

Light scattering and excess thermodynamic quantities in the cyclohexane—thiophene mixture

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The fundamental characteristics of light scattering in the symmetric cyclohexane—thiophene mixture were studied at 25°C. The concentration dependence of isotropic scattering indicated the presence only of low extent of the A—A and B—B interactions. The activity coefficients determined by light scattering are in excellent agreement with the test of reliability in the sense of the theories introduced by Redlich or Wilson. The values of ΔG^E are also compared with the values obtained ebulliometrically at 45°C.

Были изучены основные характеристики рассеяния света в симметрической смеси циклогексан—тиофен при 25°C. Концентрационная зависимость изотропного рассеяния показала на присутствие только низкой степени взаимодействий А—А и В—В. Коэффициенты активности, полученные по данным рассеяния света, статистически очень хорошо соответствуют теории Редлиха и Вильсона. Были сравнены также значения ΔG^E с эбуллиометрическими данными при 45°C.

It is known that the fundamental thermodynamic quantities of binary liquid mixtures can be determined by the method of light scattering, too. As a matter of fact, we must estimate the fluctuations in concentration in the sense of the relationship [1]

$$1 - \frac{R_{id}}{R_c} = - \frac{x_2}{RT} \frac{d\mu_2^E}{dx_2} \quad (1)$$

where R_c expresses the fluctuations in composition of a real solution, R_{id} is concentration scattering of an ideal solution, x_2 is mole fraction, and μ_2^E stands for the excess chemical potential of component 2. By integrating this equation, we obtain for the activity coefficients

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$$\ln f_1 = \int_0^{x_2} \left(\frac{1}{x_1}\right) \left\{1 - \left(\frac{R_{id}}{R_c}\right)\right\} dx_2 \quad (2)$$

$$\ln f_2 = \int_0^{x_1} \left(\frac{1}{x_2}\right) \left\{1 - \left(\frac{R_{id}}{R_c}\right)\right\} dx_1 \quad (3)$$

The excess Gibbs energy of mixing is to be determined on the basis of the following equation

$$\Delta G^E = RT (x_1 \ln f_1 + x_2 \ln f_2) \quad (4)$$

If interactions of the A—A and B—B type prevail in a mixture, the fluctuations in concentration assume greater values in comparison with fluctuations in ideal mixtures. On the other hand, if the A—B bonds are preferred in a system, a decrease in these fluctuations is to be observed when compared with ideal solution [2, 3].

This paper deals with the determination of thermodynamic parameters of the cyclohexane—thiophene mixture by the method of light scattering and analyzes them from the view-point of the theories of *Redlich* [4] and *Wilson* [5]. These theories were selected because the *Wilson* equation excellently describes the behaviour of binary mixtures and the *Redlich* procedure is useful from the view-point of graphical verification of the presence of associates [4].

Experimental

Cyclohexane (anal. grade, Lachema, Brno) and thiophene (purum, Reachim) were carefully purified by distillation in an efficacious column. The dust particles were removed by pressure filtration through a glass frit *G5* (Schott, Jena). The solutions of different

Table 1

Refractive indices of the cyclohexane—thiophene mixture at $25 \pm 0.1^\circ\text{C}$ and wavelength 546 nm ,
 x_1 — mole fraction of cyclohexane

x_1	n	x_1	n
0.000	1.5292	0.521	1.4627
0.037	1.5235	0.630	1.4535
0.075	1.5182	0.745	1.4438
0.154	1.5068	0.869	1.4350
0.238	1.4951	0.925	1.4309
0.327	1.4843	1.000	1.4269
0.422	1.4735		

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 refractive indices of pure liquids and their mixtures were determined with an Abbé refractometer. The values thus obtained (Table 1) were used for checking the composition of mixtures and correcting the measured values from the view-point of divergence of scattered light (correction n^2) on the boundary measured system—environment.

The light scattering was measured with a photogoniodyffusometer (Sofica) at the wavelength of 546 nm and $25 \pm 0.2^\circ\text{C}$. Benzene ($R_u^{\text{tot}} = 16.2 \times 10^{-6} \text{ cm}^{-1}$) was used as a standard for calculating individual scattering quantities.

Results and discussion

The calculation of concentration scattering is based on the following equations [6]

$$R_u^{\text{tot}} = R_u^{\text{iso}} + R_u^{\text{an}} \quad (5)$$

$$R_u^{\text{iso}} = R_u^{\text{d}} + R_u^{\text{c}} \quad (6)$$

where R_u represents the Rayleigh ratio at nonpolarized primary beam for total (R_u^{tot}), isotropic (R_u^{iso}), anisotropic (R_u^{an}), and concentration (R_u^{c}) light scattering. R_u^{iso} has been calculated on the basis of experimental determination of R_u^{tot} and depolarization $D_u = H_u/V_u$ (H_u and V_u are the Rayleigh ratios of horizontally and vertically polarized components of scattered light) by means of the equation [6]

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

The value of R_u^{d} has been calculated according to the equation

$$R_u^{\text{d}} = \left(\frac{\pi^2 kT}{2\lambda_0^4} \right) \beta_T \left(\frac{\partial \varepsilon}{\partial \rho} \right)_T^2 \quad (8)$$

where β_T , ρ , and ε are isothermal compressibility of liquid mixture, density, and relative permittivity of this mixture, respectively. The increment of permittivity and the value of β_T have been calculated from the following equations [6]

$$\rho \left(\frac{\partial \varepsilon}{\partial \rho} \right)_T = (1 - 0.073) [(n^2 - 1)(n^2 + 2)] \cdot \frac{1}{3} \quad (9)$$

$$\beta_T = - \left[x_1 \left(\frac{\partial V_1}{\partial P} \right)_T + x_2 \left(\frac{\partial V_2}{\partial P} \right)_T \right] \cdot \frac{1}{V} \quad (10)$$

where V and n are molar volume of the mixture and its refractive index, respectively. For calculating V , the validity of the subsequent relationship is assumed

$$V = x_1 V_1 + x_2 V_2$$

Simultaneously, it holds for the concentration scattering in ideal mixture R_{id} [6]

$$R_{id} = \left(\frac{2\pi^2 V x_1 x_2}{\lambda_0^4 N_A} \right) \left(n \frac{\partial n}{\partial x_2} \right)_{p,T}^2 \quad (11)$$

The concentration dependences of R_u^{tot} , R_u^{iso} , R_u^d , R_c , and R_{id} are to be seen in Fig. 1 and we may state that they correspond to the character of components of this so-called symmetric mixture: the molecules of cyclohexane and thiophene are, in principle, of globular shape and possess similar properties. For this reason, the course of total and isotropic scattering, too, suggests only a low degree of interactions of the type A—A or B—B [3].

The relations between concentration and activity coefficients are represented in Fig. 2. In order to verify the reliability of the obtained results, we applied the *Redlich* procedure [4] first. By introducing the quantity $Q = x_1 \log f_1 + x_2 \log f_2$, we

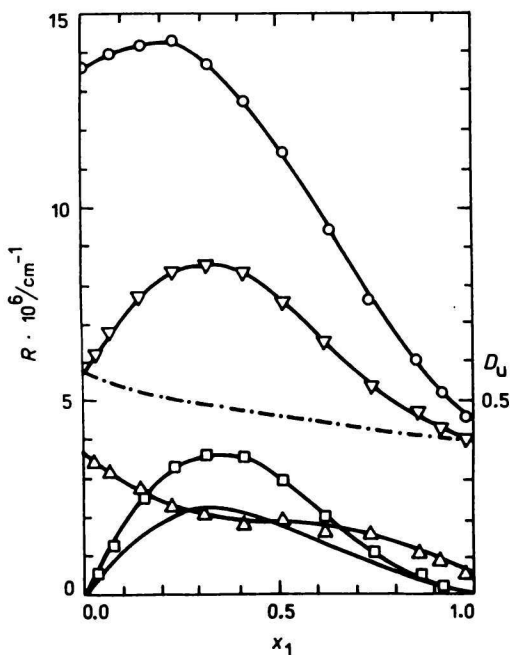


Fig. 1. Concentration dependence of scattering quantities R_u^{tot} (○), R_u^{iso} (▽), R_c (□), R_{id} (—), R_d (---), and D_u (△) in the cyclohexane—thiophene mixture.
 x_1 — mole fraction of cyclohexane.

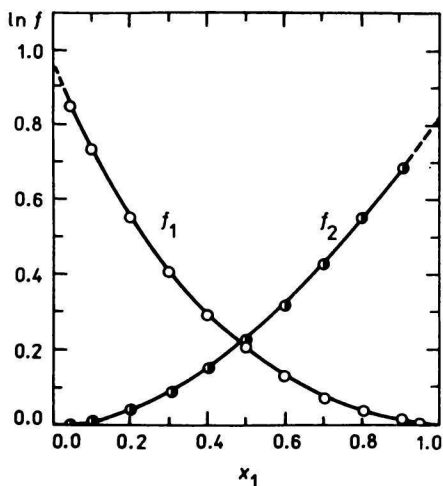


Fig. 2. Variation of activity coefficients of cyclohexane (f_1) and thiophene (f_2) with composition of the mixture at 25°C.

x_1 — mole fraction of cyclohexane; O, ● experimental values; — theoretical curve.

obtain the equation $\log (f_1/f_2) = dQ/dx_1$ and because $Q=0$ for $x_1=0$ and $x_1=1$, it results

$$\int_0^1 \log \left(\frac{f_1}{f_2} \right) dx_1 = 0 \quad (12)$$

This fact has been fully confirmed for the investigated system because the experimental data of the relationship $\log (f_1/f_2) = x_1$ are on a straight line and the area under this straight line is equal to zero in accordance with eqn (12).

For algebraic expression of the relationship between activity coefficients and state quantities Wilson [5] put forward the following equations

$$\ln f_1 = -\ln (x_1 + \lambda_{12}x_2) + x_2 \left[\frac{\lambda_{12}}{x_1 + \lambda_{12}x_2} - \frac{\lambda_{21}}{x_2 + \lambda_{21}x_1} \right] \quad (13)$$

$$\ln f_2 = -\ln (x_2 + \lambda_{21}x_1) - x_1 \left[\frac{\lambda_{12}}{x_1 + \lambda_{12}x_2} - \frac{\lambda_{21}}{x_2 + \lambda_{21}x_1} \right] \quad (14)$$

In order to estimate the consistence of this theory with the values of activity coefficients obtained by us, we drew the curves resulting from the Wilson equation through the experimental points. The parameters λ_{12} and λ_{21} were so optimized that the sum of squared deviations M expressed by the equation

$$M = \sum_n \{ [(\ln f_1)_{\text{exp}} - (\ln f_1)_{\text{theor}}]^2 + [(\ln f_2)_{\text{exp}} - (\ln f_2)_{\text{theor}}]^2 \} \quad (15)$$

was minimum. For the parameters of the Wilson expansion thus optimized, the values $\lambda_{12}=0.55$ and $\lambda_{21}=0.73$ were found. The points in Fig. 2 designate the experimental values while the curves were obtained from the Wilson equations.

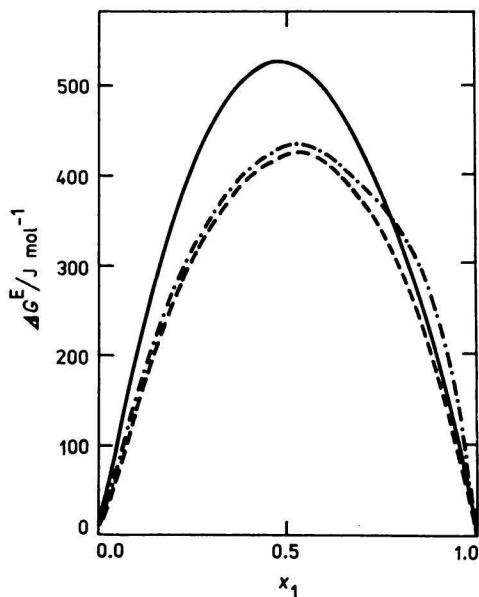


Fig. 3. Variation of ΔG^E of the cyclohexane—thiophene mixture with mole fraction of cyclohexane x_1 . Values obtained by light scattering at 25°C (—) and by ebulliometry at 45°C (--- [7], - · - · - [8]).

The values of ΔG^E obtained by light scattering at 25°C and by ebulliometry [7, 8] at 45°C are represented in Fig. 3. The comparison of these values shows that the deviation of the system from ideality decreases with increasing temperature, which is consistent with generally accepted assumption.

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