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Abstract

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Light Scattering and the Stability of Solutions

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In recent years a number of experimental studies have been carried out on the intensity of light scattering in nonstratifying solutions. To explain the observed results, certain particular assumptions have been put forward. In the present work we wished to show that no additional assumptions are required to explain the experimental facts. They can all be explained on the basis of the theory of Rayleigh scattering of light, taking into account the modern thermodynamic theory of solutions. The theory of Rayleigh scattering for two-component systems was developed by Einstein (^{1}) and Raman (^{2}), and for multicomponent systems by Kirkwood (^{3}).

In a two-component solution, for the Rayleigh constant due to scattering on concentration fluctuations, the theory (^{3}) gives

$$R = \frac{\pi^2 R_0 T}{2\lambda^4 N_A \rho_1} \left(\frac{\partial \varepsilon}{\partial c}\right)_{p,T} M_2 \Big/ \left(\frac{\partial \mu_2}{\partial c}\right)_{p,T}. \tag{1}$$

Here ρ_1 is the mass of the first component per unit volume; $c = m_2/m_1$ is the ratio of the masses of the components; M_2, μ_2 are the molecular weight and molar chemical potential of the second component; ε is the optical dielectric constant; R_0 is the universal gas constant; N_A is Avogadro’ s number.

For convenience in comparing with the conclusions of the thermodynamic theory of solutions, let us express the concentrations in mole fractions and introduce the molar free enthalpy $\bar{G} = \bar{H} - T\bar{S}$ ($\bar{H}$ is the molar enthalpy, $\bar{S}$ the molar entropy of mixing). Then we have

$$R = \frac{\pi^2 R_0 T}{2\lambda^4 N_A} x_1 x_2 \left(\frac{\partial \varepsilon}{\partial x_2}\right)^2 v \Big/ x_2 \left(\frac{\partial \mu}{\partial x_2}\right)_{p,T}; \tag{2}$$

x_i is the molar concentration of the i-th component, v is the volume of 1 mole of mixture.

Since $\bar{G} = x_1\mu_1 + x_2\mu_2$, using the Gibbs—Duhem equation:

$$x_1 \left(\frac{\partial \mu_1}{\partial x_2}\right)_{p,T} + x_2 \left(\frac{\partial \mu_2}{\partial x_2}\right)_{p,T} = 0,$$

we obtain

$$x_2 \left(\frac{\partial \mu_2}{\partial x_2}\right)_{p,T} = x_1 x_2 \left(\frac{\partial^2 \bar{G}}{\partial x_2^2}\right)_{p,T}. \tag{3}$$

Substituting (3) into (2), we finally have:

$$R = \frac{\pi^2 R_0 T}{2\lambda^4 N_A} \left(\frac{\partial \varepsilon}{\partial x_2}\right)_{p,T} v \Big/ \left(\frac{\partial^2 \bar{G}}{\partial x_2^2}\right)_{p,T}. \tag{4}$$

In order to express the scattering intensity in terms of quantities directly measured experimentally, it is necessary in the last formula to make

the following replacement (substitution) (^{4}):

$$\left(\frac{\partial^2 \bar{G}}{\partial x_2^2}\right)_{p,T} = \frac{dp}{dx_2} \left[\frac{v_\text{v} - v}{y_2 - x_2} - \left(\frac{\partial v}{\partial x_2}\right)_{p,T}\right], \tag{5}$$

where p is the total vapor pressure of the mixture; v_v is the molar volume of the mixture in the vapor phase; y_2 is the molar concentration of the second component in the vapor.

This formula can be simplified if one neglects the compression of the mixture upon a change in concentration and the molar volume of the liquid in comparison with the vapor volume. If, in addition, the vapor phase is taken to be an ideal gas, then, after some transformations using the Morgules–Duhem equation, instead of (5) we obtain

$$\left(\frac{\partial^2 \bar{G}}{\partial x_2^2}\right)_{p,T} = \frac{R_0 T}{x_1} \frac{\partial \ln p_2}{\partial x_2}. \tag{5a}$$

Substitution of this expression into formula (4), with simultaneous replacement of molar concentrations by the relative concentration $C = m_2/m_1$, gives Einstein' s well-known formula for the intensity of concentration scattering (^{1}). The conditions formulated above indicate the limits of applicability of Einstein' s formula.

Formula (4) makes it possible to state the most general considerations concerning light scattering caused by concentration fluctuations. The criterion of phase stability states that a binary mixture of arbitrary composition is stable with respect to decomposition into phases of adjacent composition if and only if (^{5}):

$$\left(\frac{\partial^2 \bar{G}}{\partial x_2^2}\right)_{p,T} \geqslant 0. \tag{6}$$

At the very boundary of stability:

$$\left(\frac{\partial^2 \bar{G}}{\partial x_2^2}\right)_{p,T} = 0. \tag{6a}$$

(Formula (4) does not apply to this case.)

At constant temperature (above the upper or below the lower critical temperature) the system will be closest to the stability boundary at the critical concentration. At this concentration the denominator in (4) will be minimal, and the scattering maximal (if there are no extrema on the refractive-index-composition curve). It follows from this that concentration scattering will make the greatest contribution to isotropic scattering at concentrations closest to the stability boundary.

For a more concrete specification of the theory with respect to different types of solutions investigated, we introduce the excess molar free enthalpy

$$\bar{G}^E = \bar{G} - \bar{G}_{\mathrm{id}}; \quad \bar{G}_{\mathrm{id}} = x_1\mu_{01} + x_2\mu_{02} + R_0T(x_1 \ln x_1 + x_2 \ln x_2)$$

—the molar free enthalpy of an ideal mixture. Then, instead of condition (6), we have:

$$\left(\frac{\partial^2 \bar{G}^E}{\partial x_2^2}\right)_{p,T} \geqslant -\frac{R_0T}{x_1x_2}. \tag{7}$$

It follows from (7) that, near the stability boundary, $\bar{G}^E > 0$, and appreciable concentration scattering can be observed only in systems with a positive excess molar free enthalpy. In the thermodynamics of solutions it has been shown that, for a binary liquid mixture,

$$\bar{G}^E = x_1x_2\left[A(p,T) + B(p,T)(x_1 - x_2) + C(p,T)(x_1 - x_2)^2 + \cdots\right].$$

Otmer and co-workers (^{6}) considered 110 liquid binary mixtures of nonelectrolytes and showed that 2 systems are ideal, while 28 are described rather well by

with one parameter, 34 with two, 37 with three, and four parameters are needed to describe 7 systems. From these data it is clear that approximately one-third of the systems studied should be assigned to the so-called regular solutions. The molar excess free enthalpy for such solutions may be represented in the form: $\overline{G}^E = Ax_1x_2$. Then

$$\left(\frac{\partial^2\overline{G}}{\partial x_2^2}\right)_{p,T} = \frac{R_cT}{x_1x_2} - 2A. \tag{8}$$

For $A > 0$, stratification occurs if $\overline{G}^E = R_0T/2 \simeq T$ cal/mol (at room temperature $\simeq 300$ cal/mol). The minimum of (8) is found at

[Figure 1 and Figure 2]

Fig. 1. Dependence of the relative intensity of isotropic scattering of aqueous solutions of γ-picoline on concentration x ($t = 20°$).

Fig. 2. Dependence of the relative intensity of isotropic scattering of aqueous solutions of γ-picoline on temperature:
1—$x = 1$; 2—0.356; 3—0.156; 4—0.090; 5—0.058; 6—$x = 0.031$.

$x = 0.5$. At this same concentration the system has the lowest stability. According to (4), the scattering here will also be maximal.

Scattering in non-stratifying solutions close to regular ones was investigated by M. I. Shakhparonov and N. G. Shlenkina (7), and they found that the scattering maximum lies in the indicated region.

The available thermodynamic data on some non-stratifying systems in which scattering was studied (7) indicate that they are located near the stability boundary. Thus, in the systems CCl_4—CH_3OH and C_6H_6—CH_3OH, G^E reaches 300 cal/mol at room temperature (8).

Table 1

Substance	T_n	x	T_v	x
γ-Picoline			Miscible	
β-Picoline	49	0.07	153	0.09
2,4-Lutidine	22.5	0.054	189.6	0.09
2,4,6-Collidine	6	0.05	190	

To verify the conclusion concerning the relation of scattering in non-stratifying systems to stratification phenomena, we investigated solutions of γ-picoline in water. The choice of this system is due to the fact that solutions in water of some homologues of pyridine possess partial miscibility and have upper (T_v) and lower (T_n) critical solution temperatures (9), indicated in Table 1.

The measurements were carried out for a wavelength of 5461 Å. The accuracy of the results obtained for intensity is no worse than 10%, and for temperature ±2°. The method of measurement and calculation is similar to that described earlier

(10). From Fig. 1 it follows that the scattering maximum of non-stratifying solutions of γ-picoline is observed in the concentration region where the critical solution point of the methyl derivatives of pyridine is located (see Table 1). At these concentrations

aqueous solutions of γ-picoline have the least stability, and fluctuations are strongly developed in them.

Next, the temperature dependence of the intensity of isotropic scattering by γ-picoline and its solutions was investigated (Fig. 2). It is clear from the figure that the scattering intensity of solutions whose concentration is close to the concentration of the solution of least stability ($x = 0.058$) passes, as the temperature is increased, through a sharply pronounced maximum. This phenomenon was observed earlier by M. F. Vuks and L. I. Lisnyanskii in a pyridine–water solution, but less distinctly (11). Such a course of the intensity is consistent with the presence of a lower critical temperature in pyridine homologues. At the temperature of inversion of the intensity, the solution has the least stability.

As Fig. 2 shows, the scattering maxima for solutions of different concentrations lie at somewhat different temperatures. This is in agreement with the fact that the upper critical point of pyridine homologues (Table 1) is shifted in concentration relative to the lower one.

It is possible that the intense development of concentration fluctuations should explain the anomalous absorption of ultrasound in some non-mixing solutions (for example, acetone–water). According to our calculations, the acetone–water system is less stable than the pyridine–water system.

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