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Abstract

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DIELECTRIC PERMITTIVITY AND MOLECULAR STRUCTURE OF SOLUTIONS HAVING A CRITICAL REGION OF PHASE SEPARATION

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If large positive deviations from ideality are observed in the thermodynamic properties of solutions, i.e., if the concentration fluctuations are large, then, as was shown in ([1]), the experimentally measured effective dielectric permittivity of solutions ε must be smaller than the average local dielectric permittivity $\bar{\varepsilon}_l$

$$\varepsilon = \bar{\varepsilon}_l - \frac{\left(\partial\bar{\varepsilon}_l/\partial\varphi\right)^2 \overline{(\Delta\varphi)^2}}{\left(2 + \dfrac{\partial\bar{\varepsilon}_l/\partial\varphi}{\partial\varepsilon/\partial\varphi}\right)\varepsilon}. \tag{1}$$

In order to study the effect of concentration fluctuations $\overline{(\Delta\varphi)^2}$ (φ –volume fractions) on ε, we measured ε, the density ρ_4^t, and the refractive index n_D of solutions of nitrobenzene in cyclohexane, *n*-hexane, *n*-heptane, and *n*-octane. According to our data, the critical point of phase separation of these solutions is located, respectively, at temperatures 4.0; 20.0; 19.3; 19.1° and at nitrobenzene concentrations (in mole percent) 48.0; 43.15; 47.5; 51.0%. Measurements of ε were made at a frequency of 700 kc by the beat method. A capacitor of capacitance 10 pF was thermostated with an accuracy of ±0.005°. The random error in the measurements of ε did not exceed 0.05%. The mean relative error of the measurements of ε did not exceed 0.5%.

The substances used by us were characterized by the following constants. Nitrobenzene: m.p. 5.75°, n_D^{20} 1.5528, ρ_4^{20} 1.2034, b.p. 211.0° at 765 mm. Cyclohexane: n_D^{20} 1.4290, ρ_4^{20} 0.7797, b.p. 80.5° at 745 mm. *n*-Hexane: n_D^{20} 1.3755, ρ_4^{20} = 0.6597, b.p. 68.7° at 756 mm. *n*-Heptane: n_D^{20} 1.3882, ρ_4^{20} 0.6850, b.p. 98.0° at 758 mm. *n*-Octane: n_D^{20} 1.4003, ρ_4^{20} 0.7060, b.p. 125.5° at 750 mm.

Measurements were made over a wide range of concentrations and at temperatures from 10 to 45°.

The data obtained make it possible to construct isotherms of ε, some of which are shown in Fig. 1. The solid lines are the values of ε, the dashed lines are the values of $\bar{\varepsilon}_l$, calculated from the Onsager equation ([2]), equation (36),

$$\left(1-\sum \vartheta_i\right)(\bar{\varepsilon}_l-1)+(2\bar{\varepsilon}_l+1)\sum \vartheta_i \frac{\bar{\varepsilon}_l-n_i^2}{2\bar{\varepsilon}_l+n_i^2}=\frac{4\pi N_i \mu_i \mu_i^*}{3kT}, \qquad (2)$$

which is justified in those cases when orientational ordering of dipolar molecules is absent and, consequently, is applicable to solutions of nitrobenzene in hydrocarbons ([1]).

From the data on ε, $\bar{\varepsilon}_l$, $\partial\bar{\varepsilon}_l/\partial\varphi$, and $\partial\varepsilon/\partial\varphi$, the values of $\overline{(\Delta\varphi)^2}$ were calculated. The dependence of $\overline{(\Delta\varphi)^2}$ on t and φ is analogous in all four systems.

In the region of values $\varphi \approx 0.6$—0.7, $\overline{(\Delta\varphi)^2}$ passes through a broad maximum. $\overline{(\Delta\varphi)^2}$ decreases only slightly with temperature. The values of $\overline{(\Delta\varphi)^2}$ change very little when one hydrocarbon is replaced by another.

In Fig. 2, for nitrobenzene–n-hexane solutions at 40°, the values of $\bar{\varepsilon}_l-\varepsilon$ and $\overline{(\Delta\varphi)^2}$ are compared with the values of I_k, the intensity of Rayleigh light scattering, $\lambda = 5780$ Å, by concentration fluctuations ([3]). The figure shows that the maximum of $\overline{(\Delta\varphi)^2}$ is much broader than the maximum of I_k, and is shifted, relative to the maximum of I_k, into the region of higher concentrations of $C_6H_5NO_2$.

Light scattering in the optical range is due mainly to fluctuations whose linear dimensions are greater than $\lambda/20$, i.e. not less than 25-30 Å. As for the quantities $\bar{\varepsilon}_l-\varepsilon$ and $\overline{(\Delta\varphi)^2}$, here the principal role is played by fluctuations whose linear dimensions amount to no more than 2-3 molecular diameters ([1]), i.e., for low-molecular-weight solutions, less than 20 Å. Let us assume, for simplicity, that the volumes of the molecules of the components of the binary solution are identical.

Figure 1 and Figure 2 diagrams

Fig. 1. Isotherms of ε and $\bar{\varepsilon}_l$ for solutions of nitrobenzene: 1 –in cyclohexane; 2 –in n-hexane; 3 –in n-heptane; 4 –in n-octane at 25°. Solid lines: ε; dashed lines: $\bar{\varepsilon}_l$

Fig. 2. Dependence of $\bar{\varepsilon}_l-\varepsilon$, I, and $\overline{(\Delta\varphi)^2}$ on the concentration of nitrobenzene in volume fractions φ in nitrobenzene–n-hexane solutions at 40°

Then

$$\bar{N}^4\overline{(\Delta\varphi)^2}=\bar{N}_1^2\overline{(\Delta N_2)^2}-2\bar{N}_1\bar{N}_2\overline{\Delta N_1\Delta N_2}+\bar{N}_2^2\overline{(\Delta N_1)^2}, \qquad (3)$$

where $\bar{N}$ is the mean number of molecules 1 and 2 in the volume element dV; $\bar{N}_1, \bar{N}_2$ are the mean numbers of molecules; ΔN_1 and ΔN_2 are the fluctuations

of N_1 and N_2 in dV. Using the expression for $\overline{\Delta N_i \Delta N_j}$ in the statistical theory of fluctuations ([4]), we obtain

$$\bar{N}\,\overline{(\Delta\varphi)^2} = x_1^2 x_2 \left\{1 + \frac{4\pi x_2}{v}\int_d^V [g_{22}(q)-1]\,dq\right\} - \frac{8\pi}{v}x_1^2 x_2^2 \int_d^V [g_{12}(q)-1]\,dq + x_1 x_2^2 \left\{1 + \frac{4\pi x_1}{v}\int_d^V [g_{11}(q)-1]\,d \right. \tag{4}$$

To estimate $\overline{(\Delta\varphi)^2}$, in accordance with what was said above, we shall confine ourselves to taking into account the interactions of neighboring molecules.

X-ray structural studies of the structure of liquids show that the function $g(q)$ within the limits of the first coordination sphere depends only weakly on temperature. If (as is the case in hydrocarbon (i)–nitrobenzene (j) systems) the potential energy of the j—j interactions is considerably greater than the energy of the i—i and i—j interactions, then the relatively largest contribution to $\overline{(\Delta\varphi)^2}$ will be made by the term containing $g_{jj}(q)$, and the maximum of $\overline{(\Delta\varphi)^2}$ should lie in the concentration region where there is an excess of j molecules. Since at small distances $g_{ii}-1$, $g_{ij}-1$, and $g_{jj}-1$ have the same order of magnitude, the maximum of $\overline{(\Delta\varphi)^2}$ should be comparatively flat and broad. With increasing size of dV, the maximum of $\overline{(\Delta\varphi)^2}$ should gradually shift into the region of those concentrations which correspond to the minimum value of $\partial P_i/\partial x_i$, and at the same time become sharper.

Differentiating (1) with respect to t, we obtain:

$$\left(\frac{\partial\varepsilon}{\partial t}\right)_\varphi = \frac{\varepsilon\varphi_2 - \frac{2}{3}\overline{(\Delta\varphi)^2}(\varepsilon_2-\varepsilon_1)}{2\varepsilon-\varepsilon_l}\frac{\partial\varepsilon_2}{\partial t} - \frac{1}{3}\frac{(\varepsilon_2-\varepsilon_1)^2}{2\varepsilon-\varepsilon_l}\frac{\partial\overline{(\Delta\varphi)^2}}{\partial t}, \tag{5}$$

where ε_2 is the dielectric constant of nitrobenzene. Calculations show that $\partial\overline{(\Delta\varphi)^2}/\partial t$ assumes its largest values near the critical point of demixing of the solutions. If the critical point is the upper one, then $\partial\overline{(\Delta\varphi)^2}/\partial t < 0$, and one may expect a noticeable decrease in the absolute values of $(\partial\varepsilon/\partial t)_\varphi$ of the solutions on approaching the critical point. But if the critical point of demixing is the lower one, then $\partial\overline{(\Delta\varphi)^2}/\partial t > 0$, and $(\partial\varepsilon/\partial t)_\varphi$, correspondingly, will increase.

Figure 3

Fig. 3. Plots of $\varepsilon = f(t)$ near the critical point of demixing.
1 –nitrobenzene–n-heptane solution, $x_{C_6H_5NO_2} = 0.489$;
2 –nitrobenzene–n-octane solution, $x_{C_6H_5NO_2} = 0.514$.
Branches 1a and 2a –before demixing, 1b and 2b –after demixing.

In Fig. 3 are presented the results of measurements of ε in the temperature region near the point of demixing of nitrobenzene solutions. In agreement with what was said above, the derivative $(\partial\varepsilon/\partial t)_\varphi$ decreases near the demixing point,

which is especially clearly observed at concentrations and temperatures close to the critical state.

Thus, the indications available in the literature ([5]) of the existence of maxima of ε in the critical region are not confirmed.

A thermodynamic analysis of the critical state does not provide grounds for asserting the presence of maxima of ε on the curves $\varepsilon = f(t)$ in the critical region.

From the works of J. W. Gibbs ([6]), p. 185, it follows that there is no strict and general thermodynamic proof of the validity of relations of the form

$$\left(\frac{\partial X_i}{\partial x_i}\right)_{x_j} = 0, \qquad \left(\frac{\partial^2 X_i}{\partial x_i^2}\right)_{x_j} = 0 \tag{6}$$

in the critical region. In each particular case the applicability of such relations requires experimental verification or theoretical proof on the basis of molecular models. Let us further note that in a heterogeneous system the intensities of the electric and magnetic fields **E** and **H** do not possess the properties of "generalized forces" in the thermodynamic sense, since under thermodynamic equilibrium of phases a and b the conditions are not fulfilled···

conditions of the form

$$E_a = E_b, \qquad H_a = H_b, \tag{7}$$

analogous to the conditions $\mu_{ia} = \mu_{ib}$, $p_a = p_b$, $T_a = T_b$. Therefore equations of the form $(\partial E/\partial D) = 1/\varepsilon = 0$ in the critical region have no physical meaning.

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Note: Figure translations are in progress. See original paper for figures.