

## Opalescence phenomena in liquid mixtures

It is well known that liquids which mix completely above a certain critical temperature, e.g. phenol and water, exhibit a strong and characteristic opalescence as the temperature of the mixture is lowered to a point slightly above that at which the components separate. A quantitative theory of this phenomenon was put forward by Einstein (*Annalen der Physik*, vol. 33, 1910) on the basis of thermodynamical reasoning, the spontaneous local fluctuations of *concentration* of the mixture being taken into account and the light-scattering due to the resulting fluctuations of refractive index being evaluated. He obtained as the expression for the light-scattering

$$\pi^2(M/N\lambda^4) \cdot v \left( \frac{\partial \mu^2}{\partial \kappa} \right)^2 \bigg/ \frac{\partial(\log p)}{\partial \kappa} \quad \text{per unit volume,}$$

where  $\mu$  is the refractive index of the mixture and  $\partial(\log p)/\partial \kappa$  expresses the rate of change of the vapour pressure of one of the components with concentration, a quantity which becomes very large as the critical temperature and concentration are approached, thus giving rise to a marked opalescence. It should be pointed out, however, that Einstein's expression does not include the whole effect, for we have also to consider the result of the *fluctuation of density of either component taken separately*, and to add to Einstein's formula

$$(\pi^2/18)(RT/N\lambda^4)[\beta_1(\mu_1^2 - 1)^2(\mu_1^2 + 2)^2 + \beta_2(\mu_2^2 - 1)^2(\mu_2^2 + 2)^2],$$

where  $\beta_1, \beta_2, \mu_1, \mu_2$  are respectively the compressibilities and refractive indices of the components. Further, the light-scattering due to the anisotropy and arbitrary orientation of the molecules of the components has also to be added.

The result of these corrections of Einstein's investigation may briefly be indicated. Very near the temperature at which the mixture separates into two phases, the fluctuations of *concentration* contribute by far the larger portion of the effect. But at higher and lower temperatures the effects of fluctuations of *density* and molecular anisotropy are no longer negligible, and when the temperature is sufficiently removed from the critical point they form a substantial part of the whole. Further, the increase in relative importance of the effect of molecular anisotropy in these circumstances should result in an increase in the proportion of *unpolarised* light in the transversely-scattered beam as we recede from the critical temperature.

The foregoing indications of theory have been confirmed generally in a series of experiments over a wide range of temperatures on light-scattering in phenol-

water mixtures undertaken under the writer's direction by Mr V S Tamma. It is found that the increased opalescence of the mixture over and above the effects due to the components taken separately can be traced at temperatures far higher than the critical point, and the indicated changes in the polarisation of the scattered light are also easily observed.

It is clear that the case of liquids which are completely miscible at ordinary temperatures stands on the same footing as that of imperfectly miscible liquids above the critical temperature, and the recent observations of W H Martin on this point (*J. Phys. Chem.*, Jan. 1922) agree with the indications of the theory outlined above.

I may take this opportunity of directing attention to a very important result observed in experiments on light-scattering in liquids conducted by Mr Seshagiri Rao and the writer. It is found that the molecular anisotropy which results in a scattering of unpolarised light is noticeably *a function of the frequency of the incident light*. This indicates that the anisotropy is really due to the difference of the optical frequencies of the molecule in different directions, a conclusion which has a bearing on the recent interesting work of Havelock (*Proc. R. Soc.*, May 1922). Debye and others have suggested that some molecules possess an appreciable permanent electric moment, and would thus exercise perceptible orienting influences on each other even in the gaseous and liquid states. Indications are already forthcoming that this may exercise an observable influence on the phenomena of molecular scattering of light.

Finally, it may be mentioned that a very carefully carried out series of experiments on the light-scattering in ether, benzene, and normal pentane, over a large range of temperatures above and below the critical temperature, has confirmed quantitatively the Einstein-Smoluchowski theory of molecular scattering of light.

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