

Quadrupolarizability of liquid mixtures

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Abstract

Theoretical expressions for the macroscopic polarizability and quadrupolarizability of a quadrupolar mixture are derived. The theory is demonstrated on the example of a liquid mixture of methane and nitrogen (non-quadrupolar plus quadrupolar component). It turns out that the dielectric permittivity (the “dipole strength” of the liquid) of this mixture changes little with the composition, while the quadrupolar length (“quadrupolar strength”) almost triples as the fraction of nitrogen approaches one. A set of such mixtures can be used as standard quadrupolar solvents to study systematically phenomena such as quadrupolar solvatochromism, the effect of the solvent on the rate of a reaction etc.

Keywords: quadrupole moment, quadrupolarizability, Onsager cavity model, liquid mixtures, dielectric constant, quadrupolar length

1 Introduction

Molecules that build up continuous media are either polar or non-polar depending on whether they possess dipole moment; we accordingly speak of polar or non-polar media. Higher order electric moments of the molecules (quadrupole moment, octupole moment etc.) are usually ignored when continuous description of a medium is sought – indeed, there are no quadrupoles and octupoles in the macroscopic Maxwell equations. However, the quadrupole moment and quadrupolarizability of the molecules may significantly affect the properties of dense media and have important role in certain physical phenomena. For example, small polar molecules orientate at the boundary between two phases according to their quadrupole moment. For instance, the water molecules at its surface are orientated with their oxygen atom pointing to the gas phase due to the asymmetric field produced by water’s quadrupole moment [1, 2]. The quadrupole interactions contribute to the surface tension [3], and the structure of the interface as a whole [4]. Quadrupolarization of the medium also contributes to the self-energy of a dissolved ion [5, 6, 7], activity coefficients [8] and slightly but measurably to the dielectric constant [9, 10, 11]. Quadrupolarizability of the medium causes solvatochromism in different non-polar solvents [12, 13], could affect the rate of chemical reactions [14-16] and chemical equilibrium [17-19] etc.

The characteristic of the polarity of a medium is the macroscopic polarizability α_p (related to the dielectric constant ε as $\alpha_p = \varepsilon - \varepsilon_0$). The polarizability can be called *polar strength* as it is related to the dipole moment \mathbf{p} of the molecules as $\alpha_p \propto C\mathbf{p} \cdot \mathbf{p}$ (here C is the particle density). In order to take into account the quadrupole moment \mathbf{q} of the molecules, we need another macroscopic characteristic of the continuous medium – *quadrupolar length* L_Q . The macroscopic quadrupolarizability α_Q is related to L_Q as $\alpha_Q = 3\varepsilon L_Q^2$, and is approximately proportional to the *quadrupolar strength*, $\alpha_Q \propto C\mathbf{q}:\mathbf{q}$. Therefore, $L_Q^2 \propto \mathbf{q}:\mathbf{q} / \mathbf{p} \cdot \mathbf{p}$ and the effect of quadrupoles is more distinct when the medium is non-polar or slightly polar.

The dielectric constant measures how the electric field of a point charge is reduced by the presence of dipoles. The presence of quadrupoles reduces the electric field intensity of a point charge even further [7]. The effect of the quadrupole moment of the molecules on macroscopic fields has been analyzed for the first time by Fokker [20] and Frenkel [21]. One of the reasons that Maxwell equations for quadrupolar media are not commonly applied to practical problems is that the quadrupolar length of the medium L_Q is unknown. In our previous work [9, 10, 11] we have developed a theoretical model for L_Q of liquids, which generalizes Onsager’s spherical cavity model for the dielectric constant ε [22] to quadrupolar media. As a result, the quadrupolar length of more than ten liquids has been calculated as a function of the temperature and the liquid density. The value of the theoretically calculated L_Q of methanol [9, 10] is in agreement with that obtained independently from data for the mean activity coefficient of NaBr in CH₃OH [8].

In order to experimentally investigate systematically the effect of the solvent quadrupole moment on the properties of a solute [12-19], it will be beneficial to formulate a set of “standard” solvents or solvent mixtures with permittivity ε that is approximately constant but of different L_Q – an idea that belongs to Dorairaj, Jeon and Kim [23]. The mixtures of benzene and cyclohexane is particularly suitable for this aim [23]. Both components are non-polar (intrinsic dipole moment, $\mathbf{p}_0 = 0$), and have similar molecular polarizability α_p [24] and size. As a result, they have similar dielectric constants: for benzene $\varepsilon = 2.3 \times \varepsilon_0$, for cyclohexane $\varepsilon = 2.0 \times \varepsilon_0$. On the other hand, one can expect that their quadrupolar lengths are different: benzene has a very large permanent quadrupole moment and large $L_Q \in 1.6-1.8 \text{ \AA}$; for cyclohexane L_Q is much lower, probably in the order of 0.5 \AA [9, 10].

However, to design “standard” mixtures of benzene and cyclohexane of L_Q in the range of 0.5-2 Å, we need *to be able to predict the quadrupolar length of these mixtures*. Therefore, in the present study we try to extend our theory of quadrupolarizability of a medium to liquid mixtures. Benzene and especially cyclohexane are relatively complicated molecules and require detailed quantum computation study in addition to theory of L_Q of mixtures (cf. Ref. [11]). To avoid this, we demonstrate the results for simpler and better studied mixture composed of N_2 (which has an intrinsic quadrupole moment \mathbf{q}_0) and CH_4 (no \mathbf{q}_0).

2 Theoretical methods. Spherical cavity model of quadrupolar liquid mixtures

Probably the most widely used relation between the dielectric constant ε and the composition of N -component mixture of gases or non-interacting liquids is the Clausius-Mossotti-Debye formula [25]

$$\frac{\varepsilon - \varepsilon_0}{\varepsilon + 2\varepsilon_0} = \sum_i^N \left(\alpha_{p,i} + \frac{p_{0,i}^2}{3k_B T} \right) C_i, \quad (1)$$

where ε_0 is the dielectric constant of vacuum, $\alpha_{p,i}$ is the molecular polarizability of i -th molecule, $p_{0,i}$ is its permanent dipole moment, k_B – the Boltzmann constant, T – absolute temperature, and C_i the particle density of i -th component which is given by

$$C_i = \frac{y_i}{\sum_i y_i v_i}. \quad (2)$$

Here, y_i is mole fraction and v_i is partial molecular volume of component i in the mixture (full list of symbols, see S1). The Clausius model assumes that a central molecule (a point dipole that is polarizable) is placed in the centre of a cavity. The local electric field acting on the central molecule is the sum of the external field \mathbf{E}_0 and the field created by the constant homogenous polarization of the medium outside the cavity.

Onsager proposed a more realistic model where the polarization of the medium is non-homogenous and depends on the field created by the central molecule. He obtained for the dielectric constant and polarizability $\alpha_{p,O}$ of a liquid mixture [22] the formula

$$\alpha_{p,O} = \varepsilon - \varepsilon_0 = \sum_i^N \frac{Y_{\text{cav}}}{1 - \alpha_{p,i} X_{\text{react},i}} \left(\alpha_{p,i} + \frac{1}{1 - \alpha_{p,i} X_{\text{react},i}} \frac{p_{0,i}^2}{3k_B T} \right) C_i. \quad (3)$$

Here, the index “O” subscript is for “Onsager”, and

$$X_{\text{react},i} = \frac{1}{2\pi\varepsilon_0 R_{\text{cav},i}^3} \frac{\varepsilon - \varepsilon_0}{2\varepsilon + \varepsilon_0}, \quad Y_{\text{cav}} = \frac{3\varepsilon}{2\varepsilon + \varepsilon_0}. \quad (4)$$

In Eqs. (3)&(4), $X_{\text{react},i}$ is a factor of proportionality (for the i -th species) in Onsager’s reaction field $\mathbf{E}_{\text{react},i} = X_{\text{react},i} \mathbf{p}_i$, which indicates how the polarizable medium around the central dipole reacts to the intrinsic field of the dipole \mathbf{p}_i . The factor Y_{cav} is the coefficient of proportionality in Onsager’s cavity field $\mathbf{E}_{\text{cav}} = Y_{\text{cav}} \mathbf{E}_0$, which is the field in the center of the cavity due to the external field \mathbf{E}_0 only, in the absence of a dipole in the centre. The polarizability of the mixture $\alpha_{p,O}$ is presented as the sum (3) of the effective polarizabilities that come from each component multiplied by its concentration.

The generalization of the Onsager spherical cavity model for N -component mixture to *quadrupolarizable* media is straightforward: we use the expressions for the reaction field, cavity field, reaction field gradient, and cavity field gradient in quadrupolarizable fluid as

derived in Ref. [9, 10]. Then, in the computation of the total polarization of the medium in external field, and the total quadrupolarization in external field gradient, we sum over all components. The results for α_p and α_Q are:

$$\alpha_p = \varepsilon - \varepsilon_0 = \sum_i^N \frac{Y_{E,i}}{1 - \alpha_{p,i} X_{p,i}} \left(\alpha_{p,i} + \frac{1}{1 - \alpha_{p,i} X_{p,i}} \frac{p_{0,i}^2}{3k_B T} \right) C_i, \quad (5)$$

$$\alpha_Q = 3\varepsilon L_Q^2 = \sum_i^N \frac{Y_{\nabla E,i}}{1 - \alpha_{q,i} X_{q,i}} \left(\alpha_{q,i} + \frac{1}{1 - \alpha_{q,i} X_{q,i}} \frac{\mathbf{q}_{0,i} : \mathbf{q}_{0,i}}{10k_B T} \right) C_i. \quad (6)$$

Here $\mathbf{p}_{0,i}$ and $\mathbf{q}_{0,i}$ are the intrinsic dipole and quadrupole moment of the i -th molecule in gas phase, $\alpha_{p,i}$ and $\alpha_{q,i}$ are their molecular polarizability and quadrupolarizability. The four Onsager factors $X_{p,i}$, $Y_{E,i}$, $X_{q,i}$, and $Y_{\nabla E,i}$ in Eqs. (5)&(6) are the coefficients in the formulae for the reaction field $\mathbf{E}_{\text{react},i} = X_{p,i} \mathbf{p}_i$, the cavity field $\mathbf{E}_{\text{cav},i} = Y_{E,i} \mathbf{E}_0$, the reaction field gradient $(\nabla \mathbf{E})_{\text{react},i} = X_{q,i} \mathbf{q}_i$, and the cavity field gradient $(\nabla \mathbf{E})_{\text{cav},i} = Y_{\nabla E,i} (\nabla \mathbf{E})_0$. They are related to ε and L_Q of the mixture and the radii of cavitation $R_{\text{cav},i}$ as [9, 10]:

$$X_{p,i} = \frac{1}{2\pi\varepsilon_0 R_{\text{cav},i}^3} \frac{\varepsilon - f_{p,i} \varepsilon_0}{2\varepsilon + f_{p,i} \varepsilon_0}; \quad Y_{E,i} = \frac{3f_{E,i} \varepsilon}{2\varepsilon + f_{p,i} \varepsilon_0}; \quad (7)$$

$$X_{q,i} = \frac{9}{4\pi\varepsilon_0 R_{\text{cav},i}^5} \frac{\varepsilon - f_{q,i} \varepsilon_0}{3\varepsilon + 2f_{q,i} \varepsilon_0}; \quad Y_{\nabla E,i} = \frac{5\varepsilon f_{\nabla E,i}}{3\varepsilon + 2\varepsilon_0 f_{q,i}}. \quad (8)$$

Here, the f -factors stand for:

$$f_{p,i} = \frac{2 + 8x_i}{2g_{p,i} + 9x_i^2 + 9x_i^3}; \quad f_{E,i} = \frac{2g_{p,i}}{2g_{p,i} + 9x_i^2 + 9x_i^3};$$

$$g_{p,i} = 1 + 4x_i + 9x_i^2 + 9x_i^3; \quad (9)$$

$$f_{q,i} = \frac{1 + 6x_i + 6x_i^2}{g_{q,i} + 12x_i^2 + 18x_i^3 + 18x_i^4}; \quad f_{\nabla E,i} = \frac{g_{q,i}}{g_{q,i} + 12x_i^2 + 18x_i^3 + 18x_i^4};$$

$$g_{q,i} = 1 + 6x_i + 24x_i^2 + 54x_i^3 + 54x_i^4, \quad (10)$$

where $x_i = L_Q/R_{\text{cav},i}$. When the medium is non-quadrupolarizable ($L_Q = x_i = 0$), all quadrupole f -factors become equal to 1, then Eq. (6) is unnecessary and Eqs. (5)&(7) simplify to the respective results of Onsager Eqs. (3)&(4), [22].

In the ideal gas limit (where $R_{\text{cav},i} \rightarrow \infty$), one has $X_{p,i}, X_{q,i} \rightarrow 0$, $Y_{E,i}, Y_{\nabla E,i} \rightarrow 1$, and the polarizability Eq. (5) and quadrupolarizability Eq. (6) of the mixture simplify to:

$$\alpha_{p,\text{id}} = \varepsilon - \varepsilon_0 = \sum_i^N \left(\alpha_{p,i} + \frac{p_{0,i}^2}{3k_B T} \right) C_i, \quad (11)$$

$$\alpha_{Q,\text{id}} = 3\varepsilon L_Q^2 = \sum_i^N \left(\alpha_{q,i} + \frac{\mathbf{q}_{0,i} : \mathbf{q}_{0,i}}{10k_B T} \right) C_i. \quad (12)$$

The last equation generalizes to mixtures the respective result of Jeon and Kim for pure liquids [6]. By chance, a Clausius-Mossotti-Debye type of model for the macroscopic quadrupolarizability produces the same result (12) for α_Q ; this is because a homogeneously quadrupolarized medium outside a cavity creates zero electric field gradient in the centre of the cavity [9, 10].

Equations (5) and (6) have too many unknown variables. If the molecular characteristics $\mathbf{p}_{0,i}$, $\alpha_{p,i}$, $\mathbf{q}_{0,i}$, and $\alpha_{q,i}$ are known, then we have only two equations for $N + 2$ unknowns (ε and

L_Q of the mixture and N radii of cavitation $R_{\text{cav},i}$). Therefore, we need an additional condition to determine $R_{\text{cav},i}$. One possible relation for $R_{\text{cav},i}$ was proposed by Onsager [22], who assumed that the cavities have spherical shape of radius $R_{\text{cav},i}$ and volume equal to the partial molecular volume v_i :

$$\frac{4}{3}\pi R_{\text{cav},i}^3 = v_i. \quad (13)$$

We will refer to the above dependence as the *Onsager relation for $R_{\text{cav},i}(v_i)$* . Another possible relation can be postulated by analogy with the respective formula for single component fluids from Ref. [9, 10] (Eq. (57)):

$$\frac{m_i}{4/3\pi R_{\text{cav},i}^3} = k_{\rho,i}\rho_i + k_{0,i}, \quad (14)$$

where ρ_i stands for m_i/v_i , m_i is the molecular mass, and the coefficients $k_{\rho,i}$ and $k_{0,i}$ are specific for each pure component (see **Table 1** in the next section). Let us denote Eq. (14) as $R_{\text{cav},i}(\rho_i)$. We can also assume a third mixing rule based on scaling arguments:

$$\frac{R_{\text{cav},i}^3}{R_{\text{cav},j}^3} = \frac{v_i}{v_j}. \quad (15)$$

Equation (13) is a special case of this *proportionality rule*.

3 Results and discussion. Computation of the quadrupolar length of the mixture

Let us demonstrate the theory of quadrupolarizable mixtures by applying it to two-component mixture of methane CH₄ and nitrogen N₂. Both have non-polar ($\mathbf{p}_0 = 0$) but polarizable ($\alpha_p \neq 0$) and quadrupolarizable ($\alpha_q \neq 0$) molecules (see **Table 1**). Due to its symmetry, the methane molecule does not possess intrinsic quadrupole moment ($\mathbf{q}_0 = 0$) but nitrogen has quadrupole moment $\mathbf{q}_0 \neq 0$. In our previous work [9, 10] we have obtained the quadrupolar lengths of the pure components as a function of the liquid density (see S2) and determined the coefficients $k_{\rho,i}$ and $k_{0,i}$ in Eq. (14), see **Table 1**.

If the cavity radii are known, formulae (5)&(6) for ε and L_Q are predictive. We have several options to calculate $R_{\text{cav},i}$, see Eqs. (13)-(15). To compare these options, we tested each of them against experimental data for the dielectric constant of a mixture of methane and nitrogen at different temperatures and pressures measured by Pan *et al.* [26] and Singh and Miller [27]. For all T and p ($T = 91\text{-}115$ K, $p = 0.1\text{-}20$ MPa) the static ε changes from approximately $1.6 \times \varepsilon_0$ for methane-rich mixture to $1.3 \times \varepsilon_0$ for nitrogen-rich mixture.

The application of Eqs. (5)&(6) to the permittivity data requires the computation of the density ρ of the mixture as well; moreover, the empirical formulae (13)-(15) contain also the partial molar volumes v_i of each component. For their computation we use the Hankinson-Thomson technique [28, 29] as explained in S3. We double-checked the result for ρ by comparing it with the GERG-2008 equation of state [30] as implemented in Aspen Plus 11. The results differ by less than 0.9 %.

Table 1. Values of the molecular multipole moments and polarizabilities of CH₄ and N₂, and the coefficients in the dependence (14) of $R_{\text{cav},i}$ on ρ_i from Ref. [10].

	Dipole moment p_0 [C m] $\times 10^{30}$	Polarizability $\alpha_p/4\pi\varepsilon_0$ [\AA^3]	Quadrupole moment $(\mathbf{q}_0:\mathbf{q}_0)^{1/2}$ [C m ²] $\times 10^{40}$	Quadrupolarizability $\alpha_q/4\pi\varepsilon_0$ [\AA^5]	k_0 [kg/m ³]	k_ρ [\AA^3]
CH ₄	0	2.597	0	1.681	122.84	0.7019
N ₂	0	1.739	4.08	1.120	342.20	0.5445

We tested several computational procedures to analyze our model and to compare it with the experimental results. The first kind of procedures that we tested predicts the dielectric constant and the quadrupolar length of the mixture via Eqs. (5)&(6), using the known values of the molecular characteristics from **Table 1** and one of the models for the radii of cavitation $R_{cav,i}$:

procedure cp1) we solve Eqs. (5)&(6) for the polarizability and the quadrupolarizability of the mixture where we substitute $R_{cav,i}$ with $R_{cav,i}(\rho_i)$ from Eq. (14). The result is ε and L_Q .

Procedure cp2) we solve Eqs. (5)&(6) with the aid of the Onsager relation for $R_{cav,i}(v_i)$, Eq. (13); this gives again ε and L_Q .

For comparison, we also applied **procedure cp0)**, using the classical Onsager cavity model, i.e. we solve Eq. (3) together with the Onsager relation (13) for $R_{cav,i}(v_i)$, to receive ε .

We also attempted a different approach, based on the work of Böttcher [31], who used data for ε of single component fluids to compute the respective cavity radius. To apply this procedure to mixtures, we substitute the experimental values for ε from Ref. [26, 27] in Eqs. (5)&(6). Together with the proportionality rule Eq. (15), this makes three equations for three unknown parameters: the quadrupolar length L_Q , methane's cavity radius $R_{cav,1}$, and nitrogen's cavity radius $R_{cav,2}$ in the mixture.

The values of ε and L_Q calculated by applying the first computational procedure (cp1) are presented in **Figure 1**. As one can see, both ε and L_Q have lower values at high temperatures and low pressures, mainly due to the respective drop in density of the mixture. The resulting value of the dielectric constant (**Figure 1a**) does not differ significantly from the value obtained by the Onsager model (cp0) – the percentage deviation between the two computed ε is about 0.2 %. The pure component quadrupolar lengths obtained previously [9, 10] (**Figure 4, S2**) agree with the values for L_Q obtained here for methane-rich and nitrogen-rich mixture **Figure 1b**. The computed dielectric constant (**Figure 1a**) is compared to the experimentally measured one [26, 27] in **Figure 2**, where the percentage difference between the two is presented for all measured mixture composition. Maximum percentage error is 1.0 % and the average error is 0.5 %. This is a reasonable result; the error is due most of all to the error in the computed molar volumes estimates which is around 1 % for hydrocarbon + nitrogen mixtures, see *Table 5* in Ref. [32]. The errors in the molecular quadrupolarizability and quadrupole moment are also of the same order of magnitude [11].

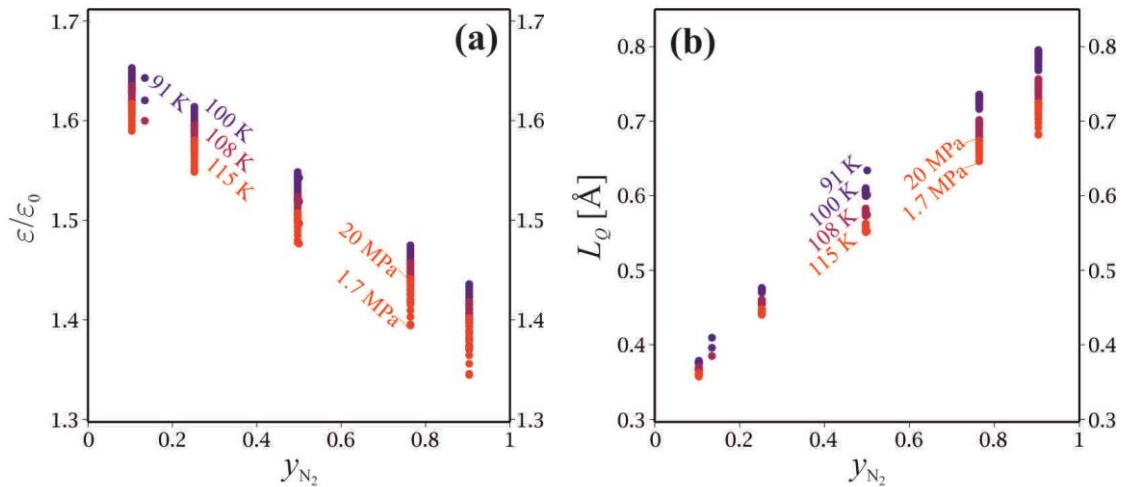


Figure 1. Dielectric constant ε (a) and quadrupolar length L_Q (b) of liquid methane + nitrogen ($\text{CH}_4 + \text{N}_2$) mixture as a function of the nitrogen mole fraction y_{N_2} . Here ε and L_Q are obtained using the first computational procedure (cp1). The color indicates the temperature. The dispersion of the points is due to them being calculated for a range of pressures: at each temperature, pressures varies from 0.1 to 20 MPa.

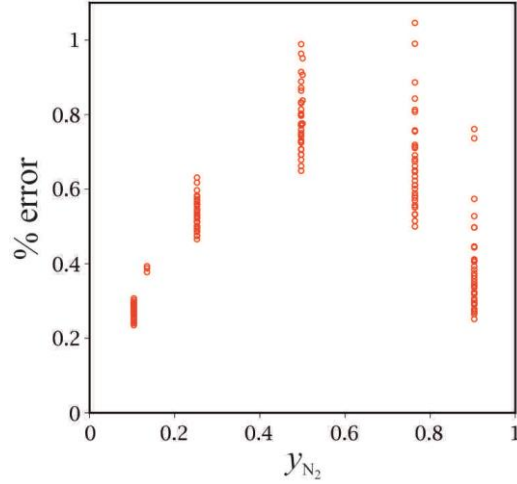


Figure 2. Difference between the calculated (using the first computational procedure (cp₁)) and experimentally measured value of the dielectric constants from Ref. [26, 27].

As already mentioned, the dielectric constant and the quadrupolar length of the mixture depend on temperature and pressure. That is illustrated in **Figure 3**, where ϵ and L_Q are calculated (using the additional condition (14) for $R_{cav,i}(\rho_i)$) for a range of T and p at each mixture composition. The quadrupolar length has a more prominent temperature and pressure dependence at a higher amount of nitrogen in the mixture. This is due to the fact that nitrogen has a non-zero quadrupole moment in contrast to methane (**Table 1**), resulting in significant contribution of the $\mathbf{q}_{0,CH_4} : \mathbf{q}_{0,CH_4} / k_B T$ term to α_Q in Eq. (6). The quadrupolar length in ideal gas approximation is also depicted in **Figure 3b**. We obtained it by solving Eqs. (11)&(12) together with the empirical relation for $R_{cav,i}(\rho_i)$, Eq. (14). As seen, the ideal gas formulae give lower values for L_Q compared to those following from the Onsager cavity model.

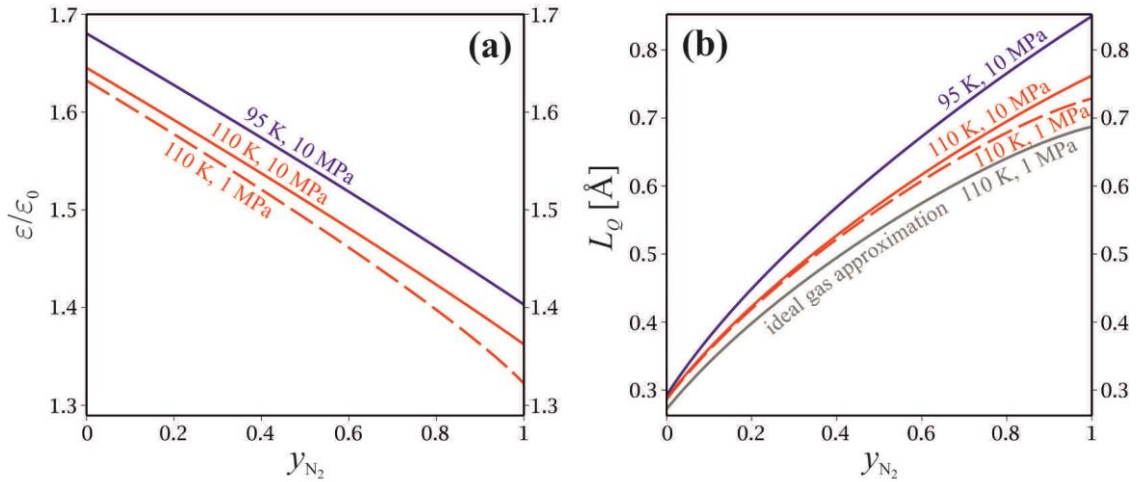


Figure 3. Dielectric constant **(a)** and quadrupolar length **(b)** of a mixture methane + nitrogen as a function of the composition for different temperatures and pressures. The results are obtained by solving Eqs. (5) and (6) together with the additional condition (14) for the cavity radii $R_{cav,i}(\rho_i)$ (cp₁), with values of the molecular characteristics from **Table 1**. Methane and nitrogen partial molar volumes are calculated using Hankinson-Thomson technique [28, 29].

All tested computational procedures described above give close values for the dielectric constant ϵ and the quadrupolar length L_Q . The difference between the computed values of ϵ from the three procedures is small compared with the experimental error in **Figure 2**. However, when the cavity radii $R_{cav,i}$ are computed via the Böttcher technique applied to mixtures, the results for the cavity radius itself appear to be illogical (see S4). All three

techniques ((cp₁), (cp₂), and Böttcher's method) predict approximately the same L_Q – the maximum percentage difference between the computed quadrupolar lengths is 1.4 % and the average absolute difference is 0.6 %. Therefore, the value obtained for L_Q does not depend significantly on the model used for the cavity radii $R_{cav,i}$ (i.e. L_Q is not very sensitive to $R_{cav,i}$), so we can conclude that the cavity model (5)&(6) we developed can be used to predict the macroscopic quadrupolar length of mixtures with adequate accuracy of the order of 1-2 %.

4 Conclusions

The main intention of the present study was to provide a recipe for the formulation of a series of “standard” quadrupolar mixtures with a relatively stable (not varying with the composition) dielectric constant ε and *known* varying quadrupole length L_Q . Such standard solvent are necessary [23] to investigate the role of the quadrupolarizability on chemical and physical phenomena such as quadrupolar solvatochromism [12, 13], effect of solvent's quadrupole moment on the rate of a reaction [14-16], solubility [23] etc. For the purpose of computing L_Q , we generalized Onsager's spherical cavity model for mixtures by including explicitly the quadrupoles and the field gradient in the model. The obtained theoretical equations (5)&(6) allow the polarizability and quadrupolarizability of a mixture to be computed from the molecular properties ($p_{0,i}$, $\alpha_{p,i}$, $q_{0,i}$, and $\alpha_{q,i}$, which can be obtained by quantum-mechanical computations).

We demonstrated the ability of our model to predict ε and L_Q on the example of the relatively simple and well-studied liquid mixture of methane and nitrogen. Furthermore, we demonstrate that this mixture has the desired properties – approximately constant dielectric permittivity ($\varepsilon \in 1.3 \div 1.6 \times \varepsilon_0$), while the quadrupolar length L_Q almost trebles with the change in composition (from 0.3 Å to 0.8 Å).

A problem of the model, already present in the original theory of Onsager [22], is that the cavity radius $R_{cav,i}$ is an ill-defined parameter. We tried several different recipes for defining $R_{cav,i}$ when computing the quadrupolar length L_Q . We have shown that the choice of how $R_{cav,i}$ is calculated has little effect on the computed L_Q : three rather different computational procedures predict almost identical values for L_Q . From the comparison of these procedures, we conclude that our model predicts L_Q with accuracy of the order of ± 2 %.

In the near future, we intend to apply the theory to the more complex system cyclohexane-benzene, which requires supplementary quantum-mechanical computation of the molecular parameters of cyclohexane (cf. Ref. [11]). We will also demonstrate how, by the addition of a balancing third component, we can produce a set of ternary mixtures with exactly the same dielectric permittivity and very different macroscopic quadrupolarizabilities.

Supporting information description. (S1) a list of symbols; (S2) pure component quadrupolar length of methane and nitrogen; (S3) Hankinson-Thomson technique for calculation of the molar volumes of the components; (S4) additional information about the radii of cavitation; (S5) a sample code.

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Quadrupolarizability of liquid mixtures

Supporting information

S1. List of symbols

C	particle density [m^{-3}]
E_0	external electric field
E_{cav}	cavity electric field
E_{react}	reaction electric field
∇E_0	external field gradient
$f_p, f_q, f_E, f_{\nabla E}, g_p, g_q$	quadrupole factors
k_B	Boltzmann constant
k_0, k_ρ	coefficients in the empirical dependence Eq. (14) between density and cavity radius
L_Q	quadrupolar length of the medium
m	mass of a molecule
\mathbf{p}	dipole moment of a molecule in external field
\mathbf{p}_0	permanent (intrinsic) dipole moment of a molecule
\mathbf{q}	quadrupole moment of a molecule in external field gradient
\mathbf{q}_0	permanent (intrinsic) quadrupole moment of a molecule
R_{cav}	radius of the cavity
T	absolute temperature [K]
v_i	partial molecular volume
X_p	reaction field factor
X_q	reaction field gradient factor
$x = L_Q/R_{\text{cav}}$	
y_i	mole fraction of i -th component
Y_E	cavity field factor
$Y_{\nabla E}$	cavity field gradient factor
α_p	mean polarizability of a molecule
α_P	macroscopic polarizability of the medium
α_q	mean quadrupolarizability of a molecule
α_Q	macroscopic quadrupolarizability of the medium
ε	dielectric permittivity of the medium
ε_0	dielectric permittivity of the vacuum
ρ	mass density
$\rho_i = m_i/v_i$	

S2. Pure component quadrupolar lengths

We supplement here just for comparison the pure component quadrupolar lengths of methane and nitrogen liquids as calculated in Ref. [9, 10].

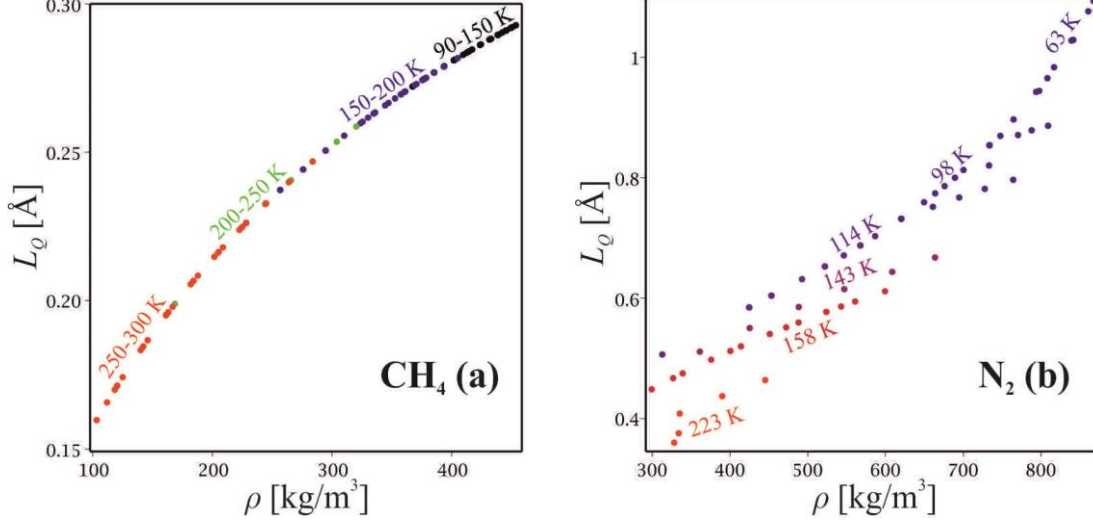


Figure 4. Pure component quadrupolar lengths L_Q of methane CH_4 (a) and nitrogen N_2 (b) liquids as function of mass density ρ .

S3. Calculation of the molar volumes of the components

According to Hankinson-Thomson technique [28, 29] the compressed liquid molar volume of a mixture is given by the Tait equation:

$$V = V_{sm} \left(1 - C \ln \frac{B + p}{B + P_{sm}} \right), \quad (16)$$

where the volume is in $[\text{m}^3]$ and the pressure is in $[\text{Pa}]$. The coefficients B and C are

$$B / P_{cm} = -1 + a_1 (1 - T_{Rm})^{1/3} + b_1 (1 - T_{Rm})^{2/3} + d_1 (1 - T_{Rm}) + e_1 (1 - T_{Rm})^{4/3}, \quad (17)$$

$$C = j_1 + k_1 \omega_{\text{SRK}m}. \quad (18)$$

Here the coefficient e_1 is given by

$$e_1 = \exp(f_1 + g_1 \omega_{\text{SRK}m} + h_1 \omega_{\text{SRK}m}^2) \quad (19)$$

and all other constants are summarized in **Table 2**. The saturated volume of the mixture V_{sm} is

$$V_{sm} = V_m^* V_R^{(0)} \left[1 - \omega_{\text{SRK}m} V_R^{(\delta)} \right], \quad (20)$$

where

$$V_R^{(0)} = 1 + a_2 (1 - T_{Rm})^{1/3} + b_2 (1 - T_{Rm})^{2/3} + c_2 (1 - T_{Rm}) + d_2 (1 - T_{Rm})^{4/3}, \quad (21)$$

$$V_R^{(\delta)} = \left[e_2 + f_2 T_{Rm} + g_2 T_{Rm}^2 + h_2 T_{Rm}^3 \right] / (T_{Rm} - 1.00001). \quad (22)$$

Table 2. Values of the constants in Eqs. (17)-(22).

Constants in Eqs. (17), (18) and (19)	Constants in Eqs. (21) and (22)
$a_1 = -9.070217$	$a_2 = -1.52816$
$b_1 = 62.45326$	$b_2 = 1.43907$
$d_1 = -135.1102$	$c_2 = -0.81446$
$f_1 = 4.79594$	$d_2 = 0.190454$
$g_1 = 0.250047$	$e_2 = -0.296123$
$h_1 = 1.14188$	$f_2 = 0.386914$
$j_1 = 0.0861488$	$g_2 = -0.0427258$
$k_1 = 0.0344483$	$h_2 = -0.0480645$

The saturated pressure of the mixture P_{sm} is calculated by the relation

$$P_{sm} = P_{cm} P_{Rm}. \quad (23)$$

Here the critical pressure P_{cm} is

$$P_{cm} = (Z_{cm} R T_{cm}) / V_m^* \quad (24)$$

and the compressibility factor Z_{cm} is calculated using the following expression

$$Z_{cm} = 0.291 - 0.080 \omega_{SRKm}. \quad (25)$$

The reduced pressure of the mixture P_{Rm} is given by

$$\log P_{Rm} = P_{Rm}^{(0)} + \omega_{SRKm} P_{Rm}^{(1)}, \quad (26)$$

where

$$P_{Rm}^{(0)} = 5.8031817 \log T_{Rm} + 0.07608141 \alpha, \quad (27)$$

$$P_{Rm}^{(1)} = 4.86601 \beta, \quad (28)$$

$$\alpha = 35.0 - 36.0 / T_{Rm} - 96.736 \log T_{Rm} + T_{Rm}^6, \quad (29)$$

$$\beta = \log T_{Rm} + 0.03721754 \alpha. \quad (30)$$

Reduced temperature T_{Rm} is

$$T_{Rm} = T / T_{cm}. \quad (31)$$

Hankinson, Brobst, and Thomson propose the following mixing rules:

$$T_{cm} = \frac{\sum_i \sum_j y_i y_j (V_i^* T_{ci} V_j^* T_{cj})^{1/2}}{V_m^*}, \quad (32)$$

$$V_m^* = \frac{1}{4} \left[\sum_i y_i V_i^* + 3 \left(\sum_i y_i V_i^{*2/3} \right) \left(\sum_i y_i V_i^{*1/3} \right) \right], \quad (33)$$

and

$$\omega_{SRKm} = \sum_i y_i \omega_{SRKi}. \quad (34)$$

In these equations y_i is the component mole fraction, T_{ci} and V_i^* are the pure component parameters which are given for methane and nitrogen in **Table 3** (for other compounds see *Table 3-10*, p. 57 in Ref. [29]).

Table 3. Pure component parameters for the Hankinson-Brobst-Thomson model.

	T_c [K]	ω_{SRK} [/]	V^* [L/mol]
CH ₄	190.58	0.0074	0.0994
N ₂	126.25	0.0358	0.0901

Substituting Eqs. (17)-(34) and the parameters from **Table 2** and **Table 3** in Eq. (16) yields liquid mixture volume V as a function of the composition (for given T and p). Then for two-component mixture we can calculate the molar volume of the components by

$$v_1 = V + y_2 \left(\frac{\partial V}{\partial y_1} \right)_{y_2} \quad (35)$$

and

$$v_2 = V - y_1 \left(\frac{\partial V}{\partial y_1} \right)_{y_2}, \quad (36)$$

where $y_2 = 1 - y_1$.

A sample Maple code that computes the mixture volume and the molar volumes of two-component mixture is given below. The example is written for methane + nitrogen mixture for temperature 110 K and pressure 1 MPa with methane mole fraction 0.75.

```
> restart;
> # 1. Tait equation of the mixture volume.
V:=Vsm*(1-C*ln((B+P)/(B+Psm))); # Eq. (16)
B:=Pcm*(-1+a1*(1-Trm)^(1/3)+b1*(1-Trm)^(2/3)+d1*(1-Trm)+e1*(1-Trm)^(4/3)):
# Eq. (17)
C:=j1+k1*omega: # Eq. (18)
e1:=exp(f1+g1*omega+h1*omega^2): # Eq. (19)

Vsm:=Vm*Vr0*(1-omega*Vrd): # Eq. (20), saturated volume of the mixture
Vr0:=1+a2*(1-Trm)^(1/3)+b2*(1-Trm)^(2/3)+c2*(1-Trm)+d2*(1-Trm)^(4/3):
# Eq. (21)
Vrd:=(e2+f2*Trm+g2*Trm^2+h2*Trm^3)/(Trm-1.00001): # Eq. (22)

Psm:=Prm*Pcm; # Eq. (23); saturated pressure of the mixture
Pcm:=(Zcm*R*Tcm)/Vm: # Eq. (24)
Zcm:=0.291-0.08*omega: # Eq. (25)
Prm:=10^(Prm0+omega*Prm1): # Eq. (26)
Prm0:=5.8031817*log[10](Trm)+0.07608141*alpha: # Eq. (27)
Prm1:=4.86601*beta: # Eq. (28)
alpha:=35.0-36.0/Trm-96.736*log[10](Trm)+Trm^6: # Eq. (29)
beta:=log[10](Trm)+0.03721754*alpha: # Eq. (30)

Trm:=T/Tcm; # Eq. (31); reduced temperature
> # 2. Mixing rule.
Tcm:=(y1^2*V1*Tc1+2*y1*y2*sqrt(V1*V2*Tc1*Tc2)+y2^2*V2*Tc2)/Vm; # Eq. (32)

Vm:=1/4*(y1*V1+y2*V2+3*(y1*V1^(2/3)+y2*V2^(2/3))*(y1*V1^(1/3)+y2*V2^(1/3)));
# Eq. (33)

omega:=y1*omega1+y2*omega2; # Eq. (34)
> # 3. Mole fraction.
y2:=1-y1;

> Digits:=15:
> # 4. Constants in Eqs. (17)-(22)
# 4.1 Constants in Eqs. (17), (18) and (19) from Table 2.
a1:=-9.070217:
b1:=62.45326:
d1:=-135.1102:
f1:=4.79594:
g1:=0.250047:
h1:=1.14188:
j1:=0.0861488:
k1:=0.0344483:
# 4.2 Constants in Eqs. (21) and (22) from Table 2.
a2:=-1.52816:
b2:=1.43907:
c2:=-0.81446:
d2:=0.190454:
e2:=-0.296123:
f2:=0.386914:
```

```

g2:=-0.0427258;
h2:=-0.0480645;
> # 5. Pure component parameters for methane+nitrogen mixture from Table 3.
# 5.1 Pure component parameters for methane (index "1"):
Tc1:=190.58; # [K]
omegal:=0.0074;
V1:=0.0994*1e-3; # [m³/mol]
# 5.2 Pure component parameters for nitrogen (index "2"):
Tc2:=126.25; # [K]
omega2:=0.0358;
V2:=0.0901*1e-3; # [m³/mol]
> # 6. Scientific constants.
with(ScientificConstants):
NA:=evalf(Constant('N[A]')); # Avogadro constant
kB:=evalf(Constant('k')); # Boltzmann constant [J/K]
R:=NA*kB; # gas constant [J/mol/K]
> # 7. Temperature, pressure.
T := 110; # temperature [K]
P := 10^6; # pressure [Pa]
> # 8. Molar volumes
v1:=evalf(V+y2*diff(V,y1)): # Eq. (35); molar volume of the first component
(methane)
v2:=evalf(V-y1*diff(V,y1)): # Eq. (36); molar volume of the second component
(nitrogen)
> # 9. Mole fraction.
y1:=0.75;
> # 10. Final results.
'V'=evalf(V*1e6); # mixture volume [cm³/mol]
'v1'=evalf(v1*1e6); # molar volume of the first component (methane) in
[cm³/mol]
'v2'=evalf(v2*1e6); # molar volume of the second component (nitrogen) in
[cm³/mol]

```

S4. Radii of cavitation

Böttcher technique is to substitute experimentally measured dielectric constant into Onsager expression for the polarizability of a medium [31]. However, for quadrupolar mixtures we do not have in advance experimentally measured quadrupolar length of the mixture. So we use additional condition – the proportionality rule, Eq. (15). We substitute the experimental ε from Refs. [26, 27] into the polarizability Eq. (5) and quadrupolarizability Eq. (6) of a mixture and then solve these three equations (Eqs. (5), (6), and (15)) for L_Q , methane cavity radius $R_{cav,1}$, and nitrogen cavity radius $R_{cav,2}$. The results are presented in **Figure 5**. As one can see, the obtained $R_{cav,i}$ using Böttcher procedure applied to mixtures are quite illogical.

Furthermore, inconsistent results for $R_{cav,i}$ are also obtained when this approach is applied to the classical Onsager model for liquid mixtures. We solve Eq. (3) together with proportionality rule (15); this gives again $R_{cav,1}$ and $R_{cav,2}$. At some mixture composition the obtained cavity radii are in the order of 0.7-0.8 Å, which is below the Curie point 1.3-1.4 Å (see Eq. (55)&(56) in Ref. [9]).

In **Figure 5** are presented also $R_{cav,i}$ according Onsager relation Eq. (13) for $R_{cav,i}(v_i)$ and the semi-empirical relation $R_{cav,i}(\rho_i)$ from Eq. (14) (where $\rho_i = m_i/v_i$).

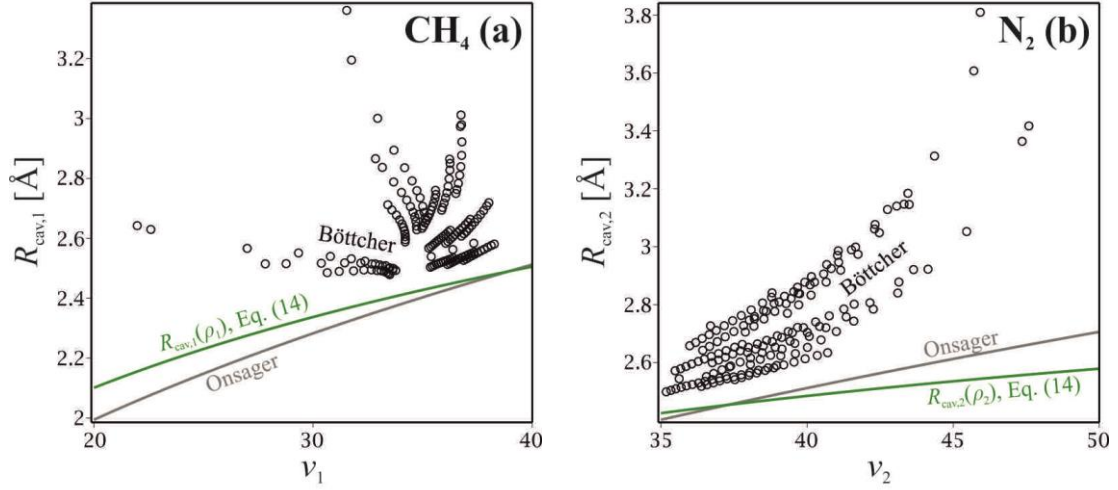


Figure 5. Methane cavity radius $R_{\text{cav},1}$ (a) and nitrogen cavity radius $R_{\text{cav},2}$ (b) as a function of the respective molar volumes v_1 and v_2 . Unfilled circles are obtained using Böttcher technique. Gray curves represent Onsager relation Eq. (13) for $R_{\text{cav},i}(v_i)$; green curves are the semi-empirical relations $R_{\text{cav},i}(\rho_i)$ from Eq. (14).

S5. Computational procedures

A Maple code that computes the quadrupolar length of $\text{CH}_4 + \text{N}_2$ mixture using different computational procedures (as described in the main text) is supplemented below.

```
> restart;
> # 1. Polarization and quadrupolarization of liquid quadrupolar mixture.
eqAP:=epsilon-1=YE1/(1-ap1*Xp1)*(ap1*C1/epsilon0+C1/epsilon0/(1-
ap1*Xp1)*p01^2/3/kB/T)+YE2/(1-ap2*Xp2)*(ap2*C2/epsilon0+C2/epsilon0/(1-
ap2*Xp2)*p02^2/3/kB/T); # Eq. (5)
eqAQ:=3*epsilon=YDE1/(1-aq1*Xq1)*(aq1*C1/epsilon0/LQ^2+C1/epsilon0/LQ^2/(1-
aq1*Xq1)*q012/10/kB/T)+YDE2/(1-aq2*Xq2)*(aq2*C2/epsilon0/LQ^2+C2/epsilon0/LQ^2/(1-
aq2*Xq2)*q022/10/kB/T); # Eq. (6)
> # 2. Onsager factors for both components.
# Eq. (7)
Xp1:=1/2/Pi/epsilon0/Rc1^3*(epsilon-fp1)/(2*epsilon+fp1):
Xp2:=1/2/Pi/epsilon0/Rc2^3*(epsilon-fp2)/(2*epsilon+fp2):

YE1:=3*fE1*epsilon/(2*epsilon+fp1):
YE2:=3*fE2*epsilon/(2*epsilon+fp2):
# Eq. (8)
Xq1:=9/4/Pi/epsilon0/Rc1^5*(epsilon-fq1)/(3*epsilon+2*fq1):
Xq2:=9/4/Pi/epsilon0/Rc2^5*(epsilon-fq2)/(3*epsilon+2*fq2):

YDE1:=5*epsilon*fDE1/(3*epsilon+2*fq1):
YDE2:=5*epsilon*fDE2/(3*epsilon+2*fq2):
> # quadrupolar f-factors:
# Eq. (9)
fp1:=(2+8*x1)/(2*gp1+9*x1^2+9*x1^3):
fp2:=(2+8*x2)/(2*gp2+9*x2^2+9*x2^3):

fE1:=(2*gp1)/(2*gp1+9*x1^2+9*x1^3):
fE2:=(2*gp2)/(2*gp2+9*x2^2+9*x2^3):

gp1:=1+4*x1+9*x1^2+9*x1^3:
gp2:=1+4*x2+9*x2^2+9*x2^3:
# Eq. (10)
fq1:=(1+6*x1+6*x1^2)/(gq1+12*x1^2+18*x1^3+18*x1^4):
fq2:=(1+6*x2+6*x2^2)/(gq2+12*x2^2+18*x2^3+18*x2^4):
```



```

fDE1:=gq1/(gq1+12*x1^2+18*x1^3+18*x1^4):
fDE2:=gq2/(gq2+12*x2^2+18*x2^3+18*x2^4):

gq1:=1+6*x1+24*x1^2+54*x1^3+54*x1^4:
gq2:=1+6*x2+24*x2^2+54*x2^3+54*x2^4:
> # x_i = L_Q/R_cav,i
x1:=LQ/Rc1:
x2:=LQ/Rc2:
> # 3. Onsager polarization of liquid mixture; Eq. (3).
eqAPO:= subs(LQ=0,eqAP);
> # 4. Particle density; Eq. (2).
# Partial molar volumes are in [cm³/mol].
C1:= NA/1e-6*y1/(v1*y1+v2*y2);
C2:= NA/1e-6*y2/(v1*y1+v2*y2);
> # 5. Onsager relation for R_cav,i(v_i); Eq. (13).
eqRA10:=4/3*Pi*Rc1^3/(v1*1e-6/NA)=1;
eqRA20:=4/3*Pi*Rc2^3/(v2*1e-6/NA)=1;
> # 6. Semi-empirical relation for R_cav,i(rho_i); Eq. (14).
eqRA1:=m1/(4/3*Pi*Rc1^3)-(krho1*rho1+k01);
eqRA2:=m2/(4/3*Pi*Rc2^3)-(krho2*rho2+k02);
# where
rho1:=m1*NA/(v1*1e-6);
rho2:=m2*NA/(v2*1e-6);
> # 7. Proportionality rule; Eq. (15).
eqV:=v1/v2=(Rc1/Rc2)^3;
> # 8. Scientific constants.
with(ScientificConstants):
NA:=evalf(Constant('N[A]')): # Avogadro constant
kB:=evalf(Constant('k')): # Boltzmann constant [J/K]
epsilon0:=evalf(Constant('epsilon[0]')): # dielectric permittivity of the vacuum
[F/m]
mH:=evalf(Element('H,atomicweight')): # mass of hydrogen atom [kg]
mC:=evalf(Element('C,atomicweight')): # mass of carbon atom [kg]
mN:=evalf(Element('N,atomicweight')): # mass of nitrogen atom [kg]
# index "1" subscript is for methane
# index "2" subscript is for nitrogen
m1:=mC+4*mH: # mass of methane molecule [kg]
m2:=2*mN: # mass of nitrogen molecule [kg]
# Convert the units of cavity radii and quadrupolar length in Angstroms.
Rc1:=RA1*10^(-10):
Rc2:=RA2*10^(-10):
LQ:=LA*10^(-10):

# 9. Molecular characteristics and parameters in Eq. (14) from Table 1.
# Dipole moment [C m]
p01:=0:
p02:=0:
# Molecular polarizability [F m²]
ap1:=2.597*evalf(4*Pi*epsilon0*1e-30):
ap2:=1.739*evalf(4*Pi*epsilon0*1e-30):
# Quadrupole moment [C m²]
q012:=0:
q022:=(4.08*1e-40)^2:
# Molecular quadrupolarizability [F m⁴]
aq1:=1.681*evalf(4*Pi*epsilon0*1e-50):
aq2:=1.120*evalf(4*Pi*epsilon0*1e-50):

# Parameters in Eq. (14)
k01:=122.84: # [kg/m³]
k02:=342.20: # [kg/m³]
krho1:=0.7019: # [/]
krho2:=0.5445: # [/]

> # 10. Additional parameters.
T:=100: # temperature [K]
P:=20.01e6: # pressure [Pa]
# Partial molar volumes, calculated using Hankinson-Thomson technique; Ref. [28,29]
v1:=35.30689: # methane partial molar volume [cm³/mol]

```

```

v2:=35.50899: # nitrogen partial molar volume [cm3/mol]
# Mole fractions
y1:=0.7462: # methane mole fraction [/]
y2:=1-y1: # nitrogen mole fraction [/]
# Experimental dielectric constant of the mixture from Ref. [27]
epsilon__exp:=1.60552; # [/]
> # 11. Computational procedures.
# 11.1 Computational procedure (cp1) (Eqs. (5), (6), and (14)).
fsolve({subs([RA1=solve(eqRA1,RA1)[1],RA2=solve(eqRA2,RA2)[1]],eqAP),
subs([RA1=solve(eqRA1,RA1)[1],RA2=solve(eqRA2,RA2)[1]],eqAQ)},
{LA=0..2,epsilon=1..5});
> # 11.2 Computational procedure (cp2) (Eqs. (5), (6), and (13)).
fsolve({subs([RA1=solve(eqRA1O,RA1)[1],RA2=solve(eqRA2O,RA2)[1]],eqAP),
subs([RA1=solve(eqRA1O,RA1)[1],RA2=solve(eqRA2O,RA2)[1]],eqAQ)},
{LA=0..2,epsilon=1..5});
> # 11.3 Computational procedure (cpO) (Eqs. (3) and (13)).
fsolve(subs([RA1=solve(eqRA1O,RA1)[1],RA2=solve(eqRA2O,RA2)[1]],eqAPO),
epsilon=1..5);
> # 12. Minimal cavity radii according Curie point (see Eq.(55)&(56) in Ref. [9]).
R__C1:=max(evalf((ap1/(4*Pi*epsilon0))^(1/3))*1e10,
evalf((3*aq1/(4*Pi*epsilon0))^(1/5))*1e10);
R__C2:=max(evalf((ap2/(4*Pi*epsilon0))^(1/3))*1e10,
evalf((3*aq2/(4*Pi*epsilon0))^(1/5))*1e10);
> # 13. Böttcher technique applied to mixtures.
fsolve({subs(epsilon=epsilon__exp,eqAP),
subs(epsilon=epsilon__exp,eqAQ),
eqV},
{RA1=R__C1..4,RA2=R__C2..4,LA=0..2});

```