

Local Structure of Ideal and Real Solutions by Rayleigh Light Scattering

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Received 11 December 1996

Rayleigh light scattering was observed for three characteristic binary solutions at various composition. The compositional scattering was reduced to concentration fluctuation and experimental results were compared with theoretical consideration of this fluctuation. According to such comparison in the cyclohexane—carbon tetrachloride solution molecular mixing is present, in the pyridine—acetic acid mixture the existence of an associated complex of the form $2C_2H_5N \cdot 3CH_3COOH$ is evident; in the solution benzene—methanol one has considered the effect of both dissociation and association. The results obtained are in perfect agreement with the liquid—vapour equilibrium data.

The local fluctuation of the concentration is considered to afford information which is useful in understanding mixing from a molecular point of view. In this connection we can distinguish the solutions with molecular and nonmolecular mixing and the mixtures characteristic with chemical interaction between components. Based on this belief in the present study we would like to analyze the composition dependence of the concentration fluctuation through the Rayleigh light scattering in the three mixtures: cyclohexane—carbon tetrachloride (H—CT), benzene—methanol (B—M), and pyridine—acetic acid (P—HAc).

THEORETICAL

Concentration fluctuation and thermodynamic properties of the solution are connected through the well known relation

$$\overline{(\Delta x)^2}v = kT \left(\frac{\partial^2 G}{\partial x^2} \right)^2 V_{12} \quad (1)$$

where x is the mole fraction of the components, Δx the deviation of mole fraction from its mean value in the volume v , V_{12} the solution molar volume, G the solution molar Gibbs energy, and kT has its usual significance. On the other hand, the concentration fluctuation is responsible for concentration light scattering, which is given by

$$R_c = \pi^2 (2\lambda^4)^{-1} \left(\frac{\partial \epsilon_r}{\partial x} \right)^2 kT \left(\frac{\partial^2 G}{\partial x^2} \right)^{-1} V_{12} \quad (2)$$

Here ϵ_r is the relative permittivity and λ the wavelength of the primary unpolarized light. The Rayleigh ratio R_c is a part of total scattering R_t

$$R_t = R_{is} + R_{an} = R_c + R_d + R_{an} \quad (3)$$

where R_{is} , R_{an} are isotropic and anisotropic scattering and R_{is} can be split into a compositional and density component, R_c , R_d ; the Rayleigh ratio is defined as

$$R = \frac{(I_{90}/I_0)r^2}{V} \quad (4)$$

where I_0 is the intensity of incident beam and I_{90} is the intensity of light scattered at 90° with respect to the light source, at a distance r from the scattering volume V

By combining eqns (1) and (2) and assuming $\epsilon_r \approx n^2$ (n is the refractive index) eqn (5) directly relates R_c with concentration fluctuation

$$\overline{(\Delta x)^2}v = \frac{2\lambda^4 R_c}{\pi^2 \left(\frac{\partial n^2}{\partial x} \right)^2} \quad (5)$$

and from (5) we can determine $\overline{(\Delta x)^2}v$ experimentally. We cannot, however, determine the mole fraction fluctuation in the form $\overline{(\Delta x)^2}$; by theoretical interpretation of $\overline{(\Delta x)^2}$ Kato and Fujiyama [1] on the basis of statistical physics consider this fluctuation within the region which contains a constant number, N , of molecules by the term $N(\Delta x)^2$, hereby between $\overline{(\Delta x)^2}v$ and $N(\Delta x)^2$ exists the relation

$$\overline{(\Delta x)^2}v = \frac{N}{\rho_n} \overline{(\Delta x)^2} \quad (6)$$

where ρ_n is the number density ($\rho_n = N[(\rho/\overline{M})N_A]^{-1}$, \overline{M} is the average relative molecular mass and ρ is the

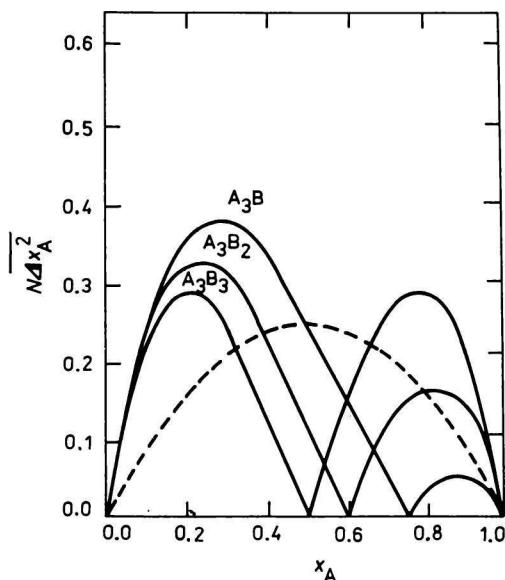


Fig. 1. Theoretical values of the concentration fluctuation calculated from eqns (7) (dashed line) and (8) for $l=3$ and $m=1, 2, 3$.

density of solution). In the paper cited authors give the expressions for calculation of $N(\Delta x)^2$ for typical cases, e.g. the ideality (molecular mixing) or the associated complex model. So the ideal binary solution is described by the relation

$$N(\Delta x)_A^2 = \bar{x}_A(1 - \bar{x}_A) \quad (7)$$

and for the case, when the binary mixture is composed of A and A_lB_m complex molecules for \bar{x}_A small and of B and A_lB_m molecules for \bar{x}_A large, it stands

$$\begin{aligned} N(\Delta x_A)^2 &= \bar{x}_A(1 - \bar{x}_A)[l - (l+m)\bar{x}_A] \\ N(\Delta x_A)^2 &= \bar{x}_A(1 - \bar{x}_A)[(l+m)\bar{x}_A - l] \end{aligned} \quad (8)$$

Some theoretical values of the concentration fluctuation calculated on the basis of eqns (7, 8) are depicted in Fig. 1.

It is customary in this part to take into consideration these general remarks. From thermodynamics we know, $(\partial^2 G / \partial x^2)_{T,p}$ serves as a measure of binary mixture stability and in the critical point $(\partial^2 G / \partial x^2)_{T,p} = 0$. From eqn (1) then it is evident, the lower $(\partial^2 G / \partial x^2)_{T,p}$, the higher is the concentration fluctuation. Analogically we can also assume that in the eutectic point of a solution this fluctuation will be lower than in the regions out of this point. Simultaneously we must remember that the vapour pressure over the solution reflects the physical circumstances in a solution and then by a low degree of the concentration fluctuation in a liquid mixture we can expect also a low vapour pressure. So in this way the concen-

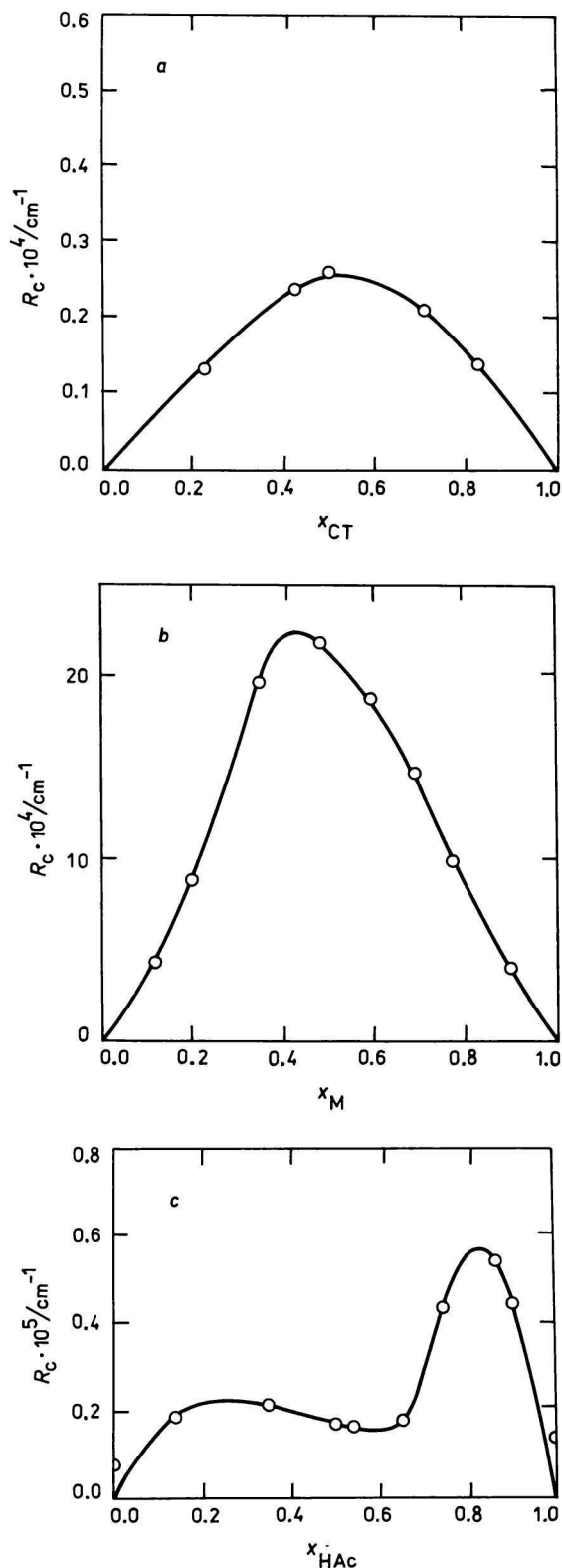


Fig. 2. Concentration dependence of the light scattering quantity R_c in the solutions: cyclohexane—carbon tetrachloride (a), benzene—methanol (b), and pyridine—acetic acid (c).

tration fluctuation, the compositional light scattering and the vapour pressure are directly connected.

EXPERIMENTAL

The instrumentation and techniques utilized for obtaining the light scattering data on the mixtures cyclohexane— CCl_4 and benzene—methanol are described in [2]. A modified Fica 50 photometer was used, each measurement was obtained by taking the average of 100 consecutive readings within about 30 s and this average was reproducible within $\pm 0.5\%$, $\lambda = 546\text{ nm}$, $\theta = 20^\circ\text{C}$.

In the case of pyridine—acetic acid the light scattering instrument was a Brice—Phoenix apparatus and further experimental treatments required were made in usual manner [3]; $\lambda = 436\text{ nm}$, $\theta = 20^\circ\text{C}$.

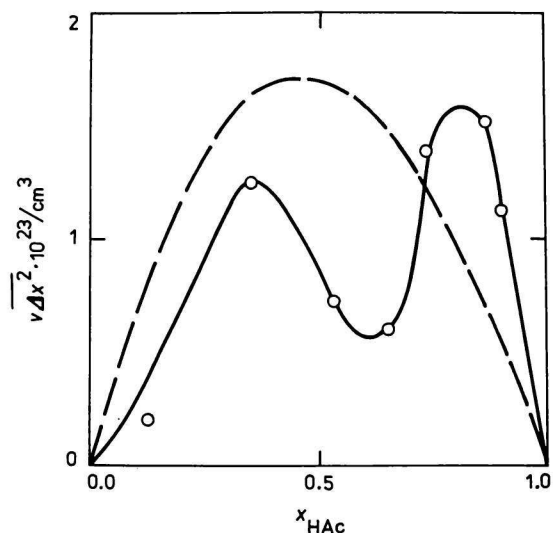
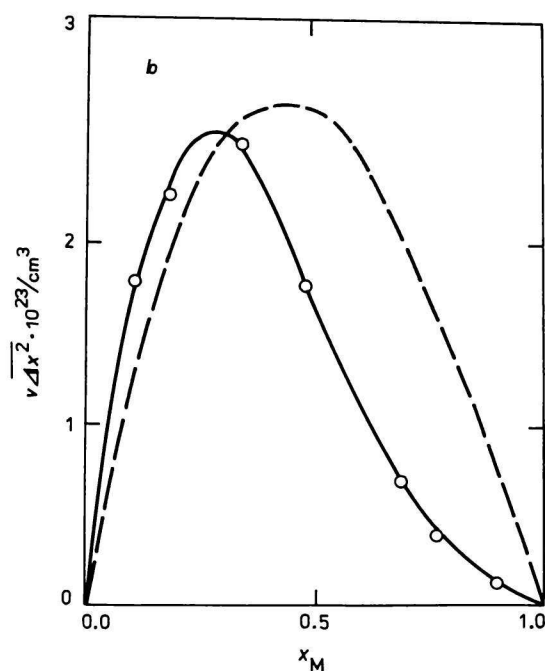
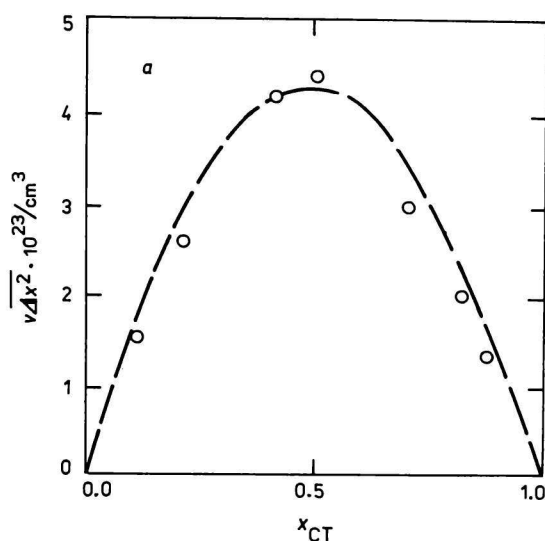


Fig. 3. Concentration fluctuation observed (o) and expected for an ideal solution (dashed line) in the systems cyclohexane—carbon tetrachloride (a), benzene—methanol (b), and pyridine—acetic acid (c).

All experimental data from [2] and [3] were extracted.

RESULTS AND DISCUSSION

In Fig. 2 the dependences of the compositional light scattering on the mole fraction of component B for binary systems H—CT, B—M, and P—HAc are depicted and we can see that a high difference in the molecular interactions in considered mixtures exists. For further description of these interactions let us to investigate the concentration fluctuation.

The experimental and theoretical course of the concentration fluctuation in the mixture H—CT is depicted in Fig. 3a. The experimental values of $(\overline{\Delta x})^2 v$ were computed according to the relation (5). Hereby the values of R_c and the dependences of the solutions refractive index n on the mixture composition were selected from [2]. Linear or polynomial functions for the evaluation of the dependence $n = f(x)$ were used. The experimental data were fitted by the least-squares method and the coefficients obtained were used in calculation of $(\partial n^2 / \partial x)^2$.

The theoretical values of $(\overline{\Delta x})^2 v$ were computed on the basis of eqns (6, 7), hereby for ρ_n the ideal mixing rule was assumed. From the comparison of theoretical and experimental curves in Fig. 3 it is evident that for the mixture H—CT the assumption of the molecular miscibility from the standpoint of concentration fluctuation is correct. Also the vapour pressure measurements give evidence for such a statement, hereby the limit activity coefficients, computed according to the Margules equation, have the values $\gamma_1^\infty = 1.12$ and $\gamma_2^\infty = 1.10$ [4].

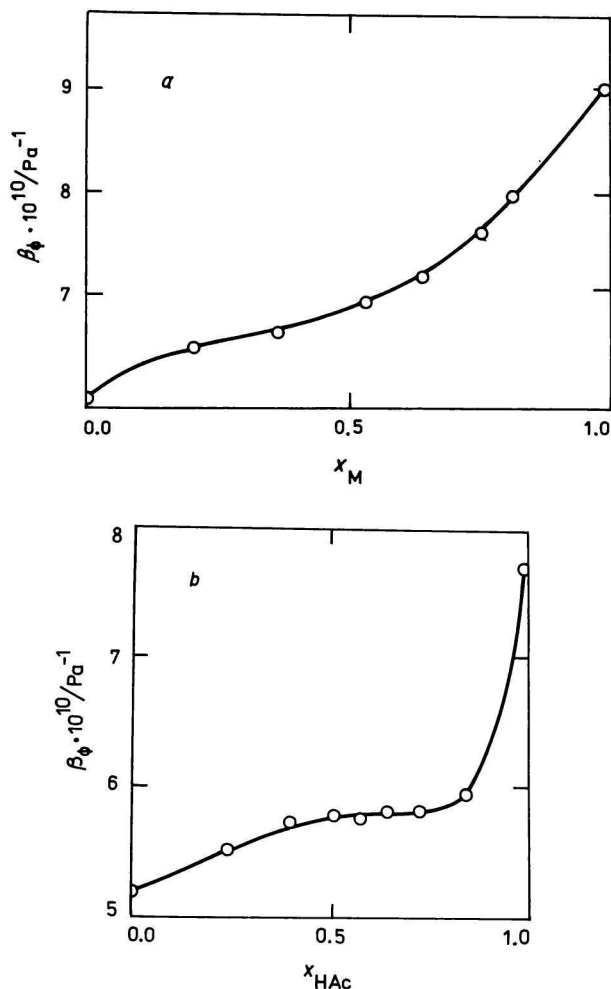


Fig. 4. Adiabatic compressibility in the benzene—methanol (a) and pyridine—acetic acid (b) mixtures [5].

To explain experimental results on the B—M mixture (Fig. 3b) one has to consider the effect of both dissociation and association between the molecules, which is evident from the study of the compressibilities of this mixture [5]. The benzene molecule has a planar structure and a high value of polarizability and so a big dissociating effect on the associating groups of any liquid, that may be introduced in it. Then, in the first stage of mixing with a large number of benzene molecules the alcohol molecules will be far apart each other. This will decrease the cohesive energy between the alcohol molecules and as this decrease is greater than the increase in cohesive energy between B—M molecules the net effect is a decrease in cohesive energy which tends to increase the compressibilities from the ideal mixture value. With a larger content of M molecules there is a tendency for association and this results in an increase of cohesive energy, hereby the compressibility curve (Fig. 4a) exhibits a point of inflexion at about $x_M = 0.3$. As we can see (Fig. 5) in this region the deviation in vapour pressure from its ideal mixture value is maximum and also in this region (Fig.

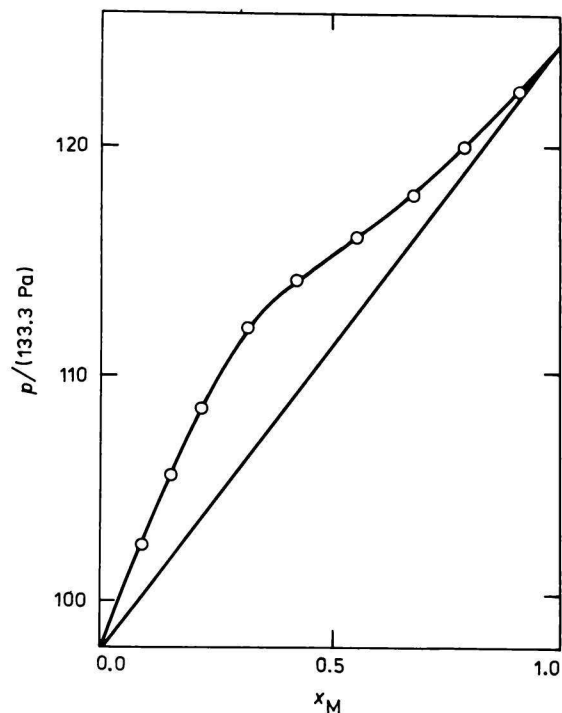


Fig. 5. Concentration dependence of the vapour pressure at 25°C in the benzene—methanol mixture [6].

3b) the experimental dependence $(\overline{\Delta x})^2 v = f(x_M)$ has a maximum. In this way it is possible to conclude that the transition stage from one solution structure to another is characterized by a maximum value of concentration light scattering.

Let us now to discuss the results on the mixture P—HAc, shown in Fig. 3c. As we can see, here the concentration dependence of composition fluctuation exhibits two distinct maxima. It is possible to observe such maxima also in Fig. 1 and the general similarity between the theoretical curve A_3B_2 and the experimental one (Fig. 3c) is remarkable. In accordance with the results of the compressibility measurements on P—HAc mixture (Fig. 4b) it seems that in the region between $x_{\text{HAc}} = 0.35$ and $x_{\text{HAc}} = 0.8$ the molecules enter in a more compact equilibrium arrangement (this may constitute formation of associated complexes); consequently, the increase in the cohesive energy of the mixture and decrease of the concentration fluctuation are expected. In connection with formation of the complexes it is known, pyridine has a pronounced proton-acceptor character, therefore an ionization of acid in this mixture should be expected and so specific interactions may be present.

Thus, on the basis of the course of the concentration fluctuation we can judge that in the mixture P—HAc a compound of the composition $2C_2H_5N \cdot 3CH_3COOH$ is present. The same conclusion was made by Swearingen and Ross [7] on the basis of the boiling points measurements. These authors in agreement with the above-mentioned general assumption

have found that the mixture containing 58.4 mole % of acetic acid has the maximum boiling point 138.35°C under a pressure of 760 mm Hg.

Finally, on the basis of Figs. 1, 3c, and 4b also in the case of the P—HAc mixture we can state that transition from one local structure to another with a maximum of concentration fluctuation is indicated.

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Translated by J. Vavra