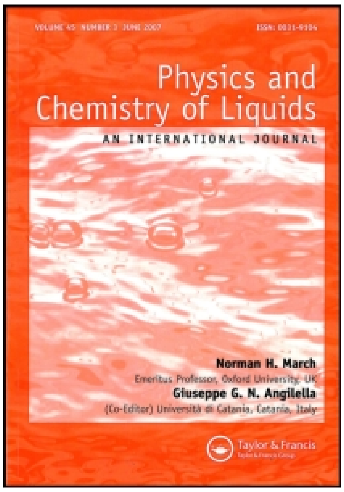

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LIGHT SCATTERING OF BINARY LIQUID SYSTEMS III. THE RESIDUAL GIBBS POTENTIAL OF SOLUTIONS

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The intensity of light scattered by 14 binary liquid mixtures and their depolarization measured at 20°C and at a wavelength of $\lambda = 632.8$ nm., were used to evaluate the composition fluctuation function, f and the residual Gibbs potential G^E for these systems as a function of mixture composition. The rule of hydrogen bond in our investigated mixtures has been discussed.

KEY WORDS: Rayleigh scattering, Gibbs potential.

INTRODUCTION

Rayleigh scattering ratios considered as a fast and simple method for probing thermodynamic interactions in binary mixtures[1–4] and have been used for deriving important thermodynamic values such as the composition fluctuation 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 better than the other thermodynamic values.

According to Prigogine[5] a large influence on the micro-mixing materials seems due to temperature, concentration, molecular dimensions ratio, ρ, and the relative differences of interaction energies, δ. Conformably with the thermodynamical point of view, the properties of solutions may be characterized by the value of the residual Gibbs potential G^E which connected with the root-mean square quantity of the composition fluctuation.

In this work, light scattering is used to evaluate the Rayleigh ratios and the thermodynamic fluctuation f. From these values one can compute the value of the residual Gibbs potential G^E for the following binary systems: nitrobenzene-alcohols, pyridine-alcohols, pyridine-hydrocarbons and water-(pyridine, acetone and dioxane).

THEORY

The total reduced intensity R, (Rayleigh ratio) is defined as

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

where I_0 is the intensity of the incident 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 decomposed into anisotropic scattering, R_{an} and isotropic scattering, R_{is}. The latter part is decomposed further into compositional scattering, R_{c}, and density scattering, R_{d}, hence:

$$R = R_{\mathrm{is}} + R_{\mathrm{an}} = R_{\mathrm{c}} + R_{\mathrm{d}} + R_{\mathrm{an}} \tag{2}$$

The expression for R_{c} in a binary mixtures reads[6,7]

$$R_{\mathrm{c}} = (\pi^2/\lambda^4)\,(\partial\varepsilon/\partial x)^2\overline{\Delta x^2}v \sin^2 \phi \tag{3}$$

Here x serves to indicate the use of mole fractions as a concentration unit, v is the volume of one mole of the mixture, λ is the wavelength of the primary light, $(\partial\varepsilon/\partial x)$ 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 or the direction of scattered light. For the scattering of nonpolarized light, we have

$$R_{\mathrm{c}} = (\pi^2/2\lambda^4)(\partial\varepsilon/\partial x)^2\,\overline{\Delta x^2}\,v \tag{4}$$

R_{c} can be related to the Gibbs function through the relation,

$$R_{\mathrm{c}} = (\pi^2/2\lambda^4 N_A)(\partial\varepsilon/\partial x)^2 R_0\, T(\partial^2\mathrm{G}/\partial x^2)^{-1}_{P,T} V_{12} \tag{5}$$

Here N_A is the Avogadro's number, $R_0\mathrm{T}$ has its usual meaning, G is the thermodynamical potential Gibbs, and V_{12} is the volume of one mole of the mixture.

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

$$1/f = (x_1x_2/R_0T)\,(\partial^2\mathrm{G}/\partial x^2)_{P,T} \tag{6}$$

Combining Eqs. (5) and (6) we have

$$R_{\mathrm{c}} = (\pi^2/2\lambda^4 N_{\mathrm{A}})(\partial\varepsilon/\partial x)^2 x_1 x_2 V_{12} f \tag{7}$$

The function f can be expressed in terms of the residual thermodynamical Gibbs potential G^E, as

$$1/f = 1 + (x_1x_2/R_0T)(\partial^2G^E/\partial x^2) \tag{8}$$

According to Eq. (7) we need to calculate: $(\partial n/\partial x)$, V_{12} and f. The derivative $\partial n/\partial x$ is evaluated as,

$$\partial n/\partial x_1 = (\partial n/\partial c_1)(c_1/x_1)^2(M_2M_1) \tag{9}$$

Here M_i's and C_i's are the molecular weights and the weight fractions of the system components.

The macroscopic value of $\partial n/\partial x$ connected with the fluctuational value appearing in Eq. (7) by the relation[8],

$$(\partial n/\partial x)_{\mathrm{fluc}} = (\partial n/\partial x)\{3n^2/(2n^2+1)\}\{3/(n^2+2)\} \tag{10}$$

The second interest value V_{12} defined as

$$V_{12} = M_{12}/\rho = (x_1M_1 + x_2M_2)/\rho \tag{11}$$

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

$$V_{12} = x_1V_1 + x_2V_2$$

and the compositional scattering Rayleigh ratio R_c, reads

$$R_c = (\pi^2/\lambda^4N_A)\{2n(\partial n/\partial x)\}^2\{9n^2/(2n^2-1)\,(n^2+2)\}^2x_1x_2V_{12}f \tag{12}$$

In the free volume theory[9–11] the thermodynamical functions can be expressed through molecular parameters (molecular dimensions and molecular interaction forces of the components of solutions)[12]. The problem of calculating the different interactions in solutions has been solved[10] supposing that, the potential energy of molecular interactions may be written as,

$$\varepsilon^*_{\mathrm{A,B}}(r) = -|\varepsilon^*_{\mathrm{A,B}}|\{2(r^*_{\mathrm{A,B}}/r)^6 - (r^*_{\mathrm{A,B}}/r)^{12}\} \tag{13}$$

and the residual free energy of the solution according to the above theory is given as

$$\begin{aligned} E = N\Lambda_{11}\{&1.453[\vartheta + (4.5\rho)]x_1x_2 + 10.8R_0T/\Lambda_{11}[-2\vartheta - 0.759^2 + \vartheta^2 \\ &+ \delta\vartheta(1+2x_2) - 38.13\rho\delta^2 - 5.55\rho\delta + 11.1\rho\vartheta(x_2 - x_1)]x_1x_2\} \end{aligned} \tag{14}$$

where the thermodynamical functions ρ, δ and ϑ defined as

$$\rho = (r_{22}^{*} - r_{11}^{*})/r_{11}^{*}; \qquad \delta = (1/\Lambda_{11})(\Lambda_{22} - \Lambda_{11});$$

$$\vartheta = \{(1/\Lambda_{11})[\Lambda_{12} - (\Lambda_{11} + \Lambda_{22})/2]\}$$

Here $\Lambda_{11} = Z|\varepsilon_{11}|$; Z is the coordination number, ε is the depth of the potential well and r is the radius of the molecule.

The above theory is applicable for solutions whose components have spherical shapes, a different radii and different interaction potentials, for example in the cases of the dispersive forces ($\vartheta = \delta^2/8$). For liquid states Roshina[12] used the assumption $16 < (\Lambda_{11}/R_0T) < 20$. So, the residual Gibbs free energy can be rewritten as,

$$(G^E/N\Lambda_{11}) = x_1x_2(3.43\rho^2 - 0.32\rho\delta + 0.2\delta^2),$$

or

$$(\partial^2 G^E/\partial x^2)_{P,T}/N = (R_0T/x_1x_2N) - 2(3.43\rho^2 - 0.32\rho\delta + 0.2\delta^2)\Lambda_{11}$$

$$(\partial^2 G^E/\partial x^2)_{P,T} = (R_0T/x_1x_2) - 2A$$

and the compositional scattering Rayleigh ratio R_c reads

$$R_c = \frac{(\pi^2/\lambda^4 N_A)4n^2(\partial n/\partial x)^2\{9n^2/(2n^2 - 1)(n^2 + 2)\}^2 x_1x_2V_{12}}{[1 - 2(x_1x_2/R_0T)A]} \qquad (16)$$

In our previous works[13–15] we proved that the molecular dimensions difference and the interaction energies can be determined using the composition fluctuation growth and the deviation from the ideality of the solutions. Also we proved that the above theory can be applicable in these cases when the components of the solutions have a non-spherical form, interacted not only with dispersive forces but also with intermediate forces and finally if the dimensions difference and the molecular interactions are very small.

EXPERIMENTAL SECTION

The equipment and techniques utilized for obtaining the various experimental quantities presented here have been described in detail in our previous papers[16,17]. Samples of purity typically higher than 99% supplied by Merck were further purified from dust particles and air bubbles by thorough filtration using a 0.45 μm Teflon filter. 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

In order to calculate R_c from R_{is}, the density scattering R_d must be estimated. The relation for R_d reads[17]

$$R_d = (\pi^2/2\lambda^4)KT\beta_T(n^2-1)^2\{3n^2/(2n^2+1)\}^2 \tag{17}$$

Another method for calculating R_d is the additive scheme $R_d = \phi_1 R_1 + \phi_2 R_2$ where R_i's are the density scattering by pure components and ϕ_i's are the volume fractions of the components.

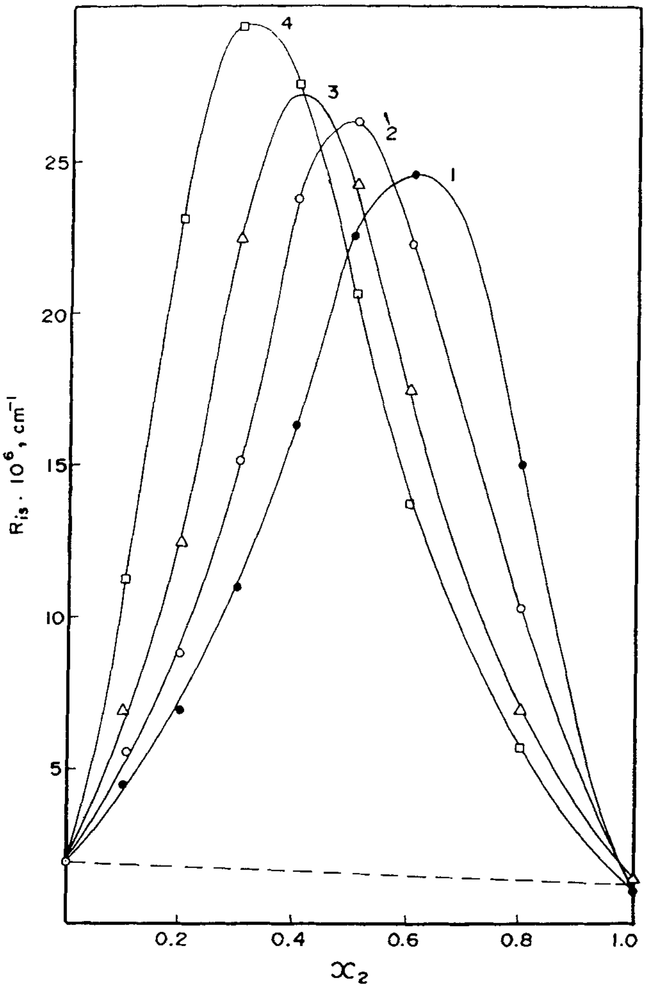

Figure 1a Rayleigh light scattering ratio R_{is} for the binary systems: (1) nitrobenzene-methanol; (2) nitrobenzene-ethanol; (3) nitrobenzene-propanol; (4) nitrobenzene-butanol, ($\lambda = 632.8$ nm, 20°C). The dashed lines represent the theoretical estimate of R_d

1 *Mixtures of Nitrobenzene*

The quantities of R_{is} for: nitrobenzene-methanol, nitrobenzene-ethanol, nitrobenzene-propanol and nitrobenzene-butanol mixtures are plotted as a function of composition in Figure 1a. The dashed lines represent the theoretical estimate of R_d calculated by Eq. (17). The intensity of scattered light from the above systems has a higher value than all the previously measured systems[18]. This not means that the composition fluctuation is also very high. The calculated function f has a maximum value equal to 7.28, which is slightly differs from one system to another $6.9 < f_{max} < 7.3$ (see Table 1). This means that a weak hydrogen bond between the molecules of nitrobenzene and alcohols are occurred comparing with that between the molecules of aniline and alcohols[18].

If the components of the solution have a little difference in their molecular dimensions and intermolecular interaction energies, the composition fluctuation will be weakly increase. This is characterizing for molecular-miscibility systems where the isotropic scattered light basically due to density fluctuation. Any increase in the difference between the molecular dimensions and the interaction energies will be accompanied with an increase in the deviation of these systems from the ideality. The values of the f function (Table 1) indicate that nitrobenzene solutions are not ideal. Therefore, its deviation from the ideality has a significant value and the values of ρ and δ differ from zero. Such solutions may be related to the molecular-immiscibility type.

From expression (15) one can see that higher values of ρ and δ give a strong growth in the composition fluctuation of the solution. Using the values of R_c and n, the parameter A in Eq. (15) has been evaluated, from which the values of the residual Gibbs potential, G^E are calculated. The dependence of G^E on the concentration is shown in Figure 1b. Going from nitrobenzene-methanol to nitrobenzene-butanol mixtures, the calculated values of ρ, the values of δ, deduced from the light scattering measurements (at low temperatures), and the G^E values are found to decrease significantly. This result may support the dependence of the original Gibbs potential on the molecular dimensions ratio and on the relative differences of interaction energies of the mixture components.

2 *Mixtures of Pyridine*

Figures 2a and 2b show the Rayleigh scattering rations R_{is} and the Gibbs potential G^E for pyridine-methanol, pyridine-ethanol, pyridine-propanol and pyridine-butanol systems as a function of alcohol's volume fractions x_2. In all tested mixtures a very weak compositional scattering has been detected. According to the thermodynamic properties, our tested systems near to the ideal solution. Such deduction may be weightless because spectroscopic data indicate that, between molecules of pyridine and alcohol a very strong hydrogen bond has been occurred. It seems that such special interaction must lead to a deviation from the ideal solution properties. Additionally the molecular properties and structure of pyridine and alcohol are largely differ. Pyridine and alcohol formed quasi-ideal mixtures, in spite of that, these

Table 1 Experimental values of the depolarization Δ and the calculated values of the function *f* and the Gibbs potential G^E for the Mixture Systems Studied (at $\lambda = 632.8$ nm, 20°C)

x_2	Δ.*10*	*f*	G^E *cal/mol*	x_2	Δ.10	*f*	G^E *cal/mol*
	Nitrobenzene-Methanol				Nitrobenzene-Ethanol		
0.00	6.68	1.00	0.000	0.00	6.70	1.00	0.000
0.10	5.03	1.35	234.5	0.10	4.64	1.74	97.31
0.20	4.02	2.45	416.9	0.20	3.17	2.64	172.9
0.30	2.66	3.72	547.3	0.30	2.36	4.12	227.0
0.40	1.85	5.25	625.4	0.40	1.19	5.84	259.5
0.50	0.95	6.94	651.5	0.50	0.95	7.02	270.3
0.60	0.59	6.20	625.4	0.60	0.79	4.90	259.5
0.80	0.36	2.47	416.9	0.80	0.54	2.11	172.9
1.00	0.83	1.00	0.000	1.00	0.63	1.00	0.000
	Nitrobenzene-Propanol				Nitrobenzene-Butanol		
0.00	6.70	1.00	0.000	0.00	6.63	1.00	0.000
0.10	4.16	2.68	28.26	0.10	3.06	3.08	1.520
0.20	2.71	3.81	50.24	0.20	1.54	5.71	2.702
0.30	1.54	5.30	65.94	0.30	1.12	7.28	3.547
0.40	1.23	7.10	75.37	0.40	1.04	6.12	4.053
0.50	1.00	5.52	78.51	0.50	1.14	4.08	4.222
0.60	0.95	3.75	75.37	0.60	1.08	3.00	4.053
0.80	1.20	2.04	50.24	0.80	1.53	1.57	2.702
1.00	0.88	1.00	0.000	1.00	2.47	1.00	0.000
	Pyridine-Methanol				Pyridine-Ethanol		
0.00	4.89	1.00	0.000	0.00	4.89	1.00	0.000
0.10	4.82	1.04	117.8	0.10	4.73	1.06	36.85
0.20	4.74	1.22	209.5	0.20	4.60	1.28	65.52
0.40	4.62	1.38	314.3	0.40	4.39	1.42	98.27
0.50	3.94	1.51	327.4	0.50	3.60	1.64	102.3
0.60	2.86	1.30	314.3	0.60	2.70	1.60	98.27
0.80	2.37	1.09	209.5	0.80	2.54	1.22	65.52
1.00	0.79	1.00	0.000	1.00	0.64	1.00	0.000
	Pyridine-Propanol				Pyridine-Butanol		
0.00	4.89	1.00	0.000	0.00	4.89	1.00	0.000
0.10	4.52	1.12	2.423	0.10	4.29	1.26	12.81
0.20	4.04	1.31	4.307	0.20	3.67	1.40	22.78
0.40	3.81	1.46	6.461	0.40	3.24	1.58	34.18
0.50	3.35	1.94	6.730	0.50	2.93	2.31	35.60
0.60	2.34	1.81	6.461	0.60	2.00	2.06	34.18
0.80	2.06	1.30	4.307	0.80	2.10	1.64	22.78
1.00	0.90	1.00	0.000	1.00	2.33	1.00	0.0000
	Pyridine-Octane				Pyridine-Decane		
0.00	4.82	1.00	0.000	0.00	4.83	1.00	0.000
0.10	2.59	1.65	210.7	0.10	2.97	1.32	359.1
0.20	1.88	3.80	374.7	0.20	2.06	2.08	638.5
0.30	1.44	5.64	491.8	0.30	1.75	3.80	838.0
0.40	1.23	5.40	562.1	0.40	1.60	4.41	957.7
0.60	1.39	2.56	562.1	0.60	1.84	2.01	957.7
0.80	1.61	1.54	374.7	0.80	2.29	1.26	638.5
1.00	1.13	1.00	0.000	1.00	1.55	1.00	0.000

(*continued*)

Table 1 *Continued*

x_2	Δ.10	f	G^E cal/mol	x_2	Δ.10	f	G^E cal/mol
	Pyridine-Hexane				Water-Pyridine		
0.00	4.82	1.00	0.000	0.00	0.91	1.00	0.00
0.10	2.06	2.31	86.45	0.05	0.14	2.44	855
0.20	1.44	4.50	153.6	0.08	0.19	4.86	1325
0.30	1.11	6.28	201.7	0.10	0.32	6.32	1620
0.40	0.98	5.90	230.5	0.20	0.77	3.25	2881
0.60	1.15	3.42	230.5	0.40	2.01	1.36	4321
0.80	1.37	2.26	153.6	0.70	4.22	1.04	3781
1.00	0.90	1.00	0.000	1.00	4.80	1.00	0.00
	Water-Dioxane				Water-Acetone		
0.00	0.91	1.00	0.00	0.00	0.91	1.00	0.00
0.06	0.56	1.68	1099	0.05	0.43	1.52	717
0.10	0.50	2.32	1754	0.10	0.89	2.06	1359
0.20	0.42	3.15	3119	0.20	1.17	2.80	2417
0.30	0.40	3.71	4094	0.40	1.17	3.62	3625
0.40	0.49	4.26	4678	0.50	1.27	5.10	3777
0.50	0.46	5.02	4873	0.60	1.46	—	3625
0.70	0.73	3.74	4093	1.00	1.73	1.00	0.00
0.80	0.94	2.02	3119				
1.00	1.20	1.00	0.0				

two substances considered as dissimilarly (the similar substances produce ideal mixtures). In this case the formation of such mixture achieved on the expense of the initiation of the hydrogen bond between pyridine and alcohol molecules.

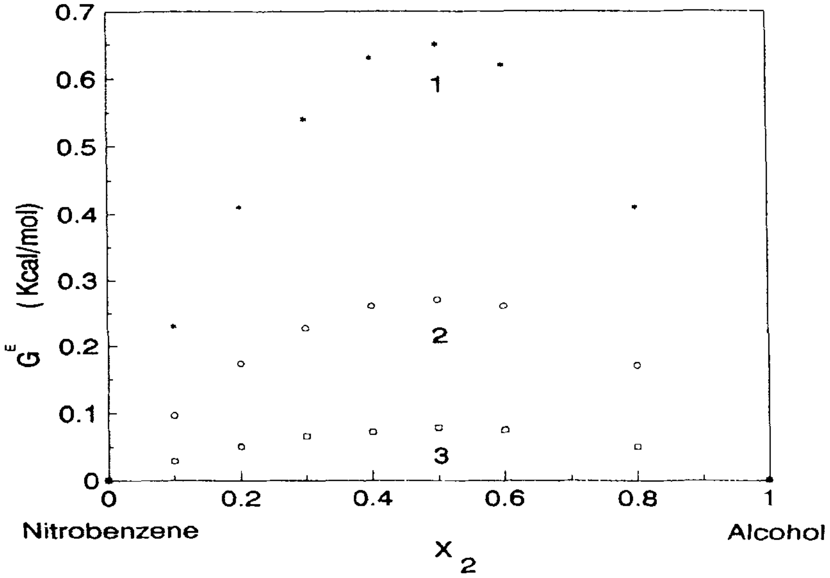

Figure 1b The residual Gibbs Potential G^E as a function of the volume fraction of the second component x_2 for the binary systems: (1) nitrobenzene-methanol; (2) nitrobenzene-ethanol; (3) nitrobenzene-propanol.

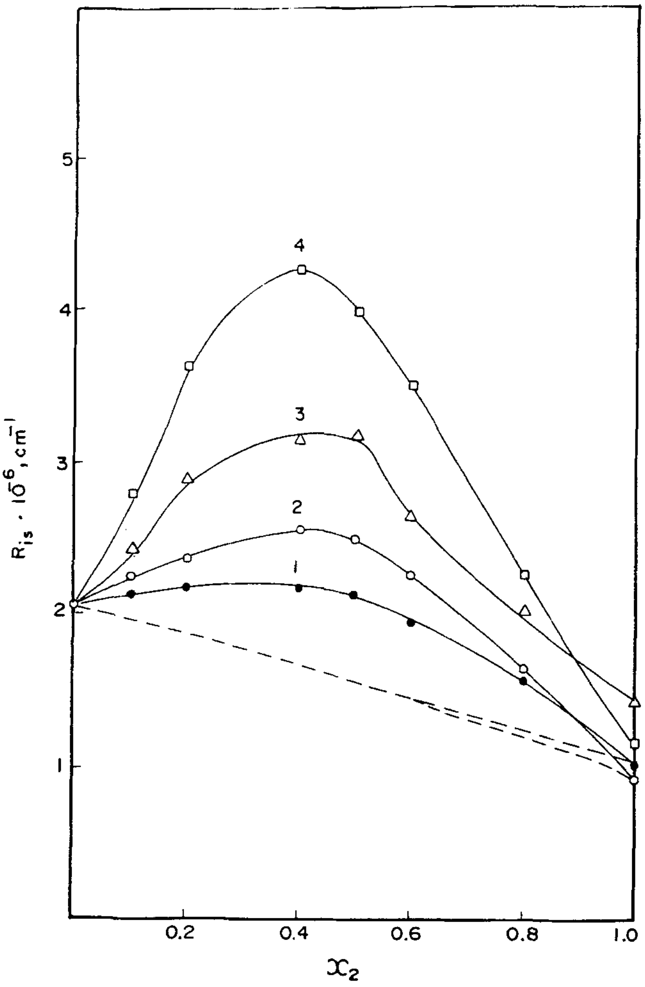

Figure 2a Dependence of the isotropic scattering R_{is} on the volume fraction of component 2 for the binary systems: (1) pyridine-methanol; (2) pyridine-ethanol; (3) pyridine-propanol; (4) pyridine-butanol. ($\lambda = 632.8$ nm, 20°C).

To explain the rule of hydrogen bond in pyridine-alcohol mixtures, the systems of pyridine-paraffin hydrocarbons (hexane, octane and decane) were studied. In the three systems, significant compositional scattering has been observed (Figure 3a) The calculated composition fluctuation f has a high maximum $f \cong 6$ in the region of $x_2 = 0.3 \div 0.4$. Hydrocarbons differ from alcohols in the absence of hydroxide groups. The experiments dealing with the mixtures of pyridine-hydrocarbons showed clearly that the lower level of the composition fluctuation in pyridine-alcohol mixtures is due to the formation of hydrogen bond between pyridine and alcohol molecules.

The dependence of the potential G^E on the molecular dimensions ratio of the two

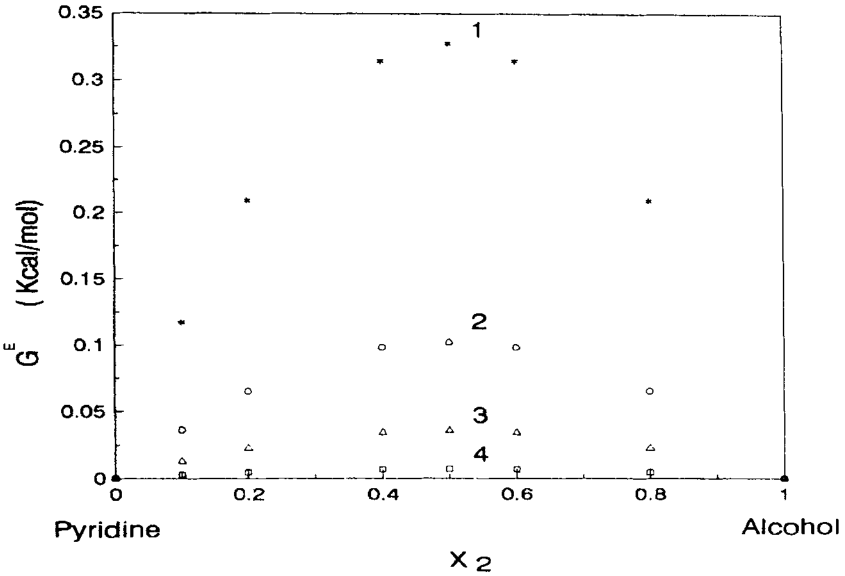

Figure 2b The residual Gibbs potential G^E for the systems: (1) pyridine-methanol; (2) pyridine-ethanol; (3) pyridine-butanol; (4) pyridine- propanol.

components agree with the conditions of the validity of expression (15), while the values of the relative interaction energies inversely proportional to the G^E values. This may be attributed to the absence of the hydroxide groups in the paraffin hydrocarbons (see Figure 3b).

3 *Mixtures of Water*

The study of the thermodynamic interactions in aqueous mixtures has a significant value. Such systems have a number of specific distinctions which must be carefully investigated. In our opinion, the technique of light scattering can be successfully employed for the indication of some special structure of the aqueous mixtures.

The quantity of R_{is} for the water-pyridine system is plotted in Figure 4 as a function of composition. The dashed lines represent the theoretical estimate of R_d calculated by Eq. (17). The calculated values of the composition fluctuation function f (see Table 1) has a sharp maximum in the region of the low concentrations of pyridine (at $x_2 = 0.10$). In this system the valuable composition fluctuation can be observed in the area of low concentrations from $x_2 = 0.05$ to $x_2 = 0.20$ only. At the high concentrations region the composition fluctuation is nearly close to the ideal fluctuation level.

The Rayleigh scattering ratio, R_{is} for the water-acetone mixture is plotted in Figure 5a as a function of acetone's volume fractions x_2. Although the compositional scattering intensities, here, has very low values but the composition fluctuation

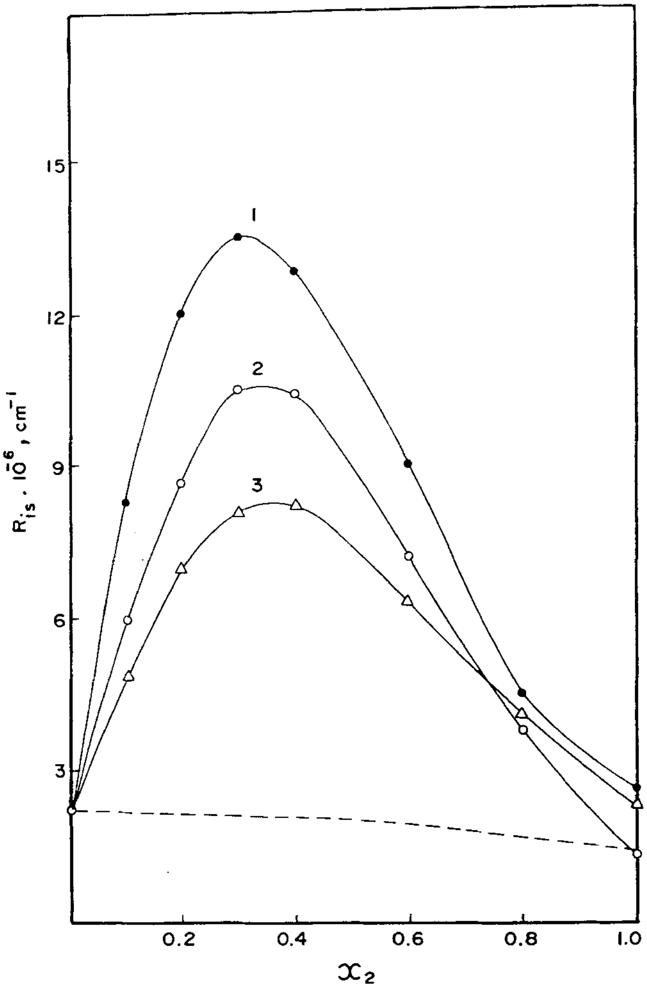

Figure 3a Light scattering ratio R_{is} for the systems: (1) pyridine-hexane; (2) pyridine-octane; (3) pyridine-decane. ($\lambda = 632.8$ nm, 20°C).

function f has sufficiently high values. This may be credible because the refractive indices of both water and acetone slightly differ from each other. So the derivative of $\partial n/\partial x$ has a very low value for all concentrations from $x_2 = 0.02$ to $x_2 = 1$. The observable compositional scattering has been detected at the low concentration region of acetone (at $x_2 = 0.2$ only).

The study of infrared spectroscopy of water $v = 5180\,\text{cm}^{-1}$ indicates that[19] the addition of acetone caused a shift of the absorption bands to the side of the more lower frequencies until the concentration of acetone near to the value of $x_2 = 0.06$, after which the shift stopped. This behavior similar to that for water-alcohol

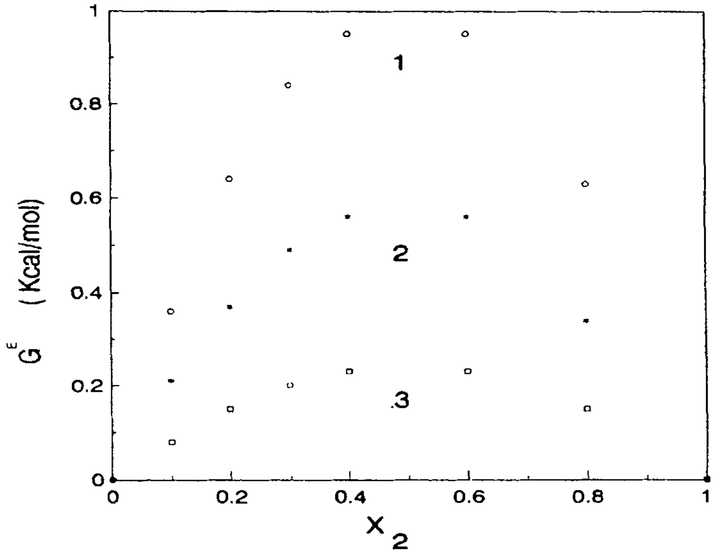

Figure 3b The residual Gibbs potential G^E for the systems: (1) pyridine-decane; (2) pyridine-octane; (3) pyridine-hexane.

mixtures[18]. The shift value for the mixtures of acetone is very lower than that for the alcohol's mixtures. In our opinion, the shift value in the absorption band $\nu = 5180\ \mathrm{cm}^{-1}$ may be served as a measure degree of the co-operative in the phase transition[20].

In the water-dioxane system (Figure 5a) it is clear that the composition fluctuation is intensely developed. Besides the composition fluctuation maximum at $x_2 = 0.5$, one can observe an additional maximum at $x_2 = 0.2$. The occurrence of the additional scattering maximum can be explained as a structure fluctuation or structure re-arrangement of water[21,22], which, in the present cases, not related with the temperature but with the concentration. The dependence of G^E on the volume fractions of the second component are shown in Figure 5b and in Table 1. It is clear from these results that the aqueous mixtures have a very high potential G^E compared with all the other investigated mixtures.

SUMMARY AND CONCLUDING REMARKS

A large effect on the micro-mixing materials is due to concentration, molecular dimensions ratio and relative differences in interaction energies. The technique of Light scattering from micro-mixing liquids can be successfully employed for studying the molecular structure, properties and intermolecular interactions of various sol-

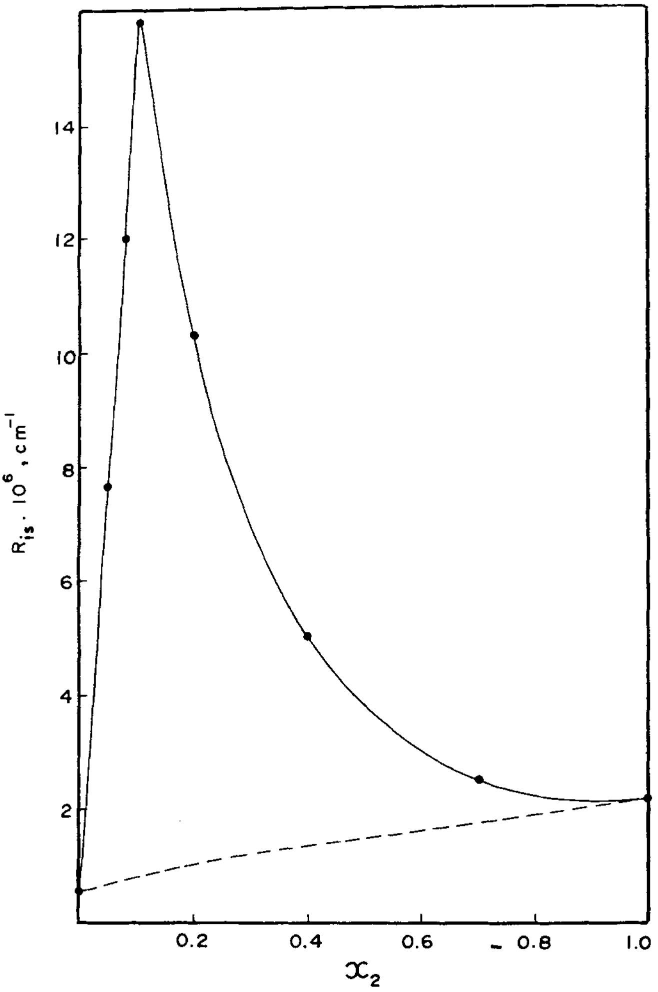

Figure 4 Light scattering ratio R_{is} for the system: water-pyridine. (λ = 632.8 nm, 20°C).

vents. We summarize here our main results: (1) An equal composition fluctuation level and a weak hydrogen bond between the molecules of nitrobenzene-alcohol were observed, the deviation of these systems from the ideality has a significant value and the values of ρ and δ differ from zero. In going from nitrobenzene-methanol to nitrobenzene-butanol mixtures the calculated values of ρ, the values of δ and the G^E values decrease significantly. (2) A very weak composition fluctuation, due to the formation of a very strong hydrogen bond, has been detected in pyridine-alcohol mixtures. (3) The additional scattering maximum in water-dioxane mixtures can be explained as a structure rearrangement of the water molecules. Since no experimental or theoretical data are available for G^E in the literature, the comparison cannot be performed.

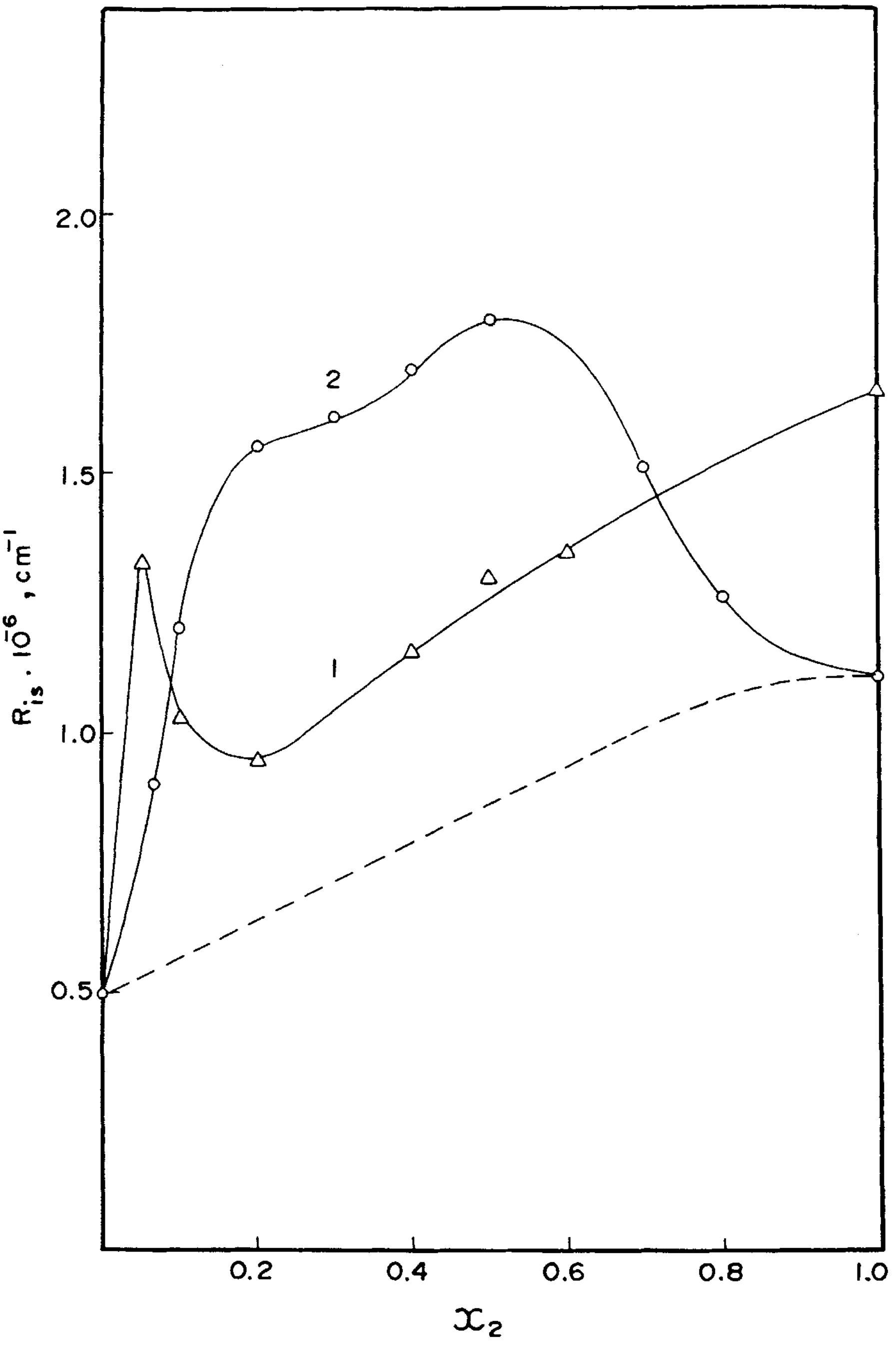

Figure 5a Light scattering ratio R_{is} for the systems: (1) water-acetone; (2) water-dioxane. ($\lambda = 632.8$ nm, 20°C)

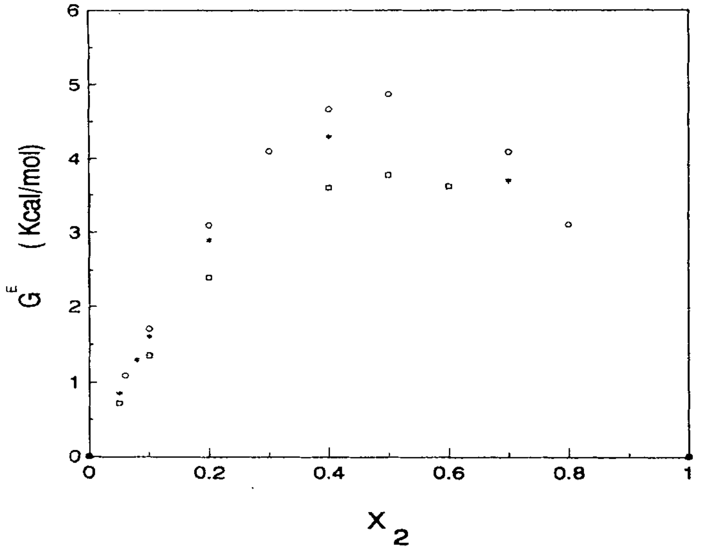

Figure 5b The residual Gibbs Potential G^E for the binary systems: (○) water-dioxane; (*) water-pyridine; (□) water-acetone.

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