Θ, temperature at sample—gas boundary in photoacoustic cell; W, temperature at sample—base boundary; μ, thermal diffusion length; γ, ratio of specific heats at constant pressure and constant volume; P_0, pressure level of gas in photoacoustic cell; T_0, temperature level of gas in cell.

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METHOD OF MEASURING THE KINETIC AND THERMODYNAMIC PROPERTIES IN BINARY STRATIFIED SYSTEMS BY MEANS OF SCATTERED LIGHT SPECTRA

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A method and results of investigating the kinetic and thermodynamic parameters of the mutual diffusion coefficient in binary stratified liquid mixtures are described.

Diffusion in nonideal solutions has been investigated slightly. This refers especially to diffusion processes near the critical stratification point.

The possibilities of the combined utilization of optical mixing spectroscopy and the measurement of scattered radiation intensity to investigate the kinetic and thermodynamic properties of the mutual diffusion coefficient in a broad temperature range and in the neighborhood of the critical stratification point are described below.

From a consideration of the kinetics of concentration fluctuations, it follows that for the hydrodynamic approximation the unbiased component of the Rayleigh scattering spectrum is related to the thermodynamic force of the system $(\partial x/\partial\mu)_{P,T}$ and the mutual diffusion coefficient $D_{1,2}$ by the relationship [1]

$$J(q,\ \omega)\sim\left(\frac{\partial x_2}{\partial\mu_2}\right)_{P,T}\frac{x_1T\cdot 2D_{1,2}q^2}{\omega^2+(D_{1,2}q^2)^2}, \tag{1}$$

where $q = (4\pi n/\lambda)\sin(\theta/2)$. For the Lorentz form of the spectral line, $D_{1,2}$ is determined by the halfwidth of this line:

$$\Delta\omega_{1/2}=D_{1,2}q^2.$$

The integrated scattered light intensity for a given concentration x_i is determined entirely, as follows from (1), by the thermodynamic properties of the solution

$$J^{-1}(T)\sim x_j\left(\frac{\partial\mu_i}{\partial x_i}\right)_{P,T}T^{-1}, \tag{2}$$

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where $\mu = \mu(T)$.

To measure the half width of the central scattering spectrum component, the technique of heterodyne detection was used with the device whose block diagram is shown in Fig. 1. The reference beam 0 and the ray C shaping the scattered (signal) radiation intersected in the cuvette at a certain angle θ. Adjustment was with respect to the reference ray which seemingly selected the necessary spatial components from the scattered radiation. In this case the condition of the ideal photomixing that occurred in the plane of the photodetector 7 within its sensitive area bounded by the diaphragm D_2 were satisfied. The conditions for optimal heterodyning of an optical mixer were discussed in [2]. The signal voltage from the photodetector was detected at the intermediate heterodyne frequency of the spectrum analyzer and was averaged by the circuit 12 permitting a stepwise change in the averaging time from 0.1 to 10 sec. The averaged signal voltage governing the spectrum being investigated was recorded by the digital voltmeter 9 or was inscribed on the X–Y plotter 11. The spectrum inscription time could vary between 3 sec and 5 min.

The stroboscopic modulator 2 was used to measure the integrated scattering intensity. The variable component of the photocurrent at the modulation frequency $f_M = 40$ Hz was recorded by the digital voltmeter 9'. Control of the laser intensity was by the photodiode 15–voltmeter 9" system.

If the spectral distribution of the signal voltage during heterodyning is a Lorentz line, as is ordinarily satisfied for the temperature ranges $(T - T_c) \geqslant 0.01°$ then

$$u_s = u_t - u_b = \frac{u_0}{2\pi} \frac{\Delta f_{1/2}}{(f - f_0)^2 + \Delta f_{1/2}^2}. \tag{3}$$

The center of this line with half width $\Delta f_{1/2}$ is located at the phase modulation frequency f_0. Equation (3) is linearized by the expression

$$\frac{1}{u_s} = A + B(f - f_0)^2, \tag{4}$$

where the ratio between the coefficients yields the desired magnitude of the half width of the spectral distribution of the spectrometer signal voltage

$$A/B = \Delta f_{1/2}^2.$$

Satisfying the relationship of the form (4) for the quantities being measured is a criterion for the applicability of the hydrodynamic approximation as the critical state sets in.

To determine the parameters A, B, f_0, the spectra were processed on an electronic computer by least squares. The maximum error in measuring the spectrum half width as a function of the closeness to the stratification temperature varied between 5 and 1%.

A binary nitrobenzene–heptane stratifying system with a concentration of $x = 0.4697$ molar fractions of nitrobenzene ($x_c = 0.4696$ molar fractions of nitrobenzene [3]) was used for the research. The cuvette with the solution to be investigated was placed in the furnace 5 whose temperature stability was ±0.02°K for 5-6 h and better than ±0.005°K for 1 h. The time between measurements which is required to build up thermal equilibrium was on the order of 1 h for $T > T_c$ and 2-4 h for $T < T_c$. The specimens were cleared of dust by multiple distillation in a vacuum. Conservation of the concentration was estimated by the reproducibility of the stratification temperature and its comparison with data obtained for the coexistence curve [3].

The nitrobenzene–heptane system is a strongly scattering mixture. To eliminate the influence of multiple scattering, the factor I/I_{meas} that takes account of attenuation of the scattered light on the path between the scattering volume and the boundaries of the opalescing cuvette [4] was introduced into (2). The intensity of the primary scattering was calculated from the formula

$$J = J_{meas} \frac{I}{I_{meas}}.$$

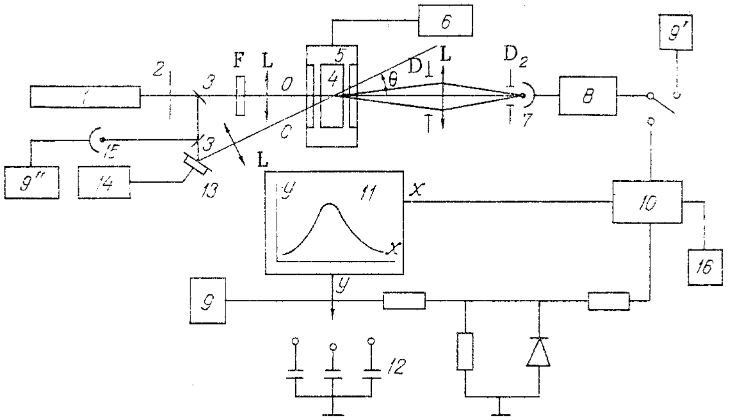

Fig. 1. Block diagram of an optical heterodyne spectrometer: 1) He–Ne laser LG-38; 2) stroboscopic modulator $f_M = 40$ Hz; 3) divider plate; 4) cuvette with the scattering specimens; 5) furnace for temperature stabilization; 6) temperature control and maintenance module; 7) photodetector FÉU-79; 8) resonance amplifier Y2-6; 9, 9', 9") digital voltmeters B7-16; 10) spectrum analyzer C4-12; 11) X–Y plotter PDS-02; 12) rectification circuit and post-detection filter; 13) piezoceramic modulator $f_M = 60$ kHz; 14) generator GZ-33; 15) photodiode FT-3; 16) frequency meter. The lens L and diaphragm D system forms an optical mixer.

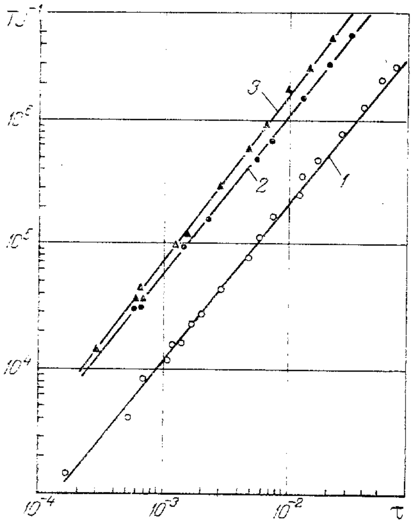

Fig. 2

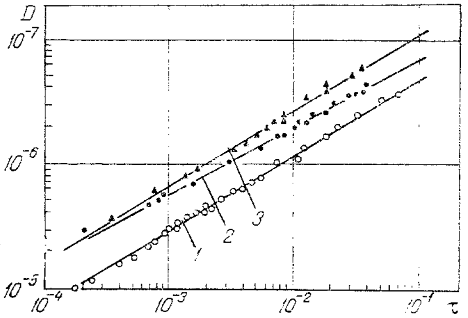

Fig. 3

Fig. 2. Dependence of the reciprocal scattered light intensity (rel. units) on the degree of approach to the critical stratification point τ for θ = 15°: 1) $T > T_c$; 2) $T < T_c$ (lower phase); 3) $T < T_c$ (upper phase).

Fig. 3. Temperature dependence of the mutual diffusion factor $D_{1,2}$ (m²/sec) for θ = 15°. Notation the same as in Fig. 2.

The results of measuring the temperature dependences of the reciprocal scattered light intensity and the mutual diffusion coefficient in the nitrobenzene–heptane mixture, whose concentration is close ot the critical value, are presented in Figs. 2 and 3. The measurements were performed both above and below the stratification temperature in the range $10^{-4} \leqslant \tau \leqslant 10^{-1}$, where $\tau = (T - T_c)/T_c$.

As is seen from the figures, the dependences $TJ^{-1}(\tau)$ and $D(\tau)$ remain linear in a logarithmic scale for a given temperature range and can be represented by the power-law functions

$$TJ^{-1} = (TJ^{-1})_0 \tau^{\gamma}, \qquad (5)$$

$$D_{1,2} = D_0 \tau^{\nu^*}, \qquad (5a)$$

where $(TJ^{-1})_0$ and D_0 are numerical coefficients whose values are presented in the table, where numerical values are also given for the exponents in (5) for the homogeneous and heterogeneous states of the system. It is seen from the graphs and the table that for $T < T_c$ the properties of the two coexistent phases are characterized by different exponents and coefficients. The asymmetry in the properties of the coexistent phases is obtained experimentally and discussed for the critical mixture phenol—water in [5, 6]. In a number of theoretical papers the asymmetry in the properties of the phases is explained by several reasons: the nonsymmetry of the thermodynamic functions of the system [7, 8], the strong concentration dependence of the macroscopic mobility of the components [6], and the influence of impurities [8].

According to the fluctuation—dissipation theorem [9], the mutual diffusion factor of a mixture can be represented in the form of a product of the thermodynamic derivative $(\partial \mu_i / \partial x_i)_{P,T}$ and the macroscopic mobility of the component b_i

$$D_{1,2} = x_i b_i \left(\frac{\partial \mu_i}{\partial x_i} \right)_{P,T}. \qquad (6)$$

It follows from (2), (5), (6) that

$$b_i \sim \frac{D_{1,2}}{TJ^{-1}} \sim \tau^{-\psi}, \qquad (7)$$

where $\Psi = \gamma - \nu^*$. A weak divergence for b_i near T_c was assumed in [10]. From the results presented in Table 1 it follows that $\Psi' = 0.70 \pm 0.04$ for $T < T_c$ and $\Psi = 0.66 \pm 0.04$ for $T > T_c$. From an analysis of the Van der Waals' model, Fixman found that $\Psi = 0.5$ [11]. The computations of Kadanoff and Swift [10, 12] result in $\Psi' = \Psi = 0.67$. The data we obtained are close to the results in [12], but disagreement between the values Ψ' and Ψ is obtained here for the states of the system below and above the critical mixing temperature. This same property should also be noted for the exponents γ and ν^*.

TABLE 1. Results of Processing Measurement Data for the Processed Scattered Light Intensity and the Mutual Diffusion Factor in a Nitrobenzene—Heptane System with Concentration x = 46.97 mole % Nitrobenzene

Measurement range	ν^*	$D_0 \cdot 10^7$, m^2/sec	γ	$(J^{-1}T)_0 \cdot 10^{-7}$ (rel. units)
$T > T_c$	0,62±0,03	2,1±0,2	1,28±0,03	8,1±0,5
$T < T_c$ (lower phase)	0,53±0,05	2,3±0,5	1,23±0,03	26±2
$T < T_c$ (upper phase)	0,61±0,03	4,5±0,3	1,31±0,03	55±4

NOTATION

μ_i, x_i, chemical potential and concentration of the i-th component of the solution; T, temperature; T_c, x_c, critical temperature and concentration; q, modulus of the scattering vector; ω, cyclic frequency; f, frequency; n, refractive index of the solution; λ, radiation wavelength in a vacuum; θ, scattering angle; u_s, u_t, u_b, signal voltages at the spectrum analyzer output: the investigated, total, and background; u_0, coefficient dependent on the heterodyne spectrometer parameters; I, I_{meas}, reference beam intensities before and after passing the opalescent cuvette; J, J_{meas}, intensities of the primary and measured scattered radiation; the upper phase is heptane rich, and the lower is nitrobenzene rich.

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MEASUREMENT OF UNSTEADY GAS FLOW UNDER ANISOTHERMIC CONDITIONS

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We describe a dynamic method for measuring unsteady gas flow under anisothermic conditions. We show that the value of the flow sensitivity determined under isothermal conditions can be used for molecular flow.

In measuring gas flow, the volume in which gas is generated or absorbed (reactor volume) and the volume directly connected to the recording equipment ("instrument" volume) may be at different temperatures.

Static and dynamic methods of measurement can be used. The static method can be used when the interconnected reactor and instrument volumes are hermetically sealed. The gas flow is determined from the rate of change of pressure in the instrument volume. The presence of a temperature gradient along the gas route from the reactor volume to the instrument volume requires corrections because of the thermomolecular pressure difference [1]. The dynamic method involves measuring the pressure drop of the gas across the port connecting the evacuation system (in the case of gas generation) or the pressure system (in the case of gas absorption) with the instrument and reactor volumes which, just as in the static method, are interconnected. In the molecular flow regime the gas flow through the port is proportional to the measurable pressure drop.

The fact that no information on the effect of anisothermicity on the results of dynamic measurements of gas flows is presently available in the literature stimulated the writing of the present paper.

In discussing the dynamic method in the presence of a temperature gradient (Fig. 1), we make three assumptions: 1) gas is generated in the reactor volume; 2) the gas flow regime is molecular; 3) the gas in the exhaust system is much less dense than that in the instrument volume ($n_0 << n_2$). In this case the equations for the balance of gas molecules are [2]

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