Molecular aelotropy in liquids

A very remarkable feature shown by many liquids in experiments on the molecular scattering of light is that the scattered beam in a direction transverse to the primary rays shows a large admixture of *unpolarised* light, the proportion of this to polarised light in the scattered beam being several times greater than in the case of the same substance in the condition of vapour at atmospheric pressure. This fact seemed at first very puzzling; an explanation is, however, now forthcoming. A theory of the phenomenon has been worked out by the writer which not only explains the facts in a simple and quantitative manner, but has also pointed out the way to further fruitful research. It may be briefly indicated as follows:

   The polarised and unpolarised parts of molecularly scattered light may be conceived as arising in two distinct ways; the former is a *mass-effect* arising from the thermal fluctuations of density in the fluid, and its magnitude is given by the Einstein–Smoluchowski formula

$$\frac{\pi^2}{18}\frac{RT\beta}{N\lambda^4}(\mu^2-1)^2(\mu^2+2)^2,$$

and as we pass from the condition of vapour to that of liquid in which the molecules are more closely packed together, it increases much less than in proportion to the increased density. The *unpolarised* part of the scattered light is, on the other hand, a *molecular* effect, and its magnitude increases simply in proportion to the number of molecules per unit volume. The ratio of unpolarised to polarised part of the scattered light should therefore be considerably enhanced. This is exactly what is observed. If I and $2I_2$ are respectively the polarised and unpolarised parts of the transversely scattered light, the ratio $I_2/(I_1+I_2)$ may be determined experimentally by analysis with the aid of a double-image prism and a nicol. The table below shows in the second column the value of this ratio as determined by Lord Rayleigh for certain substances in the state of vapour, in the third column the value of the ratio for the liquid state at ordinary temperature as calculated from the writer's theory, and in the fourth column the value as determined by Mr K Seshagiri Rao in the present writer's laboratory. The agreement is significant.

   We may also view the matter in another way. When a substance is in the state of vapour under small pressures, both the positions and orientations of its molecules are absolutely at random, and assuming the molecules to be aelotropic, the

Ratio of components of polarisation

Substance	Observed, vapour (%)	Calculated, liquid (%)	Observed, liquid (%)
Ethyl ether	1·7	10·9	8·2
Benzene	6·0	39·8	39·8
Chloroform	3·0	18·2	15·5

degree of imperfection of polarisation of the light scattered by it may easily be calculated, as has been done by the late Lord Rayleigh. On the other hand, in the liquid state, the packing of the molecules is so close that their ordering in space is no longer at random; but we may still, at least in the case of ordinary liquids, consider the orientations to be arbitrary without serious error. If we take this into account in determining the resultant effect of the waves scattered by the individual molecules, we should be led to the same result as has been indicated above.

The theory put forward has other notable successes to its credit. The Einstein–Smoluchowski formula indicates that though the density of a liquid diminishes with rise of temperature, its scattering power should increase and become very large as the critical temperature is approached. Similarly, as the temperature is increased, the scattering power of the saturated vapour should increase much more rapidly than in proportion to its density. Accordingly, in both cases, we should expect the polarisation of the scattered light to improve steadily with rise of temperature and become practically complete as the critical temperature of the liquid is approached. Experiments with benzene liquid and vapour made by Mr K R Ramanathan have quantitatively confirmed this prediction. A similar improvement in polarisation has also been observed by Mr V S Tamma in experiments on the scattering of light in *binary liquid mixtures* as the critical temperature for separation into two phases is approached.

C V RAMAN

210 Bowbazaar Street, Calcutta
11 May 1922