

# Isotropic and Anisotropic Light Scattering in Ideal and Real Liquid Mixtures

J. VAVRA

Department of Physical Chemistry, Faculty of Chemical Technology,  
Slovak Technical University, CS-812 37 Bratislava

Received 4 March 1992

Concentration dependence of basic light scattering quantities in ideal and real low-molecular mixtures was studied. Depolarization ratio alone may serve as a sensitive measure of the presence of specific interactions; on the basis of the course of this ratio one can speak about positive or negative deviations from Raoult's law. Experimental data of anisotropic scattering were in harmony with the idea that the parameters determining molecular orientation should be considered as continuous probability variables. Transition from one local structure to another with a maximum of concentration fluctuations and thus of isotropic scattering is indicated.

In the previous papers [1, 2] the Raman as well as Rayleigh scattering was applied to study binary mixtures of pyridine with carboxylic acids. Both methods indicated the presence of strong intermolecular interactions with formation of a complex. In spite of this fact the aim of this paper is to investigate the isotropic and anisotropic light scattering in the mixture pyridine (P)—acetic acid (HAc) in more detail. For comparison the light scattering behaviour of the mixtures methanol—benzene (M—B) [3] and dimethylformamide—tetrahydrofuran (DMF—THF) is presented.

## THEORETICAL

Local fluctuations in the density, concentration, and anisotropy are considered to afford information which is useful to understand the state of mixing from

a molecular point of view. The relationship between these equilibrium fluctuations and Rayleigh intensities is established through basic characteristics [4]  $R_u^{\text{tot}}(\theta) = R_u^{\text{is}}(\theta) + R_u^{\text{anis}}(\theta)$  ( $R_u$  is the Rayleigh ratio for unpolarized primary ray for total, isotropic and anisotropic light scattering,  $\theta$  is the angle of observation), where the isotropic contribution by a liquid mixture may be regarded as a sum of fluctuations in density and concentration [5]

$$R_u^{\text{is}}(\theta) = R_u^{\text{d}}(\theta) + R_u^{\text{c}}(\theta) \quad (1)$$

The scattering parameters  $R^{\text{is}}$ ,  $R^{\text{anis}}$  can be calculated on the basis of experimental determination of  $R_u^{\text{tot}}$  and depolarization  $D_u = H_u/V_u$  ( $H_u/V_u$  is the Rayleigh ratio of the horizontally and vertically polarized components of the scattered light at  $\theta = 90^\circ$ ), and using the well-known equations

$$R_u^{\text{is}} = R_u^{\text{tot}} (6 - 7D_u)/(6 + 6D_u) \quad (2)$$

$$R_u^{\text{anis}} = R_u^{\text{tot}} (13D_u)/(6 + 6D_u) \quad (3)$$

In connection with isotropic scattering the density term is given by the relation [6]

$$R_u^{\text{d}} = (\pi^2 kT/2\lambda_0^4) \beta_T (\rho \partial \epsilon / \partial \rho)_T^2 \quad (4)$$

where  $\beta_T$  is the isothermal compressibility of the liquid mixture,  $\rho$  is the density and  $\epsilon$  permittivity. Then, on the basis of relations (1), (2), (4) it is possible to compute  $R_u^{\text{c}}$  of the mixtures.

$R_u^{\text{anis}}$  denotes translational-orientational fluctuations of anisotropically polarizable molecules and according to papers [7, 8] the anisotropic scattering is given by

$$R_u^{\text{anis}} = QN \left[ g^2 + \frac{z}{2} \sum_i \sum_j \alpha_i \alpha_j (3 \cos^2 \eta_{ij} - 1) \right] \quad (5)$$

$i, j = x, y, z$

where

$$Q = \frac{104}{45} \frac{\pi^4}{\lambda_0^4} \frac{(n^2 + 2)}{3} \quad (6)$$

( $n$  is the refractive index of the scattering medium,  $\lambda_0$  the vacuum wavelength of the incident light) and

$$g^2 = \frac{1}{2} \left[ (\alpha_x - \alpha_y)^2 + (\alpha_y - \alpha_z)^2 + (\alpha_z - \alpha_x)^2 \right] \quad (7)$$

is the anisotropy of the polarizability;  $\alpha_x$ ,  $\alpha_y$ ,  $\alpha_z$  are the main polarizability axes of the molecules;  $N$  denotes the number of molecules per unit volume and  $\eta_{ij}$  is the angle between the axes of symmetry of a pair of molecules; if the number of molecules in the first coordination sphere is  $z$ , the coefficient  $z/2$  stands for the summation over all interacting molecules.

So by estimating concentration dependences  $R_u^{\text{is}}$ ,  $R_u^{\text{anis}}$ , and  $D_u$  it is possible to obtain information on

the structure or intermolecular interactions in a liquid mixture.

## EXPERIMENTAL

The solvents were purified by twofold distillation in an efficient column. THF was subjected to action of KOH for several days and afterwards it was distilled with pure KOH and subsequently with metallic sodium.

The dust particles were removed by pressure filtration through a porous glass filter G5 (Schott, Jena). The solvent solutions of different composition were prepared by pipetting directly into measuring cells in dust-free medium. The tabulated values of density were used for calculating the concentrations.

The light scattering was measured with a photogoniometer Sofica at the wavelength of 546 nm at 25 °C. Benzene was used as a standard for the calculation of individual scattering quantities ( $R_u^{\text{tot}} = 16.2 \times 10^{-6} \text{ cm}^{-1}$ ).

The error of  $R_u^{\text{tot}}$  determinations was 3–5 %, for  $D_u$  5–8 % (repeated preparation and measurement of individual mixtures).

## RESULTS AND DISCUSSION

Fig. 1 shows concentration dependences of light scattering quantities in the investigated mixtures.

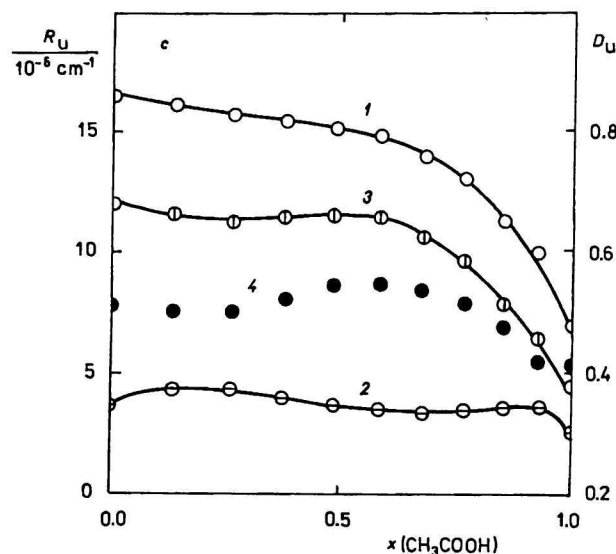
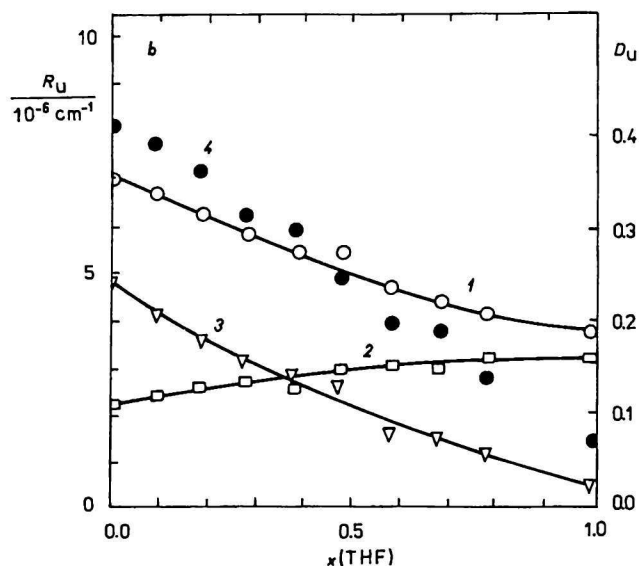
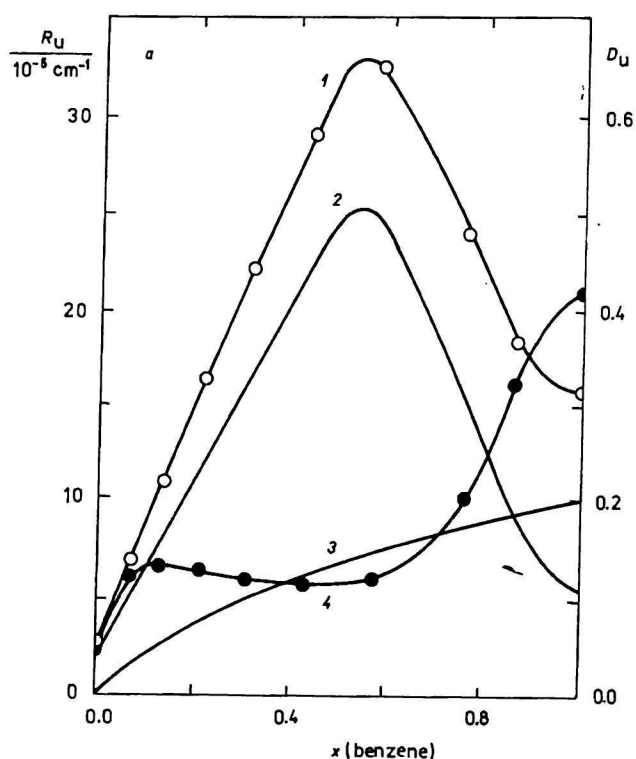


Fig. 1. Concentration dependences of the basic light scattering quantities  $R_u^{\text{tot}}$  (1),  $R_u^{\text{is}}$  (2),  $R_u^{\text{anis}}$  (3) at  $\Theta = 90^\circ$  and  $D_u$  (4). a) Methanol—benzene; b) dimethylformamide—tetrahydrofuran; c) pyridine—acetic acid.  $x$  – mole fraction.

In connection with discussion of these dependences it should be mentioned that generally the scattering molecule is anisotropic and is considered to be an ellipsoid of polarizable "material", which causes some depolarization of scattered light even at  $\Theta = 90^\circ$  and  $D_u$  is a quantitative measure of this depolarization. Similarly in the case of mixtures pair correlations give a fluctuating field at the scattering particles and depolarization can be expected, too.

Provided the solutions are molecular mixtures (without associates and complexes) with components of comparable molecular dimensions or energies of interactions, all pairs of molecules starting from A—A through A—B to B—B will be oriented randomly and the  $D_u$ —concentration dependence should have a linear character. As example of such a behaviour THF—DMF mixture can serve (Fig. 1b) if we judge the affinity of the components by the value of their solubility parameters  $\sigma$  and hydrogen bond indexes  $\Theta_H$  [9]: for DMF  $\sigma/(\text{J cm}^{-3})^{1/2} = 50.6$ ,  $\Theta_H = 18.9$ , for THF  $\sigma = 41.4$ ,  $\Theta_H = 12.0$  ( $\Theta_H$  reflects the ability of a molecule to form the hydrogen bond).

In the system M—B (Fig. 1a) methanol and benzene are quite different chemical species, thus in the region of pure components some degree of structuring of molecules of the same type can occur, but with the growing mutual presence of the components in the mixture this ordering declines. Simultaneously depolarization of the scattered light declines, too and maximum negative deviation from linearity reaches near the equimolar composition just in the region, which is characterized by a high disordering and thus by a maximum of composition fluctuations.

Fig. 1c informs us about the mixture P—HAc, which from the point of view of concentration dependence of  $D_u$  in comparison with the solution M—B has an opposite character. Here we suppose pronounced intermolecular interaction in the region between  $x_{\text{HAc}} = 0.35$  and  $x_{\text{HAc}} = 0.8$  and this interaction is also evident from the course of  $R_u^{\text{anis}}$ . In harmony with this statement we assume that in this concentration region the components of the mixture exhibit a high degree of ordering (orientation), which is accompanied by the marked increase of depolarization of the scattered light.

It is interesting to compare the experimental course of  $R_u^{\text{anis}}$  in the systems P—HAc and DMF—THF with some ideas of description of anisotropic scattering according to *Beke and Keszei* [8]. These authors consider that the parameters determining molecular orientation should always be regarded as continuous probability variables. They introduced a probability density function for the angle  $\eta$  between the spatial positions of two neighbouring molecules in the form

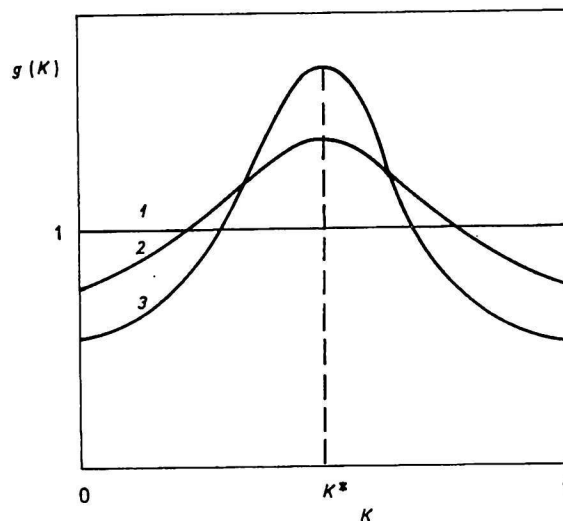


Fig. 2. Probability density of the function  $g(K)$  for chaotic (1) and ordered (2, 3) orientation of neighbouring molecules [8].

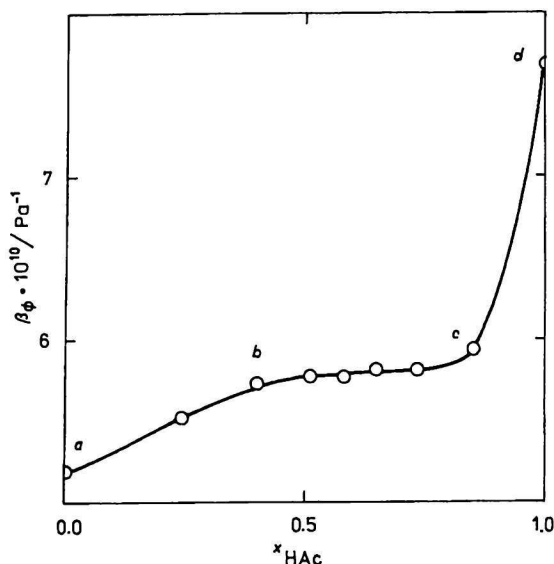


Fig. 3. Adiabatic compressibility in the pyridine—acetic acid mixture [10].

$$g(K) = f(K) \frac{d\eta}{dK}, \quad \text{where } K = -\cos \eta \quad (8)$$

Though the one-variable function  $g(K)$  represents orientation only in the case of one-degree orientational freedom, considerations concerning the probability density of the function  $g(K)$  (Fig. 2) are helpful for the explanation of the problem of specific interactions between molecules A—B [8]. Curve 1 shows the uniform distribution. Curve 2 indicates a kind of order in orientation; mutual positions close to  $K^*$  dominate. Curve 3 represents an orientation where positions close to  $K^*$  are more probable than

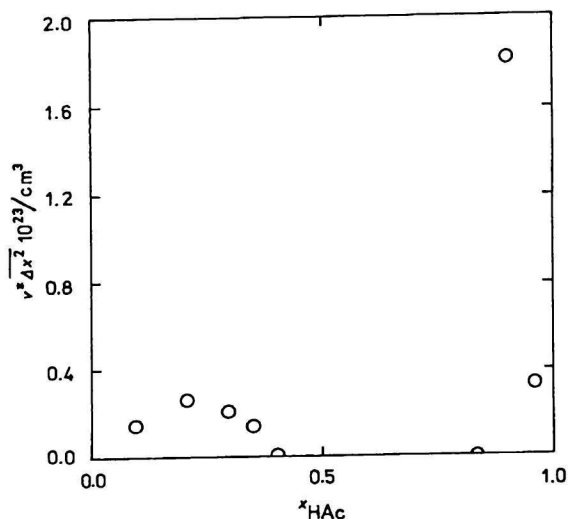


Fig. 4. Concentration dependence of concentration fluctuations for the pyridine-acetic acid system at 25 °C.

in the previous case. So in this way the curve 1 may be adopted as an indicator of linear experimental dependence of  $R_u^{\text{anis}} = f(c)$  in the mixture DMF-THF and curve 2 as theoretical background for the explanation of experimental course of  $R_u^{\text{anis}}$  in the solution P-HAc.

In accord with the results of the compressibility measurements on P-HAc mixture [10] (Fig. 3) it seems that in the considered region with pronounced interactions the molecules enter a more compact equilibrium arrangement (this may be formation of associated complexes); consequently the cohesive energy of the mixture is increased and a decrease of the concentration fluctuations is expected.

These fluctuations  $\overline{\Delta x^2}$  in a volume element  $v^*$  can be quantitatively judged on the basis of the relation

$$v^* \overline{\Delta x^2} = \frac{2\lambda^4 R_u^c}{\pi^2 \left( \frac{\partial n^2}{\partial x} \right)^2} \quad (9)$$

and experimental values of  $R_u^c$  and  $(\partial n/\partial x)$  published in paper [2]. (Iwasaki *et al.* [11] call this  $v^* \overline{\Delta x^2}$  the "fluctuation ability".) Fig. 4 demonstrates  $v^* \overline{\Delta x^2}$  as a function of concentration in the mixture P-HAc. As it can be seen, the concentration fluctuations are zero just in the region, where the compressibility of the mixture is constant (Fig. 3); hereby remarkable agreement between lower compressibility in the region a, b (Fig. 3) and lower degree of fluctuations in this region, respectively higher compressibility and higher degree of fluctuations in the region c, d, exists.

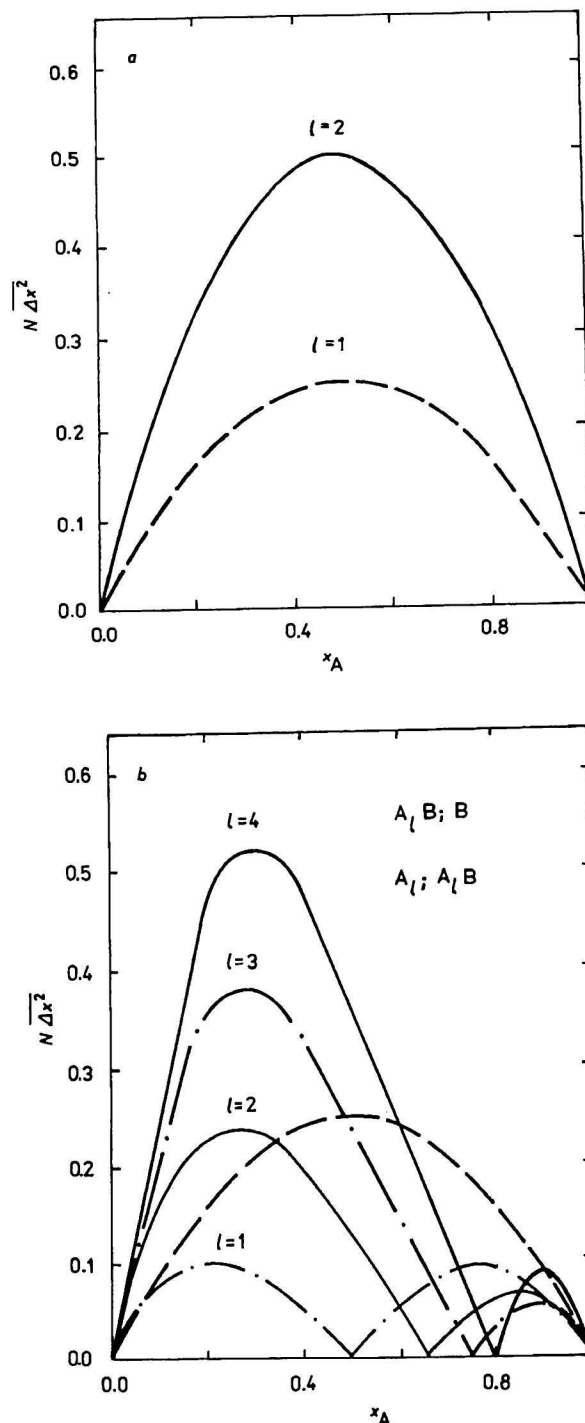


Fig. 5. Theoretical values of concentration fluctuations in systems with associated molecules in the form of  $A_l$  and  $B_m$  [12]; a)  $l = m$ ; b)  $m = 1$  and  $l = 1, 2, 3, 4$ .

Ideas of associated complex formation in a binary solution from the light scattering point of view are discussed in paper [12]. Fig. 5 may serve as an example of theoretical considerations where theoretical values of concentration fluctuations for various types of local structures are plotted. ( $N = \rho_n v^*$ ,  $\rho_n$  is the number density.) From Fig. 5b it is evident

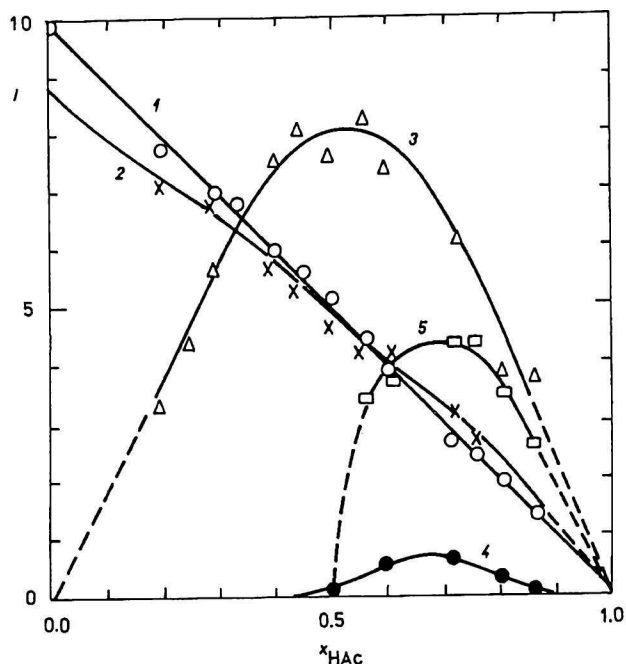


Fig. 6. Intensity of the Raman lines in the mixture pyridine—acetic acid [1] at wavenumbers  $\tilde{\nu}/\text{cm}^{-1}$ : 1. 990; 2. 1030; 3. 1007; 4. 1542; 5. 1020.

that concentration fluctuations can take on zero value at certain mole fractions. Therefore  $\Delta\bar{x}^2$  curves have two distinct maxima, what is the case of the mixture P—HAc (Fig. 4), too. On the basis of Figs. 5a, 5b, 1a and 4 we can judge that transition from one local structure to another with a maximum of composition fluctuations is indicated.

The conclusions about the state of mixing in P—HAc solution obtained from isotropic and anisotropic light scattering are in a full agreement with the results of Raman spectroscopy in this mixture [1]. In this connection Fig. 6 informs about the origin or extinction of the Raman line at  $\tilde{\nu} = 1007 \text{ cm}^{-1}$  just at concentrations, where maximum composition fluctuations are observed (Fig. 4). Simultaneously the region of zero values of these fluctuations starts by  $x_{\text{HAc}} \approx 0.35$ , where the pyridine lines at  $\tilde{\nu} = 990 \text{ cm}^{-1}$  and  $1030 \text{ cm}^{-1}$  (Fig. 6, curves 1 and 2) are of identical intensity as the line at  $\tilde{\nu} = 1007 \text{ cm}^{-1}$  (curve 3), and ends by  $x_{\text{HAc}} \approx 0.8$ , where the lines at  $\tilde{\nu} = 1542 \text{ cm}^{-1}$  and  $1020 \text{ cm}^{-1}$  (curves 4 and 5) become extinct. Hereby the new Raman lines at  $\tilde{\nu} = 1007 \text{ cm}^{-1}$  and  $1020 \text{ cm}^{-1}$  are attributed to the presence of a complex of the proton donor-acceptor type [1].

## CONCLUSION

Results of this study can be summarized as follows:

1. In agreement with Raman spectroscopy the concentration curves of the depolarization ratio and of the isotropic and anisotropic light scattering indicated the presence of a strong intermolecular interaction in the mixture of pyridine with acetic acid.
2. Depolarization ratio alone can serve as a sensitive measure of the presence of specific interactions; on the basis of variation of this ratio with concentration we may speak about positive or negative deviations from Raoult's law.
3. Transition from one local structure to another with a maximum of concentration fluctuations and thus of isotropic scattering is indicated.
4. The isotropic scattering factor of ideal liquid mixtures varies monotonously with concentration.
5. Experimental data of anisotropic scattering were in harmony with the idea that the parameters determining molecular orientation should be considered as continuous probability variables.
6. Light scattering behaviour of the mixture pyridine—acetic acid is in harmony with the conclusion that the anisotropic scattering is independent of the composition fluctuations occurring in the liquid [13].

## REFERENCES

1. Schwab, G. M. and Glatzer, G., *Z. Elektrochem.* 61, 1028 (1957).
2. Vavra, J. and Rosenbergerová, A., *Z. Phys. Chem. (Leipzig)* 260, 1073 (1979).
3. Coumou, D. J., Hijmans, J., and Mackor, E. L., *Trans. Faraday Soc.* 60, 2244 (1964).
4. Kielich, S., *Acta Phys. Pol. A* 19, 149 (1960).
5. Kirkwood, J. G. and Goldberg, R. J., *J. Chem. Phys.* 18, 54 (1950).
6. Einstein, A., *Ann. Phys. (New York)* 33, 1275 (1910).
7. Shakhparonov, M. I., *Physics and Physical Chemistry of Liquids*, 2nd Edition (in Russian). Publishing House of the Moscow University, Moscow, 1973.
8. Beke, Gy. and Keszei, E., *Acta Chim. Hung.* 104, 363 (1980).
9. Kumar, R. and Prausnitz, J. M., in *Solutions and Solubilities, Part I.* (Dack, M. R. J., Editor.) P. 259. Wiley, New York, 1975.
10. Balachandran, C. J., *J. Indian Inst. Sci.* 36, 10 (1954).
11. Iwasaki, K., Tanaka, M., and Fujiyama, T., *Bull. Chem. Soc. Jpn.* 49, 2719 (1976).
12. Kato, T. and Fujiyama, T., *J. Phys. Chem.* 80, 2771 (1976).
13. Kerker, M., *The Scattering of Light*, p. 591. Academic Press, New York, 1969.

Translated by J. Vavra