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similar systems

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M Śliwińska-Bartkowiak

Institute of Physics, A Mickiewicz University, Grunwaldzka 6, Pl-60780 Poznań, Poland

Abstract. The second virial coefficient for mixtures of o-nitrotoluene and nitrobenzene with n-alkanes, characterized by a limited miscibility with a critical point, and for m-nitrotoluene mixtures with n-alkanes, characterized by a far pre-critical effect, is determined.

On the grounds of the formal analogies of the value of the second virial coefficient in the critical systems, the hypothetical critical temperature 'T_c' of the m-nitrotoluene mixtures with n-alkanes was estimated.

The 'T_c'-values found in this way are in agreement with those determined from the non-linear dielectric effect (NDE) measurements in these mixtures, assuming the exponential character of the NDE behaviour near the critical point.

1. Introduction

Studies of the non-linear dielectric effect (NDE), i.e. the change in the permittivity of a system in a strong electric field [1,2], as well as the results of dielectric constant measurements [3] carried out for *o*-nitrotoluene with some *n*-alkanes, proved that in a certain concentration range these mixtures show limited miscibility with a critical point. The critical concentrations x_c (expressed as a molar fraction of the dipole liquid) of *o*-nitrotoluene mixtures with *n*-alkanes were found to satisfy the dependence [4]

$$x_c = 0.1543n^{0.54} \tag{1}$$

where n is the number of carbon atoms in an *n*-alkane molecule.

Analogous studies for *m*-nitrotoluene mixtures with *n*-alkanes [1,2,4] showed also, in these mixtures, NDE anomalies typical of critical solutions at temperatures higher than their critical temperature T_c. The concentrations 'x_c' at which an anomalous increase in NDE was observed in these mixtures also satisfied equation (1). On this basis it was concluded that the *m*-nitrotoluene mixtures with *n*-alkanes revealed a far pre-critical effect. However, they solidify from the homogeneous phase so that the solidification temperature is higher than the hypothetical critical temperature of the mixtures. It was found that the group of *o*- and *m*-nitrotoluene mixtures with cycloalkanes [5] and methylcycloalkanes reveal similar pre-critical properties, where the modified dependence (1) is also satisfied [6].

Analysis of the dielectric properties of these mixtures [3,7] revealed that, in the concentration ranges distinguished by the anomalous NDE increase, the system was

found to be highly ordered and the energy of intermolecular interactions was observed to increase, in a similar way as for critical mixtures at temperatures significantly higher than T_c [8–13]. The possibility of describing the critical concentration values x_c as well as the concentrations 'x_c' by equation (1) suggests a relation between the formation of the critical (or pre-critical) state and the geometry of the solvent molecules, or more exactly their linear size. From this point of view the linear sizes of o- and m-nitrotoluene are the same. The change in the NO_2 group position from the ortho to the meta compound, which results in an increase in the dipole moment μ of m-nitrotoluene relative to o-nitrotoluene (see table 2 later), influences only the value of critical temperature of mixtures of those liquids with a given n-alkane and does not affect the possibility that the pre-critical state occurs.

These conclusions have been supported by the results of an investigation of mixtures of o- and m-nitrotoluene with hydrocarbons which differ from the corresponding n-alkanes only in the position of the CH_2 group and have the same number n of carbon atoms in a molecule. From the viewpoint of the molecular geometry this situation is comparable with the replacement of o-nitrotoluene by m-nitrotoluene in a mixture with the same alkane. The replacement of n-octane by iso-octane in the mixture with m-nitrotoluene resulted in the appearance of the classical phase separation phenomenon in this kind of mixture; thus the value of T_c must have increased with respect to the hypothetical value of 'T_c' of an m-nitrotoluene–n-octane system. On the other hand, the values of the critical concentrations x_c and 'x_c' fulfilling the dependence (1) for $n = 8$, remained the same in both systems [14]. The replacement of n-octane by iso-octane in a mixture with o-nitrotoluene also gave an increase in T_c of the mixture with respect to the o-nitrotoluene–n-octane system with the same values of critical concentrations of both mixtures preserved and estimated according to (1) for $n = 8$ [14].

The above-presented facts confirm the suggested rule of the phenomena discussed. The critical concentration values x_c (or 'x_c') as well as the ranges of limited miscibility are determined by a factor related to the geometry of molecules, whereas T_c depends on an energy factor corresponding to a given structure.

Investigation of the solubility of hydrocarbons from a homologous series in water indicated that they behaved similarly [15]. Using the Scatchard–Hildebrand equations the solubility of hydrocarbons in water was expressed as a function of the molar volumes V_m of both components of the mixture and their solubility parameters; the values of the critical concentration x_c depended only on the molar volume of both substances and T_c determined V_m and the parameters of solubility of both components [16]. In the work of Hermann [17] and Amidon *et al* [18] the solubility of hydrocarbons in water was related to the surface area of the molecules rather than to their volume. Medir and Giralt [19] estimated the same solubility as a function of the dipolar moment and the structural parameter introduced by Randic [20], the so-called 'branching index' λ defined by

$$\lambda = \sum_{i,j \text{ bonds}} r_i r_j^{-1/2} \tag{2}$$

where r_i and r_j are the numbers of bonds from atom i and atom j forming the given bond. According to all these findings the solubility of hydrocarbons in water decreases with increasing size of the hydrocarbon molecule. The fundamental role of the molecular geometry in these phenomena is also proved.

In the considerations presented in this paper, the molecule geometry and the factor related to the interaction of molecules were approximated by the corresponding parameters of the Lennard-Jones potential. It seemed interesting to estimate molecular interactions in the mixtures of o-nitrotoluene with n-alkanes, which show the classical phase separation effect, and to compare them with the interactions in the mixtures of m-nitrotoluene with n-alkanes showing the pre-critical effect. In order to verify the results obtained we also studied the mixtures of nitrobenzene with some alkanes, which also show limited miscibility with a critical point.

2. The Lennard-Jones potential of mixtures of o- and m-nitrotoluene and nitrobenzene with n-alkanes

The behaviour of a system near the phase transition point is characterized by molecular fluctuations of the correlation range far greater than the range of intermolecular forces. Because these correlations occur over regions containing many molecules, the detailed nature of the intermolecular forces has little effect on the behaviour of the properties. Thus, critical phenomena in widely varying types of fluid (inert gases, polar fluids, superfluids, etc) show a remarkable similarity—a situation known as universality [15,21]. Far from the critical point, the intermolecular correlations in fluids have a range similar to that of the intermolecular forces and then the fluid properties are very markedly affected by the nature of these forces. However, the location of the critical point and the extent of the critical region in the (P, V, T) diagram are strongly affected by the nature of the intermolecular forces [21,22].

According to the results of molar refraction studies of o-nitrotoluene mixtures in n-alkanes [23,24] the intermolecular central interactions have the dominant role here (their contribution is up to 96–98%) and angular interactions play a much less important role. Therefore, the application of the one-centre Lennard-Jones potential

$$\rho_{ab}(r) = 4\epsilon_{ab}[(\sigma_{ab}/r_{ab})^{12} - (\sigma_{ab}/r_{ab})^6] \tag{3}$$

to estimate the intermolecular forces in the mixture considered seems to be a reasonably good approximation. Determination of the function of the intermolecular potential energy $\rho_{ab}(r)$ for molecular pairs (where r_{ab} is the distance between molecules a and b, σ_{ab} the parameter of collisions expressed in the units of length and ϵ_{ab} the maximum attraction energy of two molecules) required the estimation of σ_{ab} and ϵ_{ab} for the liquids considered.

In view of the divergence of data in the literature as to the potential constants of given substances, when a group of compounds is studied, it is recommended [22,25] that values of these constants determined by the same method are used. Since we have not found the values of the potential constants of all the relevant alkanes determined by one method, we had to estimate the values of potential constants of non-dipolar substances from the relations recommended in [22] based on the rule of corresponding states:

$$\epsilon_{ab}/k = 1.15T_b \tag{4}$$

$$b_0 = \tfrac{2}{3}\pi N_A \sigma_{ab}^3 = 2.0V_b^l \tag{5}$$

where b_0 is the second virial coefficient for a gas composed of hard spheres, T_b the boiling point of a given substance, V_b^l the molar volume of the liquid at the boiling point under normal pressure, k the Boltzmann constant and N_A the Avogadro constant. From among the different methods for the estimation of V_b^l we chose the Le Bas [26] method because of its relatively good accuracy for n-alkanes (an error of about 1% [27]). The values of V_b^l are presented in table 1. The values of σ_{11} and ϵ_{11}/k found for the alkanes under consideration from equations (4) and (5) are also presented in table 1. They are compared with the values obtained from viscosity measurements [22,25] and from vapour pressure and orthobaric liquid densities [28]. Unfortunately, the latter values, which were determined also as a function of temperature, do not refer to the whole group of n-alkanes studied; however, they also reveal a systematic increase in the parameters σ_{11} and ϵ_{11}/k with increasing length of the hydrocarbon chain.

The interaction potential for a pair of polar molecules may be described by the Stockmayer potential, which is a superposition of the Lennard-Jones potential and the electrostatic energy of the interaction between two dipoles. In order to estimate the constants of the intermolecular potential for the molecules of o- and m-nitrotoluene and nitrobenzene with relatively large dipole moments (table 2) we had to find the values of σ_{22} and ϵ_{22}/k in the Stockmayer potential of these compounds.

In the case of polar substances, whose intermolecular potential depends on the dipole moment of molecules, the reduced constants $P^* = P\sigma_{ab}^3/\epsilon_{ab}$, $V^* = V/N_A\sigma_{ab}^3$ and $T^* = kT/\epsilon_{ab}$ (where P, V and T are the pressure, volume and temperature of the substance) are also functions of the reduced dipole moment $\mu^* = \mu/\sqrt{\epsilon_{ab}\sigma_{ab}^3}$ [22]. When we take this into account, the critical compressibility factor $Z_c = P_c V_c/RT_c$ (R is the gas constant, and the subscript c refers to the values at the critical gas–liquid point) is studied as a function of $t^* = \mu^{*2}/\sqrt{8}$ [29]. From the $Z_c = f(t^*)$ dependences presented in [22,29] we concluded that t^* for the substances studied may be approximated by $t^* \simeq 0.35$, which corresponds to the Z_c-values calculated for those compounds falling in the range 0.244–0.249. The values of T_c, P_c and V_c of the dipole substances studied, calculated by the Lydersen [30] method of critical constant estimation, are presented in table 2 as well. The reduced values $T_c^* = kT_c/\epsilon_{ab}$ and $V_c^* = V_c/b_0$ for $t^* \simeq 0.35$ lead [22,29] to the following dependences.

$$\epsilon_{ab}/k = 0.87T_c \tag{6}$$

$$b_0 = 0.588V_c \qquad \sigma_{ab} = 0.775V_c^{1/3}. \tag{7}$$

These relations are very close to the dependences obtained by Stiel and Thodos [31] and derived for polar molecules without hydrogen bonds:

$$\epsilon_{ab}/k = 0.887T_c \tag{8}$$

$$\sigma_{ab} = 0.785V_c^{1/3}. \tag{9}$$

According to Stiel and Thodos, the error in σ_{ab} and ϵ_{ab} for the substances that they studied varied between 5 and 20%.

If we consider a mixture of polar and non-polar molecules where the latter are polarized in the electric field produced by the former, the intermolecular potential

Table 1. Basis set and values of σ_{11} and ϵ_{11}/k calculated for alkanes.

Alkane	$(4\pi\epsilon_0)^{-1}$ ($10^{30}\alpha$ m^{-3})	T_b (K)	V_b^l (m^3 kmol^{-1})	Calculated from equations (4) and (5)		Determined from measurements [27,28]	
				σ_{11} (10^{-10} m)	ϵ_{11}/k (K)	σ_{11} (10^{-10} m)	ϵ_{11}/k (K)
n-pentane	9.95	309.16	0.118	5.728	355.52	5.769[a], 5.449[b]	345.0[a], 402.49[b]
n-hexane	11.78	342.16	0.141	6.065	393.47	5.910[a], 5.748[b]	413.0[a], 450.68[b]
n-heptane	13.61	371.16	0.163	6.369	426.83	8.880[c], 6.029[b]	282.0[c], 492.28[b]
n-octane	15.44	398.16	0.185	6.644	457.87	7.455[a]	320.0[a]
n-decane	19.16	446.16	0.229	7.140	513.07		
n-dodecane	22.75	489.66	0.274	7.574	563.09		
n-hexadecane	30.07	561.16	0.363	8.318	645.32		
Iso-octane	15.53	383.86	0.185	6.644	441.43	6.52 [37]	

[a] Determined from viscosity measurements [27].
[b] Determined via orthobaric and vapour pressure [28].
[c] Calculated from virial coefficients [27].

Table 2. Basis set and values of σ_{22} and ϵ_{22}/k calculated for dipolar liquids.

| Dipolar liquid | μ (10^{-30} C m) | T_b (K) | Estimated by the Lydersen method | | | Calculated from equations (6) and (7) | |
			V_c (m^3 kmol^{-1})	P_c (MPa)	T_c (K)	σ_{22} (10^{-10} m)	ϵ_{22}/k (K)
o-nitrotoluene	12.30	494.65	0.389	3.755	718.86	5.660	625.41
m-nitrotoluene	13.90	505.66	0.389	3.755	734.86	5.660	639.33
nitrobenzene	13.36	484.16	0.339	4.340	719.02	5.408	625.65

should include the terms describing the interactions between dipoles and induced dipoles [22]:

$$\rho_{12}(r) = 4\epsilon_{12}[(\sigma_{12}/r_{12})^{12} - (\sigma_{12}/r_{12})^6] - \alpha_1\mu_2^2/r_{12}^6 \qquad (10)$$

where the subscripts 1 and 2 refer to non-polar and polar substances respectively, and α is the polarizability of a non-polar molecule.

Equation (10) may be transformed into a form of the Lennard-Jones potential (2), when we rewrite the mixed potential parameters as [22]

$$\sigma'_{12} = \sigma_{12}\xi^{-1/6} \qquad (11)$$

$$\epsilon'_{12} = \epsilon_{12}\xi^2 \qquad (12)$$

where

$$\sigma_{12} = \tfrac{1}{2}(\sigma_{11} + \sigma_{22}) \qquad (13)$$

$$\epsilon_{12} = \sqrt{(\epsilon_{11}\epsilon_{22})} \qquad (14)$$

and

$$\xi = \left[1 + (\tfrac{1}{4}\alpha_1\mu_2^{*2}/\sigma_{11}^3)\sqrt{\epsilon_{22}/\epsilon_{11}}\right]. \qquad (15)$$

The parameters of the Lennard-Jones potential obtained for the mixtures of o- and m-nitrotoluene and nitrobenzene with the alkanes considered, according to equations (11) and (12), are given in tables 3–5. As follows from the presented data, the values of σ'_{12} for the mixtures of o- and m-nitrotoluene with the same alkanes are very similar. This is a consequence of the fact that the σ_{22}-values are the same for o- and m-nitrotoluene (table 2) and that these liquids have almost the same molar volume V_m (tables 3 and 4). The situation is analogous for the mixtures of these liquids with n-octane and iso-octane because of the same σ_{11}-value for these hydrocarbons and their very similar molar volumes V_{1m} (tables 3 and 4). As follows from the experimental results [4,14], the values of x_c (or 'x_c') are for these mixtures almost the same. The critical concentrations x_c of the mixtures of o-nitrotoluene and nitrobenzene in the appropriate alkanes (tables 3–5) can be expressed in the form of the volume fraction of the dipolar component:

$$\Phi_c = x_c V_{2m}/[(1 - x_c)V_{1m} + x_c V_{2m}]. \qquad (16)$$

Then, for a given value of V_{1m}, the values of Φ_c (figure 1) are almost the same in both types of mixture. Thus, the ratios of critical concentrations x_c^{nb} and x_c^{nt} in mixtures of nitrobenzene and o-nitrotoluene with a given n-alkane, if $\Phi_c^{nb} = \Phi_c^{nt}$, must obey the following relations:

$$x_c^{nb}/x_c^{nt} \simeq (1 - x_c^{nb})V_{2m}^{nt}/(1 - x_c^{nt})V_{2m}^{nb} \simeq (1 - x_c^{nb})\sigma_{22}^{3nt}/(1 - x_c^{nt})\sigma_{22}^{3nb} \qquad (17)$$

assuming that the molar volume V_{2m} of the liquid equals approximately σ_{22}^3 [23]. In the calculations presented, $V_{2m}^{nt}/V_{2m}^{nb} = 1.151$ and $\sigma_{22}^{3nt}/\sigma_{12}^{3nb} = 1.148$, which gives a difference of 0.25%. This justifies the application of the parameter σ_{ab} as an effective radius of the molecule in these phenomena. If the mixture of m-nitrotoluene with a given alkane is compared with a mixture of o-nitrotoluene with this alkane, then it follows from the dependence (17) that, if the V_{2m} or σ_{22}-values for these liquids are the same, then 'x_c'= x_c, which was experimentally proved.
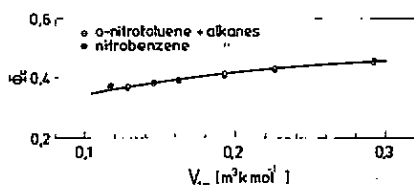

Figure 1. Critical concentrations Φ_c of the mixtures of o-nitrotoluene and nitrobenzene in alkanes versus V_{1m}, the molar volume of n-alkanes.
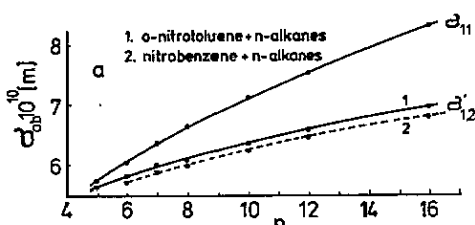
Figure 2. σ_{11} and σ_{12}' versus n, the number of carbon atoms of the molecule of alkane.

Table 3. Critical parameters and values of σ_{12}' and ϵ_{12}'/k calculated from equations (11) and (12) as well as values of B_{12} for the mixtures of o-nitrotoluene with alkanes.

| | o-nitrotoluene, $V_m = 0.118$ m^3 kmol^{-1} | | | | | |
Alkane	V_m (m^3 kmol^{-1})	x_c	T_c (K)	σ_{12}' (10^{-10} m)	ϵ_{12}'/k (K)	B_{12} (m^3 kmol^{-1})
n-pentane	0.118	0.368[a]	275.25[a]	5.679	485.51	−1.592
n-hexane	0.131	0.405[a]	272.35[a]	5.849	510.53	−1.950
n-heptane	0.146	0.442[a]	271.65[a]	6.001	531.09	−2.282
n-octane	0.163	0.478[a]	272.45[a]	6.140	549.72	−2.583
n-decane	0.195	0.535[b]	276.35[b]	6.387	580.82	−3.153
n-dodecane	0.227	0.590[b]	281.55[b]	6.604	607.76	−3.688
n-hexadecane	0.292	0.682[b]	290.86[b]	6.976	649.58	−4.638
Iso-octane	0.165	0.476[a]	280.75[a]	6.138	539.90	−2.385

[a] Estimated by the visual method [14] and equation (1).
[b] Determined from density measurements [38].

Figures 2 and 3(a) present the calculated values of σ_{11} and σ_{12}' and of ϵ_{11}/k and ϵ_{12}'/k, respectively, as functions of n, the number of carbon atoms in a molecule of a given n-alkane for all three kinds of the mixture studied. Figure 3(b) illustrates the

Table 4. Critical and hypothetical critical parameters and values of σ'_{12} and ϵ'_{12}/k, calculated from equations (11) and (12) as well as values of B_{12} for the mixtures of m-nitrotoluene and alkanes.

			T_c [a]	'T_c' [c]	'T_c'	σ'_{12}	ϵ'_{12}/k	B_{12}
Alkane	x_c [a]	'x_c' [b]	(K)	(K)	(K)	(10^{-10} m)	(K)	(m^3 kmol^{-1})
n-pentane		0.368			269.95	5.676	495.42	−1.732
n-hexane		0.405			267.10	5.845	520.15	−2.100
n-heptane		0.442			266.45	5.997	540.93	−2.438
n-octane		0.478		270.05	269.62	6.137	559.56	−2.762
n-decane		0.535			272.59	6.383	591.19	−3.360
n-dodecane		0.590			277.03	6.601	618.36	−3.922
n-hexadecane		0.682		286.41	286.74	6.973	660.69	−4.895
Iso-octane	0.472	0.478	277.40	277.32	277.25	6.129	556.24	−2.561

[a] Determined by the visual method [14].
[b] Calculated from equation (1).
[c] Estimated from NDE measurements [14].

Table 5. Critical parameters and values of σ'_{12} and ϵ'_{12}/k, calculated from equations (11) and (12) for the mixtures of nitrobenzene with alkanes.

	Nitrobenzene, $V_m = 0.103$ m^3 kmol^{-1}			
		T_c	σ'_{12}	ϵ'_{12}/k	B_{12}
Alkane	x_c	(K)	(10^{-10} m)	(K)	(m^3 kmol^{-1})
n-hexane	0.426[a]	293.21[a]	5.719	517.46	−1.630
n-heptane	0.470[a]	292.22[a]	5.869	538.46	−1.909
n-octane	0.505[a]	292.30[a]	6.008	556.88	−2.182
n-decane	0.561[b]	296.25[b]	6.255	588.17	−2.658
n-dodecane			6.472	615.08	
n-hexadecane	0.718[b]	309.59[b]	6.844	656.90	−3.963

[a] Determined from viscosity measurements [39].
[b] Determined by the visual method.

dependence of ϵ'_{12}/k on σ'_{12} for the mixtures studied. It was found that the functions presented in figure 3(b) are best approximated by a second-degree polynomial. With an accuracy of 0.002% it was determined that for the mixtures of o-nitrotoluene with n-alkanes,

$$\epsilon'_{12}/k = -14.72\sigma'^2_{12} + 312.57\sigma'_{12} - 814.62 \tag{18}$$

for m-nitrotoluene with n-alkanes,

$$\epsilon'_{12}/k = -13.93\sigma'^2_{12} + 303.51\sigma'_{12} - 778.27 \tag{19}$$

and, for nitrobenzene with n-alkanes,

$$\epsilon'_{12}/k = -14.27\sigma'^2_{12} + 303.05\sigma'_{12} - 748.82. \tag{20}$$

The character of the functions relating the energy parameter ϵ'_{12}/k and the structural parameter σ'_{12} is similar in all three kinds of mixture. Comparing the values σ'_{12}

and ϵ'_{12}/k of the mixtures of *o-* and *m-*nitrotoluene with the same *n-*alkanes we find that, whereas the values of σ'_{12} (which are physically interpreted as the effective radius of molecules 1 and 2 involved) of these systems are almost the same, their ϵ'_{12}/k-values are different. Higher values of the parameter ϵ'_{12}/k in the mixtures of *m-*nitrotoluene and *n-*alkanes may, with the same geometry of system preserved, have an essential influence on the observed decrease in critical temperatures of these systems when compared with those of the corresponding mixtures with *o-*nitrotoluene. These conclusions have been confirmed by the analysis of intermolecular interactions estimated within the approximation of the second virial coefficient in these mixtures.
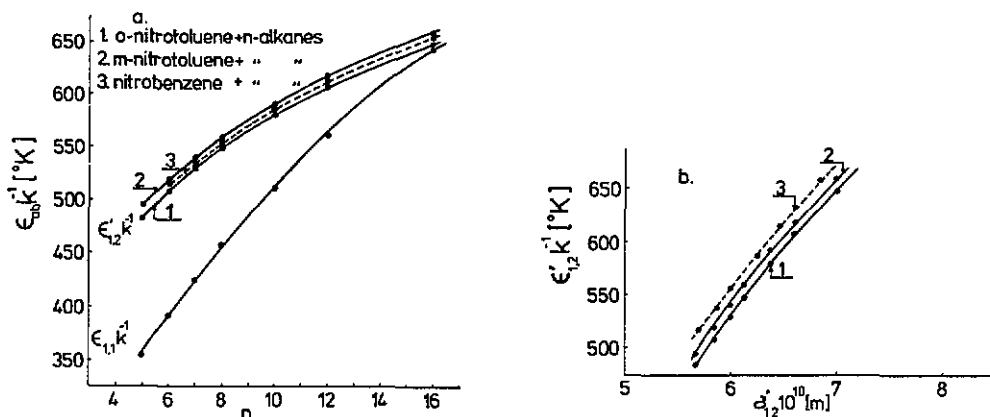

Figure 3. (*a*) ϵ_{11}/k and ϵ'_{12}/k versus *n*, the number of carbon atoms of the molecule of alkane for systems of *o-* and *m-*nitrotoluene and nitrobenzene with *n-*alkanes; (*b*) ϵ'_{12}/k versus σ'_{12} for systems of *o-* and *m-*nitrotoluene and nitrobenzene with *n-*alkanes.

3. Second virial coefficient

In general terms, liquids and dense gases are treated either as non-ideal gases, the molecules of which are subject to repeated collisions, or as defected crystals in which the long-range ordering disappears. The assumption of the Lennard-Jones potential, which is mainly applicable to gases, justifies the description of the mixtures considered from the point of view of gases. Such an approach leads to the equation of state in the virial form, where the second virial coefficient is expressed as

$$B(T) = b_0 B^*(T^*) \tag{21}$$

and the reduced second virial coefficient as

$$B^*(T^*) = \frac{4}{T^*} \int_0^\infty r^{*2} \left(-\frac{12}{r^{*12}} + \frac{6}{r^{*6}} \right) \exp\left[-\frac{4}{T^*} \left(\frac{1}{r^{*12}} - \frac{1}{r^{*6}} \right) \right] dr^* \tag{22}$$

where

$$r^* = r_{ab}/\sigma_{ab}. \tag{23}$$

The expansion of the expression $\exp[(4/T^*)r^{*-6}]$ allows us to express $B^*(T^*)$ in the form [22]

$$B^*(T^*) = \sum_{j=0}^{\infty} b^{(j)} T^{-(2j+1)/4} \tag{24}$$

where the coefficients $b^{(j)}$ are expressed through Γ functions [22]. In the case of binary mixtures, the second virial coefficient $B_{\mathrm{m}}(T)$ of the mixtures is expressed as follows:

$$B_{\mathrm{m}}(T) = x_1^2 B_{11}(T) + 2x_1 x_2 B_{12}(T) + x_2^2 B_{22}(T) \tag{25}$$

where x_1 and x_2 are the molar fractions of components 1 and 2, respectively, $B_{11}(T)$ and $B_{22}(T)$ determine the second virial coefficient of the pure components and $B_{12}(T)$ is the second virial coefficient determining the interaction of mixed molecule pairs 1 and 2. It seemed interesting to determine the interaction of molecular pairs as functions of concentration and temperature, and then to compare them in the mixtures revealing the classical phenomenon of phase separation (*o*-nitrotoluene– or nitrobenzene–*n*-alkanes) with those in the mixtures revealing a far pre-critical effect (*m*-nitrotoluene–*n*-alkanes). $B_{\mathrm{m}}(T)$-values were calculated from (25), (24) and (21), using the σ_{ab}- and ϵ_{ab}/k-values presented in tables 1–5 and the tabulated function $B^*(T^*)$ given in [22].

Figures 4 and 5 show the B_{m}-values and the contributions from the interactions of molecular pairs of the solvent ($x_1^2 B_{11}$) and dipole liquids ($x_2^2 B_{22}$) as well as both types of molecule ($2x_1 x_2 B_{12}$) in the mixtures of *o*- and *m*-nitrotoluene with *n*-octane and iso-octane, respectively, to this value at various temperatures as functions of concentration x_2. On analysing figure 4(*a*) we can see that, at a temperature $T = 272.4$ K (for this mixture it is the critical value T_c; see table 3), $x_1^2 B_{11}$ and $x_2^2 B_{22}$ are equal for a concentration $x_2 = 0.478$ which is the critical concentration x_c for this mixture. There are two more characteristic points on the plot: a concentration of $x_2 \simeq 0.27$, for which $x_1^2 B_{11}$ and $2x_1 x_2 B_{12}$ assume the same value and a concentration of $x_2 \simeq 0.70$ for which $x_2^2 B_{22} = 2x_1 x_2 B_{12}$. Hence, three concentration ranges can be differentiated in the plot: range I, $0 \lesssim x_2 \lesssim 0.27$, where interactions of the $x_1^2 B_{11}$ type are predominant, whereas the other two have only small contributions to B_{m}; range II, $0.27 \lesssim x_2 \lesssim 0.70$, where the mixed interactions $2x_1 x_2 B_{12}$ are predominant (also, within the concentration range $0.27 \lesssim x_2 \lesssim x_c$ the contribution comparable with that of $2x_1 x_2 B_{12}$ also comes from $x_1^2 B_{11}$ for, at x_c, $2x_1 x_2 B_{12} = x_1^2 B_{11} + x_2^2 B_{22}$, whereas within the concentration range $x_c \lesssim x_2 \lesssim 0.70$, besides the interaction of $2x_1 x_2 B_{12}$ type, $x_2^2 B_{22}$ also plays an important role); range III, $0.70 \lesssim x_2 \lesssim 1$, where the $x_2^2 B_{22}$-type interactions are predominant. Hence, it can be concluded that the properties of the system within the concentration range I are determined by the properties of component 1, concentration range II is characterized by very strong mixed interactions (hence some processes determining the system miscibility must occur there) and in range III the properties of the system are determined by the properties of component 2.

The total value of the second virial coefficient B_{m} given as a function of concentration in figure 4(*a*) testifies to the fact that the total intermolecular interaction does not depend linearly on concentration but exhibits a mild increase within the concentration range where the mixed interactions are predominant.
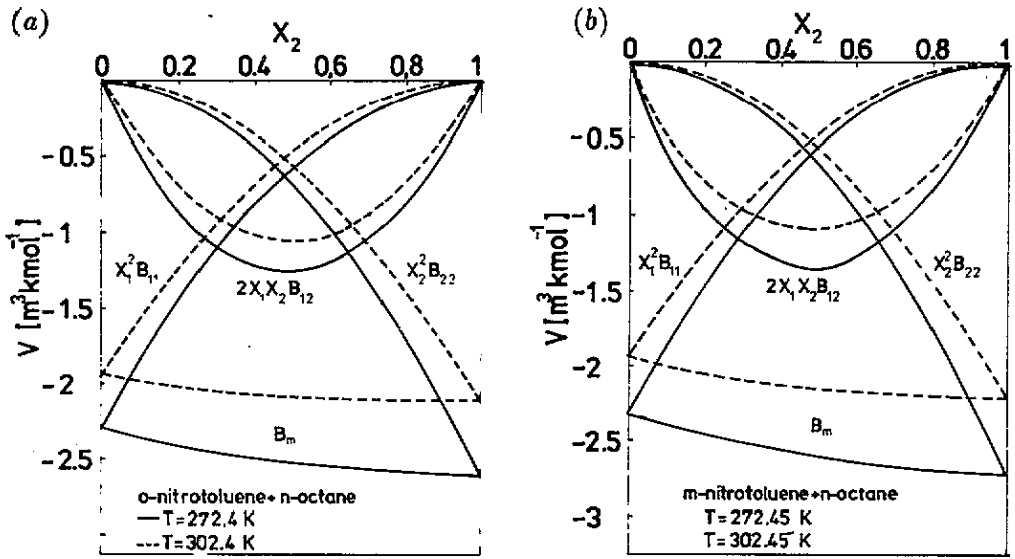
Figure 4. Second virial coefficient versus concentration at various temperatures for the following systems: (*a*) *o*-nitrotoluene–*n*-octane; (*b*) *m*-nitrotoluene–*n*-octane.
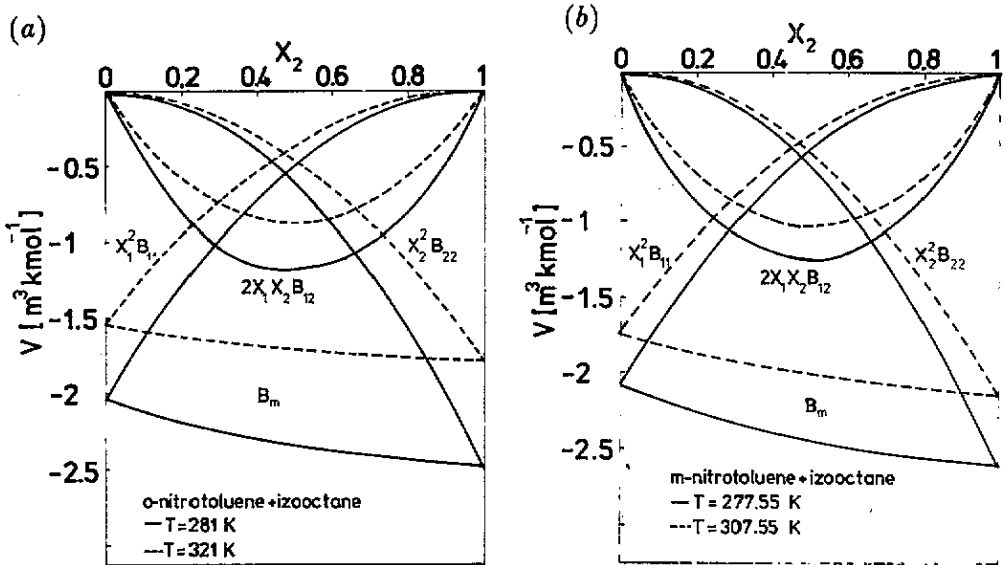

Figure 5. Second virial coefficient versus concentration at various temperatures for the following systems: (*a*) *o*-nitrotoluene–iso-octane; (*b*) *m*-nitrotoluene–iso-octane.

It is very significant that intermolecular interactions in the mixture are also distributed in a similar way at higher temperatures. Although the contributions to B_m (figure 4(*a*)) coming from particular types of interaction, at a temperature $T_c + 30$ K are relatively lower (higher energy of molecular thermal motion), their distribution as a function of concentration has similar concentration ranges as in the case of lower temperatures. Hence, it may be expected that even at very high temperatures the division into three characteristic concentration ranges in which appropriate types of predominant interaction determine the behaviour of the system will still occur.

According to this approach, the properties of the mixture at various temperatures will be determined by the parameter $T^* = kT/\epsilon_{11}$ in the concentration range I, $T^* = kT/\epsilon'_{12}$ in range II and $T^* = kT/\epsilon_{22}$ in range III.

The different behaviours of the mixture in the three different concentration ranges are evidenced by experimental data. On comparison of figure 1(*a*) in [14] with figure 4(*a*) it can be observed that the concentration range for which positive anomalies of NDE resulting from the pre-transition effect occur exactly overlaps range II in which mixed interactions are prevalent. Below the critical temperature T_c the phase coexistence curve includes the same concentration range [14].

The dependences presented in figure 5 which determine the second virial coefficient B_m and the values of $x_1^2 B_{11}$, $x_2^2 B_{22}$ and $2x_1 x_2 B_{12}$ as functions of concentration for the *o*- and *m*-nitrotoluene mixtures with iso-octane may be analysed in an analogous way. In this case we can also differentiate between three characteristic concentration ranges within which the behaviours of the mixtures are different, and which are almost the same for both systems studied. As follows from the discussion presented in the previous section, this is because the values of σ_{11} and σ_{22} determining the b_0-value in equation (21) are the same for both systems. Hence, it appears that these systems differ only in the values of ϵ_{22} and ϵ'_{12}, which are higher for the *m*-nitrotoluene mixture with iso-octane, leading to a reduction in the critical temperature T_c (table 4) with respect to the *o*-nitrotoluene–iso-octane system. It also becomes apparent when we compare figures 2(*a*) and 2(*b*) in [14] with figures 5(*a*) and 5(*b*), that the concentration range characterized by NDE anomalies above T_c as well as the range of concentrations under the phase coexistence curve below T_c correspond to concentrations which in figure 5 are determined by the dominant value $2x_1 x_2 B_{12}$. Stronger intermolecular interactions in the *m*-nitrotoluene mixtures with alkanes cause a reduction in their critical temperature with respect to the *o*-nitrotoluene mixtures but, on the other hand, their melting point is higher [32]. The second virial coefficient as a function of concentration in the *m*-nitrotoluene–*n*-octane mixture presented in figure 4(*b*) shows a concentration range (analogous to those in figure 4(*a*)) where phase separation may be expected to occur, with almost the same x_c-value. Yet the mixture solidifies in the homogeneous phase, although the NDE anomalies (figure 1(*b*) in [14]) indicate a pre-transition effect.

A similar situation is illustrated in figure 6, where the second virial coefficient in the *o*- and *m*-nitrotoluene mixtures with *n*-hexadecane is presented as a function of concentration at a temperature which is the critical temperature for the *o*-nitrotoluene–*n*-hexadecane mixture. As figure 6 clearly indicates, the concentration ranges with mixed interactions predominate for the systems considered, and also their x_c and 'x_c' concentrations are comparable. NDE anomalies resulting from the pre-transition effect were confirmed to occur in this concentration range of these mixtures [2].

The finding that the concentration ranges in which the mixture shows limited miscibility with a critical point are determined by the characteristic distribution of intermolecular interactions has been confirmed by the results of calculations of B_m for nitrobenzene–*n*-alkane mixtures. Figure 7 presents the second virial coefficient as a function of concentration for the nitrobenzene–*n*-hexane mixture at the critical temperature and higher. Pre-transition anomalies of NDE for this system were also found within the concentration range in which mixed interactions prevail [9,33]. The dependences observed in figures 4–7 are also reported for the remaining dipolar-liquid–alkane mixtures studied and in each case the concentration range II is
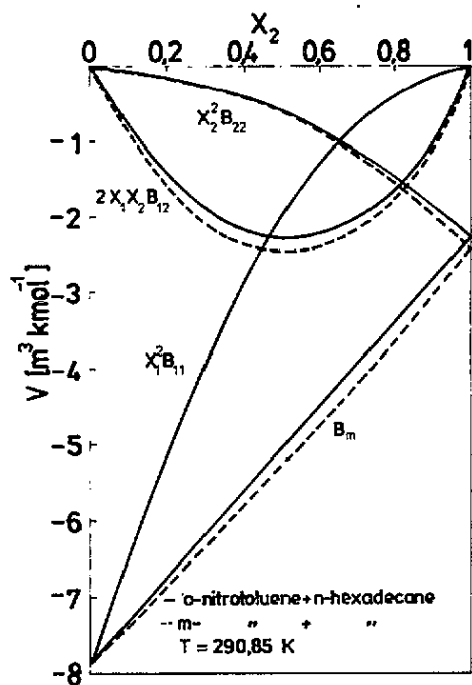
Figure 6. Second virial coefficient versus concentration for *o*- and *m*-nitrotoluene with *n*-hexadecane.
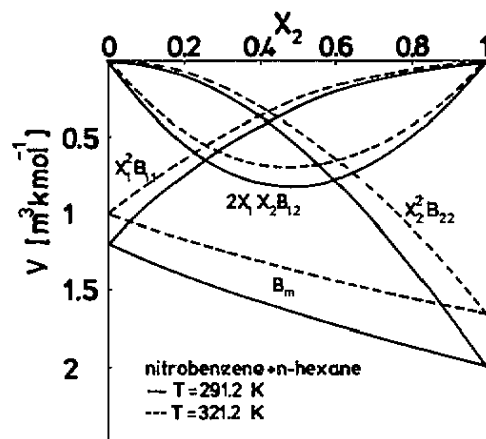
Figure 7. Second virial coefficient versus concentration for nitrobenzene–*n*-hexane at various temperatures.

distinguished in the NDE studies as a concentration region with critical NDE anomalies present [34].

On examination of the reduced temperature $T^* = kT_c/\epsilon'_{12}$ as a function of ϵ'_{12} for systems showing phase separation (mixtures of *o*-nitrotoluene and nitrobenzene with *n*-alkanes) (figure 8) it was found that T_c, which is generally close to $T^* \simeq 0.5$, changes depending on ϵ'_{12}; the T^*-values are lower for molecules of large molar volume (nitrotoluene mixtures with alkanes) and higher for mixtures of molecules of smaller volume. In the case of *o*- and *m*-nitrotoluene mixtures with a given alkane, for which the molecular volumes are the same, T^* is a function of only ϵ'_{12} (figure 8).

Thus, when we formally express the coefficient B_{12} in (21) for the phase separation temperatures (tables 3 and 5) as a function of ϵ'_{12}/k for the mixtures considered (figure 9), we obtain similar curves for *o*-nitrotoluene and nitrobenzene mixtures with alkanes. The curves are well approximated by a second-degree polynomial; in the case of *o*-nitrotoluene–*n*-alkane systems this dependence is as follows:

$$B_{12} = -0.02976(\epsilon'_{12}/k)^2 + 15.3482\epsilon'_{12}/k - 2030.5240 \tag{26}$$

and the accuracy of the approximation obtained is about 0.2%. In the case of nitrobenzene–*n*-alkane mixtures, this dependence, approximated with the same accuracy, is

$$B_{12} = -0.0307(\epsilon'_{12}/k)^2 + 19.3575\epsilon'_{12}/k - 3423.0527. \tag{27}$$

Since the second virial coefficient B_{12} is a function of both σ'_{12} and ϵ'_{12}/k, by combining (26) and (18) or (27) and (20), it is possible to determine the value of B_{12} as a function of both parameters for the mixtures considered.
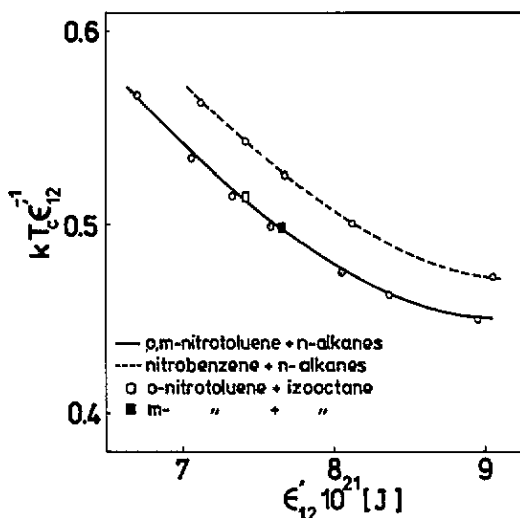
Figure 8. Reduced temperature T_c^* versus ϵ_{12}' for o- and m-nitrotoluene with alkanes and for nitrobenzene with alkanes.
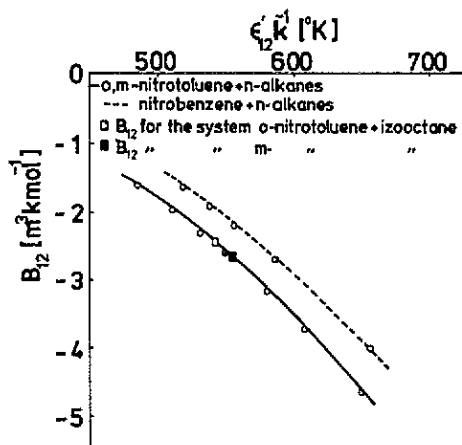
Figure 9. Second virial coefficient B_{12} versus ϵ_{12}'/k for o- and m-nitrotoluene with alkanes and for nitrobenzene with alkanes.

Assuming a formal analogy of the above description, and combining equations (26) and (19), we can estimate B_{12} for mixtures of m-nitrotoluene and n-alkanes at their hypothetical 'T_c' and at the same time on the basis of equation (24) we can calculate this temperature. The coefficients B_{12} obtained in this way as well as 'T_c' corresponding to them, calculated with the accuracy of $T^* \pm 0.002$, are compiled in table 4. When the coefficient B_{12} of the m-nitrotoluene mixture with iso-octane is determined likewise, its value is found to be $B_{12} = -2.561$ m^3 kmol^{-1}, which corresponds to $T_c = 277.25$ K. This value is in good agreement with the actually observed critical temperature $T_c = 277.40$ K (figure 3 in [14]) for this mixture. Hypothetical values of 'T_c' for m-nitrotoluene mixtures with some alkanes were also estimated on the basis of the exponential law, which describes the behaviour of the NDE in the vicinity of the critical point [14]. The 'T_c'-values reported therein for o-nitrotoluene mixtures with n-octane and n-hexadecane are also presented in table 3 and are in good agreement with the values estimated in the way proposed in this work. The melting points, determined in the case of m-nitrotoluene mixtures with n-decane and n-hexadecane [32], and which for their 'x_c' concentrations are $T_m = 282.55$ K and $T_m = 288.35$ K, respectively, are higher than the 'T_c' of these mixtures.

If we express the coefficients B_{12} of nitrobenzene–n-alkane mixtures at the critical temperatures as a function of both potential parameters (figure 10), we arrive at a kind of phase surface f(B_{12}, σ_{12}', ϵ_{12}'/k) including the region in which the mixtures studied exist in the homogeneous phase. Outside this surface in the region which corresponds to temperatures lower than T_c, heterogeneity of these systems is observed. Similar surfaces can be found for o- and m-nitrotoluene mixtures with alkanes but for m-nitrotoluene mixtures it has a purely hypothetical value.

Since the phenomenon that the critical temperature is lower than the melting point was found for a very wide group of mixtures [1, 2, 5, 14], it is not unlikely that it may be observed in many other liquid mixtures. Then, the experimentally observed courses of many physical quantities sensitive to inhomogeneities of the medium, whose
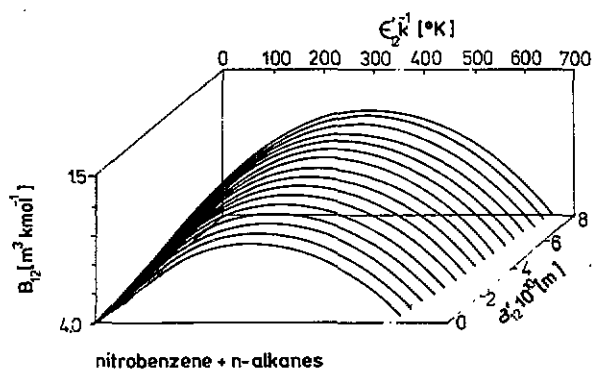
Figure 10.   Phase surface $f(B_{12}, \sigma'_{12}, \epsilon'_{12}/k)$ for the nitrobenzene–alkane systems.

anomalies depend strongly on temperature, may be related to the presence of a far pre-critical effect in the systems studied.

4. Conclusions

On the basis of the classical theory assuming the presence of van der Waals intermolecular forces, we determined the second virial coefficient of liquid mixtures showing the classical critical effect (*o*-nitrotoluene and nitrobenzene with *n*-alkanes) as well as of mixtures showing a pre-transitional effect (*m*-nitrotoluene with *n*-alkanes). It was found that the concentration region in which the strongest intermolecular interactions are detected correspond to the concentration ranges for which the phenomenon of phase separation in these mixtures is observed. In mixtures showing the pre-transitional effect in this very concentration range, at temperatures close to their melting points, molecular clusters characteristic of pre-critical states were found [32]. The considerations presented confirm the fact that the geometry of molecules plays a crucial role in the formation of these concentration regions, which is in agreement with the results of studies on hydrocarbon solubility in water [15–20].

On the basis of a formal analogy of the values of second virial coefficients in the systems studied, we determined hypothetical critical temperatures 'T_c' of mixtures of *m*-nitrotoluene with *n*-alkanes in which the melting point is higher than the hypothetical 'T_c'. The values found are in good agreement with the 'T_c'-values *calculated for mixtures of m-nitrotoluene with some alkanes. The latter were* determined from NDE measurements performed on these mixtures, assuming that NDE behaviour near phase transitions is exponential in character [14]. The dependences found allowing a determination of the critical temperature of these mixtures on the basis of the Lennard-Jones potential parameters are also fulfilled in the case of mixtures studied of the polar liquids with cycloalkanes [34]; thus, it can be said that they assume a more general character.

The results obtained prove the dependence of the critical parameters of the mixtures studied on their σ_{ab}- and ϵ_{ab}-values. From the viewpoint of the percolation approach [35,36] to molecular cluster formation, where the criterion on the formation of clusters is given by the condition that two occupied neighbouring sites are bonded, the parameters σ_{ab} and ϵ_{ab} might characterize the percolation lattice, the sites of which are occupied randomly.

Acknowledgments

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