

## THE VAN DER WAALS MODEL AND THE APPROXIMATE EQUATION OF STATE FOR A BINARY SOLUTION NEAR ITS STRATIFICATION TEMPERATURE

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On the basis of the van der Waals model, an extended equation of state for binary solutions near their critical stratification temperature has been proposed, the parameters of which have a definite physical meaning. The equation has been used to analyze the temperature dependence of the concentration of some binary solutions nitrobenzene + alkane in terms of different order parameters. It has been shown that the mole concentration of the solutions has to be used as the order parameter for the systems under study. The parameters of the extended equation of state for the mole concentration have been demonstrated to be linear functions of the number of carbon atoms in alkanes. For the volume and mass concentrations, the dependences of those parameters on the number of carbon atoms in alkanes is very weak.

The derivation of the equation of state for binary solutions near the critical stratification temperature remains to be a challenging task for condensed matter physics [1–4]. In the framework of this research direction, we suggest an extended equation for the binary solution coexistence curve, which is based on the fluctuation theory of phase transitions (FTPT) [5] and the van der Waals model [6, 7]. For this purpose, by analogy with works [6, 7], we took into account [8, 9] the characteristic volume of order parameter fluctuations,  $v_f = \frac{4}{3}\pi R_c^3$ , and the interaction forces between fluctuations at distances  $r > R_c$ , where  $R_c$  is the correlation length. Then, the fluctuation part of the free energy of a system  $F_f$  which (by analogy with work [7]) makes allowance for the formation of order-parameter fluctuation quasiassociations [10] looks like

$$F_f = \frac{F_0}{\omega} \left(1 + \frac{1-\omega}{\omega} \Delta c_0\right) \left(1 - \frac{n-1}{n} x\right) - AC_0^2 R_c^{-4}. \quad (1)$$

On the basis of Eq. (1) and the results of work [5], the extended equation for the coexistence curve is

$$\Delta c_i^* = dF_\Phi/d\mu = \pm B_{i0}t^\beta \pm B_{i1}t^{n_1} +$$

$$+ B_{i2}t^{n_2} + B_{i3}t^{n_3} + B_{i4}t^{n_4} \dots \quad (2)$$

Here,  $\Delta c_i^* = (c_i - c_{ic})/c_{ic}$ ;  $\omega = (1 - V_f/V_c)$ ;  $\Delta\mu = (\mu - \mu_c)/\mu_c$ ;  $t = (T - T_c)/T_c$ ;  $c_{ic}$ ,  $\mu_c$ , and  $T_c$  are the reduced critical values of concentration, chemical potential, and temperature of the solution, respectively;  $n_1 = \beta + \Delta$ ;  $n_2 = 2\beta$ ;  $n_3 = 1 - \alpha$ ;  $n_4 = \beta + \nu$ ;  $\beta$ ,  $\Delta$ , and  $\alpha$  are the critical indices [5];  $c_i$  stand for the molar,  $c_\mu(t)$ , volume,  $c_v(t)$ , and mass,  $c_m(t)$ , concentrations, respectively;  $\rho_f = \rho_c/(1 - \omega)$  is the substance density in a fluctuation;  $\rho_c$  is the critical density;  $A$  is a constant that characterizes interaction forces between fluctuation clusters at distances  $r \geq R_c$ ;  $F_0 = N_f k_B T = C_0 R_c^{-3}$  is the fluctuation part of the thermodynamic potential in the symmetric approximation of the FTPT [5];  $\Delta c_0 = dF_0/d\mu$ ; the parameter  $x = N_{fn}/N_f = x_0 t^{\Delta_0}$ , according to works [7, 10], determines the association degree of fluctuations in the system;  $N_f$  is the total number of fluctuations of the order parameter per mole of the substance, which occupy the volume  $V_f = \frac{4}{3}\pi R_c^3 N_f$ ;  $V_c$  is the molar critical volume; and  $N_{fn}$  is the number of fluctuations that form complexes with  $n$  fluctuations.

Let us analyze the physical meaning of the parameter  $\omega = (1 - V_f/V_c)$ . It is natural to represent the volume of all fluctuations  $V_f$  in one mole of a substance as a sum of two independent terms:  $V_f = \Delta V_1 + \Delta V_2$ . Here,  $\Delta V_1 = b = \text{const}$  is the volume of all molecules in a mole of a substance (analogously to that in the conventional van der Waals equation [6]), and  $\Delta V_2 = V_f - b$  is a “disordered” contribution to  $V_f$ , which is governed by the average distance between molecules of a substance in an order parameter fluctuation and which changes, when moving away from the critical point. The quantity  $\Delta V_2$  is a function of the change  $\Delta S_\mu = S_\mu - S_{\mu c}$  of the entropy  $S_\mu$  of one mole of a substance with respect to its value  $S_{\mu c}$  at the critical point:  $\Delta V_2 = \Delta V_2(\Delta S_\mu)$ . This means that the volume of all order parameter fluctuations in

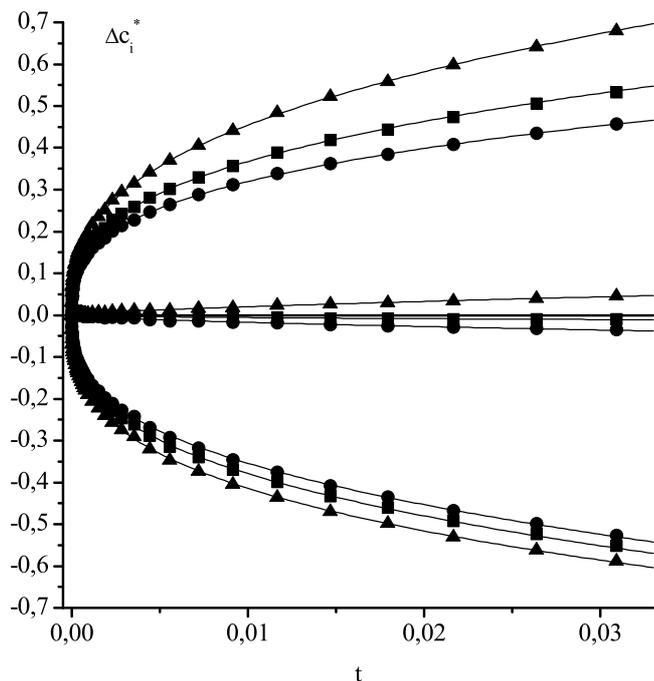


Fig. 1. Temperature dependences of the molar (square), volume (triangles), and mass (circles) concentrations of a nitrobenzene-heptane solution

one mole of a substance can be expressed in the form  $V_f = b + (\partial V_2 / \partial S_\mu)_{N_f} \Delta S_\mu$ , and  $\omega = \omega_0(1 - \text{const} \Delta S_\mu)$ , where  $\omega_0 = 1 - b/V_c$ . According to the operation rules for scale dimensions [5], the scale dimension of molar entropy  $\Delta S_\mu = \Delta(S/N)N_A$  is equal to that of specific entropy  $\Delta(S/V) \sim t^{3\nu-1} = t^{1-\alpha}$  divided by the scale dimension of number density  $\Delta(N/V) \sim t^{3\nu-\beta\delta} = t^\beta$ . Then  $\Delta(S/N) \sim \Delta S_\mu \sim t^{1-\alpha-\beta}$ , and we obtain that  $1/\omega \approx 1/\omega_0(1 + \text{const} \Delta S_\mu) = 1/\omega_0(1 + \text{const}' t^{1-\alpha-\beta})$ .

The obtained equation (2) agrees with the results of other theoretical calculations [1–4] which were successfully applied to the analysis of experimental data near the critical point and far from it.

In this work, we used the equation of state (2) to analyze the temperature dependences of concentrations  $c_i(T)$  for a number of alkane (heptane – tetradecane) solutions in nitrobenzene [11] along the interface in the temperature range  $t_f = 10^{-5} \div 10^{-2}$ . Such an interval was specially confined by us by the fluctuation region,  $t_f \ll Gi$  [6] ( $t_f \leq 10^{-2}$ ), only, which allowed us to neglect crossover components [1] in the equation of state of a substance.

In the work, we used experimental data [11] on the temperature dependences of the molar concentration of those solutions (squares in Fig. 1). On the basis of these

data and with the help of relations [12]

$$\left(\frac{1}{c_{v_1}} - 1\right) \frac{1}{\rho_1} = \left(\frac{1}{c_{m_1}} - 1\right) \frac{1}{\rho_2};$$

$$\left(\frac{1}{c_{v_1}} - 1\right) \frac{\mu_1}{\rho_1} = \left(\frac{1}{c_{m_1}} - 1\right) \frac{\mu_2}{\rho_2};$$

$$\left(\frac{1}{c_{m_1}} - 1\right) \mu_1 = \left(\frac{1}{c_{\mu_1}} - 1\right) \mu_2, \quad (3)$$

we plotted similar dependences for the volume (triangles in Fig. 1) and mass (circles in Fig. 1) concentrations. The comparative analysis of those data is demonstrated in Fig. 1. One can see that the molar concentration has the most symmetric temperature dependence. Therefore, proceeding from the conclusions drawn in works [13, 14], just this concentration should be selected as the order parameter of solutions.

On the basis of those data, we calculated the parameters  $B_n$  in the equation of state (2) which are presented in Fig. 2. The figure exhibits the dependences of the coefficients  $B_0$  (Fig. 2,a),  $B_1$  (Fig. 2,b),  $B_2$  (Fig. 2,c),  $B_3$ , and  $B_4$  (Fig. 2,d) of the extended equation for the curve of coexistence on the number of carbon atoms  $N^c$  in alkane that composes a solution with nitrobenzene. When calculating  $B_n$ , the following values of the critical indices obtained by the introduction of small parameters [15] into the FTPT relations [5] were used:  $\nu = 0.636$ ,  $\beta = 0.337$ ,  $\alpha = 0.091$ , and  $\Delta = 0.5$  [1].

Let us analyze the dependences  $B_n(N^c)$  presented in Figs. 2,a to d. Panel a demonstrates that the asymptotic term  $B_0(N^c)$  of Eq. (2) behaves differently for different order parameters  $\Delta c_\mu^*$ ,  $\Delta c_v^*$ , and  $\Delta c_m^*$ . For instance, in the cases of mass,  $c_m$ , and volume,  $c_v$ , concentrations, the value of  $B_0(N^c)$  is almost independent of the number of carbon atoms in dissolved alkane. Therefore, they cannot be selected as physical characteristics of the given solutions. At the same time, only for the molar concentration  $c_\mu$ , the coefficient  $B_0(N^c)$  depends considerably on the number of carbon atoms in alkanes. Just for this reason, the coefficient  $B_0(N^c)$ , which governs the asymptotic behavior of the molar concentration  $\Delta c_\mu^*$  along the curve of liquid–liquid equilibrium, is the physical characteristic of the solutions nitrobenzene–alkane under investigation.

From Fig. 2,b, one can also see that the non-asymptotic term  $B_1(N^c)$  is very small ( $B_1(N^c) \approx 0$ ) ( $B_1|t|^{\beta+\delta} \ll B_0|t|^\beta$ ) for all order parameters  $\Delta c_\mu^*$ ,  $\Delta c_v^*$ , and  $\Delta c_m^*$ . This fact testifies that the complexes of fluctuations  $N_f$  [10] play a tiny role in those solutions in the

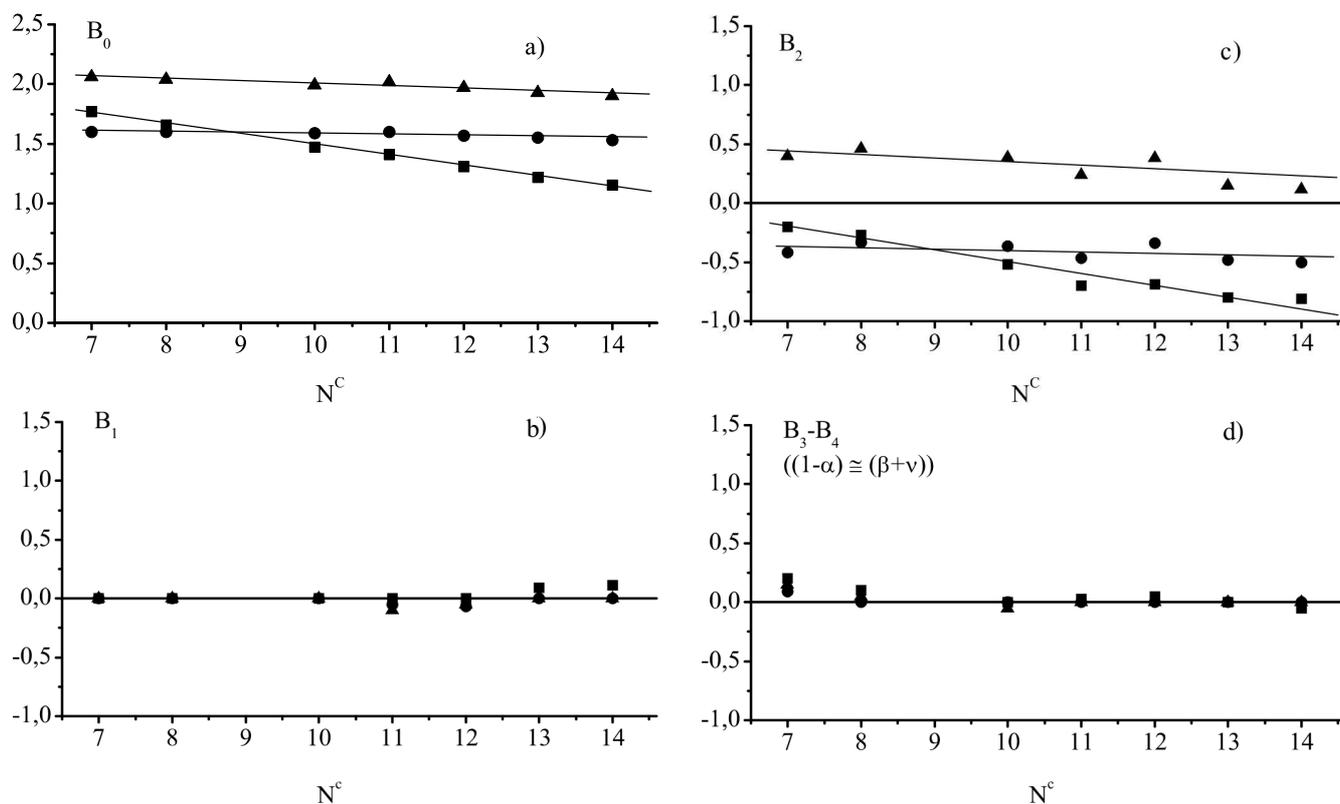


Fig. 2. Dependences of the coefficients  $B_0$  (a),  $B_1$  (b),  $B_2$  (c),  $B_3$ , and  $B_4$  (d) in the extended equation for the coexistence curve on the number of carbon atoms  $N^c$  in alkanes

selected temperature interval  $t \leq 10^{-2}$ . Therefore, in the temperature interval  $t \leq 10^{-2}$ , the symmetric part of the equation of state for a binary solution is described by a single asymptotic term  $B_0|t|^\beta$ .

At the next stage of our research, we found the asymmetric terms of the extended equation for the coexistence curve (2):  $B_2$ ,  $B_3$ , and  $B_4$ . The corresponding results are presented in Figs. 2,c and d. Their analysis testifies that the asymmetric terms of this equation can be described by only one term  $B_2|t|^{2\beta}$  (Fig. 2,c). This figure also demonstrates that the dependences  $B_2(N^c)$  are essentially different for different order parameters  $\Delta c_\mu^*$ ,  $\Delta c_\nu^*$ , and  $\Delta c_m^*$ . For the mass,  $\Delta c_m^*$ , and volume,  $\Delta c_\nu^*$ , concentrations, the quantity  $B_2(N^c)$  changes weakly with the variation of the number of carbon atoms  $N^c$ . At the same time, for the molar concentration  $\Delta c_\mu^*$ , the parameter  $B_2(N^c)$  linearly depends on  $N^c$ .

The analysis of experimental data shows (Fig. 2,d) that the influence of the terms  $B_3|t|^{1-\alpha}$  and  $B_4|t|^{\beta+\nu}$  on the shape of the nitrobenzene-alkane solution coexistence curve is not significant in the selected temperature interval  $t_f \ll 10^{-2}$ :  $B_2|t|^{2\beta} \gg (B_3|t|^{1-\alpha} - B_4|t|^{\beta+\nu})$ ,

$(1-\alpha) \approx (\beta+\nu)$ . This can be related to the fact that the terms are approximately equal by their absolute values:  $|B_3| > 0 \approx |-B_4| < 0$ . However, they enter into Eq. (2) with different signs and, consequently, partially compensate each other.

The behavior of the order parameters  $\Delta c_\mu^*$ ,  $\Delta c_\nu^*$ , and  $\Delta c_m^*$  (Fig. 1) can be explained on the basis of theoretical calculations [12]. That work presents the formulas for the transition from one order parameter to another one obtained on the basis of the van der Waals model [8, 9]. For instance, if we pass from the molar order parameter to the volume one, the coefficients are transformed by the formulas

$$B'_0 = |B_0|/(1 - \rho^* \mu^* c_{\mu c});$$

$$B'_1 = |B_1|/(1 - \rho^* \mu^* c_{\mu c});$$

$$B'_2 = B_2/(1 - \rho^* \mu^* c_{\mu c}) + (B'_0)^2 \rho^* \mu^* c_{\mu c}. \quad (4)$$

The transition from the volume order parameter  $\Delta c_\nu^*$  to the mass one is determined by the formulas

$$B''_0 = |B'_0|/(1 - \rho^* c_{\nu c});$$

$$B_1'' = |B_1'|/(1 - \rho^* c_{vc});$$

$$B_2'' = B_2'/(1 - \rho^* c_{vc}) + (B_0'')^2 \rho^* c_{vc} \quad (5)$$

Here,  $\rho^* = (\rho_2 - \rho_1)/\rho_2$  and  $\rho^* \mu^* = (\rho_1 \mu_2 - \rho_2 \mu_1)/\rho_1 \mu_2$ .

According to formulas (4) and (5), the change of the value or the sign of a coexistence curve asymmetry is governed by individual characteristics of solution components – the densities  $\rho_1$  and  $\rho_2$ , the molecular masses  $\mu_1$  and  $\mu_2$ , and the critical concentration value, either  $c_{\mu c}$  or  $c_{vc}$ .

The dependences of the parameters  $B_n$  in the equations of state (2) on the number of carbon atoms  $N^c$  in alkanes and the signs of those parameters, which are exhibited in Fig. 2, completely agree with relations (4) and (5) describing the transition from the molar concentration to the volume and mass ones.

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МОДЕЛЬ ВАН-ДЕР-ВААЛЬСА ТА НАБЛИЖЕНЕ РІВНЯННЯ СТАНУ ПОДВІЙНИХ РОЗЧИНІВ ПОБЛИЗУ КРИТИЧНОЇ ТЕМПЕРАТУРИ РОЗШАРУВАННЯ

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Резюме

У роботі на основі моделі Ван-дер-Ваальса запропоновано розширене рівняння стану подвійних розчинів поблизу критичної температури розшарування, параметри якого мають конкретний фізичний зміст. Це рівняння було використано для аналізу температурної залежності концентрації ряду подвійних розчинів нітробензол + алкан у термінах різних параметрів порядку. Проведений аналіз показав, що як параметр порядку досліджених систем необхідно використовувати мольну концентрацію розчину. Показано, що параметри розширеного рівняння стану саме для мольної концентрації є лінійними функціями числа атомів вуглецю в алканах. Для об'ємної та масової концентрацій ці параметри дуже слабо залежать від числа атомів вуглецю.