PERTURBATION THEORY OF SOLUTIONS OF NON-ELECTROLYTES. THE EFFECT OF PERMANENT AND INDUCED MULTIPOLE INTERACTIONS ON EXCESS THERMODYNAMIC FUNCTIONS OF BINARY SYSTEMS

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Received March 20th, 1979

Dedicated to Professor E. Hála on the occasion of his 60th birthday.

Perturbation theory proposed to describe fluids with the multipole interactions was extended to the systems with significant induced interactions. The relations obtained were used to study the effect of the permanent and induced multipole interactions on excess thermodynamic functions of binary solutions formed by a simple fluid (interacting according to the Lennard–Jones pair potential) and a fluid with anisotropic intermolecular forces. Model solutions were studied first; the same procedure was then used to predict behaviour of the real systems cyclopentane–chloroform at 298·15 K and xenon–hydrogen chloride at 195·4 K. A considerable effect of anisotropic interactions on excess quantities of the model- as well as actual solutions was proved.

The determination of thermodynamic properties of non-associating molecular liquids requires to include a sufficiently accurate description of intermolecular interactions into the statistical-thermodynamic theory. It concerns both the short-range intermolecular interactions (repulsive interactions) and the long-range intermolecular interactions (dispersion, multipole and induced interactions). The important methods which allow to consider the long-range anisotropic interactions in the statistical-thermodynamic description are the perturbation methods with the reference liquid formed by particles of spherical shape. However, the anisotropy of repulsion can be incorporated in these theories only in a rather approximative way (or it is fully neglected); therefore these methods are suitable for the description of liquids with mildly non-spherical molecules and with significant long-range interactions. The general formulation of these methods was proposed by Pople[1] in 1954. The first concrete calculations[2], however, were carried out only in 1972 when the radial distribution function of the hard sphere system and of the Lennard–Jones 12-6 (LJ) particles, which were used as the reference systems, were already sufficiently well known. The computations for pure liquids were performed by Stell, Rasaiah and coworkers[2–4], McDonald[5] and Ananth, Gubbins and Gray[6]. The study of solutions was dealt with by Chambers and McDonald[7] and Gubbins, Gray and coworkers[8–10].

A variant of the perturbation theory formulated by the last authors is the basis of procedure used in this work; the theory was extended by including the induced interactions and then employed to study the effect of the multipole- and induced interactions on excess thermodynamic quantities of several model and actual systems of non-electrolytes.

THEORETICAL

To express the intermolecular interactions in pure constituents and in solution the pair potential given as the sum of the LJ potential and the perturbation potential, u^{p}, was used:

$$u_{\mathrm{ab}}(r_{12}, \omega_1, \omega_2) = u_{\mathrm{ab}}^{\mathrm{LJ}}(r_{12}) + u_{\mathrm{ab}}^{\mathrm{p}}(r_{12}, \omega_1, \omega_2)\,. \tag{1}$$

This potential describes the interactions of particle 1 of the type a and particle 2 of the type b whose mutual position is given by the intermolecular distance r_{12} and the solid angles ω_1, ω_2.

To express the perturbation potential we utilized the potentials of the multipole interactions[11]

$$u_{\mathrm{ab}}^{\mu} = C\mu_{\mathrm{a}}\mu_{\mathrm{b}}r^{-3}(2c_{\mathrm{a}}c_{\mathrm{b}} + s_{\mathrm{a}}s_{\mathrm{b}}c_{\mathrm{ab}})\,, \tag{2}$$

$$u_{\mathrm{ab}}^{\mathrm{q}} = \tfrac{3}{4}Cq_{\mathrm{a}}q_{\mathrm{b}}r^{-5}(1 - 5c_{\mathrm{a}}^2 - 5c_{\mathrm{b}}^2 + 17c_{\mathrm{a}}^2c_{\mathrm{b}}^2 + 2s_{\mathrm{a}}^2s_{\mathrm{b}}^2c_{\mathrm{ab}}^2 + 16s_{\mathrm{a}}s_{\mathrm{b}}c_{\mathrm{a}}c_{\mathrm{b}}c_{\mathrm{ab}}) \tag{3}$$

and of the induced interactions[11]

$$u_{\mathrm{ab}}^{\alpha\mu} = -\tfrac{1}{2}\,Cr^{-6}[\alpha_{\mathrm{b}}\mu_{\mathrm{a}}^2(3c_{\mathrm{a}}^2 + 1) + \alpha_{\mathrm{a}}\mu_{\mathrm{b}}^2(3c_{\mathrm{b}} + 1)]\,, \tag{4}$$

$$u_{\mathrm{ab}}^{\mathrm{q}\alpha} = -\tfrac{9}{8}Cr^{-8}[\alpha_{\mathrm{b}}q_{\mathrm{a}}^2(1 - 2c_{\mathrm{a}}^2 + 5c_{\mathrm{a}}^4) + \alpha_{\mathrm{a}}q_{\mathrm{b}}^2(1 - 2c_{\mathrm{b}}^2 + 5c_{\mathrm{b}}^4)]. \tag{5}$$

In the given potentials, μ is the dipole moment, q the quadrupole moment, α the dipole polarizability, $c_{\mathrm{i}} \equiv \cos\theta_{\mathrm{i}}$, $s_{\mathrm{i}} \equiv \sin\theta_{\mathrm{i}}$ $(i = \mathrm{a, b})$ and $c_{\mathrm{ab}} \equiv \cos\phi$ (angles θ_{i}, ϕ represent angular orientations of axially symmetric molecules), $C = (4\pi\varepsilon_0)^{-1}$, ε_0 is the permitivity of vacuum.

On using Eq. (*1*), it is possible to express the configurational Helmholtz free energy of a solution by the expansion

$$F = F_{\mathrm{LJ}} + F_1 + F_2 + F_3 + \ldots\,. \tag{6}$$

Here F_{LJ} is the contribution of the LJ interactions and F_1, F_2, F_3 are the perturbation terms of the first to third order. For their expressing the general relations[12] were found, *e.g.*

$$F_1 = \frac{\varrho^2}{2}\sum_{\mathrm{ab}} x_{\mathrm{a}}x_{\mathrm{b}} \int u_{\mathrm{ab}}^{\mathrm{p}}(r_{12}, \omega_1, \omega_2)\, g_{\mathrm{ab}}^{\mathrm{LJ}}(r_{12})\, \mathrm{d}\mathbf{r}_1\, \mathrm{d}\mathbf{r}_2\, \mathrm{d}\omega_1\, \mathrm{d}\omega_2\,. \tag{7}$$

In the last equation, ϱ is the particle density, $x_{\mathrm{i}}(i = \mathrm{a, b})$ are the mole fractions of components and $g_{\mathrm{ab}}^{\mathrm{LJ}}(r_{12})$ the distribution function of the LJ solution. F_{LJ} and further thermodynamic quantities of the LJ solution were calculated from the $v\,\mathrm{d}W1$ approximation[13] by means of the equations of McDonald and Singer[14]. The cross LJ parameters were calculated from the relations

$$\sigma_{ab} = \tfrac{1}{2}(\sigma_a + \sigma_b) \tag{8}$$

$$\varepsilon_{ab} = \xi(\varepsilon_a \varepsilon_b)^{1/2}\,, \tag{9}$$

where ξ is the semi-empirical parameter whose value is close to unity.

The concrete expression of the perturbation terms is obtained by inserting the perturbation potentials into the general relations and by carrying out the angular averaging. Considering the induced interactions to the first perturbation order and the multipole interactions to the third perturbation order, we obtain for a solution of polarizable polar liquids, on using the potentials (*2*), (*4*), the relations

$$F_1 = F_1^{\text{ind}} = -2\pi\varrho NC \sum_{ab} x_a x_b (\alpha_a \mu_b^2 + \alpha_b \mu_a^2) \left(\frac{1}{\sigma_{ab}^3}\right) J_{ab}^{(6)}\,, \tag{10}$$

$$F_2^{\text{mult}} = \frac{2\pi\beta\varrho N}{3}\, C \sum_{ab} x_a x_b \mu_a^2 \mu_b^2 \left(\frac{1}{\sigma_{ab}^3}\right) J_{ab}^{(6)}\,, \tag{11}$$

$$F_3^{\text{mult}} = \left(\frac{14\pi}{5}\right)^{1/2} \frac{32\pi^3\beta^2\varrho^2 N}{135}\, C^3 \sum_{abc} x_a x_b x_c \mu_a^2 \mu_b^2 \mu_c^2 \left(\frac{1}{\sigma_{ab}\sigma_{ac}\sigma_{bc}}\right) K_{abc}(222, 333)\,, \tag{12}$$

and for a solution of polarizable quadrupolar liquids, on using the potentials (*3*), (*5*), the realtions

$$F_1 = F_1^{\text{ind}} = -3\pi\varrho NC \sum_{ab} x_a x_b (\alpha_a q_b^2 + \alpha_b q_a^2) \left(\frac{1}{\sigma_{ab}^5}\right) J_{ab}^{(8)}\,, \tag{13}$$

$$F_2^{\text{mult}} = -\frac{14\pi\beta\varrho N}{5}\, C^2 \sum_{ab} x_a x_b q_a^2 q_b^2 \left(\frac{1}{\sigma_{ab}^7}\right) J_{ab}^{(10)}\,, \tag{14}$$

$$F_3^{\text{mult}} = \frac{144\pi\beta^2\varrho N}{245}\, C^3 \sum_{ab} x_a x_b q_a^3 q_b^3 \left(\frac{1}{\sigma_{ab}^{12}}\right) J_{ab}^{(15)} +$$

$$+ \frac{32\pi^3}{2025}(2002)^{1/2}\beta^2\varrho^2 N C^3 \sum_{abc} x_a x_b x_c q_a^2 q_b^2 q_c^2 \left(\frac{1}{\sigma_{ab}^3\sigma_{ac}^3\sigma_{bc}^3}\right) K_{abc}(444, 555)\,. \tag{15}$$

In expressions (*10*)–(*15*), N is the number of particles of the system $\beta = 1/kT$;

$$J^{(n)}_{ab} = \sigma_{ab}^{n-3} \int_0^\infty r_{12}^{-(n-2)} g^{LJ}_{ab}(r_{12})\, dr_{12} \qquad (16)$$

and $K_{abc}(l, l', l'', n, n', n'')$ are the dimensionless integrals which can be calculated providing that the radial distribution function of the LJ liquid is known. In this paper, the values of integrals were calculated in the same way as in refs[10,15] (approximation 2).

The multipole interactions and anisotropy of polarizability have no effect on F_1. Therefore the polarizability in potentials (*3*), (*5*) is considered as isotropic.

The complete configurational Helmholtz free energy of solution was approximated by the relation

$$F \approx F_{LJ} + F_1^{ind} + \frac{F_2^{mult}}{1 - (F_3^{mult}/F_2^{mult})} \cdot \qquad (17)$$

To express the contribution of multipole interaction the Padé approximant, proposed by Stell and coworkers[3], was used. The relations for the other thermodynamic

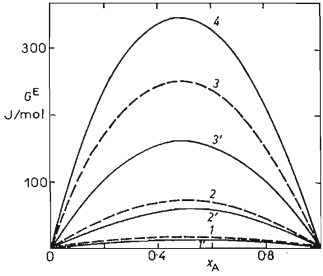

FIG. 1

G^E of the System LJ Liquid(A)-Stockmayer Liquid(B) at 115·8 K and Zero Pressure

Parameters: $\sigma_A = \sigma_B = 3{\cdot}405 \,.\, 10^{-10}$ m, $\varepsilon_A/k = \varepsilon_B/k = 119{\cdot}8$ K; *1* $\mu_B^* = 0{\cdot}5$, *2* 0·75, *3* 1·0, *4* 1·25. Dashed lines correspond to the perturbation theory to the second order and solid lines to the complete description.

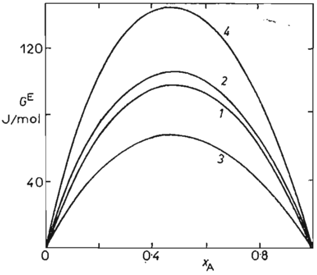

FIG. 2

G^E of the System Polarizable LJ Liquid(A)–Polarizable Quadrupolar Liquid(B) at 115·8 K and Zero Pressure

Parameters: $\sigma_A = \sigma_B = 3{\cdot}405 \,.\, 10^{-10}$ m, $\varepsilon_A/k = \varepsilon_B/k = 119{\cdot}8$ K; $q_B^* = 0{\cdot}65$; *1* $\alpha_A^* = \alpha_B^* = 0$, *2* $\alpha_A^* = \alpha_B^* = 0{\cdot}05$, *3* $\alpha_A^* = 0{\cdot}08$, $\alpha_B^* = 0{\cdot}02$, *4* $\alpha_A^* = 0{\cdot}02$, $\alpha_B^* = 0{\cdot}08$.

quantities can be obtained from Eq. (*17*) using the fundamental thermodynamic relations[9].

RESULTS

The calculations were performed for several model systems of the type LJ liquid–liquid with anisotropic interactions and for two real systems.

Some results for the model systems are given in Figs 1–4. Fig. 1 shows the effect of reduced dipole moment $\mu^* = \mu/(C\varepsilon\sigma^3)^{1/2}$ on excess free enthalpy G^E of the system LJ liquid (A)–Stockmayer liquid (B) for $\sigma_A = \sigma_B = 3{\cdot}405 \,.\, 10^{-10}$ m and $\varepsilon_A/k = \varepsilon_B/k = 119{\cdot}8$ K. Dashed line denotes the results on neglecting the third-order perturbation term. From Fig. 2, the influence of induced interaction on G^E is evident in case of the solution of polarizable LJ liquid (A)–polarizable quadrupolar liquid (B). It is obvious that the G^E values corresponding to the pure quadrupole interaction can be increased or decreased by an induced interaction with regard to the fact whether the induced interaction increases more the attractive forces in pure component B or in solution. (The reduced quadrupole moment and polarizability are given

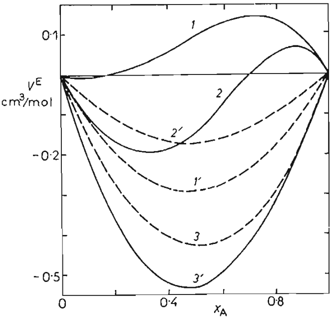

FIG. 3

V^E of the System Polarizable LJ Liquid(A)–Polarizable Quadrupolar Liquid(B) at 97 K and Zero Pressure

Parameters: $\sigma_A = 3{\cdot}40 \,.\, 10^{-10}$ m, $\varepsilon_A/k = 120{\cdot}0$ K; $\sigma_B/\sigma_{AB} = 1{\cdot}05$, *1* $\varepsilon_B/\varepsilon_{AB} = 0{\cdot}95$, *2* 1·1, *3* 1·2; *1*, *2* $q_B^* = 0{\cdot}6$, *3* 0·4; $\alpha_A^* = 0{\cdot}05$, $\alpha_B^* = 0{\cdot}06$. Dashed lines refer to the LJ description and solid lines to the complete description.

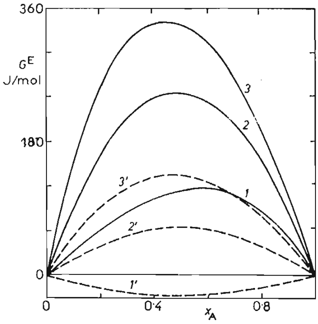

FIG. 4

G^E of the System Polarizable LJ Liquid(A)–Polarizable Polar Liquid(B) at 192 K and Zero Pressure

Parameters: $\sigma_B = 3{\cdot}50 \,.\, 10^{-10}$ m, $\varepsilon_B/k = 350{\cdot}0$ K; $\varepsilon_A/\varepsilon_{AB} = 0{\cdot}9$, *1* $\sigma_A/\sigma_{AB} = 0{\cdot}95$, *2* 1·0, *3* 1·05; $\mu_B^* = 0{\cdot}75$; *1* $\alpha_A^* = 0{\cdot}04$, *2* 0·05, *3* 0·06; $\alpha_B^* = 0{\cdot}05$. Dashed lines refer to the LJ description and solid lines to the complete description used.

by the relations $q^* = q/(C\varepsilon\sigma^5)^{1/2}$ and $\alpha^* = \alpha/\sigma^3$.) Fig. 3 shows the effect of a change in the ratio $\varepsilon_B/\varepsilon_{AB}$ on the excess molar volume of solutions of the type polarizable LJ liquid (A)–polarizable quadrupolar liquid (B) for $\sigma_B/\sigma_{AB} = 1{\cdot}05$ and the temperature $T = 97$ K. The calculated values are plotted by solid line, V^E for the corresponding LJ interactions is plotted by the dashed line. The effect of change in the ratio σ_A/σ_{AB} on G^E of solutions of the type polarizable LJ liquid (A)–polarizable polar liquid (B) for $\varepsilon_A/\varepsilon_{AB} = 0{\cdot}9$ and $T = 192$ K is shown in Fig. 4.

In Figs 5–8, the results are presented of interpretation of excess thermodynamic quantities of the real systems cyclopentane–chloroform (298·15 K) and xenon–hydrogen chloride (195·4 K). The solutions were considered partly as a solution of LJ liquids (dashed curves) and partly as a solution formed by polarizable LJ liquid-polarizable polar liquid (solid curves). Circles denote experimental data[16,17]. (Experimental values of H^E for the xenon–hydrogen chloride system are not known.)

The parameters σ, ε/k for pure substances were fitted to the experimental data on the dependence of density of pure liquid on temperature; the values of μ and α were taken over from the literature. Besides the computations for $\xi = 1$, also the results are given for ξ values adjusted to the experimental data on excess volumes.

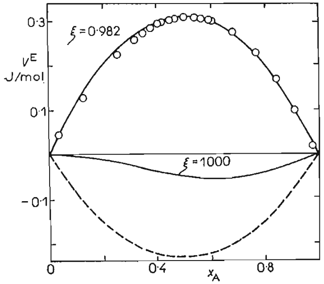

FIG. 5

Experimental and Computed Values of V^E in the Cyclopentane(A)–Chloroform(B) System at 298·15 K

LJ description (dashed line): $\sigma_A = 5{\cdot}060 \,.\, 10^{-10}$ m, $\varepsilon_A/k = 370{\cdot}0$ K, $\sigma_B = 4{\cdot}816 \,.\, 10^{-10}$ m, $\varepsilon_B/k = 403{\cdot}0$ K. Complete description (solid lines): $\sigma_B = 4{\cdot}833 \,.\, 10^{-10}$ m, $\varepsilon_B/k = 395{\cdot}1$ K, $\mu_B^* = 0{\cdot}484$, $\alpha_B^* = 0{\cdot}073$, $\alpha_A^* = 0{\cdot}069$.

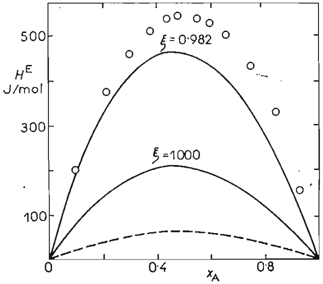

FIG. 6

Experimental and Computed Values of H^E in the Cyclopentane(A)–Chloroform(B) System at 298·15 K

Parameters as in Fig. 5.

DISCUSSION

From the calculations carried out, a considerable effect of multipole interactions on the magnitude and shape of excess thermodynamic quantities of systems studied follows. The influence of induced interactions is more pronounced in such a case when the molecules of both components have rather different value of α^* (at sufficiently large value μ^* or q^*). For most systems, the contributions of anisotropic interactions to excess quantities had positive values, which is in agreement with the results, of Gubbins, Gray and coworkers[8,9] or Chambers and McDonald[7]. However, it was found that in some cases these contributions could have even negative values (Fig. 3). The concentration dependences of excess quantities were often rather asymmetric; even S-shaped dependence occurred (Fig. 3).

In the real systems, the improved description of intermolecular interactions resulted in a better agreement of computed and experimental values of excess thermodynamic quantities. The results attained are better than those obtained in terms of other versions of perturbations theory[7,17] (in all the cases the value $\xi = 1$ is considered). The good agreement of computed and experimental values was attained, however, only after adjusting the parameter ξ to the experimental values of V^E.

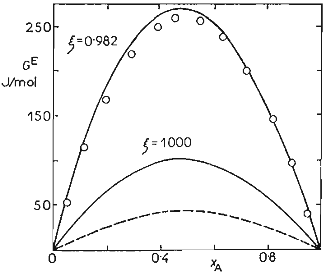

FIG. 7

Experimental and Computed Values of G^E in the Cyclopentane(A)–Chloroform(B) System at 298·15 K.

Parameters as in Fig. 5.

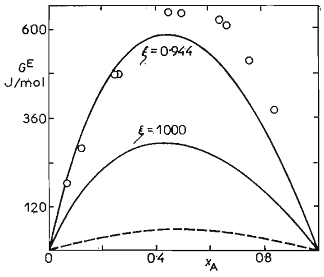

FIG. 8

Experimental and Computed Values of G^E in the Xenon(A)–HCl(B) System at 195·4 K.

LJ description (dashed line): $\sigma_A = 3{\cdot}955 \,.\, 10^{-10}$ m, $\varepsilon_A/k = 226{\cdot}0$ K, $\sigma_B = 3{\cdot}480 \,.\, 10^{-10}$ m, $\varepsilon_B/k = 252{\cdot}0$ K. Complete description (solid lines): $\sigma_B = 3{\cdot}521 \,.\, 10^{-10}$ m, $\varepsilon_B/k = 228{\cdot}6$ K, $\mu_B^* = 0{\cdot}878$, $\alpha_B^* = 0{\cdot}060$, $\alpha_A^* = 0{\cdot}065$.

The main reason of the disagreement is most probably the insufficient description of intermolecular interactions in the real systems considered.

The discussion performed rests, besides the results reported in this work, upon additional calculations contained in ref.[18], too.

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Translated by J. Linek.