

VISCOSITY AND ACTIVATION ENERGY OF THE SYSTEM NITROBENZENE/CYCLOHEXANE

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Viscosity coefficients η are determined in the system nitrobenzene/cyclohexane vs concentration and temperature, and the Frenkel and Hill formulas are checked. From experimental η vs T^{-1} curves, and applying the method of tangents, the activation energy of viscosity E is determined as a function of concentration and temperature. The maximum of E (decreasing with increasing T), observed in the critical concentration range, is related to a change in microstructure of the liquid resulting from fluctuations in the critical region. The present results are compared with earlier dielectric saturation studies in the same binary system.

1. Introduction

The system nitrobenzene/cyclohexane is a critical solution, the upper critical miscibility temperature of which lies at 269 K [1]. Various physical studies point to the presence of microscopic inhomogeneities (fluctuations in density and concentration) already at temperatures considerably higher than critical while the solution still presents macroscopic homogeneity in the entire range of concentrations. Molecular light scattering studies [2] have revealed a marked maximum of the isotropic scattering coefficient of nitrobenzene/cyclohexane at 293 K, i. e. far from the critical point, in contradistinction to the system nitrobenzene/carbon tetrachloride, where no such maximum occurs.

The study of non-linear electric polarization (dielectric saturation effect) in nitrobenzene/cyclohexane [3] very clearly reveals the presence of microscopic changes in the neighbourhood of the molecules. Near the critical concentration (about 0.3 molar fractions of nitrobenzene in cyclohexane), a pronounced maximum of dielectric saturation occurs, which increases with decreasing temperature.

Also in studies of fundamental physical properties (density, viscosity) versus the temperature and concentration, especial attention is given to the critical region of the system.

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Viscosity depends (like the optical and electric phenomena cited) on the structure and interactions of the molecules. The present work is a study of the viscosity coefficient of the system nitrobenzene/cyclohexane as a function of temperature and concentration leading to the determination of the activation energy of the viscosity.

2. Some theoretical aspects

The theoretical approach to the viscosity of solutions is beset with difficulties. Numerous equations have been proposed for the viscosity coefficient as a function of the concentration and molecular properties of the components [4-8].

According to Frenkel, the viscosity of a two-component solution can be written in the form [8]

$$\lg \eta^F = f_A^2 \lg \eta_A + f_B^2 \lg \eta_B + 2f_A f_B \lg \eta_{AB}^F, \quad (1)$$

where η_A , η_B , f_A and f_B denote, respectively, the viscosity coefficients and concentrations (in molar fractions) of the components, whereas η_{AB}^F is the coefficient of "mutual viscosity", characterizing the interaction between their molecules.

Nora E. Hill [9] extended Andrade's viscosity theory of liquids to the case of binary solutions. According to Andrade, the molecules of liquids vibrate at a frequency ν about an equilibrium position which varies very slowly in time. The transfer of angular momentum in a viscous liquid between layers moving with different velocities occurs by way of collisions. The viscosity coefficient η can then be expressed as follows:

$$\eta = \frac{1}{3} c \nu m / \sigma, \quad (2)$$

where m is the mass of the molecule, σ the mean distance between the molecules, and c the collision probability; c varies as $\exp(-E/kT)$, with E denoting the difference in mutual potential energy of the molecules at collision.

In a binary solution, three types of collision occur: (AA) between molecules of component A ; (BB) between molecules of component B ; and (AB) involving a molecule of A and one of B . With these interactions taken into account, the viscosity coefficient η^H of the solution takes the form:

$$\eta^H = f_A^2 \eta_A \sigma_A / \sigma_m + f_B^2 \eta_B \sigma_B / \sigma_m + 2f_A f_B \eta_{AB}^H \sigma_{AB} / \sigma_m, \quad (3)$$

with η_A and η_B the viscosity coefficients of the components A and B , and η_{AB}^H the "mutual viscosity", defined as

$$\eta_{AB}^H = \frac{1}{3} c_{AB} \frac{\nu_A + \nu_B}{\sigma_{AB}} \frac{m_A m_B}{m_A + m_B}, \quad (4)$$

with σ_{AB} — the mean distance between a molecule of the species A and an adjacent one of the species B , and σ_A , σ_B — the mean distances between similar molecules.

If the viscosity coefficient of the system obeys the Arrhenius equation

$$\ln \eta = \ln \eta_0 + E/RT, \quad (5)$$

where η_0 is a constant, R the gas constant and T the Kelvin temperature, it becomes possible to calculate the activation energy E of the viscosity defining the potential barrier which a molecule of the liquid has to traverse in order to pass from one equilibrium position into another. The magnitude of E depends on the molecular interactions in the nearest neighbourhood of the molecule [10].

In organic liquids consisting of spherical molecules (e. g. CCl_4) with considerable freedom of rotation, Eq. (5) is fulfilled throughout the entire liquid range, from the temperature of ebullition to that of freezing [11]. Most organic liquids obey Arrhenius' equation in a restricted range of temperatures: at some temperature, specific for the compound, Eq. (5) ceases to be valid. This is the case of organic compounds the molecules of which can reorient themselves about two or more axes [11]. In such cases, the activation energy cannot be determined directly from Eq. (5).

3. Experimental

Viscosity coefficients of solutions of nitrobenzene in cyclohexane were measured with an Ubbelohde viscometer with an accuracy to 0.5% in the entire range of concentrations, from 273 to 323 K. The temperature of the liquid in the viscometer was measured to within 0.1 K. The density of the solutions was determined pycnometrically with an accuracy of 0.04%.

Nitrobenzene of purity grade, from VEB Jenapharm. Laborchemie Apolda, was distilled twice under reduced pressure and dried with Al_2O_3 of chromatographic grade. Cyclohexane, of pro analysi purity, produced in Poland, was distilled twice under normal pressure.

4. Results and discussion

The results of our measurements of the viscosity coefficients η of the solutions versus the concentration in molar fractions of nitrobenzene are plotted in Fig. 1.

The concentration-dependence of η is not linear. The deviations of η from linearity,

$$\Delta\eta = \eta - (\eta_A f_A + \eta_B f_B) \quad (6)$$

are negative and become pronouncedly larger as the temperature of the binary system decreases (Fig. 2).

According to Frenkel [12], this behaviour of η vs concentration is exhibited by liquids where the process of solution involves an intake of heat. Now an endothermal process of solution is evidence that the forces of interaction between like molecules exceed those active between different molecules.

The concentration-dependent behaviour of the viscosity coefficient at the temperatures 273 and 280.3 K, where a moderate, diffluent maximum occurs in the concentration range from $f_2 = 0.2$ to 0.5, is attributable to the circumstance that the system forms a critical solution. An increase in viscosity coefficient near the critical temperature is observed for other systems as well [13-15].

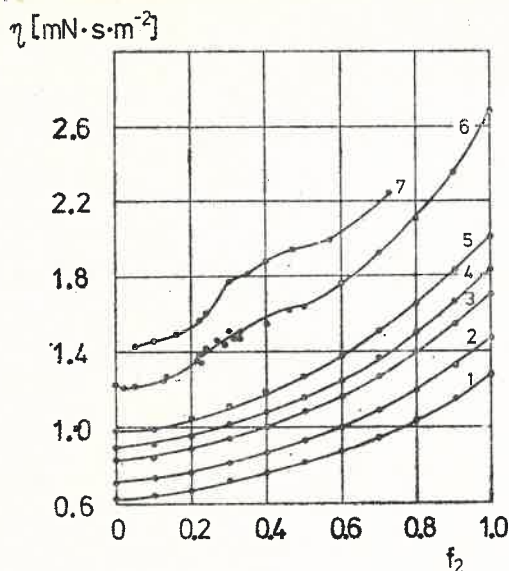


Fig. 1. Viscosity coefficient η of the system nitrobenzene/cyclohexane as a function of nitrobenzene concentration f_2 at the temperatures: 1 — 323 K; 2 — 313 K; 3 — 303 K; 4 — 298 K; 5 — 293 K; 6 — 280.3 K; 7 — 273 K

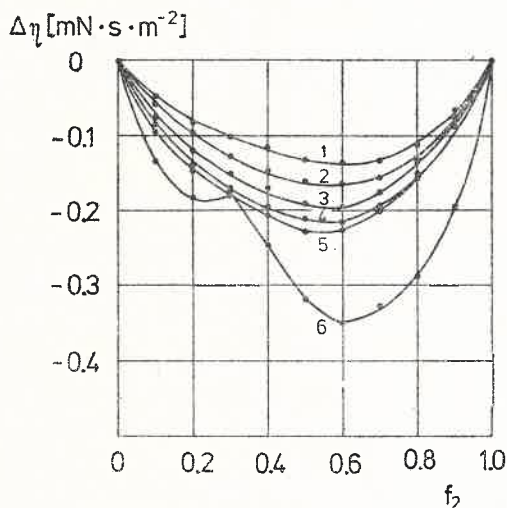


Fig. 2. Viscosity coefficient excess $\Delta\eta$ of the system nitrobenzene/cyclohexane as a function of nitrobenzene concentration f_2

The experimentally determined viscosity coefficients, and those calculated from the formulas of Frenkel (1) and Nora Hill (3), are compared in Table I.

The values of η_{AB}^F and $\eta_{AB}^H \times \sigma_{AB}$, occurring in Eqs (1) and (3), were calculated with the experimental value of η obtained at the concentration $f_2 = 0.5$, and represent values characteristic for a given system and temperature. On assuming these values as independent

TABLE
 Experimental (η) and calculated (η^F and η^H) values of the viscosity coefficients of nitrobenzene/cyclohexane solutions. $\eta, \eta^F, \eta^H, \Delta\eta^F, \Delta\eta^H$ [mN s/m²]; $\Delta\eta^F = \eta - \eta^F$; $\Delta\eta^H = \eta - \eta^H$

f_2	$T = 280.3 \text{ K}$										$T = 293 \text{ K}$					$T = 323 \text{ K}$				
	η	η^F	η^H	$\Delta\eta^F$	$\Delta\eta^H$	η	η^F	η^H	$\Delta\eta^F$	$\Delta\eta^H$	η	η^F	η^H	$\Delta\eta^F$	$\Delta\eta^H$	η	η^F	η^H	$\Delta\eta^F$	$\Delta\eta^H$
	0	1.228	1.228	1.228	0	0	0.987	0.987	0.987	0	0	0.623	0.623	0.623	0	0	0.623	0.623	0.623	0
0.1	1.243	1.281	1.262	-0.038	-0.019	0.994	1.022	1.011	-0.028	-0.017	0.643	0.650	0.643	-0.007	0	0.643	0.650	0.643	-0.007	0
0.2	1.321	1.346	1.318	-0.025	0.003	1.044	1.068	1.051	-0.024	-0.007	0.676	0.683	0.673	-0.006	0.003	0.676	0.683	0.673	-0.006	0.003
0.3	1.494	1.427	1.401	0.067	0.093	1.115	1.125	1.107	-0.010	0.008	0.722	0.722	0.713	0	0.009	0.722	0.722	0.713	0	0.009
0.4	1.567	1.525	1.509	0.042	0.058	1.194	1.194	1.182	0	0.012	0.772	0.769	0.764	0.003	0.008	0.772	0.769	0.764	0.003	0.008
0.5	1.643	1.643	1.643	0	0	1.277	1.277	1.277	0	0	0.825	0.825	0.825	0	0	0.825	0.825	0.825	0	0
0.6	1.758	1.784	1.801	-0.026	-0.043	1.381	1.377	1.387	0.004	-0.006	0.885	0.891	0.896	-0.006	0	0.885	0.891	0.896	-0.006	0
0.7	1.927	1.955	1.986	-0.028	-0.059	1.508	1.497	1.517	0.011	-0.009	0.956	0.966	0.978	-0.010	-0.022	0.956	0.966	0.978	-0.010	-0.022
0.8	2.113	2.158	2.195	-0.045	-0.082	1.665	1.640	1.667	0.025	-0.002	1.044	1.056	1.071	-0.012	-0.027	1.044	1.056	1.071	-0.012	-0.027
0.9	2.343	2.400	2.431	-0.057	-0.088	1.831	1.811	1.834	0.020	-0.003	1.155	1.162	1.174	-0.007	-0.019	1.155	1.162	1.174	-0.007	-0.019
1.0	2.693	2.693	2.693	0	0	2.019	2.019	2.019	0	0	1.287	1.287	1.287	0	0	1.287	1.287	1.287	0	0

of concentration, theoretical values of the viscosity coefficients η^F and η^H were calculated in the entire range of concentrations.

On inspection of Table I one notes that the equations of Frenkel and Nora Hill adequately describe the concentration-dependence of the viscosity coefficient for the system nitrobenzene/cyclohexane in the range of higher temperatures (293 and 323 K) but fail to do so at lower temperatures (280.3 K), where the coefficient exhibits a diffuent maximum.

As already stated, the higher temperature range is characterized by a monotonical increase in η vs concentration and a negative deviation of η from linearity. In this temperature range, the system obeys the Frenkel equation (1), the Hill equation (2), as well as that of Arrhenius (5), permitting the calculation of the viscosity activation energy from Eq. (5). Since the temperature-dependence of the viscosity coefficient is found to be a non-Arrhenius one in the entire range of temperatures studied ($\ln \eta$ vs $1/T$ is not linear), in pure nitrobenzene as well as in its solutions in cyclohexane, the activation energy cannot be determined unequivocally from Eq. (5).

Hence, in the present work, we decided to apply a procedure similar to that of Ref. [16], taking into account the dependence of the activation energy E on temperature as determined by the method of tangents (at steps of $\Delta(1/T) = 2 \times 10^{-5} \text{ K}^{-1}$) from the curve of η vs $1/T$ on the basis of the following formula:

$$E = R \frac{d \ln \eta}{d(1/T)} \approx R \frac{\Delta \ln \eta}{\Delta(1/T)} = R \frac{1}{\eta} \frac{\Delta \eta}{\Delta(1/T)}. \quad (7)$$

In this way, we calculated the viscosity activation energy E in the system nitrobenzene/cyclohexane for the entire range of concentrations. Fig. 3a shows E vs T for various concentrations f_2 of nitrobenzene in cyclohexane.

Quite generally, when analyzing E vs T in pure nitrobenzene and its solutions in cyclohexane, E is found in all cases to be the largest at temperatures close to the point of solidification. This can be explained in terms of the occurrence of microinhomogeneities due to the fluctuations in the solution. This effect hinders the process of viscous flow i. e. enhances the activation energy required for the process. An increase in temperature, lowering the fluctuations, lowers the activation energy as can be observed in all cases (Fig. 3a).

In the pure solvent ($f_2 = 0$), E varies but insignificantly with temperature. This may be due to the circumstance that the molecules of cyclohexane possess a non-spherical, temperature-dependent structure, somewhat restricting the freedom of their rotation. For comparison, Fig. 3b shows E vs T , calculated as above, for carbon tetrachloride, on the basis of available data [17]; one notes that E is entirely independent of temperature proving the Arrhenius-type behaviour of viscosity in CCl_4 [11] resulting from the complete freedom of rotation of its spherical molecules.

Fig. 3a shows that the temperature-dependence of E differs from one solution to another. In order to illustrate the isothermal dependence of E vs f_2 , the nitrobenzene concentration, we selected the three temperatures 288 K, 303 K and 318 K (Fig. 4).

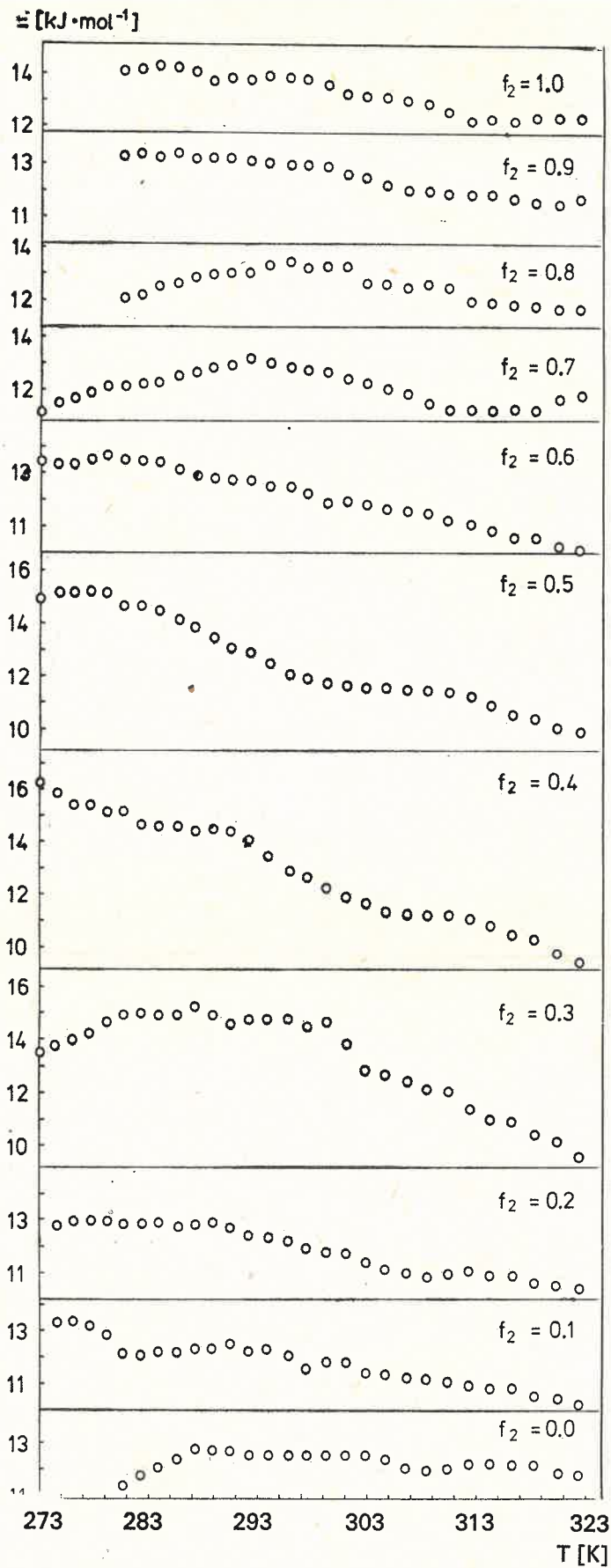


Fig. 3a. Viscosity activation energy E in the system nitrobenzene/cyclohexane as a function of temperature T for different nitrobenzene concentration f_2

At the critical concentration $f_2 \sim 0.3$, a characteristic maximum of the viscosity activation energy, decreasing with increasing temperature and vanishing at 318 K, occurs. The maximum can be attributed to a change of the structure of the system in the critical region most probably due to association of the nitrobenzene molecules — a phenomenon involving an increase in the activation energy of viscosity.

It is noteworthy that direct measurement of η as a function of temperature and concentration permits the observation of a local maximum of η in the critical concentration

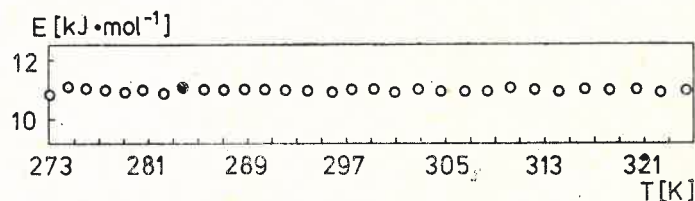


Fig. 3b. Viscosity activation energy E in carbon tetrachloride as a function of temperature T

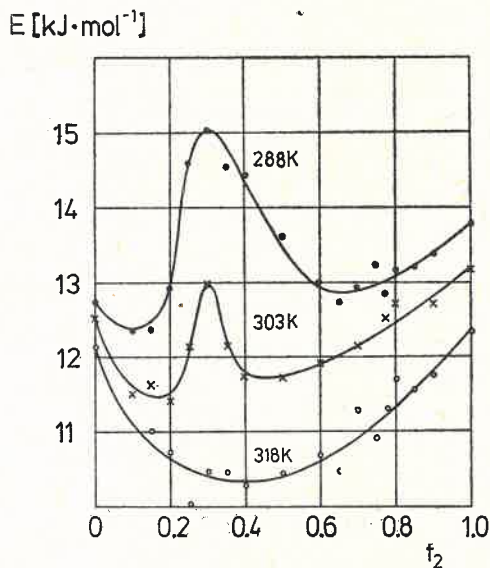


Fig. 4. Viscosity activation energy E in the system nitrobenzene/cyclohexane as a function of nitrobenzene concentration f_2

region only at temperatures close to the critical temperature of miscibility (Fig. 1), whereas the isothermal E vs f_2 dependence reveals a maximum of the activation energy (Fig. 4), related with changes in the microstructure of the solution, at a temperature considerably higher (303 K), when the system is still macroscopically homogeneous and the dependence of η on f_2 is monotonical.

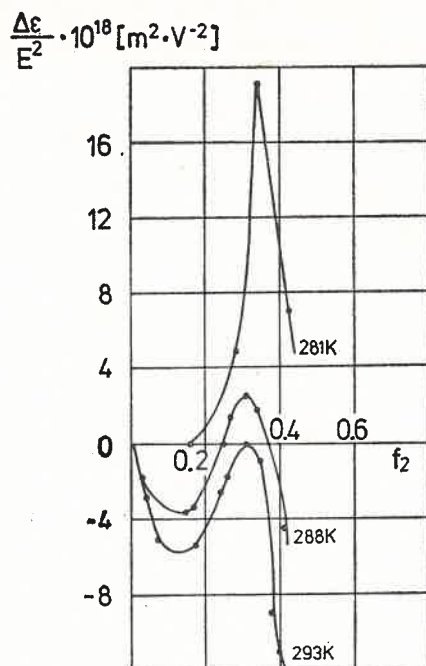


Fig. 5. Dielectric saturation $\Delta\epsilon/E^2$ versus the nitrobenzene concentration f_2 in cyclohexane [3]; E denotes electric field

The same mechanism of temperature and concentration dependent variations in the degree of association of nitrobenzene molecules leads to the well known [18] increase in mean dipole moment of nitrobenzene in strong electric fields, apparent in cyclohexane solutions by an increase in positive dielectric saturation with decreasing temperature at the critical concentration of ~ 0.3 molar fraction (Fig. 5) [3].

In conclusion it could be stated that the determination of E in the way described above is seen as a method, relating a macroscopic and a statistical quantity, namely the viscosity coefficient on the macroscopic and the phenomenon of nitrobenzene association on the molecular level.

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