3	11.9	52.8	16.4	8.8	20.8	16.2
·207	33.3	14.7	61.0	21.4	11.6	29.0	20.8
·243	39.0	18.9	64.4	27 . 1	15-8	32.4	27.3
· · 428	52.8	28.3	71.7	40.9	25.2	39.7	40.2
Vertical Slit	52.8	28.9	70.4			*****	
Horizontal Slit	11.9	3.1	32.0				

Stearic Acid Sol with Red Filter

TABLE III

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Angle of Conver- gence in radians	ρ. %	P*	Ph %	Δρ. %	Δρ. %	Δρ.	$\frac{2\Delta\rho_{\rho}}{1+\Delta\rho_{\rho}}$ %
0	8.2	2.2	32.0				
·014	8.2	2.2	32.0			•	
·021	8.2	2.2	32.0				
·051	9.4	2.8	34.7	1.2	0.6	2.7	1.2
·102	9.9	3.3	40.6	1.7	1 • 1	8.6	2.2
·149	17.2	6.5	47.3	9.0	4.3	15.3	8-3
·207	27 • 1	11 • 9	54.8	18-9	9.7	22.8	17.7
·243	37.6	18.5	70.4	29.4	16.3	38.4	28.0
· 428 ·	50.9	29.5	81.0	42.7	27.3	49·0	42-9
Vertical Slit	50.9	29.5	81.0			5 TAS	
Horizontal Slit	8.2	2.2	32.0				

Arsenic Trisulphide Sol with Red Filter .

TABLE IV

Sulphur Suspensions with Red Filter

Angle of Conver- gence in radians	ρ. %	P. %	Рж %	Δρ. %	Δρ. %	Δρ.	$\frac{2\Delta\rho_{\bullet}}{1+\Delta\rho_{\bullet}}\%$
0	18.9	2.4	14.7				
-014	18.9	2.4	14.7				
·021	18.9	2.4	14.7				
·051	19.8.	2.9	16.3	0.9	~0.5	1.6	1.0
.102	26.0	6.2	19.8	7 · 1	3.8	5 · 1	7.3
-149	33.3	10.6	28.3	14.4	8.2	13.6	15-2
·207	42.9	15.5	37.6	24.0	13.1	22.9	23.2
·243	56-8	23.8	49.0	37.9	21.4	34.3	35.3
·428	67.9	35.4	63.3	49.0	33.0	48.6	49.6
Vertical Slit	67.9	35.4	63.3				
Horizontal Slit	18.9	2.4	14.7				

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TABLE V

Gelatine Solution with Pinkish Violet Filter

Angle of Conver- gence in radians	ρ _u . %	ρ. %	ρ. %	Δρ. %	Δρ. %	Δρ <u>h</u> %	$\frac{2\Delta\rho_{,}}{1+\Delta\rho}\%$
0	2.5	0.77	47.3				
·014 ·	2.5	0.77	47.3				
-021	2.5	0.77	47.3				
·051	3.1	1.10	49.0	0.6	0.33	1.7	0.66
·102	4.5	1.98	54.8	2.0	1.21	7.5	2.4
·149	6.7	2.8	63 · 3	4.2	2.03	16.0	3.98
-207	9.5	4 · 1	67.9	7.0	3.33	20.6	6.5
·243	13.9	6.2	72.9	11.4	5.43	25.6	10.3
-428	18.9	9.4	81.0	16.4	8.63	33.7	15.9
Vertical Slit	19.4	9.4	81.0				
Horizontal Slit	2.5	0.77	47.3			5811	00000

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TABLE VI

Angle of Conver- gence in radians (2θ)	ρ ₄ %	P. %	Рл %	Δρ. %	θ²/2 %	Δρ . %	θ²/4 %	Δρ. %	$-\frac{\theta^2}{4 ho_o}\%$
0	11.5	5.77	90.1						
·012	11.5	5.77	90.1						
·018	11.5	5.77	90.1						
-045	11.5	5.77	90-1						
·091	11.7	5.77	90.1	0.2	0.11		0.053		
·133	11.9	5.99	88.5	0.4	0.23	0.22	0.12	-1.6	-1.9
·187	12.2	5.99	88.5	0.7	0.44	0.22	0.22	-1.6	-4.0
•217	12.5	6.22	86.9	1.0	0.6	0.45	0.3	-3.2	-4.8
·367	13.3	6.69	85.5	1.8	1.69	0.92	0.85	-4.6	-13.6
Vertical Slit	13.3	6.69	85.5					• • • • •	
Horizontal Slit	11.2	5.77	90.1						•

Plastic Slab with Orange Filter

Effect of Convergence on Depolarisation Measurements

TABLE VII

Angle of Conver- ence in radians (2θ)	ρ <u>u</u> %	P. %	Δρ. %	θ²/2 %	Δρ. %	θ²/4 %
0	8.2	4.3				
-0134	8.2	4.3				
-021	8.2	4.3				
·051	8.2	4.3				
-101	8.35	4.3	0.15	·13		0.07
·148	8.5	4.44	0.3	·27	0.14	0.14
·207	8.8	4.52	0.6	· 54	0.22	0.27
·240	9.1	4.71	0.9	•72	0.41	0.36
· 407	10.3	5.33	2.1	2.07	1.03	1.04
Vertical Slit	10-3	5.3				
Horizontal Slit	7.7	4.3				

Ether with Orange Filter

SI N	. Scattering o. Medium		Ржо %	ρ %	Рло %	Рид %	ρ _{υθ} %	Ржө. %	Δρ. %	Δρ. %	Δρ. %
1	Graphite .		32.0	6.2	20.8	70.4	29.5	61.0	38.4	23.3	40.2
2	Stearic acid		11.9	3.1	32.0	52.8	28.3	71.7	40.9	25.2	39.7
3	Arsenic trisulphide	:	8.2	2.2	32.0	50.9	29.5	81.0	42.7	27.3	49.0
4	Sulphur suspension	ns	18.9	2.4	14.7	67 • 9	35.4	63.3	49.0	33.0	48.6
5	Gelatine solution .		2.5	0.77	47.3	18.9	9.4	81.0	16.4	8.6	33.7
6	Plastic slab .		11.5	5.77	90.1	13.8	6.8	85.5	2.3	1.03	-4.6
7	Ether	••	8.2	4.3	100	10.5	5.45	••	2.3	1.05	••

 ρ_{u_c} , ρ_{v_0} and ρ_{h_0} are the depolarisation factors for parallel light.

 $\rho_{u\theta}$, $\rho_{v\theta}$ and $\rho_{h\theta}$ are the depolarisation factors for convergent light with the angle of convergence $2\theta = 24^{\circ}30'$.

behaviour is entirely different from what has been predicted by Ananthakrishnan for molecular scattering, namely, the decrease of ρ_h with increase in the value of θ . Besides, the increases in the values of ρ_u and ρ_v are many

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times more than the values of the theoretical correction factors, $\theta^2/2$ and and $\theta^2/4$ for the case of molecular scattering. It is therefore clear from the results reported here that the convergence corrections applicable to molecular scattering media are not applicable to colloids containing particles not small compared with the wavelength of light. It is indeed surprising to note that whatever may be the angle of convergence, $\Delta \rho_u$ is found to be nearly equal to $2\Delta \rho_v /(1 + \Delta \rho_v)$. See the values given in columns 5 and 8 of Tables I to V.

In the case of ether, the values of ρ_u , ρ_v and ρ_h vary with the angle of convergence in accordance with the formulæ given by Ananthakrishnan. Unlike in the case of the colloids, ρ_h in ether decreases as θ increases. The values of ρ_h , however, are not given in Table VII. In the case of methyl methacrylate glass (plastic slab), the variations in the values of the depolarisation factors are similar to those observed with ether. The increases in the values of ρ_u and ρ_v are nearly equal to $\theta^2/2$ and $\theta^2/4$ respectively. See columns 5, 6, 7 and 8 of Table VI. The value of ρ_h decreases from a value of 90.1% to 85.5% when 2θ increases from 0 to 0.367 of a radian. Consequently, the values of $\Delta \rho_h$ are given with a negative sign. According to Ananthakrishnan, the correction factor for ρ_h is given by $\theta^2/4\rho_{v_a}$. This factor has been evaluated for various values of 2θ and the results are given in column 10 of Table VI. It is found that the observed values of $\Delta \rho_h$ are far different from the calculated values, *i.e.*, the decrease in ρ_h as θ increases is much less than what it should be if the scattering is completely molecular in region. This observation supports the view that the scattering elements in the plastic slab cannot be considered as small compared with the wavelength of light.

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In columns 9, 10 and 11 of Table VIII are given the convergence corrections $\Delta \rho_u$, $\Delta \rho_v$ and $\Delta \rho_h$ for the various colloial solutions for a convergence angle equal to $24\frac{1}{2}^\circ$ or $\cdot 428$ of a radian. Let us confine ourselves to the first five cases only, as they represent typical colloidal solutions having particles not small compared with the wavelength of light. An examination of the values given in columns 9, 10 and 11 shows that unlike in the case of molecular scattering where the convergence correction is independent of the nature of the scattering medium, the corrections to be applied for the observed values of ρ_u , ρ_v and ρ_h are very much dependent on the nature of the colloidal solution, *i.e.*, on the size and shape of the colloidal particles. For colloids having nearly the same value of ρ_{v_o} , it is found that $\Delta \rho_v$ has a higher value in the case of the colloid which has smaller ρ_{h_o} . In the same way, for colloids having nearly the same value of ρ_{h_o} , $\Delta \rho_h$ is found to be higher, the lower the value of ρ_{v_0} . In general, the convergence corrections to be applied to the observed values of ρ_v and ρ_h may be functions of both ρ_{v_0} and ρ_{h_0} . In order to find out the exact relationship, it is necessary to examine a much larger number of colloidal solutions than has been done in the present investigation.

In the case of all the colloids investigated, the values of ρ_u , ρ_v and ρ_h obtained using a horizontal slit in the path of the incident beam are found to be the same as those for parallel light, *i.e.*, for zero angle of convergence. This fact could be easily explained on the basis of the observations made by one of us (Krishnan, 1938). The effect of introducing a horizontal slit in the path of incident beam is equivalent to using a narrow parallel beam of light and measuring the depolarisation factors for the light scattered not in the exact traverse direction, but over an extended region with the angle of scattering varying from $(\pi/2 - \theta)$ to $(\pi/2 + \theta)$, where θ is the angle subtended by the extreme rays on the central ray coming through the horizontal slit. It has been observed (Krishnan, 1938) that in the case of colloids ρ_u , ρ_v and Ph vary continuously with the angle of scattering over a small region on either side of the transverse directions, *i.e.*, $\pi/2$. The mean value of the depolarisation factor over a finite range of the scattering angle, namely from $(\pi/2 - \theta)$ to $(\pi/2 + \theta)$, may therefore be expected to be equal to that for the scattering angle $=\pi/2$, *i.e.*, for the exact transverse scattering. This is what

has been observed.

It is interesting to point out that the depolarisation factors ρ_u , ρ_v and ρ_h obtained using a vertical slit in the path of the incident beam are nearly the same as those for convergent light.

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