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LIGHT SCATTERING ARISING FROM COMPOSITION FLUCTUATIONS IN BINARY LIQUID SYSTEMS

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Rayleigh light scattering ratios were measured for 22 binary mixtures at 20°C and at a wavelength of $\lambda = 632.8$ nm. These data were used to evaluate the composition fluctuation function, f , for these systems as a function of mixture composition. The accuracy and sensitivity of the applied method depends mainly on the difference of the refractive indices of the two components of the mixture and on the values of the Rayleigh ratios.

KEY WORDS: Refractive index, Rayleigh scattering.

INTRODUCTION

The thermodynamic properties of liquid mixtures have been obtained earlier from vapour-liquid equilibria, at pressures close to the ambient pressure. Consequently, the measurements are usually restricted to temperatures near the boiling points of the solvents. At these temperatures, free energy based solvent-solvent interaction data is rare. So, the availability of a fast and simple method for probing thermodynamic interactions in binary mixtures would have a significant value¹⁻⁴.

Rayleigh scattering ratios have been used for deriving important thermodynamic values such as the compositional fluctuation function f . Determination of the function f utilized for calculating the partial pressure, the activation coefficient and the residual Gibbs potential for the components of the mixtures. In our opinion, the thermodynamic function f gives an indication about the picture of the intermolecular interaction in binary liquid mixtures rather than the other thermodynamic values.

In this work, light scattering is used to evaluate the Rayleigh ratios and the thermodynamic fluctuation function f for 22 binary systems: CCl₄-alcohols, benzene-alcohols, toluene-alcohols, aniline-alcohols and water-alcohols. Mixtures of CCl₄-cyclohexane, benzene-cyclohexane and toluene-octane were tested. The choice of water-alcohol mixtures has been based on the availability of the isothermal compressibility data in the literature. The other liquid pair selections depend mainly on the difference of the refractive indices of the components of the mixtures and on the experimental precision in the determination of Rayleigh ratios.

THEORY

The intensities of light scattered at a 90° angle by liquids and liquid mixtures are commonly expressed by means of Rayleigh's ratio, R , define as

$$R = (I_{90}/I_0)r^2 \quad (1)$$

where I_0 is the intensity of the primary light beam and I_{90} is the intensity of light scattered at 90° by a volume unit of the liquid and measured at a distance r from the scattering element. In liquid mixtures, the total scattering Rayleigh ratio R is comprised of two parts; isotropic scattering, R_{is} , and anisotropic scattering, R_{an} . Isotropic scattering can be divided into two components: scattering due to the fluctuation of concentration (compositional fluctuation), R_c , and scattering caused by density fluctuation, R_d . Hence,

$$R = R_{is} + R_{an} = R_c + R_d + R_{an} \quad (2)$$

The fluctuation of anisotropy can be expressed according to Cabannes⁵ by measuring the depolarization ratio $\Delta = R_h/R_v$, i.e., the ratio of intensities scattered when the incident light is polarized horizontally and vertically, respectively. The relation (2) reads

$$R = (R_c + R_d)(6 + 6\Delta)/(6 - 7\Delta) \quad (3)$$

The calculation of R_c for binary mixtures^{6,7} depends on the fluctuation of dielectric permittivity $\overline{\Delta\epsilon^2}$,

$$\overline{\Delta\epsilon^2} = (\partial\epsilon/\partial\rho)^2\overline{\Delta\rho^2} + (\partial\epsilon/\partial x)^2\overline{\Delta x^2}$$

where x is the molecular concentration of one of the components, and $x_1 + x_2 = 1$. The expression for R_c in a binary mixtures reads

$$R_c = (\pi^2/\lambda^4)(\partial\epsilon/\partial x)^2\overline{\Delta x^2} v \sin^2\phi \quad (4)$$

Here v is the volume of one mole of the mixture, λ is the wavelength of the primary light, $(\partial\epsilon/\partial x)$ is the derivative describing the dependence of the dielectric constant of the mixture ϵ on composition and ϕ is the angle between the direction of the electric vector of the incident light and the radius vector of the direction of scattered light.

Expression (4) defined the scattering of polarized incident light, whereas for the scattering of unpolarised light, we change $\sin^2\phi$ into $(1 + \cos^2\theta)/2$, where θ is the angle of scattering. So,

$$R_c = (\pi^2/2\lambda^4)(\partial\epsilon/\partial x)^2\overline{\Delta x^2}v \quad (5)$$

R_c can be related to the Gibbs function through the relation,

$$R_c = (\pi^2/2\lambda^4 N_A)(\partial\varepsilon/\partial x)^2 R_o T (\partial^2 G/\partial x^2)_{P,T}^{-1} V_{12} \quad (6)$$

Here N_A is the Avogadro's number, $R_o T$ has its usual meaning, G is the thermodynamical potential Gibbs, and V_{12} is the volume of one mole of the mixture.

The quantity $(\partial^2 G/\partial x^2)_{P,T}$, according to the thermodynamics of solutions, served as a standard value for measuring the stability of a solution against its separation into two phases of contiguous compositions. In the critical point the separation reduces to zero. It is clear that, the increasing of $(\partial G^2/\partial x^2)_{P,T}$ gives a decreasing in the fluctuation of concentration.

The dimensionless function f which characterized the level of the compositional fluctuation is defined as

$$1/f = (x_1 x_2 / R_o T) (\partial^2 G / \partial x^2)_{P,T} \quad (7)$$

Combining Eqs. (6) and (7) we have

$$R_c = (\pi^2/2\lambda^4 N_A)(\partial\varepsilon/\partial x)^2 x_1 x_2 V_{12} f \quad (8)$$

The function f can be expressed in terms of the residual thermodynamical Gibbs potential G^E , the chemical potential μ or finally as the activity a .

The Gibbs free energy is given as

$$G = G_{\text{ideal}} + G^E$$

for ideal mixtures

$$(\partial^2 G_{\text{ideal}}/\partial x^2) = (R_o T/x_1 x_2)$$

and Eq. (7) reads

$$1/f = 1 + (x_1 x_2 / R_o T) (\partial^2 G^E / \partial x^2) \quad (9)$$

It is obvious that, for ideal mixtures, the function $f = 1$ whilst a mixture with a positive deviation from ideality has $f > 1$ and a mixtures with a negative deviation has $f < 1$.

Using the thermodynamical relation⁸

$$G = x_1 \mu_1 + x_2 \mu_2$$

and Gibbs formula

$$x_1 (\partial \mu_1 / \partial x_1)_{P,T} + x_2 (\partial \mu_2 / \partial x_2)_{P,T} = 0$$

where μ_1 and μ_2 are the molar chemical potentials of the components of the mixture. It is easy to prove that,

$$(\partial^2 G/\partial x_1^2) = (1/x_2)(\partial\mu_1/\partial x_1)$$

Substituting into Eq. (7) yields the third expression for f

$$1/f = (x_1/R_o T)(\partial\mu_1/\partial x_1) = (x_2/R_o T)(\partial\mu_2/\partial x_2) \quad (10)$$

To obtain the compositional scattering R_c , according to Eq. (8), we need to calculate: $(\partial n/\partial x)$, V_{12} and f . The quantity of primary interest is $(\partial n/\partial x)$, the derivative of refractive indices with respect to the mole fractions of one of the components. The non-linearity of such curves leads to a miscalculation of $\partial n/\partial x$. For a good accuracy in determination this value we must plot the relation of n as a function of the weight fraction C_1 or C_2 . So,

$$\partial n/\partial x_1 = (\partial n/\partial c_1)(c_1/x_1)^2(M_2 M_1) \quad (11)$$

Here M_1 and M_2 are the molecular weights of the mixture components.

The macroscopic value of $\partial n/\partial x$ differ from the fluctuational value that enters in Eq. (8), they are related by ⁹

$$(\partial n/\partial x)_{fluc.} = (\partial n/\partial x)\{3n^2/(2n^2 + 1)\}\{3/(n^2 + 2)\} \quad (12)$$

The second interest value V_{12} is defined as

$$V_{12} = M_{12}/\rho = (x_1 M_1 + x_2 M_2)/\rho \quad (13)$$

Here M_{12} and ρ are the molecular weight and density of mixture, respectively. In many cases V_{12} stands for the molar volume of the mixture as computed from the individual molar volumes of the components V_1 and V_2

$$V_{12} = x_1 V_1 + x_2 V_2$$

The final relation for the compositional scattering Rayleigh ratio R_c , reads

$$R_c = (\pi^2/2\lambda^4 N_A)\{2n(\partial n/\partial x)\}^2\{9n^2/(2n^2 - 1)(n^2 + 2)\}^2 x_1 x_2 V_{12} f \quad (14)$$

EXPERIMENTAL SECTION

The equipment and techniques utilized for obtaining the various experimental quantities presented here have been described in detail in our previous papers¹⁰⁻¹². The liquids used had nominal purities of 99% or better. Each liquid sample was

passed through a 0.45- μm Teflon filter to ensure it was free of dust and other particulate impurities. The refractive indices of the pure liquids and mixtures were measured using a lamp and filter providing incident light at a wavelength of $\lambda = 632.8$ nm. Both the density and refractive indices were measured at 20°C.

RESULTS AND DISCUSSION

As elaborated in the theoretical discussion, the measurement of the depolarization coefficient Δ permits excluding the anisotropic scattering ratio, R_{an} . Isotropic scattering can, in turn, be split into a compositional and a density component $R_{is} = R_c + R_d$. However, in order to calculate R_c from R_{is} , the density scattering R_d must first be estimated. The relation for R_d reads¹³

$$R_d = (\pi^2/2\lambda^4)KT\beta_T(n^2 - 1)^2\{3n^2/(2n^2 + 1)\}^2 \quad (15)$$

Another method for calculating R_d is the additive scheme $R_d = \phi_1 R_1 + \phi_2 R_2$ where R_1 , R_2 are the density scattering by pure components and ϕ_1 , ϕ_2 are the volume fractions of the system components.

I Mixtures of benzene and CCl_4

The quantity of R_{is} for the systems: CCl_4 -methanol, CCl_4 -ethanol, CCl_4 -cyclohexane, benzene-methanol, benzene-ethanol, and benzene-cyclohexane is plotted as a function of composition in Figures 1 and 2. The dashed lines represent the theoretical estimate of R_d calculated by Eq. (15). From Table 1 it is clear that the compositional fluctuation level f for the CCl_4 -methanol system is greater than that for benzene-methanol system. In turn, R_c for the later system is greater than that for the first system. The reason for this difference is in the slightly different magnitude of the value of the refractive indices of the pure components (CCl_4 and methanol) for the first system than that for the second system (benzene and methanol), which produces a different magnitude of the value of $\partial n/\partial x$.

For CCl_4 -alcohols and benzene-alcohols systems, the maximum of compositional fluctuations is shifted towards the lower concentration side, while for cyclohexane systems the shift is directed towards the largest concentration.

II Mixtures of toluene

The Rayleigh scattering ratios R_{is} for the systems of toluene-methanol, toluene-ethanol, toluene-propanol, toluene-butanol and toluene-octane are plotted in Figure 3 against alcohol (and octane) volume fractions x_2 . It is easy to observe that, all curves are arranged in the same order as in the systems of benzene and CCl_4 . The general light scattering pattern is approximately similar.

To separate the compositional scattering, it is necessary to exclude the scattered light due to the density fluctuations. Figure 4 shows the dependence of the composi-

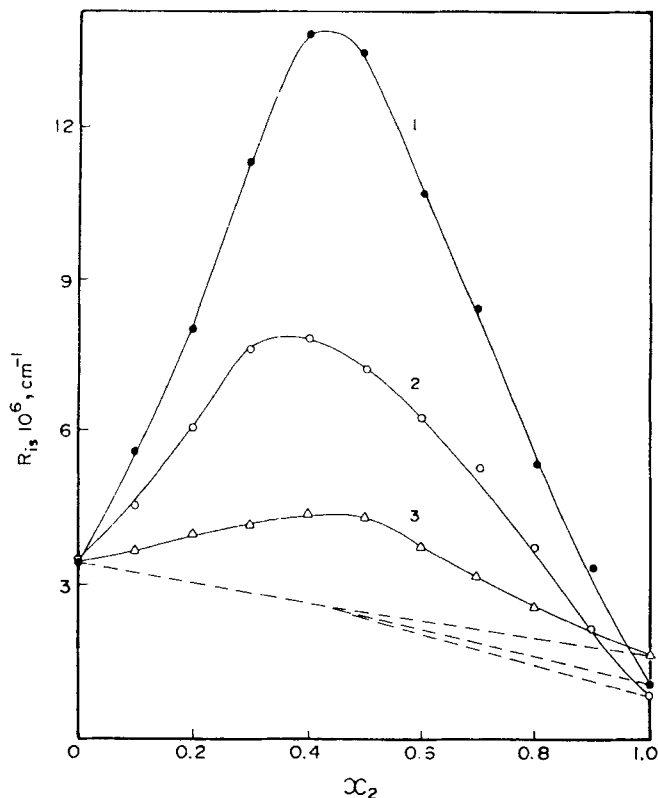


Figure 1 Isotropic Rayleigh ratios R_{is} for the binary systems: (1) CCl_4 -methanol; (2) CCl_4 -ethanol; (3) CCl_4 -cyclohexane ($\lambda = 632.8 \text{ nm}$, 20°C). The dashed lines represent the theoretical estimate of R_d .

tional fluctuation function f (calculating with the helping of Eq. 14) for the above systems on the mole fraction of alcohol, x_2 . The mixtures of toluene-octane give very weak values of compositional scattering and a very low values of f ($f \leq 1.5$).

III Mixtures of chlorobenzene

The Rayleigh scattering ratio, R_{is} for the mixtures of chlorobenzene-methanol, chlorobenzene-propanol and chlorobenzene-butanol are plotted in Figure 5 as a function of alcohol's volume fractions x_2 . The behavior of the present curves analogous to that for benzene and toluene systems. The similarity certificated the analogous of their thermodynamical properties. This deduction seems waitless, because chlorobenzene considered as a polar liquid having a large value for the dipole moment $\mu \cong 1.7$, and toluene having a very weak polarity, whilst benzene have not dipole moment. We can deduced that dipole interactions in such mixtures are not effective. In other words between molecules of chlorobenzene and alcohols a strong

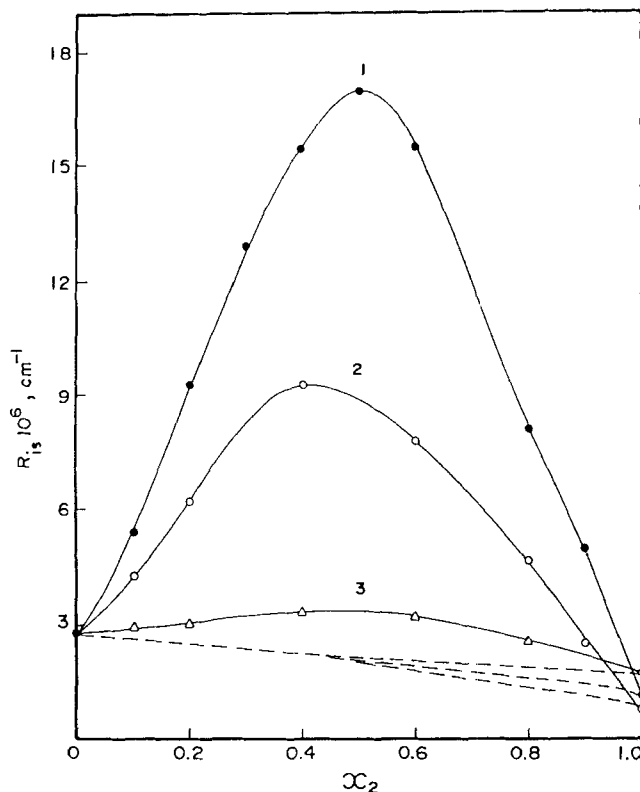


Figure 2 Rayleigh light scattering ratio R_{i_s} for the binary systems: (1) benzene-methanol; (2) benzene-ethanol; (3) benzene-cyclohexane ($\lambda = 632.8 \text{ nm}$, 20°C).

hydrogen bond not occurred, and the hydrogen bond in chlorobenzene mixtures not stronger than that in benzene and toluene mixtures.

IV Mixtures of aniline

Figure 6 shows the Rayleigh scattering ratios R_{i_s} for aniline-methanol, aniline-ethanol, aniline-propanol, aniline-butanol, and aniline-heptanol systems as a function of alcohol's volume fractions x_2 . Comparing these curves and values of R , f with those for benzene, toluene and chlorobenzene systems indicates that the dependence of the compositional fluctuations on the kind of alcohol is inverse. In other words, compositional fluctuation in the mixtures of benzene, toluene and chlorobenzene decreased by increasing the alcohol number, while these fluctuations increased in the case of aniline-alcohols system. Additionally, the general compositional fluctuation level, f , here, have a very low value. For example in aniline-methanol system maximum $f = 1.48$ while in aniline-heptanol system maximum $f = 2.87$. Such de-

Table 1 Experimental values of the depolarization Δ , Rayleigh Ratios R , R_{is} and R_c . The calculated values of the function f for the 22 Mixture Systems Studied (at $\lambda = 632.8$ nm, 20°C).

| x_2 | Rayleigh ratios $\times 10^6, \text{cm}^{-1}$ | | | | | f | x_2 | Rayleigh ratios $\times 10^6, \text{cm}^{-1}$ | | | | |
|------------------------------------|--|-------|----------|-------|-------|--------------------------------|-------|--|-------|----------|-------|-----|
| | $\Delta.10$ | R | R_{is} | R_c | f | | | $\Delta.10$ | R | R_{is} | R_c | f |
| Carbon Tetrachloride – Methanol | | | | | | Carbon Tetrachloride – Ethanol | | | | | | |
| 0.00 | 0.51 | 3.86 | 3.45 | 0.00 | 1.00 | 0.00 | 0.50 | 3.90 | 3.50 | 0.00 | 1.00 | |
| 0.10 | 0.44 | 6.21 | 5.64 | 2.42 | 4.85 | 0.10 | 0.33 | 4.86 | 4.52 | 1.30 | 4.06 | |
| 0.20 | 0.22 | 8.39 | 8.00 | 4.98 | 6.74 | 0.20 | 0.23 | 6.39 | 6.08 | 3.06 | 5.21 | |
| 0.30 | 0.11 | 11.60 | 11.33 | 8.63 | 10.02 | 0.30 | 0.17 | 7.86 | 7.57 | 4.87 | 6.43 | |
| 0.40 | 0.09 | 14.09 | 13.82 | 11.30 | 11.61 | 0.40 | 0.32 | 8.39 | 7.82 | 5.28 | 6.38 | |
| 0.50 | 0.09 | 13.77 | 13.50 | 11.16 | 9.30 | 0.50 | 0.22 | 7.50 | 7.15 | 4.88 | 4.46 | |
| 0.60 | 0.13 | 11.06 | 10.75 | 8.58 | 7.86 | 0.60 | 0.26 | 6.58 | 6.22 | 4.27 | 3.42 | |
| 0.70 | 0.17 | 6.69 | 6.45 | 4.58 | 2.68 | 0.70 | 0.26 | 5.56 | 5.25 | 3.55 | 3.01 | |
| 0.80 | 0.24 | 5.60 | 5.31 | 3.71 | 1.90 | 0.80 | 0.27 | 3.98 | 3.75 | 2.32 | 1.86 | |
| 0.90 | 0.32 | 3.65 | 3.40 | 1.94 | 1.48 | 0.90 | 0.39 | 2.37 | 2.14 | 1.02 | 1.34 | |
| 1.00 | 0.58 | 1.25 | 1.10 | 0.00 | 1.00 | 1.00 | 1.11 | 1.02 | 0.80 | 0.00 | 1.00 | |
| Carbon Tetrachloride – Cyclohexane | | | | | | Benzene – Methanol | | | | | | |
| 0.00 | 0.50 | 3.88 | 3.48 | 0.00 | 1.00 | 0.00 | 4.18 | 7.76 | 2.80 | 0.00 | 1.00 | |
| 0.10 | 0.29 | 3.94 | 3.70 | 0.48 | 3.10 | 0.10 | 2.61 | 9.84 | 5.42 | 2.82 | 3.85 | |
| 0.20 | 0.39 | 4.32 | 3.97 | 0.96 | 3.26 | 0.20 | 2.04 | 14.60 | 9.24 | 6.79 | 6.74 | |
| 0.30 | 0.35 | 4.51 | 4.18 | 1.48 | 3.41 | 0.30 | 1.56 | 18.10 | 12.80 | 10.45 | 7.68 | |
| 0.40 | 0.45 | 4.86 | 4.41 | 1.86 | 3.31 | 0.40 | 1.33 | 20.64 | 15.38 | 13.18 | 7.07 | |
| 0.50 | 0.45 | 4.77 | 4.32 | 1.86 | 3.02 | 0.50 | 1.23 | 22.16 | 16.90 | 14.80 | 6.10 | |
| 0.60 | 0.46 | 4.15 | 3.75 | 1.48 | 2.61 | 0.60 | 1.29 | 20.64 | 15.50 | 13.60 | 4.65 | |
| 0.70 | 0.39 | 3.51 | 3.22 | 1.02 | 2.06 | 0.80 | 2.16 | 13.09 | 8.04 | 6.44 | 1.93 | |
| 0.80 | 0.53 | 2.92 | 2.60 | 0.70 | 1.74 | 0.90 | 1.31 | 6.56 | 4.91 | 3.51 | 1.27 | |
| 0.90 | 0.44 | 2.38 | 2.16 | 0.36 | 1.21 | 1.00 | 0.58 | 1.25 | 1.10 | 0.00 | 1.00 | |
| 1.00 | 0.91 | 2.04 | 1.67 | 0.00 | 1.00 | | | | | | | |
| Benzene – Ethanol | | | | | | Benzene – Cyclohexane | | | | | | |
| 0.00 | 4.20 | 7.75 | 2.78 | 0.00 | 1.00 | 0.00 | 4.24 | 7.70 | 2.74 | 0.00 | 1.00 | |
| 0.10 | 3.27 | 9.24 | 4.30 | 1.61 | 2.70 | 0.10 | 4.08 | 7.84 | 2.92 | 0.31 | 2.46 | |
| 0.20 | 2.52 | 10.96 | 6.18 | 3.74 | 3.98 | 0.20 | 3.98 | 7.96 | 3.05 | 0.60 | 2.61 | |
| 0.40 | 1.88 | 14.11 | 9.26 | 7.06 | 4.23 | 0.40 | 3.87 | 8.34 | 3.30 | 1.10 | 2.35 | |
| 0.60 | 1.97 | 13.58 | 8.73 | 6.98 | 2.62 | 0.60 | 3.57 | 7.44 | 3.20 | 1.15 | 2.05 | |
| 0.80 | 2.83 | 8.84 | 4.61 | 3.33 | 1.81 | 0.80 | 3.25 | 5.51 | 2.58 | 0.78 | 1.64 | |
| 0.90 | 2.52 | 4.43 | 2.50 | 1.45 | 1.10 | 0.90 | 2.67 | 4.14 | 2.25 | 0.55 | 1.14 | |
| 1.00 | 1.13 | 1.00 | 0.78 | 0.00 | 1.00 | 1.00 | 0.83 | 2.10 | 1.75 | 0.00 | 1.00 | |
| Toluene – Methanol | | | | | | Toluene – Ethanol | | | | | | |
| 0.00 | 4.83 | 8.70 | 2.56 | 0.00 | 1.00 | 0.00 | 4.86 | 8.67 | 2.52 | 0.00 | 1.00 | |
| 0.20 | 2.38 | 14.40 | 8.40 | 6.20 | 5.80 | 0.20 | 2.89 | 12.26 | 6.30 | 4.10 | 3.48 | |
| 0.30 | 1.70 | 18.51 | 12.68 | 10.56 | 8.55 | 0.30 | 2.14 | 13.82 | 8.55 | 6.43 | 5.00 | |
| 0.40 | 1.31 | 22.74 | 17.05 | 15.09 | 10.30 | 0.40 | 1.71 | 16.12 | 11.02 | 9.05 | 5.10 | |
| 0.50 | 0.96 | 27.61 | 22.35 | 20.47 | 9.20 | 0.50 | 1.60 | 16.43 | 11.52 | 9.64 | 4.30 | |
| 0.57 | 0.82 | 26.34 | 22.00 | 20.20 | 7.72 | 0.70 | 2.15 | 10.86 | 6.70 | 5.15 | 2.65 | |
| 0.60 | 0.80 | 23.80 | 19.96 | 18.21 | 7.00 | 0.80 | 1.89 | 6.14 | 4.02 | 2.72 | 2.05 | |
| 0.70 | 0.93 | 16.55 | 13.50 | 11.80 | 5.05 | 1.00 | 1.21 | 0.98 | 0.75 | 0.00 | 1.00 | |
| 0.80 | 1.02 | 9.77 | 7.81 | 6.26 | 2.40 | | | | | | | |
| 1.00 | 0.58 | 1.27 | 1.12 | 0.00 | 1.00 | | | | | | | |

(continued)

Table 1 (Continued)

| x_2 | Rayleigh ratios $\times 10^6, \text{cm}^{-1}$ | | | | | x_2 | Rayleigh ratios $\times 10^6, \text{cm}^{-1}$ | | | | |
|------------------------|--|-------|----------|-------|------|------------------------|--|-------|----------|-------|------|
| | $\Delta.10$ | R | R_{is} | R_c | f | | $\Delta.10$ | R | R_{is} | R_c | f |
| Toluene-Propanol | | | | | | Toluene-Butanol | | | | | |
| 0.00 | 4.80 | 8.72 | 2.60 | 0.00 | 1.00 | 0.00 | 4.80 | 8.71 | 2.60 | 0.00 | 1.00 |
| 0.20 | 3.07 | 11.21 | 5.50 | 3.30 | 2.80 | 0.20 | 3.31 | 10.86 | 5.00 | 2.80 | 2.40 |
| 0.30 | 2.47 | 12.64 | 7.22 | 5.10 | 3.65 | 0.30 | 3.11 | 10.94 | 5.31 | 3.19 | 2.30 |
| 0.40 | 2.32 | 13.00 | 7.70 | 5.74 | 3.30 | 0.40 | 2.76 | 8.75 | 4.65 | 2.69 | 2.15 |
| 0.60 | 3.00 | 9.66 | 4.82 | 3.07 | 2.35 | 0.60 | 2.75 | 6.12 | 3.26 | 1.51 | 1.70 |
| 0.70 | 3.00 | 7.31 | 3.65 | 1.84 | 1.95 | 0.70 | 2.70 | 4.51 | 2.43 | 0.76 | 1.50 |
| 0.80 | 2.04 | 4.05 | 2.56 | 0.91 | 1.60 | 0.80 | 1.67 | 2.84 | 1.96 | 0.37 | 1.35 |
| 1.00 | 0.92 | 1.74 | 1.42 | 0.00 | 1.00 | 1.00 | 2.35 | 1.96 | 1.15 | 0.00 | 1.00 |
| Toluene-Octane | | | | | | Chlorobenzene-Methanol | | | | | |
| 0.00 | 4.81 | 8.68 | 2.57 | 0.00 | 1.00 | 0.00 | 5.93 | 10.96 | 2.12 | 0.00 | 1.00 |
| 0.10 | 4.79 | 8.72 | 2.60 | 0.30 | 1.15 | 0.10 | 3.90 | 13.81 | 5.41 | 3.36 | 3.96 |
| 0.20 | 4.47 | 8.05 | 2.66 | 0.36 | 1.25 | 0.20 | 2.73 | 16.86 | 9.02 | 7.07 | 4.60 |
| 0.40 | 4.25 | 7.70 | 2.72 | 0.76 | 1.50 | 0.30 | 1.87 | 21.42 | 14.10 | 12.20 | 5.63 |
| 0.50 | 3.50 | 6.41 | 2.77 | 0.89 | 1.45 | 0.40 | 1.40 | 24.74 | 18.16 | 16.31 | 7.25 |
| 0.60 | 3.79 | 5.84 | 2.36 | 0.61 | 1.35 | 0.50 | 1.17 | 26.26 | 20.31 | 18.49 | 7.20 |
| 0.80 | 3.70 | 3.91 | 1.62 | 0.21 | 1.20 | 0.60 | 0.75 | 23.51 | 19.96 | 18.24 | 6.91 |
| 1.00 | 1.42 | 1.70 | 1.24 | 0.00 | 1.00 | 0.80 | 1.21 | 15.66 | 12.00 | 10.62 | 4.00 |
| | | | | | | 0.90 | 1.47 | 8.84 | 6.38 | 5.13 | 1.96 |
| | | | | | | 1.00 | 0.59 | 1.16 | 1.02 | 0.00 | 1.00 |
| Chlorobenzene-Propanol | | | | | | Chlorobenzene-Butanol | | | | | |
| 0.00 | 5.94 | 10.90 | 2.10 | 0.00 | 1.00 | 0.00 | 5.95 | 10.86 | 2.08 | 0.00 | 1.00 |
| 0.10 | 4.30 | 13.20 | 4.60 | 2.55 | 2.40 | 0.10 | 4.84 | 12.12 | 3.55 | 1.51 | 1.48 |
| 0.20 | 3.16 | 14.60 | 7.00 | 5.05 | 2.82 | 0.20 | 3.69 | 13.96 | 5.81 | 3.86 | 2.39 |
| 0.30 | 2.70 | 16.14 | 8.70 | 6.80 | 3.61 | 0.30 | 3.58 | 14.11 | 6.05 | 4.15 | 2.28 |
| 0.40 | 2.58 | 16.76 | 9.32 | 7.47 | 3.54 | 0.40 | 3.69 | 12.53 | 5.21 | 3.36 | 1.96 |
| 0.50 | 2.52 | 14.91 | 8.40 | 6.58 | 3.36 | 0.60 | 3.58 | 8.86 | 3.80 | 2.00 | 1.48 |
| 0.60 | 2.35 | 12.74 | 7.48 | 5.67 | 3.00 | 0.80 | 1.79 | 4.11 | 2.76 | 1.06 | 1.20 |
| 0.70 | 2.52 | 9.94 | 5.61 | 3.86 | 2.11 | 1.00 | 2.38 | 1.92 | 1.12 | 0.00 | 1.00 |
| 0.80 | 2.30 | 7.56 | 4.50 | 2.78 | 1.50 | | | | | | |
| 0.90 | 1.42 | 4.31 | 3.15 | 1.50 | 1.21 | | | | | | |
| 1.00 | 0.87 | 1.73 | 1.43 | 0.00 | 1.00 | | | | | | |
| Aniline-Methanol | | | | | | Aniline-Ethanol | | | | | |
| 0.00 | 5.49 | 7.92 | 1.84 | 0.00 | 1.00 | 0.00 | 5.49 | 7.92 | 1.84 | 0.00 | 1.00 |
| 0.10 | 4.86 | 8.24 | 2.40 | 0.59 | 1.04 | 0.10 | 4.44 | 8.70 | 2.90 | 1.18 | 1.15 |
| 0.20 | 4.16 | 8.83 | 3.21 | 1.51 | 1.15 | 0.20 | 3.64 | 9.78 | 4.12 | 2.49 | 1.24 |
| 0.40 | 2.82 | 10.96 | 5.73 | 4.14 | 1.48 | 0.30 | 3.05 | 10.94 | 5.40 | 3.84 | 1.50 |
| 0.60 | 1.80 | 13.22 | 8.85 | 7.43 | 1.21 | 0.40 | 2.34 | 12.36 | 7.27 | 5.81 | 1.67 |
| 0.80 | 1.44 | 11.43 | 8.30 | 6.95 | 1.06 | 0.60 | 1.65 | 14.94 | 10.36 | 9.09 | 1.30 |
| 0.90 | 1.65 | 7.22 | 5.00 | 3.70 | 1.04 | 0.80 | 1.65 | 9.60 | 6.66 | 5.64 | 1.08 |
| 1.00 | 0.55 | 1.15 | 1.02 | 0.00 | 1.00 | 1.00 | 1.15 | 1.03 | 0.80 | 0.00 | 1.00 |
| Aniline-Propanol | | | | | | Aniline-Butanol | | | | | |
| 0.00 | 5.48 | 7.94 | 1.85 | 0.00 | 1.00 | 0.00 | 5.50 | 7.90 | 1.82 | 0.00 | 1.00 |
| 0.10 | 4.19 | 9.24 | 3.33 | 1.49 | 1.22 | 0.10 | 3.46 | 10.52 | 4.66 | 2.82 | 1.41 |

(continued)

Table 1 (Continued)

| x_2 | Rayleigh ratios $\times 10^6, \text{cm}^{-1}$ | | | | | x_2 | Rayleigh ratios $\times 10^6, \text{cm}^{-1}$ | | | | | |
|-------|--|-------|----------|-------|------|-------|--|-------|----------|-------|------|--|
| | Δ_{10} | R | R_{is} | R_c | f | | Δ_{10} | R | R_{is} | R_c | f | |
| 0.20 | 3.21 | 10.66 | 5.05 | 3.33 | 1.64 | 0.20 | 2.59 | 12.81 | 7.10 | 5.38 | 1.84 | |
| 0.30 | 2.48 | 11.94 | 6.80 | 5.15 | 1.76 | 0.40 | 1.60 | 17.46 | 12.25 | 10.63 | 2.06 | |
| 0.40 | 1.84 | 13.40 | 8.88 | 7.27 | 1.86 | 0.50 | 1.56 | 17.49 | 12.48 | 10.78 | 1.94 | |
| 0.50 | 1.43 | 14.71 | 10.72 | 9.13 | 1.81 | 0.70 | 2.22 | 11.76 | 7.13 | 5.71 | 1.22 | |
| 0.60 | 1.32 | 15.00 | 11.20 | 9.65 | 1.39 | 0.80 | 2.23 | 7.18 | 4.26 | 2.84 | 1.14 | |
| 0.80 | 1.87 | 7.60 | 5.00 | 3.57 | 1.11 | 1.00 | 2.29 | 1.91 | 1.14 | 0.00 | 1.00 | |
| 1.00 | 0.86 | 1.81 | 1.50 | 0.00 | 1.00 | | | | | | | |
| | Aniline-Heptanol | | | | | | Water-Ethanol | | | | | |
| 0.00 | 5.45 | 7.98 | 1.88 | 0.00 | 1.00 | 0.00 | 0.91 | 0.61 | 0.50 | 0.00 | 1.00 | |
| 0.10 | 2.04 | 14.62 | 9.26 | 7.43 | 1.67 | 0.10 | 0.63 | 0.70 | 0.61 | 0.13 | 1.04 | |
| 0.20 | 1.23 | 20.60 | 15.71 | 14.03 | 2.87 | 0.15 | 0.66 | 0.67 | 0.58 | 0.08 | 1.16 | |
| 0.30 | 0.97 | 19.41 | 15.69 | 13.99 | 2.82 | 0.20 | 0.73 | 0.68 | 0.58 | 0.08 | 1.30 | |
| 0.40 | 0.89 | 16.04 | 13.20 | 11.60 | 2.20 | 0.28 | 0.62 | 0.71 | 0.62 | 0.12 | 1.64 | |
| 0.60 | 1.01 | 10.26 | 8.21 | 6.77 | 1.40 | 0.31 | 0.60 | 0.73 | 0.64 | 0.14 | 2.06 | |
| 0.80 | 1.22 | 4.71 | 3.64 | 2.26 | 1.21 | 0.37 | 0.63 | 0.70 | 0.61 | 0.08 | 2.28 | |
| 1.00 | 0.89 | 1.96 | 1.61 | 0.00 | 1.00 | 0.40 | 0.52 | 0.74 | 0.66 | 0.11 | 2.20 | |
| | | | | | | 0.47 | 0.48 | 0.80 | 0.72 | 0.09 | 2.11 | |
| | | | | | | 0.50 | 0.47 | 0.82 | 0.74 | 0.06 | 1.61 | |
| | | | | | | 0.60 | 0.46 | 0.83 | 0.75 | 0.00 | — | |
| | | | | | | 0.70 | 0.46 | 0.89 | 0.80 | 0.00 | — | |
| | | | | | | 0.80 | 0.53 | 0.92 | 0.82 | 0.00 | — | |
| | | | | | | 1.00 | 1.12 | 1.10 | 0.86 | 0.00 | 1.00 | |
| | Water-Isopropyl alcohol | | | | | | Water-Tertbutyl alcohol | | | | | |
| 0.00 | 0.91 | 0.61 | 0.50 | 0.00 | 1.00 | 0.00 | 0.91 | 0.61 | 0.50 | 0.00 | 1.00 | |
| 0.02 | 0.31 | 1.82 | 1.70 | 1.15 | 1.48 | 0.03 | 0.14 | 5.18 | 5.02 | 4.25 | 2.14 | |
| 0.04 | 0.28 | 2.04 | 1.92 | 1.23 | 2.06 | 0.04 | 0.01 | 7.40 | 7.25 | 6.12 | 3.58 | |
| 0.05 | 0.26 | 2.38 | 2.25 | 1.52 | 4.68 | 0.05 | 0.12 | 5.65 | 5.50 | 4.62 | 5.87 | |
| 0.08 | 0.30 | 1.92 | 1.80 | 1.15 | 3.14 | 0.10 | 0.37 | 2.71 | 2.50 | 1.45 | 4.88 | |
| 0.12 | 0.54 | 1.36 | 1.21 | 0.50 | 3.91 | 0.15 | 0.32 | 2.84 | 2.65 | 1.45 | 4.56 | |
| 0.20 | 0.70 | 1.57 | 1.35 | 0.28 | 3.44 | 0.20 | 0.45 | 3.31 | 3.00 | 1.77 | 4.99 | |
| 0.30 | 0.61 | 1.60 | 1.40 | 0.12 | 2.80 | 0.30 | 0.74 | 2.35 | 2.00 | 0.62 | 4.08 | |
| 0.40 | 0.53 | 1.63 | 1.45 | 0.04 | 2.41 | 0.40 | 0.89 | 2.08 | 1.71 | 0.32 | 3.41 | |
| 0.60 | 0.78 | 1.78 | 1.50 | 0.00 | — | 0.60 | 0.91 | 2.20 | 1.80 | 0.15 | 2.33 | |
| 0.80 | 0.73 | 1.90 | 1.62 | 0.00 | — | 0.80 | 0.86 | 2.27 | 1.88 | 0.00 | — | |
| 1.00 | 0.82 | 1.94 | 1.62 | 0.00 | 1.00 | 1.00 | 0.86 | 2.45 | 2.03 | 0.00 | 1.00 | |

pendence may be explained as the formation of hydrogen bond between the molecules of aniline and alcohols. In the mixtures of methanol the rule of hydrogen bond is very effective. In going to ethanol, propanol, butanol and heptanol mixtures this effect decreases. This can be explained as the worsening solubility which caused the increasing of the compositional fluctuations.

V Light scattering from aqueous mixtures

In the previous studied systems, the scattered intensity due to the density fluctuation were obtained with the help of a simple additive scheme. Such a scheme is not valid

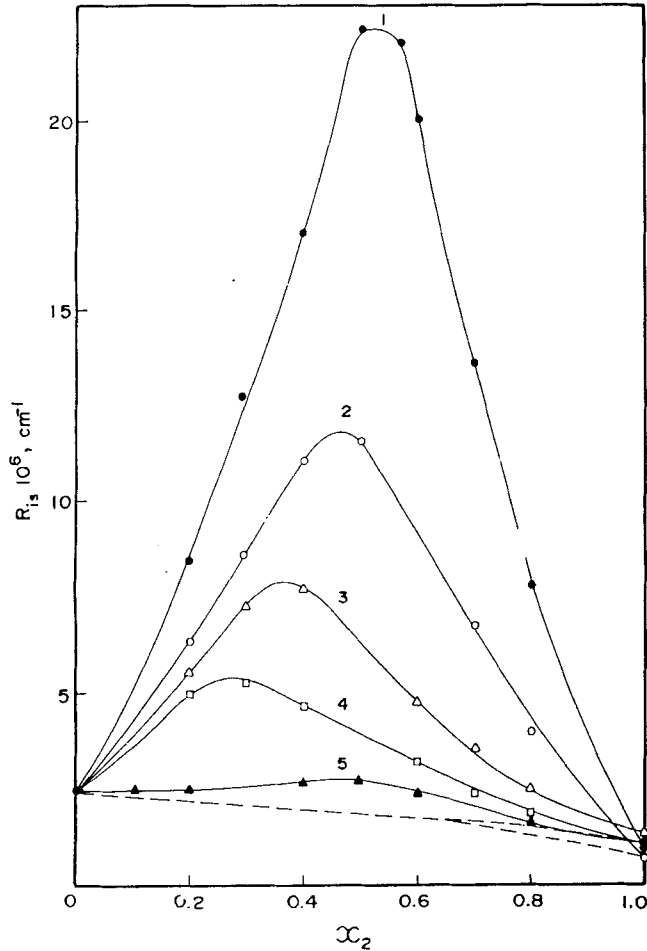


Figure 3 Dependence of the isotropic scattering R_{i_s} on the volume fraction of component 2 for five binary systems: (1) toluene-methanol; (2) toluene-ethanol; (3) toluene-propanol; (4) toluene-butanol; (5) toluene-octane ($\lambda = 632.8 \text{ nm}$, 20°C).

for aqueous mixtures. Therefore we must use expression (15). The isothermal compressibility β_T is given as

$$\beta_T = \beta_S + (\sigma^2 T / \rho C_P)$$

The coefficient of expansion σ and the heat capacity C_P for mixtures can be calculated using the additive scheme

$$\sigma = \phi_1 \sigma_1 + \phi_2 \sigma_2; \quad C_P = C_2 C_{P2}$$

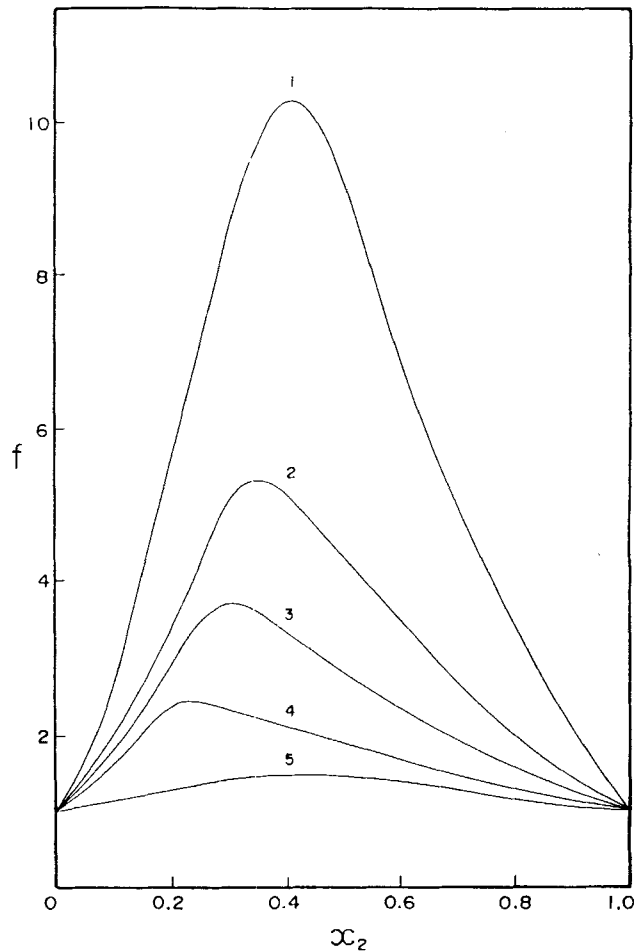


Figure 4 The compositional fluctuation function f for the binary systems: (1) toluene-methanol; (2) toluene-ethanol; (3) toluene-propanol; (4) toluene-butanol; (5) toluene-octane ($\lambda = 632.8 \text{ nm}$, 20°C).

Here σ_1 , σ_2 , C_{P1} and C_{P2} are the coefficients of expansion and specific heat of the mixture components. ϕ_1 , ϕ_2 , C_1 and C_2 are the volume fractions and weights of the mixture.

The above method for determining σ and C_P is, of course, approximate. However, by adding the value of $(\sigma^2 T / \rho C_P)$ to the adiabatic compressibility constitutes about 20–30%. So the large error in their calculation not caused appreciably error in the value of β_T .

Mixtures of water The density scattering for water-ethanol mixtures has been calculated using expression (15). The compressibility β_S is computed from the experimental data of sound velocity¹⁴. Other necessary values for determining β_T we

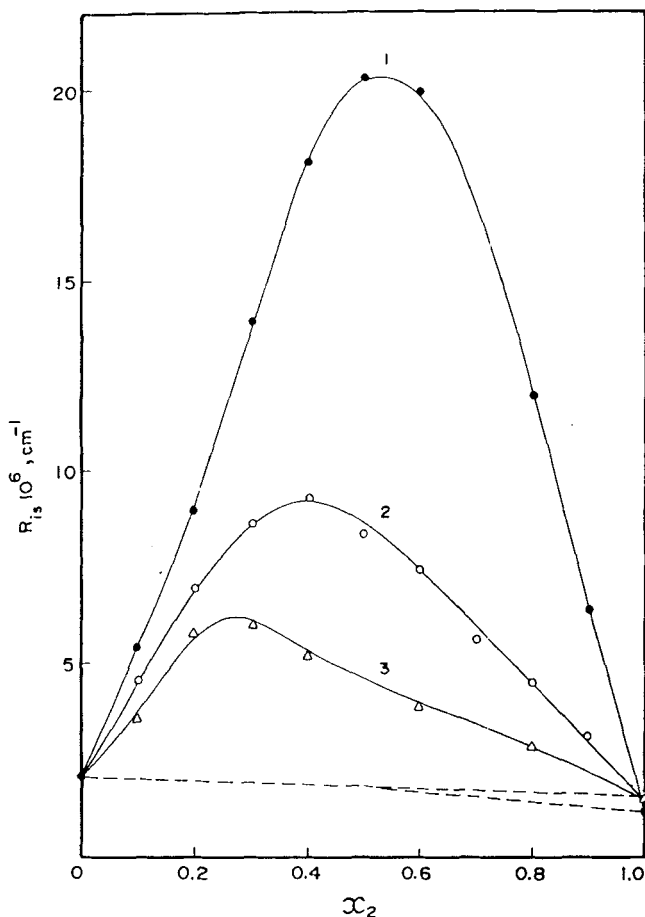


Figure 5 Rayleigh light scattering ratio R_{13} for the binary systems: (1) chlorobenzene-methanol; (2) chlorobenzene-propanol; (3) chlorobenzene-butanol ($\lambda = 632.8 \text{ nm}$, 20°C).

have obtained from the tables. The calculating values of density scattering intensity are represents in Figure 7 as dotted lines. Comparing the full curve with the dashed line indicated that, the compositional scattering in the present system is very weak, producing a little change in the total intensity, in the area of low concentration of alcohol at $x_2 \leq 0.40$ only.

In the water-isopropyl alcohol system (Figure 7) beside the sharp maximum, at $x_2 = 0.05$, which has no relation with the compositional fluctuation, we can observe a very weak compositional fluctuation maximum in the region of $x_2 = 0.20$. In our opinion, the absence of an observed maximum follows from the fact that the compositional fluctuation is very weak and because of the lower values of $\partial n/\partial x$. The theoretical calculation, on the basis of the thermodynamical data¹⁵ shows that, the compositional maximum in the present system must lie in the region of $x_2 = 0.18$.

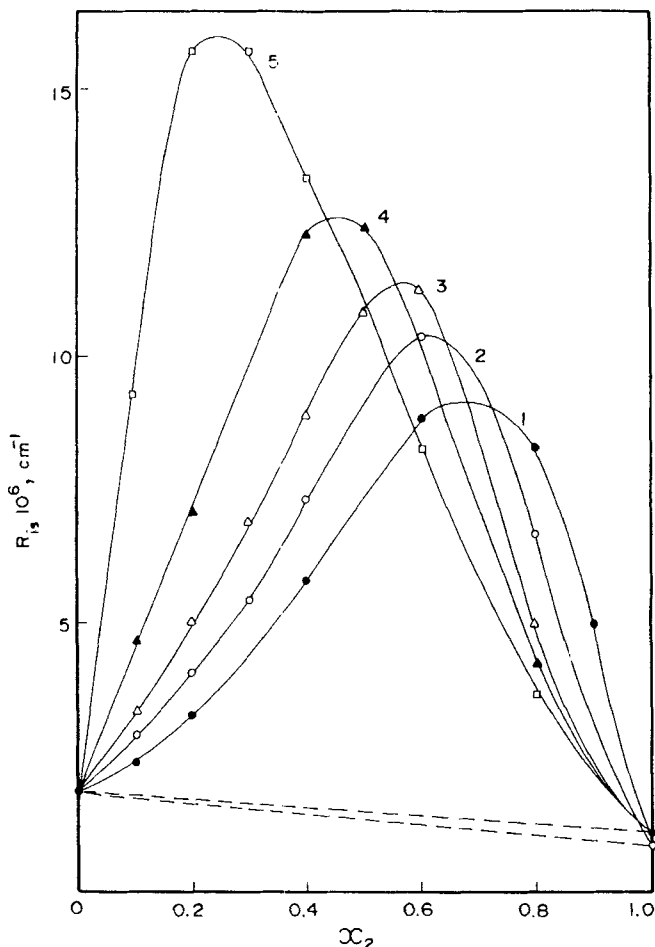


Figure 6 Light scattering ratio R_{13} for the five systems: (1) aniline-methanol; (2) aniline-ethanol; (3) aniline-propanol; (4) aniline-butanol; (5) aniline-heptanol ($\lambda = 632.8 \text{ nm}$, 20°C).

The water-tertbutyl alcohol system (Figure 7) has a very sharp maximum at $x_2 = 0.04$ and a wide-range maximum at $x_2 = 0.20$. Authors^{16,17} suggested that the compositional scattering maximum must be lied in the region of $x_2 \cong 0.15$ (at $\lambda = 546.1 \text{ nm}$, 20°C) and must have a wide-range maximum.

The nature of the anomaly scattering The occurrence of the additional scattering maximum in the water-alcohol systems can be explained as a structure fluctuation or structure rearrangement, in our cases, not connected with the temperature but with the concentration. The interaction between alcohols and water may be imagined as follows: in very low concentration of alcohols, its molecules are deeply penetrated in the water lattice, and cannot initiate the breakdown of the lattice. Such penetration

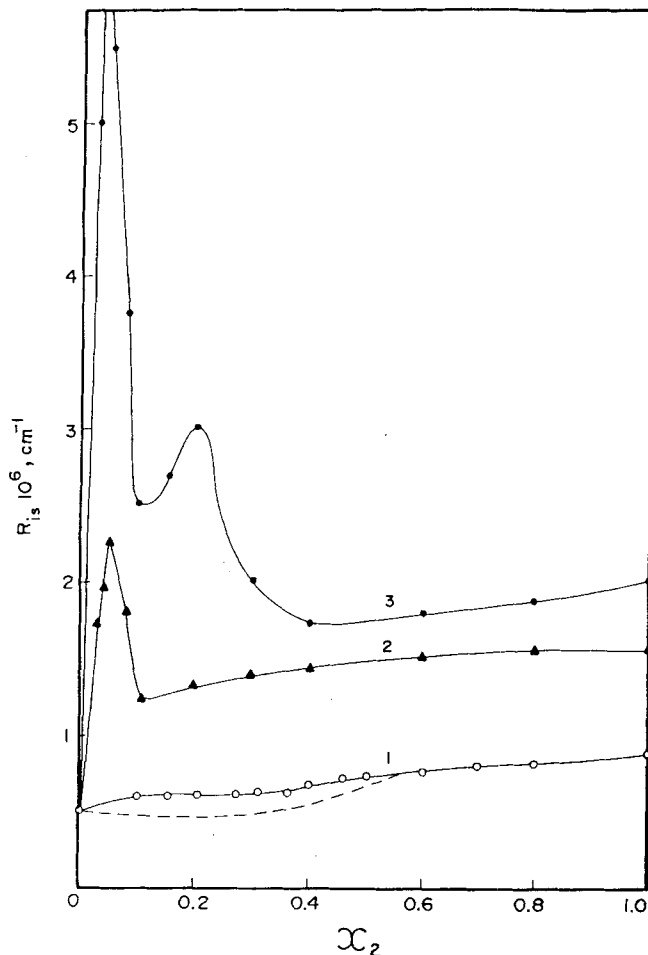


Figure 7 Light scattering ratio R_{1s} for the systems: (1) water-ethanol; (2) water-isopropyl alcohol; (3) water-tertbutyl alcohol ($\lambda = 632.8$ nm, 20°C).

can be suggested as; polar groups of OH displaced the water molecules from their lattice and the most extended hydrophobic atomic groups enter the interstitial site spaces. But alcohol molecules (except methanol) cannot occupy the space in the interstitial site of the ice-lattice. It is necessary to suppose that^{18,19} the implantation of alcohols into the water lattice caused the structure rearrangement of water, as a result of the conversion of the ice-lattice to dodecahedral with larger interstitial spaces. It is obvious that, the penetration of alcohol's molecule, without the destruction of the structure of water, may be continued only until a defined concentration. The existence of the additional maximum in the scattered light indicated that the structure rearrangement of the mixture by increasing alcohol's concentration have a co-operative character. Reconstruction occurs at an exactly defined concentration.

But we cannot exclude that the transition has a limited spreading. It means that at the transition critical point the double structures exist together in the form of a nucleus (center) or one of the structure fragments inside the other.

CONCLUSIONS

Light scattering techniques from liquids and liquid mixtures can be successfully employed to obtain binary thermodynamic interaction data for various solvents in a simple and routine manner. The technique for studying the properties of molecules and intermolecular interactions is fast and simple. The accuracy and sensitivity of the applied method depends mainly on the difference of the refractive indices of the two compounds of the mixture and on the values of the Rayleigh ratios. We summarize our main findings as follows:

- 1) The dipole interactions in all our mixtures are not effective.
- 2) Between molecules of chlorobenzene and alcohol a strong hydrogen bond has not occurred, and the hydrogen bond in chlorobenzene mixtures is not stronger than that in benzene and toluene mixtures.
- 3) Compositional fluctuation in the mixtures of benzene, toluene and chlorobenzene decreased by increasing the alcohol number, while these fluctuations increased in the case of aniline-alcohol systems.
- 4) In the mixtures of methanol the rule of hydrogen bond is very effective. In going to ethanol, propanol, butanol and heptanol mixtures, this effect decreases. This may be explained as the worsening solubility which caused the increase of the compositional fluctuations.

The occurrence of the additional scattering maximum in the water-alcohol systems may be explained as a structure fluctuation. The additional maximum of scattered light cannot be viewed as evidence that the phase transition has occurred. Such proof may be given only by studying the thermodynamical properties of mixtures.

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