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Density, speed of sound, refractive index and relative permittivity of methanol, propan-1-ol or pentan-1-ol + aniline liquid mixtures. Application of the Kirkwood-Fröhlich model

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Abstract

Densities (ρ) and speeds of sound (c) at a temperature $T = 298.15$ K, relative permittivities at 1 MHz (ϵ_r) and refractive indices at the sodium D-line (n_D) at $T = (293.15$ K to 303.15 K), all of them at a pressure $p = 0.1$ MPa, are reported for binary liquid mixtures alkan-1-ol + aniline. The alkan-1-ols considered are methanol, propan-1-ol and pentan-1-ol. Also, the values of the excess molar volume (V_m^E), excess isentropic compressibility (κ_S^E), excess speed of sound (c^E), excess refractive index (n_D^E), excess relative permittivity (ϵ_r^E) and its temperature derivative $(\partial\epsilon_r^E/\partial T)_p$ are calculated and fitted to Redlich-Kister polynomials. The agreement among the reported data and other literature sources is analysed by comparing V_m^E , n_D^E , ϵ_r^E and the deviation of c from mole-fraction linearity (Δc). The positive excess molar internal energies at constant volume ($U_{m,v}^E$) show the dominance of the breaking of interactions between like molecules in the energy balance on mixing, particularly the breaking of strong dipolar interactions between aniline molecules. This contribution is also dominant for the ϵ_r^E values, as they are negative and decrease with the length of the alkan-1-ol chain. Calculations on the concentration-concentration structure factor are consistent with these statements, revealing homocoordination in the studied systems. The V_m^E are negative, which together with the positive $U_{m,v}^E$ indicate the existence of important structural effects in the studied mixtures. The application of the Kirkwood-Fröhlich model shows that the average relative orientation of neighbouring dipoles is similar in the mixtures methanol + aniline or + pyridine, in spite of the different character of the predominant interactions in the latter mixture (heterocoordination).

Keywords: alkan-1-ol; aniline; permittivity; refractive index; density; speed of sound.

1. Introduction

The high polarizability of the aromatic ring, together with the NH_2 group, gives the aniline molecule very interesting properties. Thus, liquid mixtures of aniline and alkanes show high upper critical solution temperatures (UCSTs), as it is shown by the high value of this quantity for the heptane system, 343.11 K [1], which reveals very strong dipolar interactions between aniline molecules. Alkan-1-ol + aniline liquid mixtures are characterized by positive deviations from Raoult's law, as it is demonstrated by the following $G_m^E/\text{J}\cdot\text{mol}^{-1}$ values at equimolar composition for the solutions with methanol (515, $T=293.15$ K) [2] or ethanol (644, $T=313.15$ K) [2]. It is to be noted that systems containing an alkan-1-ol and one primary, or secondary or tertiary aliphatic amine behave in the opposite way. For example, in the case of propan-1-ol + propan-1-amine system at equimolar composition and $T=302.95$ K, $G_m^E = -752 \text{ J}\cdot\text{mol}^{-1}$ [3].

As a part of our research on liquid mixtures of alcohols and amines [4-15], we are engaged in a systematic study of the dielectric behaviour of alkan-1-ol + amine liquid mixtures by means of relative permittivities (ϵ_r), refractive indices at the sodium D-line (n_D), and the application of the Kirkwood-Fröhlich model by the calculation of the Kirkwood correlation factor [16,17], which also requires the knowledge of density (ρ) data. So far, we have reported measurements for systems containing cyclohexanamine [18,19], hexan-1-amine [13], *N*-propylpropan-1-amine [14] and *N,N*-diethylethanamine [15]. Now we aim to investigate the impact on the dielectric properties of the replacement of the mentioned aliphatic amines by aniline, as the thermodynamic behaviour of these mixtures is quite different (see above). Therefore, we provide measurements of ϵ_r at 1 MHz frequency and n_D over the temperature range (293.15 to 303.15) K and, complementarily, of ρ and the speed of sound (c) at 298.15 K, for the liquid mixtures methanol, propan-1-ol or pentan-1-ol + aniline at 0.1 MPa.

A survey of literature data using Web of Science and the Thermolite machine shows that different research groups have provided results of their measurements of these properties [20-38]. We perform a critical comparative analysis of these data, which reveals the poor precision of some of them and, more importantly, large discrepancies that make it difficult to judge their accuracy. The measurements reported in this work will, hopefully, help to reveal which of the literature datasets are more likely to be accurate.

2. Experimental

2.1. Materials

Information about the pure compounds employed in the experiments is shown in Table 1. They were used without further purification. The measured thermophysical properties at the working temperatures and their dipole moments (μ) are collected in Table 2. Comparison with literature values reveals a good agreement.

2.2. Apparatus and procedure

The mixtures were prepared in glass vessels of about 10 cm³, and the concentration was measured by mass determination using an analytical balance Sartorius MSU125p, with a standard uncertainty of 5·10⁻⁵ g. The weighing was corrected taking into account buoyancy effects. The standard uncertainty in the mole fraction is 0.0005. Molar quantities were calculated using the relative atomic mass Table of 2015 issued by the Commission on Isotopic Abundances and Atomic Weights (IUPAC) [39]. Pure liquids were stored with 4 Å molecular sieves (except methanol, because measurements were affected) in order to minimize the effects of the interaction with air components. The measurement cells (see below) were appropriately filled with the samples and closed to avoid liquid evaporation. The density of the pure compounds was measured along the experiments, remaining constant within the experimental uncertainty.

Temperatures were measured using Pt-100 resistances. They were calibrated using the triple point of water and the melting point of Ga, according to the ITS-90 scale of temperature, as reference points. The standard uncertainty of this quantity is 0.01 K for ρ and c measurements, and 0.02 K for ε_r and n_D measurements.

Densities and speeds of sound of the liquids were obtained by means of a vibrating-tube densimeter and sound analyser, Anton Paar model DSA 5000, with a temperature stability of 0.001 K. A description of the calibration procedure has been given elsewhere [40]. The relative standard uncertainty of the ρ measurements is 0.0008. The determination of the speed of sound is based on the measurement of the propagation time of short acoustic pulses of 3 MHz centre frequency [41], which are repeatedly transmitted through the sample. The standard uncertainty of the c measurements is 0.2 m·s⁻¹. The experimental technique was checked through the determination of the excess molar volume, V_m^E , and excess isentropic compressibility, κ_S^E (see equations below), of the cyclohexane + benzene mixture at $T = (293.15 \text{ to } 303.15) \text{ K}$, and there is good agreement between our results and published values [42-45].

The quantity n_D was determined by means of a Bellingham + Stanley RFM970 automatic refractometer, which determines the critical angle at the wavelength of the sodium D-line (589.3 nm) and relates it to the corresponding refractive index. The standard uncertainty of n_D is 0.00008. The temperature stability (0.02 K) is achieved by means of Peltier modules. The apparatus was calibrated following the recommendations by Marsh [46], using 2,2,4-trimethylpentane and toluene at $T = (293.15 \text{ to } 303.15) \text{ K}$.

The experimental device to determine ε_r and its calibration has been described in detail elsewhere [47]. It is based on precise impedance measurement by the auto-balancing bridge method in 4TP (Four-Terminal Pair) configuration, using a precision impedance analyser 4294A and a 16048G test lead from Agilent. A sample volume of $\approx 4.8 \text{ cm}^3$ fills a 16452A cell (parallel-plate capacitor, also from Agilent), which is immersed in a thermostatic bath LAUDA RE304, with a temperature stability of 0.02 K. The repeatability of the ε_r measurements is 0.0001. The relative standard uncertainty of ε_r was estimated to be 0.003 from the differences between our data and values available in the literature, in the range of temperature (288.15 to 333.15) K, for the following pure liquids: water, benzene, cyclohexane, hexane, nonane, decane, dimethyl carbonate, diethyl carbonate, methanol, propan-1-ol, pentan-1-ol, hexan-1-ol, heptan-1-ol, octan-1-ol, nonan-1-ol and decan-1-ol.

3. Equations

Assuming negligible dispersion and absorption of the acoustic wave in the liquid, the isentropic compressibility (κ_S) can be determined from ρ and c measurements using the Newton-Laplace equation:

$$\kappa_S = \frac{1}{\rho c^2} \quad (1)$$

The isothermal compressibility (κ_T) is related to the molar volume (V_m), the molar isobaric heat capacity (C_{pm}), the thermal expansion coefficient (α_p) and κ_S through:

$$\kappa_T = \kappa_S + \frac{TV_m(\alpha_p)^2}{C_{pm}} \quad (2)$$

The values F^{id} of the thermodynamic properties of an ideal mixture at the same temperature and pressure as the real mixture are calculated from the well-established equations from Benson and Kiyohara [48-50]:

$$F^{\text{id}} = x_1 F_1^* + x_2 F_2^* \quad (F = V_m, C_{pm}) \quad (3)$$

$$F^{\text{id}} = \phi_1 F_1^* + \phi_2 F_2^* \quad (F = \alpha_p, \kappa_T) \quad (4)$$

where F_i^* is the value of the property F of pure component i , x_i denotes the mole fraction of component i and $\phi_i = x_i V_{mi}^* / V_m^{\text{id}}$ represents the volume fraction of component i . Ideal values of κ_S and c are calculated from the formulae [48]:

$$\kappa_S^{\text{id}} = \kappa_T^{\text{id}} - \frac{TV_m^{\text{id}}(\alpha_p^{\text{id}})^2}{C_{pm}^{\text{id}}} \quad (5)$$

$$c^{\text{id}} = \left(\frac{1}{\rho^{\text{id}} \kappa_S^{\text{id}}} \right)^{1/2} \quad (6)$$

being $\rho^{\text{id}} = (x_1 M_1 + x_2 M_2) / V_m^{\text{id}}$ (M_i , molar mass of the i component).

The ideal dielectric and refractive properties are given by [51,52]:

$$\epsilon_r^{\text{id}} = \phi_1 \epsilon_{r1}^* + \phi_2 \epsilon_{r2}^* \quad (7)$$

$$n_D^{\text{id}} = \left[\phi_1 (n_{D1}^*)^2 + \phi_2 (n_{D2}^*)^2 \right]^{1/2} \quad (8)$$

$$\left[\left(\frac{\partial \epsilon_r}{\partial T} \right)_p \right]^{\text{id}} = \left(\frac{\partial \epsilon_r^{\text{id}}}{\partial T} \right)_p \quad (9)$$

Lastly, the excess properties are obtained using the relation:

$$F^{\text{E}} = F - F^{\text{id}} \quad (10)$$

4. Results

Values of $\alpha_p = -(1/\rho)(\partial\rho/\partial T)_p$ of the pure compounds at $T = 298.15$ K and $p = 0.1$ MPa were obtained from linear regressions of experimental ρ values in the range (293.15 to 303.15) K. The temperature derivative $(\partial\epsilon_r^{\text{E}}/\partial T)_p = [(\partial\epsilon_r/\partial T)_p]^{\text{E}} = (\partial\epsilon_r/\partial T)_p - (\partial\epsilon_r^{\text{id}}/\partial T)_p$ was calculated in an analogous fashion.

Experimental values of ρ , c , V_m^{E} , κ_S^{E} and c^{E} of alkan-1-ol (1) + aniline (2) liquid mixtures at $T = 298.15$ K and $p = 0.1$ MPa are collected as functions of x_1 (mole fraction of the alkan-1-ol) in Table 3. Table 4 collects their ϕ , ϵ_r and ϵ_r^{E} values of as functions of x_1 in the T

range (293.15 to 303.15) K and $p = 0.1$ MPa, while Table 5 contains the experimental x_1 , ϕ_1 , n_D and n_D^E values at the same conditions. The data of $(\partial \varepsilon_r^E / \partial T)_p$ at $T = 298.15$ K and $p = 0.1$ MPa are collected in Table 6.

The F^E data were fitted by unweighted linear least-squares regressions to Redlich-Kister polynomials [53]

$$F^E = x_1(1 - x_1) \sum_{i=0}^{k-1} A_i (2x_1 - 1)^i \quad (11)$$

The number, k , of appropriate coefficients for each system, property and temperature has been determined by the application of an F-test of additional term [54] at a 99.5% confidence level. Table 7 includes the parameters A_i obtained, and the standard deviations, $\sigma(F^E)$, defined by:

$$\sigma(F^E) = \left[\frac{1}{N - k} \sum_{j=1}^N (F_{\text{cal},j}^E - F_{\text{exp},j}^E)^2 \right]^{1/2} \quad (12)$$

where j indexes the N experimental data $F_{\text{exp},j}^E$, and $F_{\text{cal},j}^E$ is the corresponding value of the excess property F^E calculated from equation (11).

The values of V_m^E , κ_s^E and c^E versus x_1 , and those of ε_r^E , $(\partial \varepsilon_r^E / \partial T)_p$ and n_D^E versus ϕ_1 , at $T = 298.15$ K and $p = 0.1$ MPa, are plotted together with their corresponding Redlich-Kister regressions in Figures 1-6.

4.1. Comparison with literature data

Data available in the literature on ρ , c , ε_r and n_D of alkan-1-ol + aniline liquid mixtures [20-38] are analysed and compared with our measurements in Table 8 and Figures 1, 4, 5 and S1-S8 (supplementary material). For comparison purposes, the deviation from mole-fraction linearity of the speed of sound, Δc , has been computed:

$$\Delta c = c - x_1 c_1 - x_2 c_2 \quad (13)$$

From now on, we will denote by n the number of carbon atoms of the alkan-1-ol, and by $n\text{OH}$ the corresponding alkan-1-ol. We will now analyse the reliability of the data available in the literature on V_m^E , Δc , n_D^E and ε_r^E for the studied systems.

a) Density. As can be seen from Figures 1 and S1-S3, there are several sources of V_m^E values that agree well with our data for the systems with 1OH [21,22], 3OH [31] or 5OH [30]. Furthermore, references [23,33] regarding the 4OH mixture are in accordance with our V_m^E variation with n , and are very close to each other (Figure 1). From these two, only reference [23]

reports data with the same symmetry as our measurements. We are evaluating the agreement of the data taking into account that the temperature difference between sources is not large. Data from reference [34] seem, therefore, unreliable, as they give large and positive V_m^E values, in contrast with the large negative values from our data and from references [21,22]. Reference [38] presents also abnormally high V_m^E values, which are even large and positive for $n = 4,5,6$; it can be then concluded that the data from this reference have to be taken with caution. The same can be said about the data from reference [35] regarding the 3OH mixture, as their values are similar to those of reference [38]. As for the temperature dependence of V_m^E , none of the references provides enough precision to confirm any tendency. For the case of 4OH mixtures, the available references [23,33] seem to show opposite trends.

b) Speed of sound. There are few references reporting c values of the systems under study. Δc values calculated from reference [22] for the 1OH mixture agree well with our data (Figure S4), like they also do for V_m^E (see above). Reference [36] leads to Δc values for the 3OH mixture comparable to ours (Figure S5). Data from reference [38] do not agree well with our data (Figure S6), but this discordance was already observed on the very deviated values it gives for V_m^E .

c) Refractive index. Sources of n_D data are even scarcer. For the 4OH mixture, n_D^E values can be calculated using data from reference [23] (Figure 5) and, as it happened with V_m^E values from this reference, they agree rather well with our n_D^E variation with n (taking into account the large data scattering). Data from reference [21] for the 1OH mixture is not precise enough to calculate n_D^E , giving a huge data scattering (Figure 5). n_D^E from reference [37] disagree with our values (Figure 5). Given the lack of a sufficient amount of reliable references, the objective conclusion is to mark all these n_D sources as uncertain ([23,37]) or not precise enough for the calculation of n_D^E ([21]).

d) Relative permittivity. There are more sources of ϵ_r data than in the case of n_D , but they differ a lot among them and/or present a significant data scattering. For the 1OH mixture, none of the ϵ_r sources leads to ϵ_r^E values in agreement with ours (Figure S7). Nevertheless, it must be noticed that either the number of experimental points is rather low [20] or the data scattering is important [26]. We see, however, rather good agreement in ϵ_r^E of the 3OH mixture for references [24,32], although with significant data scattering (Figures 4 and S8); there is no agreement in the case of reference [28], but the data scattering in this case is enormous (Figure

S8). The rest of the references [25,27,29] do not provide the ε_r values for the pure compounds, and consequently ε_r^E cannot be evaluated consistently.

5. Discussion

In this section, if nothing else is specified, the values of the thermophysical properties are given at $T = 298.15$ K and $x_1 = 0.5$, except for dielectric properties, which will be given at $\phi_1 = 0.5$. As before, we will denote by n the number of carbon atoms of the alkan-1-ols and by $n\text{OH}$ the alkan-1-ol with n carbon atoms.

5.1. Excess molar volumes, molar enthalpies and isentropic compressibilities

$n\text{OH} + \text{aniline}$ liquid mixtures show positive, or small and negative, $H_m^E/\text{J}\cdot\text{mol}^{-1}$ values: -175 (1OH [55]), 351 (2OH [55]), 776 (3OH [55]), 944 (4OH [56]), 1011 (5OH [55]). They show an important positive contribution to this quantity coming from the rupture of interactions between molecules of the same species. In contrast, their $V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$ are negative: -0.902 (1OH, this work), -0.593 (3OH, this work), -0.398 (4OH [23]), -0.241 (5OH, this work). Positive H_m^E values occurring together with negative V_m^E values indicate the presence of relevant structural effects. In fact, it is possible to evaluate the magnitude of these effects on the H_m^E results, and subtract them by performing the calculation of the excess molar internal energy at constant volume ($U_{m,V}^E$) [57]:

$$U_{m,V}^E = H_m^E - T \frac{\alpha_p}{\kappa_T} V_m^E \quad (14)$$

Due to the lack of reliable data, in the application of equation (14) to $n\text{OH} + \text{aniline}$ mixtures both α_p and κ_T were considered ideal. Also, for pure 4OH α_p and κ_T were taken from Riddick *et al.* [58]. This gives a very reasonable approximation of the corresponding $U_{m,V}^E/\text{J}\cdot\text{mol}^{-1}$ values: 143 (1OH), 997 (3OH), 1095 (4OH), 1104 (5OH). We observe an important contribution to H_m^E coming from the equation-of-state term (the second term in equation (14)). The $U_{m,V}^E$ results are positive, revealing that, in the balance of interactional effects, there is a dominance of the rupture of interactions between like molecules, even for the 1OH mixture, which shows a positive $U_{m,V}^E$. In this balance, the breaking of the dipolar interactions between aniline molecules plays a major role. This can be seen by comparing with the largely negative H_m^E values for the $n\text{OH} + \text{hexan-1-amine}$ mixtures [59]. The importance of dipolar interactions and structural effects in $n\text{OH} + \text{aniline}$ mixtures is also supported by the

poor results obtained for these systems in the framework of the ERAS model [60]. It can also be observed that, as n takes higher values, the increment of H_m^E , or $U_{m,V}^E$, when n is incremented by 1 unit tends to decrease. This can be ascribed to a lower and weaker association of longer alkan-1-ols.

Negative values of κ_S^E are typical of solutions where there are relevant interactions between unlike molecules and/or structural effects [61,62]. $\kappa_S^E/\text{TPa}^{-1}$ values of $n\text{OH} + \text{aniline}$ liquid mixtures are moderately negative: -109.7 (1OH), -72.5 (3OH), -37.3 (5OH), and their change with n is parallel to that of V_m^E . They can be interpreted in terms of a decrease of the free volume available for the molecules due to the structural effects that make V_m^E negative, which make the mixtures less compressible. These values are consistent with the positive $c^E/\text{m}\cdot\text{s}^{-1}$ values: 139.0 (1OH), 86.5 (3OH), 44.8 (5OH).

5.2. Excess relative permittivities

The value of ε_r^E is affected negatively when interactions between like molecules are disrupted, whereas it is impacted either positively or negatively when interactions between unlike molecules are created, depending on the character of the formed multimers in terms of their effective response to an electric field. In mixtures of the type $n\text{OH} + \text{benzene}$ there is a dominance of the rupture of interactions along mixing, showing therefore negative values of ε_r^E (at 293.2 K [58,63]): -1.28 (1OH), -2.15 (3OH), -2.78 (4OH), -2.83 (6OH), -2.23 (8OH). As n increases, ε_r^E decreases and then increases again, which is a typical behaviour of $n\text{OH} + \text{alkane}$ (e.g. heptane [12,58,64,65]) or $+ \text{amine}$ (e.g. hexan-1-amine [13], propylpropan-1-amine [14], *N,N*-diethylethanamine [15], cyclohexanamine [18,19]), and can be attributed to the lower and weaker association of longer alkan-1-ols. The values of ε_r^E in $n\text{OH} + \text{aniline}$ systems are also negative: -0.778 (1OH), -1.850 (3OH), -2.082 (5OH), indicating a predominance of the rupture of $n\text{OH}-n\text{OH}$ and aniline-aniline interactions. The aniline molecule can be considered as a benzene molecule to which the $-\text{NH}_2$ group is added, so a larger negative contribution to ε_r^E from the rupture of interactions between like molecules is expected in comparison with $n\text{OH} + \text{benzene}$ mixtures. Consequently, the higher ε_r^E values presented by $n\text{OH} + \text{aniline}$ suggest that the contribution of the formation of interactions between unlike molecules is positive, in such a way that the created multimers respond more effectively to the electric field than the structures that existed in the pure liquids.

ε_r^E decreases when T is increased for the 1OH system, and increase in line with T for the mixtures with 3OH or 5OH. A similar trend is encountered when aniline is replaced by hexan-1-

amine. The negative $(\partial \varepsilon_r^E / \partial T)_p$ results for the solution containing 1OH may indicate that, at higher temperatures, the multimers in the mixture become of smaller size and/or cyclic nature and that this effect predominates over those related to the breaking of the interactions between like molecules, which should contribute positively to $(\partial \varepsilon_r^E / \partial T)_p$ as they decrease with T . Longer alkan-1-ols are more weakly self-associated and the permittivity of the ideal state decreases with the increasing of temperature more rapidly than ε_r in such a way that $(\partial \varepsilon_r^E / \partial T)_p$ values become positive.

Pyridine shows a higher dipole moment (2.21 D [66]) and relative permittivity (12.91 [58]). It is interesting that, nevertheless, the strength of amine-amine interactions in pure pyridine is lower than in pure aniline, as revealed by the upper critical solution temperatures of their mixtures with heptane: 343.11 K (aniline [1]) > 255.2 K (pyridine [67]). In contrast with aniline, the liquid mixture 1OH + pyridine shows a positive ε_r^E value (2.85 [58,68]), indicating positive contributions from the formed multimers, which are predominant over the negative contributions from the rupture of interactions. This is consistent with the fact that $H_m^E(1OH + \text{pyridine}) = -707 \text{ J} \cdot \text{mol}^{-1}$ [69] is somewhat lower than $H_m^E(1OH + \text{aniline})$ (see above), and suggests that strong 1OH-pyridine interactions could be enhancing the dipole moment of pyridine molecules in the mixed state. It is interesting to note that the results from ε_r^E are also in accordance with those from the concentration-concentration structure factor ($S_{cc}(0)$) formalism. The concentration-concentration structure factor, defined by [70,71]:

$$S_{cc}(0) = \frac{RT}{\left(\frac{\partial^2 \Delta G_m}{\partial x_1^2} \right)_{T,p}} = \frac{x_1 x_2}{1 + \frac{x_1 x_2}{RT} \left(\frac{\partial^2 G_m^E}{\partial x_1^2} \right)_{T,p}} > 0 \quad (15)$$

where ΔG_m is the molar Gibbs energy of mixing, is a way to study fluctuations in a binary mixture. For ideal mixtures, $S_{cc}(0) = x_1 x_2$. If $S_{cc}(0) > x_1 x_2$, the dominant trend in the system is homocoordination (separation of the components), whereas if $S_{cc}(0) < x_1 x_2$, the dominant trend in the solution is heterocoordination (compound formation). $S_{cc}(0)$ values have been evaluated for some $nOH + \text{amine}$ systems by means of the DISQUAC model [3,68]. For the aniline mixtures [60], $S_{cc}(0)$ values are higher than the ideal ones: 0.398 (1OH, $T = 293.15 \text{ K}$), 0.461 (3OH), 0.493 (4OH), 0.504 (5OH). They are, therefore, characterized by homocoordination. In contrast, pyridine solutions [72] show $S_{cc}(0)$ values that deviate negatively from ideality: 0.235 (1OH), 0.230 (3OH, $T = 313.15 \text{ K}$), 0.230 (4OH, $T = 313.15 \text{ K}$). Consequently, these mixtures are characterized by heterocoordination.

5.3. Molar refraction

The molar refraction, R_m , is proportional to the average electronic contribution to the polarizability, α_e , from one molecule in a macroscopic sphere of liquid [16,17], and consequently it is a measure of dispersive interactions [17,73]. It is defined by the so-called Lorentz-Lorenz equation [16,17]:

$$R_m = \frac{n_D^2 - 1}{n_D^2 + 2} V_m = \frac{N_A \alpha_e}{3\epsilon_0} \quad (16)$$

where N_A is Avogadro's constant and ϵ_0 the vacuum permittivity. The $R_m/\text{cm}^3 \cdot \text{mol}^{-1}$ values for $n\text{OH} + \text{aniline}$ mixtures (at equimolar composition) reveal more important dispersive interactions for larger n : 19.5 (1OH), 24.2 (3OH), 28.9 (5OH). The corresponding excess values, $R_m^E = R_m - R_m^{\text{id}}$, can be calculated substituting ideal values in equation (16) for R_m^{id} . For $n\text{OH} + \text{aniline}$ systems, the $R_m^E/\text{cm}^3 \cdot \text{mol}^{-1}$ values at equimolar composition are negative: -0.27 (1OH), -0.17 (3OH), -0.07 (5OH). They mean there is a loss in dispersive interactions along mixing with respect to the ideal state, in which dipoles of different components do not interact. The lower R_m^E value encountered for the methanol solution may be due, in this case, to a formation of a larger number of hydrogen bonds between the components upon mixing. A similar trend is observed for alkan-1-ol + hexan-1-amine mixtures [13].

5.4. Kirkwood-Fröhlich model

The Kirkwood-Fröhlich model for dielectrics is based on fluctuation relations at zero field. It is assumed that the molecules are in a spherical cavity of an infinitely large dielectric. The high-frequency permittivity, ϵ_r^∞ , with only induced polarizability contributions, is used to treat macroscopically the induced polarizability. There is a local field in the cavity that plays the role of long-range dipolar interactions, and is calculated considering the outside of the cavity as a continuous medium of permittivity ϵ_r . The Kirkwood correlation factor, g_K , represents the effect of short-range interactions and informs about the deviations of the relative orientation of a dipole with respect to its neighbors from randomness. For a one-fluid model of a mixture of polar liquids [74], g_K can be determined using [16,17,74,75]:

$$g_K = \frac{9k_B T V_m \epsilon_0 (\epsilon_r - \epsilon_r^\infty)(2\epsilon_r + \epsilon_r^\infty)}{N_A \mu^2 \epsilon_r (\epsilon_r^\infty + 2)^2} \quad (17)$$

Here, k_B is Boltzmann's constant; N_A , Avogadro's constant; ϵ_0 , the vacuum permittivity; and V_m , the molar volume of the liquid at the working temperature, T . For polar compounds, ϵ_r^∞ has

been estimated using $\varepsilon_r^\infty = 1.1n_D^2$ [76]. μ represents the dipole moment of the solution, estimated from the equation [74]:

$$\mu^2 = x_1\mu_1^2 + x_2\mu_2^2 \quad (18)$$

where μ_i stands for the dipole moment of component i ($= 1,2$). Calculations have been performed using smoothed values of V_m^E , n_D^E and ε_r^E at $\Delta x_1 = 0.01$. The source and values of μ_i used for alkan-1-ol + aniline mixtures are collected in Table 2.

The values of $g_K(n\text{OH}+\text{aniline})$ obtained in this work are moderately high and decrease with n (Figure 7): 1.94 (1OH), 1.72 (3OH), 1.50 (5OH). The n variation can be ascribed to the lower and weaker solvation and self-association of the alkan-1-ol as its chain becomes longer. We note that $g_K(1\text{OH} + \text{aniline})$ is considerably lower than $g_K(1\text{OH} + \text{hexan-1-amine})$ [13] (Figure 7), indicating that solvation and the self-association of the alkan-1-ol, a key feature of $1\text{OH} + \text{hexan-1-amine}$, is less important in the aniline mixture. The dependence of $g_K(1\text{OH} + \text{aniline})$ with ϕ_1 suggests that aniline is a better breaker of the 1OH network than hexan-1-amine. For the sake of comparison, we also show g_K results when aniline is replaced by benzonitrile (293.15 K, [20]), a strongly polar, non-associated compound. In fact, in this case the g_K curve increases even slowly with ϕ_1 (Figure 7), as a result of a quite effective rupture of the self-association of 1OH by benzonitrile [77]. On the other hand, if aniline is kept but 1OH is replaced by a strongly polar, non-associated compound such as *N,N*-dimethylformamide [78], the values of g_K are very low (Figure 7) as the high contribution to parallel alignment from the association of 1OH disappears.

Lastly, let us see that the g_K curve of the system $1\text{OH} + \text{pyridine}$ [68] (Figure 7) is very similar to that of the mixture $1\text{OH} + \text{aniline}$. As has been noted above, the former is characterized by homocoordination, whereas the latter by heterocoordination. The results from the model suggest that, even though the kind of interactions predominant in each mixture is different, the multimers formed by the molecules are structured in such a way that the average relative orientation of neighbouring dipoles is practically the same in both systems.

6. Conclusions

Measurements of ρ ($T = 298.15$ K), c ($T = 298.15$ K), ε_r at 1 MHz ($T = 293.15$ K to 303.15 K) and n_D ($T = 293.15$ K to 303.15 K) have been reported for the liquid mixtures methanol, propan-1-ol or pentan-1-ol + aniline at 0.1 MPa. The data have been useful to identify

inconsistencies among different literature sources on alkan-1-ol + aniline systems. Positive $U_{m,V}^E$ and negative ϵ_r^E that increase in absolute value with the length of the alkan-1-ol reveal the predominance of the breaking of the interactions between like molecules along mixing. This is supported by the application of the concentration-concentration structure factor formalism. The negative V_m^E values show the existence of important structural effects in the mixtures under study. According to the Kirkwood-Fröhlich model, the average relative orientation of neighbouring dipoles is similar in the mixtures methanol + aniline or + pyridine.

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Table 1

Sample description.

Chemical name	CAS Number	Source	Purification method	Purity ^a	Water content ^b
methanol	67-56-1	Sigma-Aldrich	none	0.999	$2 \cdot 10^{-5}$
propan-1-ol	71-23-8	Fluka	none	0.999	$1 \cdot 10^{-3}$
pentan-1-ol	71-41-0	Sigma-Aldrich	none	0.999	$3 \cdot 10^{-4}$
aniline	62-53-3	Sigma-Aldrich	none	0.999	$4 \cdot 10^{-4}$

^a In mole fraction. By gas chromatography. Provided by the supplier.^b In mass fraction. By Karl-Fischer titration.

Table 2

Thermophysical properties of the pure liquids used in this work at temperature T and pressure $p = 0.1$ MPa: dipole moment (μ), density (ρ^*), speed of sound (c^*), isobaric thermal expansion coefficient (α_p^*), isentropic compressibility (κ_S^*), molar isobaric heat capacity (C_{pm}^*), isothermal compressibility (κ_T^*), refractive index at the sodium D-line (n_D^*) and relative permittivity at frequency $f = 1$ MHz (ϵ_r^*). ^a

Property	T/K	Methanol	propan-1-ol	pentan-1-ol	aniline
μ/D		1.664 [79]	1.629 [79]	1.598 [79]	1.51 [58]
$\rho^*/g\cdot cm^{-3}$	293.15	0.79191	0.80352	0.81454	1.02166
		0.7916 [80]	0.80361 [82]	0.81468 [83]	1.02166 [30]
		0.791400 [81]			1.0217 [84]
	298.15	0.78682	0.79941	0.81081	1.01731
		0.7869 [85]	0.79960 [82]	0.81103 [83]	1.0174 [84]
		0.786884 [86]			
	303.15	0.78259	0.79547	0.80724	1.01301
		0.782158 [86]	0.79561 [82]	0.81737 [83]	1.0130 [84]
$c^*/m\cdot s^{-1}$	293.15	1119.1	1222.5	1292.4	1658.0
		1119 [87]	1223 [88]	1292 [87]	1651.3 [36]
					1657.0 [61]
	298.15	1102.1	1205.1	1275.3	1638.6
		1101.9 [89]	1206 [88]	1276 [87]	1632.8 [36]
					1638.6 [61]
	303.15	1086.6	1188.6	1259.0	1617.9
		1186.37 [90]	1189 [88]	1259 [87]	1614.5 [36]
					1619.2 [61]
$\alpha_p^*/10^{-3}K^{-1}$	298.15	1.185	1.007	0.900	0.850
		1.196 [58]	1.004 [58]	0.905 [58]	0.849 [58]
κ_S^*/TPa^{-1}	293.15	1008.2	832.7	735.0	356.1
	298.15	1046.7	861.4	758.3	366.1
		1028 [58]	849 [58]		368 [58]
$C_{pm}^*/J\cdot mol^{-1}\cdot K^{-1}$	303.15	1082.3	889.8	781.5	377.1
^b κ_T^*/TPa^{-1}	298.15	81.92 [91]	146.88 [91]	207.45 [92]	191.01 [93]
n_D^*	298.15	1254.9	1016.1	884.9	469.3
		1248 [58]	1026 [58]	884 [58]	
	293.15	1.32852	1.38513	1.41000	1.58656
		1.32859 [94]	1.38512 [95]	1.40986 [87]	1.5865 [96]
					1.58660 [21]
	298.15	1.32639	1.38309	1.40800	1.58378
		1.32652 [97]	1.38307 [87]	1.40789 [87]	1.58364 [58]
					1.5836 [98]
	303.15	1.32431	1.38101	1.40596	1.58109
		1.32457 [99]	1.38104 [87]	1.40592 [100]	1.58143 [21]
		1.32410 [87]			
ϵ_r^*	293.15	33.576	21.225	15.746	7.137
		33.61 [101]	21.15 [102]	15.63 [101]	7.07 [103]
					7.045 [104]

298.15	32.624 32.62 [101]	20.545 20.42 [102]	15.162 15.08 [105]	7.004 6.940 [104] 6.774 [106]
303.15	31.684 31.66 [101]	19.873 19.75 [102]	14.586 14.44 [101]	6.876 6.88 [107] 6.857 [108]

^a Standard uncertainties (u): $u(T) = 0.01$ K for ρ^* measurements; $u(T) = 0.02$ K for ε_r^* and n_D^* measurements; $u(p) = 1$ kPa; $u(f) = 20$ Hz; $u(c^*) = 0.2$ m·s⁻¹; $u(n_D^*) = 0.00008$. Relative standard uncertainties (u_r): $u_r(\rho^*) = 0.0008$; $u_r(\alpha_p^*) = 0.028$; $u_r(\kappa_S^*) = 0.002$; $u_r(\kappa_T^*) = 0.015$; $u_r(\varepsilon_r^*) = 0.003$.

^b Determined using experimental values measured in this work and C_{pm}^* values from the literature included in this table.

Table 3

Density (ρ), speed of sound (c), excess molar volume (V_m^E), excess isentropic compressibility (κ_s^E) and excess speed of sound (c^E) of alkan-1-ol (1) + aniline (2) liquid mixtures as functions of the mole fraction of the alkan-1-ol (x_1) at temperature $T = 298.15$ K and pressure $p = 0.1$ MPa.^a

x_1	ρ /g·cm ⁻³	c /m·s ⁻¹	V_m^E /cm ³ ·mol ⁻¹	κ_s^E /TPa ⁻¹	c^E /m·s ⁻¹	x_1	ρ /g·cm ⁻³	c /m·s ⁻¹	V_m^E /cm ³ ·mol ⁻¹	κ_s^E /TPa ⁻¹	c^E /m·s ⁻¹
methanol (1) + aniline (2) ; $T/K = 298.15$											
0.0502	1.01351	1629.5	-0.1313	-10.6	21.5	0.5508	0.94981	1464.9	-0.9268	-120.3	142.5
0.1006	1.00939	1618.6	-0.2573	-21.1	41.0	0.5977	0.94018	1441.1	-0.9491	-129.6	143.6
0.1516	1.00483	1606.5	-0.3749	-31.9	59.1	0.6507	0.92770	1410.9	-0.9354	-138.0	141.2
0.2003	1.00006	1593.9	-0.4765	-42.5	75.3	0.6971	0.91554	1381.9	-0.9090	-143.5	136.2
0.2510	0.99463	1579.6	-0.5722	-53.7	90.3	0.7501	0.90000	1345.8	-0.8596	-146.8	127.0
0.3024	0.98872	1564.0	-0.6681	-65.4	104.2	0.7997	0.88342	1307.8	-0.7821	-144.4	113.7
0.3489	0.98273	1548.5	-0.7352	-75.8	115.0	0.8497	0.86434	1265.3	-0.6684	-134.6	95.5
0.3976	0.97597	1530.9	-0.8022	-86.9	124.7	0.8992	0.84266	1218.1	-0.5141	-113.2	71.6
0.4504	0.96783	1510.1	-0.8582	-98.8	133.2	0.9500	0.81677	1163.5	-0.2948	-72.3	40.0
0.4976	0.95983	1489.8	-0.8984	-109.1	138.6						
propan-1-ol (1) + aniline (2) ; $T/K = 298.15$											
0.0498	1.00931	1621.9	-0.0891	-10.1	20.6	0.5494	0.91498	1421.7	-0.6034	-74.9	84.4
0.0994	1.00114	1604.0	-0.1741	-19.5	37.3	0.5998	0.90391	1399.9	-0.6167	-76.5	81.2
0.1508	0.99242	1585.0	-0.2551	-28.8	51.8	0.6507	0.89215	1377.0	-0.5990	-76.1	76.1
0.2002	0.98379	1566.6	-0.3260	-37.3	63.3	0.7005	0.88038	1354.5	-0.5789	-74.3	69.9
0.2478	0.97524	1547.6	-0.3882	-44.5	71.4	0.7505	0.86807	1331.4	-0.5358	-70.2	62.3
0.3001	0.96555	1526.7	-0.4472	-52.0	78.5	0.8004	0.85548	1308.1	-0.4872	-64.1	53.5
0.3518	0.95566	1505.6	-0.4961	-58.6	83.3	0.8498	0.84258	1284.5	-0.4218	-55.4	43.4
0.4015	0.94592	1485.0	-0.5399	-64.2	86.0	0.8998	0.82877	1259.3	-0.3096	-42.1	31.0
0.4500	0.93605	1464.5	-0.5673	-68.7	87.0	0.9502	0.81434	1232.8	-0.1733	-24.1	16.6
0.5003	0.92564	1443.2	-0.5987	-72.6	86.6						
pentan-1-ol (1) + aniline (2) ; $T/K = 298.15$											
0.0574	1.00395	1611.6	-0.0522	-9.1	18.4	0.5470	0.89781		-0.2430		
0.0993	0.99422	1591.5	-0.0766	-14.6	27.9	0.6010	0.88693	1392.4	-0.2384	-36.7	40.4
0.1484	0.98303	1568.6	-0.1080	-20.2	36.2	0.6509	0.87702	1374.7	-0.2303	-33.5	35.1
0.2005	0.97151	1545.3	-0.1553	-25.5	42.5	0.7004	0.86740	1359.7	-0.2278	-31.4	31.5
0.2513	0.96012	1522.7	-0.1662	-29.1	45.8	0.7512	0.85758	1344.6	-0.2118	-28.2	27.2
0.3013	0.94925	1501.6	-0.1913	-32.3	47.9	0.8004	0.84810	1330.3	-0.1805	-24.4	22.6
0.3485	0.93915	1482.4	-0.2141	-34.5	48.5	0.8506	0.83865	1316.3	-0.1563	-19.9	17.7
0.4009	0.92800	1461.8	-0.2259	-36.1	48.0	0.8999	0.82941	1302.7	-0.1181	-14.5	12.4
0.4488	0.91793	1443.8	-0.2310	-36.9	46.8	0.9501	0.82000	1289.0	-0.0585	-7.8	6.5
0.5009	0.90724	1425.0	-0.2450	-37.2	44.7						

^a Standard uncertainties (u): $u(T) = 0.01$ K; $u(p) = 1$ kPa ; $u(x_1) = 0.0005$; $u(c) = 0.2$ m·s⁻¹; $u(V_m^E) = 0.010 \cdot |V_m^E|_{\max} + 0.005$ cm³·mol⁻¹; $u(c^E) = 0.4$ m·s⁻¹. Relative standard uncertainties (u_r): $u_r(\rho) = 0.0008$.

Table 4

Volume fractions of alkan-1-ol (ϕ_1), relative permittivities at frequency $f = 1$ MHz (ϵ_r) and excess relative permittivities at $f = 1$ MHz (ϵ_r^E) of alkan-1-ol (1) + aniline (2) liquid mixtures as functions of the mole fraction of the alkan-1-ol (x_1), at temperature T and pressure $p = 0.1$ MPa.

a

x_1	ϕ_1	ϵ_r	ϵ_r^E	x_1	ϕ_1	ϵ_r	ϵ_r^E
methanol (1) + aniline (2) ; $T/K = 293.15$							
0.0502	0.0229	7.575	-0.167	0.5508	0.3525	15.591	-0.866
0.1006	0.0473	8.049	-0.339	0.5977	0.3974	16.804	-0.840
0.1516	0.0735	8.590	-0.490	0.6507	0.4526	18.355	-0.748
0.2003	0.1001	9.158	-0.626	0.6971	0.5053	19.798	-0.699
0.2510	0.1295	9.846	-0.715	0.7501	0.5713	21.646	-0.596
0.3024	0.1614	10.582	-0.822	0.7997	0.6393	23.532	-0.507
0.3489	0.1922	11.371	-0.848	0.8497	0.7151	25.655	-0.389
0.3976	0.2266	12.234	-0.894	0.8992	0.7984	27.960	-0.286
0.4504	0.2667	13.318	-0.870	0.9500	0.8940	30.590	-0.183
0.4980	0.3057	14.331	-0.888				
methanol (1) + aniline (2) ; $T/K = 298.15$							
0.0502	0.0230	7.421	-0.172	0.5508	0.3530	15.126	-0.922
0.1006	0.0474	7.872	-0.346	0.5977	0.3979	16.295	-0.903
0.1516	0.0736	8.391	-0.499	0.6507	0.4532	17.801	-0.814
0.2003	0.1003	8.934	-0.640	0.6971	0.5059	19.188	-0.777
0.2510	0.1297	9.592	-0.735	0.7501	0.5718	20.997	-0.657
0.3024	0.1617	10.297	-0.850	0.7997	0.6398	22.825	-0.571
0.3489	0.1925	11.059	-0.877	0.8497	0.7155	24.895	-0.440
0.3976	0.2270	11.888	-0.932	0.8992	0.7987	27.127	-0.340
0.4504	0.2672	12.929	-0.921	0.9500	0.8942	29.693	-0.220
0.4980	0.3062	13.908	-0.941				
methanol (1) + aniline (2) ; $T/K = 303.15$							
0.0502	0.0230	7.273	-0.174	0.5508	0.3532	14.668	-0.970
0.1006	0.0475	7.702	-0.352	0.5977	0.3982	15.814	-0.941
0.1516	0.0737	8.196	-0.508	0.6507	0.4535	17.248	-0.878
0.2003	0.1004	8.718	-0.649	0.6971	0.5062	18.600	-0.834
0.2510	0.1299	9.344	-0.755	0.7501	0.5721	20.353	-0.716
0.3024	0.1618	10.022	-0.868	0.7997	0.6400	22.136	-0.617
0.3489	0.1927	10.751	-0.906	0.8497	0.7157	24.131	-0.500
0.3976	0.2272	11.554	-0.958	0.8992	0.7989	26.324	-0.371
0.4504	0.2674	12.548	-0.962	0.9500	0.8943	28.809	-0.253
0.4980	0.3064	13.497	-0.980				
propan-1-ol (1) + aniline (2) ; $T/K = 293.15$							
0.0498	0.0412	7.463	-0.254	0.5494	0.5001	12.311	-1.871
0.0994	0.0830	7.802	-0.504	0.5998	0.5515	13.043	-1.864
0.1508	0.1272	8.175	-0.754	0.6507	0.6045	13.868	-1.785
0.2002	0.1704	8.558	-0.980	0.7005	0.6574	14.724	-1.674
0.2478	0.2128	8.952	-1.183	0.7505	0.7117	15.669	-1.494

0.3001	0.2602	9.421	-1.382	0.8004	0.7669	16.650	-1.291
0.3518	0.3081	9.926	-1.552	0.8498	0.8228	17.713	-1.016
0.4015	0.3550	10.446	-1.692	0.8998	0.8805	18.844	-0.697
0.4500	0.4017	11.014	-1.782	0.9502	0.9400	20.026	-0.354
0.5003	0.4510	11.632	-1.859				
propan-1-ol (1) + aniline (2) ; T/K = 298.15							
0.0498	0.0413	7.315	-0.248	0.5494	0.5003	11.933	-1.846
0.0994	0.0831	7.636	-0.493	0.5998	0.5517	12.636	-1.839
0.1508	0.1273	7.992	-0.736	0.6507	0.6047	13.424	-1.768
0.2002	0.1705	8.357	-0.956	0.7005	0.6576	14.246	-1.663
0.2478	0.2129	8.732	-1.155	0.7505	0.7118	15.153	-1.489
0.3001	0.2604	9.178	-1.352	0.8004	0.7671	16.100	-1.291
0.3518	0.3083	9.659	-1.520	0.8498	0.8229	17.125	-1.022
0.4015	0.3552	10.157	-1.657	0.8998	0.8806	18.222	-0.706
0.4500	0.4019	10.693	-1.753	0.9502	0.9400	19.375	-0.358
0.5003	0.4512	11.289	-1.825				
propan-1-ol (1) + aniline (2) ; T/K = 303.15							
0.0498	0.0413	7.171	-0.242	0.5494	0.5005	11.564	-1.817
0.0994	0.0832	7.476	-0.481	0.5998	0.5519	12.243	-1.806
0.1508	0.1273	7.815	-0.716	0.6507	0.6049	12.987	-1.751
0.2002	0.1706	8.164	-0.929	0.7005	0.6578	13.783	-1.642
0.2478	0.2130	8.518	-1.126	0.7505	0.7120	14.645	-1.485
0.3001	0.2606	8.944	-1.319	0.8004	0.7672	15.565	-1.282
0.3518	0.3084	9.399	-1.485	0.8498	0.8230	16.550	-1.023
0.4015	0.3554	9.878	-1.617	0.8998	0.8807	17.609	-0.713
0.4500	0.4020	10.382	-1.719	0.9502	0.9400	18.728	-0.365
0.5003	0.4514	10.956	-1.787				
pentan-1-ol (1) + aniline (2) ; T/K = 293.15							
0.0574	0.0674	7.377	-0.338	0.5470	0.5891	9.890	-2.318
0.0993	0.1157	7.548	-0.583	0.6010	0.6414	10.287	-2.371
0.1484	0.1714	7.749	-0.862	0.6509	0.6888	10.790	-2.276
0.2005	0.2294	7.972	-1.138	0.7004	0.7351	11.278	-2.187
0.2513	0.2849	8.188	-1.400	0.7512	0.7819	11.873	-1.995
0.3013	0.3386	8.415	-1.636	0.8004	0.8264	12.501	-1.750
0.3485	0.3884	8.651	-1.829	0.8506	0.8711	13.219	-1.417
0.4009	0.4427	8.929	-2.018	0.8999	0.9143	13.979	-1.029
0.4488	0.4915	9.215	-2.152	0.9501	0.9576	14.848	-0.533
0.5009	0.5437	9.550	-2.267				
pentan-1-ol (1) + aniline (2) ; T/K = 298.15							
0.0574	0.0674	7.230	-0.324	0.5470	0.5892	9.595	-2.216
0.0993	0.1158	7.392	-0.557	0.6010	0.6414	9.966	-2.271
0.1484	0.1715	7.581	-0.822	0.6509	0.6889	10.440	-2.184
0.2005	0.2295	7.793	-1.083	0.7004	0.7352	10.901	-2.101
0.2513	0.2850	7.996	-1.333	0.7512	0.7819	11.460	-1.923
0.3013	0.3387	8.210	-1.557	0.8004	0.8265	12.059	-1.688
0.3485	0.3885	8.432	-1.741	0.8506	0.8712	12.736	-1.375
0.4009	0.4428	8.694	-1.922	0.8999	0.9144	13.465	-0.999
0.4488	0.4916	8.960	-2.054	0.9501	0.9576	14.295	-0.521

0.5009	0.5438	9.275	−2.165				
pentan-1-ol (1) + aniline (2) ; $T/K = 303.15$							
0.0574	0.0675	7.088	−0.308	0.5470	0.5892	9.305	−2.114
0.0993	0.1158	7.242	−0.527	0.6010	0.6415	9.657	−2.165
0.1484	0.1715	7.418	−0.780	0.6509	0.6889	10.100	−2.087
0.2005	0.2295	7.619	−1.026	0.7004	0.7352	10.538	−2.006
0.2513	0.2850	7.808	−1.265	0.7512	0.7820	11.058	−1.847
0.3013	0.3387	8.013	−1.474	0.8004	0.8265	11.628	−1.620
0.3485	0.3885	8.218	−1.653	0.8506	0.8712	12.263	−1.330
0.4009	0.4429	8.465	−1.826	0.8999	0.9144	12.962	−0.964
0.4488	0.4917	8.714	−1.953	0.9501	0.9577	13.752	−0.508
0.5009	0.5438	9.012	−2.057				

^a Standard uncertainties (u): $u(T) = 0.02$ K; $u(p) = 1$ kPa; $u(f) = 20$ Hz; $u(x_i) = 0.0005$; $u(\phi_i) = 0.004$. Relative standard uncertainty (u_r): $u_r(\varepsilon_r) = 0.003$. Relative expanded uncertainty at 0.95 confidence level (U_r): $U_r(\varepsilon_r^E) = 0.03$.

Table 5

Volume fractions of alkan-1-ol (ϕ_1), refractive indices at the sodium D-line (n_D) and excess refractive indices at the sodium D-line (n_D^E) of alkan-1-ol (1) + aniline (2) liquid mixtures as functions of the mole fraction of the alkan-1-ol, x_1 , at temperature T and pressure $p = 0.1$ MPa. ^a

x_1	ϕ_1	n_D	$10^5 n_D^E$	x_1	ϕ_1	n_D	$10^5 n_D^E$
methanol (1) + aniline (2) ; $T/K = 293.15$							
0.0519	0.0237	1.58144	51	0.5457	0.3478	1.50271	86
0.0974	0.0457	1.57619	50	0.6459	0.4474	1.47749	79
0.1546	0.0751	1.56942	76	0.7501	0.5713	1.44514	34
0.2524	0.1303	1.55609	73	0.7981	0.6370	1.42737	-22
0.3471	0.1909	1.54138	74	0.8488	0.7136	1.40674	-53
0.4539	0.2695	1.52214	81	0.8989	0.7978	1.38391	-67
0.5022	0.3093	1.51233	87	0.9472	0.8884	1.35897	-78
methanol (1) + aniline (2) ; $T/K = 298.15$							
0.0519	0.0238	1.57872	58	0.5457	0.3483	1.50113	198
0.0974	0.0458	1.57367	76	0.6459	0.4480	1.47586	182
0.1546	0.0752	1.56691	101	0.7501	0.5718	1.44339	115
0.2021	0.1013	1.56081	117	0.7981	0.6375	1.42550	42
0.2524	0.1306	1.55384	125	0.8488	0.7141	1.40485	5
0.3471	0.1913	1.53929	141	0.8989	0.7982	1.38208	-12
0.3988	0.2279	1.53051	157	0.9472	0.8886	1.35694	-54
0.4539	0.2699	1.52030	169				
methanol (1) + aniline (2) ; $T/K = 303.15$							
0.0519	0.0238	1.57630	84	0.6459	0.4482	1.47401	246
0.0974	0.0459	1.57114	92	0.7501	0.5721	1.44193	213
0.1546	0.0753	1.56449	127	0.7981	0.6378	1.42425	157
0.2021	0.1014	1.55839	141	0.8488	0.7143	1.40373	125
0.3009	0.1609	1.54421	155	0.8989	0.7984	1.38083	90
0.3988	0.2281	1.52834	201	0.9472	0.8888	1.35538	11
0.5022	0.3100	1.50847	229				
propan-1-ol (1) + aniline (2) ; $T/K = 293.15$							
0.0548	0.0454	1.57744	-53	0.6014	0.5532	1.47692	-160
0.1050	0.0878	1.56918	-73	0.6488	0.6025	1.46704	-147
0.1455	0.1226	1.56224	-102	0.7530	0.7144	1.44442	-110
0.2543	0.2186	1.54332	-145	0.8481	0.8208	1.42262	-70
0.3488	0.3053	1.52617	-171	0.8889	0.8678	1.41298	-43
0.4500	0.4017	1.50708	-180	0.9521	0.9422	1.39733	-23
0.5527	0.5034	1.48687	-170				
propan-1-ol (1) + aniline (2) ; $T/K = 298.15$							
0.0548	0.0454	1.57478	-44	0.6014	0.5534	1.47459	-150
0.1050	0.0879	1.56657	-60	0.6488	0.6027	1.46478	-134
0.1455	0.1227	1.55968	-87	0.7530	0.7146	1.44221	-101
0.2543	0.2188	1.54082	-128	0.8481	0.8209	1.42052	-60
0.3488	0.3055	1.52373	-154	0.8889	0.8679	1.41080	-44
0.4500	0.4019	1.50466	-168	0.9521	0.9423	1.39528	-17

0.5527	0.5036	1.48450	–160				
propan-1-ol (1) + aniline (2) ; $T/K = 303.15$							
0.0548	0.0455	1.57219	–35	0.6014	0.5535	1.47251	–120
0.1050	0.0879	1.56406	–47	0.6488	0.6029	1.46267	–107
0.1455	0.1228	1.55720	–70	0.7530	0.7147	1.44013	–80
0.2543	0.2189	1.53848	–104	0.8481	0.8211	1.41845	–43
0.3488	0.3056	1.52146	–128	0.8889	0.8680	1.40876	–29
0.4500	0.4020	1.50249	–137	0.9521	0.9423	1.39320	–14
0.5527	0.5038	1.48239	–128				
pentan-1-ol (1) + aniline (2) ; $T/K = 293.15$							
0.0528	0.0621	1.57551	–66	0.5534	0.5953	1.48081	–318
0.1002	0.1168	1.56558	–138	0.5969	0.6374	1.47341	–305
0.1465	0.1693	1.55630	–178	0.6495	0.6875	1.46464	–282
0.1979	0.2266	1.54608	–224	0.6989	0.7337	1.45645	–266
0.2508	0.2844	1.53575	–266	0.7523	0.7829	1.44793	–223
0.2961	0.3331	1.52722	–279	0.7980	0.8243	1.44063	–196
0.3543	0.3945	1.51621	–315	0.8451	0.8663	1.43337	–149
0.4008	0.4426	1.50770	–326	0.8996	0.9141	1.42504	–99
0.4542	0.4970	1.49814	–327	0.9487	0.9564	1.41763	–53
0.4966	0.5394	1.49066	–326				
pentan-1-ol (1) + aniline (2) ; $T/K = 298.15$							
0.0528	0.0621	1.57276	–68	0.5534	0.5954	1.47848	–315
0.1002	0.1168	1.56294	–133	0.5969	0.6375	1.47113	–301
0.1465	0.1693	1.55362	–180	0.6495	0.6876	1.46240	–278
0.1979	0.2266	1.54353	–217	0.6989	0.7338	1.45431	–256
0.2508	0.2845	1.53314	–268	0.7523	0.7829	1.44579	–219
0.2961	0.3331	1.52455	–293	0.7980	0.8243	1.43851	–193
0.3543	0.3945	1.51372	–315	0.8451	0.8663	1.43129	–146
0.4008	0.4427	1.50515	–334	0.8996	0.9141	1.42301	–94
0.4542	0.4971	1.49568	–330	0.9487	0.9565	1.41560	–50
0.4966	0.5395	1.48826	–326				
pentan-1-ol (1) + aniline (2) ; $T/K = 303.15$							
0.0528	0.0621	1.57005	–73	0.5534	0.5954	1.47615	–317
0.1002	0.1168	1.56032	–133	0.5969	0.6375	1.46881	–304
0.1465	0.1694	1.55101	–180	0.6495	0.6876	1.46008	–284
0.1979	0.2266	1.54089	–226	0.6989	0.7338	1.45198	–266
0.2508	0.2845	1.53061	–269	0.7523	0.7830	1.44353	–224
0.2961	0.3332	1.52205	–292	0.7980	0.8243	1.43634	–194
0.3543	0.3946	1.51128	–312	0.8451	0.8663	1.42912	–150
0.4008	0.4427	1.50275	–332	0.8996	0.9141	1.42089	–96
0.4542	0.4971	1.49329	–331	0.9487	0.9565	1.41352	–51
0.4966	0.5395	1.48594	–323				

^a Standard uncertainties (u): $u(T) = 0.02$ K; $u(p) = 1$ kPa; $u(x_1) = 0.0005$; $u(\phi_1) = 0.004$, $u(n_D) = 0.00008$. Expanded uncertainty at 0.95 confidence level (U): $U(n_D^E) = 0.0002$.

Table 6

Volume fraction of alkan-1-ol (ϕ_1) and temperature derivative of the excess relative permittivity at frequency $f = 1$ MHz ($(\partial\epsilon_r^E/\partial T)_p$) of alkan-1-ol (1) + aniline (2) liquid mixtures as functions of the mole fraction of the alkan-1-ol (x_1) at temperature T and pressure $p = 0.1$ MPa. ^a

x_1	ϕ_1	$(\partial\epsilon_r^E/\partial T)_p$	x_1	ϕ_1	$(\partial\epsilon_r^E/\partial T)_p$
methanol (1) + aniline (2) ; $T/K = 298.15$					
0.0502	0.0230	-0.0007	0.5508	0.3530	-0.0104
0.1006	0.0474	-0.0013	0.5977	0.3979	-0.0101
0.1516	0.0736	-0.0018	0.6507	0.4532	-0.0130
0.2003	0.1003	-0.0023	0.6971	0.5059	-0.0135
0.2510	0.1297	-0.0040	0.7501	0.5718	-0.0120
0.3024	0.1617	-0.0046	0.7997	0.6398	-0.0110
0.3489	0.1925	-0.0058	0.8497	0.7155	-0.0111
0.3976	0.2270	-0.0064	0.8992	0.7987	-0.0085
0.4504	0.2672	-0.0092	0.9500	0.8942	-0.0070
0.4980	0.3062	-0.0092			
propan-1-ol (1) + aniline (2) ; $T/K = 298.15$					
0.0498	0.0413	0.0012	0.5494	0.5003	0.0054
0.0994	0.0831	0.0023	0.5998	0.5517	0.0058
0.1508	0.1273	0.0038	0.6507	0.6047	0.0034
0.2002	0.1705	0.0051	0.7005	0.6576	0.0032
0.2478	0.2129	0.0057	0.7505	0.7118	0.0009
0.3001	0.2604	0.0063	0.8004	0.7671	0.0009
0.3518	0.3083	0.0067	0.8498	0.8229	-0.0007
0.4015	0.3552	0.0075	0.8998	0.8806	-0.0016
0.4500	0.4019	0.0063	0.9502	0.9400	-0.0011
0.5003	0.4512	0.0072			
pentan-1-ol (1) + aniline (2) ; $T/K = 298.15$					
0.0574	0.0674	0.0030	0.5470	0.5892	0.0204
0.0993	0.1158	0.0056	0.6010	0.6414	0.0206
0.1484	0.1715	0.0082	0.6509	0.6889	0.0189
0.2005	0.2295	0.0112	0.7004	0.7352	0.0181
0.2513	0.2850	0.0135	0.7512	0.7819	0.0148
0.3013	0.3387	0.0162	0.8004	0.8265	0.0130
0.3485	0.3885	0.0176	0.8506	0.8712	0.0087
0.4009	0.4428	0.0192	0.8999	0.9144	0.0065
0.4488	0.4916	0.0199	0.9501	0.9576	0.0025
0.5009	0.5438	0.0210			

^a Standard uncertainties (u): $u(T) = 0.02$ K; $u(p) = 1$ kPa; $u(f) = 20$ Hz; $u(x_1) = 0.0005$; $u(\phi_1) = 0.004$; $u[(\partial\epsilon_r^E/\partial T)_p] = 0.0008$ K⁻¹.

Table 7

Coefficients A_i and standard deviations, $\sigma(F^E)$ (equation (12)), for the representation of F^E at temperature T and pressure $p = 0.1$ MPa for alkan-1-ol (1) + aniline liquid mixtures by equation (11).

Property F^E	alkan-1-ol	T/K	A_0	A_1	A_2	A_3	A_4	A_5	A_6	$\sigma(F^E)$
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	methanol	298.15	-3.607	-1.39	-0.75	-0.59	-0.4			0.003
	propan-1-ol	298.15	-2.370	-0.73	-0.49	-0.33				0.004
	pentan-1-ol	298.15	-0.963	-0.21	-0.19					0.005
$\kappa_S^E/\text{TPa}^{-1}$	methanol	298.15	-438.7	-434	-344	-201	-105	-186	-160	0.14
	propan-1-ol	298.15	-289.9	-125	-63	-48	-33			0.15
	pentan-1-ol	298.15	-149.0	4	-19					0.3
$c^E/\text{m}\cdot\text{s}^{-1}$	methanol	298.15	556.0	187.4	82	37	34			0.12
	propan-1-ol	298.15	346.0	-52.0	45	9	15			0.13
	pentan-1-ol	298.15	179.1	-91	68	-30				0.4
\mathcal{E}_r^E	methanol	293.15	-3.54	0.57						0.018
		298.15	-3.77	0.31						0.02
		303.15	-3.95							0.02
	propan-1-ol	293.15	-7.43	-1.86	1.05	0.8				0.007
		298.15	-7.286	-1.97	0.6	0.76	0.6			0.005
		303.15	-7.146	-2.01	0.48	0.3	0.48	0.5		0.0017
	pentan-1-ol	293.15	-9.09	-3.43	0.19	0.7				0.011
		298.15	-8.68	-3.39	0.04	0.6				0.010
		303.15	-8.25	-3.31	-0.09	0.5				0.009
	methanol	293.15	369	207	-606	-1822				11
		298.15	762	408	-690	-1903				11
		303.15	923	658	89	-1396				12
$10^5 n_D^E$	propan-1-ol	293.15	-694	196						5
		298.15	-657	151	158					4
		303.15	-535	147	176					3
	pentan-1-ol	293.15	-1305	190						5
		298.15	-1302	230						5
		303.15	-1311	212						4
	methanol	298.15	-0.037	-0.049	-0.027					0.0008
		propan-1-ol	298.15	0.0266	-0.023	-0.030				0.0005
		pentan-1-ol	298.15	0.0834	0.008	-0.028				0.0005

Table 8

Literature data on density (ρ), speed of sound (c), refractive index at the sodium D-line (n_D) and relative permittivity (ϵ_r) of alkan-1-ol (1) + aniline at pressure 0.1 MPa and temperature T . Symbols: n , number of carbon atoms of the alkan-1-ol; F^E , excess property ($F = V_m, n_D, \epsilon_r$); Δc , deviation from mole-fraction linearity of the speed of sound.

Ref.	Year	n	Properties	T/K	Comparison with our data
[20]	1964	1,2	ϵ_r	293.15	Lower ϵ_r^E ($n = 1$).
[21]	1967	1	ρ, n_D	293.15, 303.15, 313.15	Good agreement in V_m^E . Large data scattering in n_D^E .
[22]	1971	1	ρ, c	308.15	Good agreement in V_m^E . Good agreement in Δc .
[23]	1971	4	ρ, n_D	298.15, 303.15, 308.15, 313.15	V_m^E agrees with our n variation and is close to ref. [33]. Symmetry of the curve also agrees with ours. n_D^E agrees rather well with our n variation, but large data scattering.
[24]	1984	3,4	ϵ_r	307.15	Comparable ϵ_r^E values ($n = 3$), but large data scattering.
[25]	1993	3,4	ϵ_r	307.15	ϵ_r^E not computable (ϵ_r of pure compounds not provided).
[26]	1994	1	ϵ_r	283.15, 293.15, 303.15, 313.15	Much lower ϵ_r^E , and large data scattering.
[27]	1994	5,6,7,8	ϵ_r	303.15	ϵ_r^E not computable (ϵ_r of pure compounds not provided).
[28]	1999	2,3,4,6,7	ϵ_r	283.15, 293.15, 303.15, 313.15	Much higher ϵ_r^E ($n = 3$), and large data scattering.
[29]	2000	3,4,5,6,7,8	ϵ_r	303.15	ϵ_r^E not computable (ϵ_r of pure compounds not provided).
[30]	2000	5	ρ	293.15	Good agreement in V_m^E .
[31]	2001	3	ρ	294.15, 298.15, 303.15, 308.15, 313.15	Good agreement in V_m^E .
[32]	2003	3	ϵ_r	293.15, 303.15, 313.15, 323.15	Comparable ϵ_r^E values, but large data scattering.
[33]	2003	4	ρ	298.15, 303.15, 308.15, 313.15	V_m^E agrees with our n variation and is close to ref. [23]. Symmetry of the curve does not agree with ours.
[34]	2007	1	ρ	298.15	Positive V_m^E , abnormally high.
[35]	2007	3	ρ	293.15, 298.15, 303.15, 308.15, 313.15, 318.15	Higher V_m^E .
[36]	2007	3	c	293.15, 298.15, 303.15, 308.15, 313.15, 318.15	Comparable Δc values.

[37]	2010	3	n_D	293.15, 298.15, 303.15, 308.15, 313.15, 318.15	Lower n_D^E , opposite symmetry of the curve.
[38]	2019	3,4,5,6	ρ, c	303.15, 308.15, 313.15, 318.15 (for ρ) 303.15, 313.15 (for c)	Abnormally high V_m^E values, positive for $n = 4,5,6$. Large data scattering in Δc ; values lower than ours for $n = 3$ and comparable for $n = 5$.

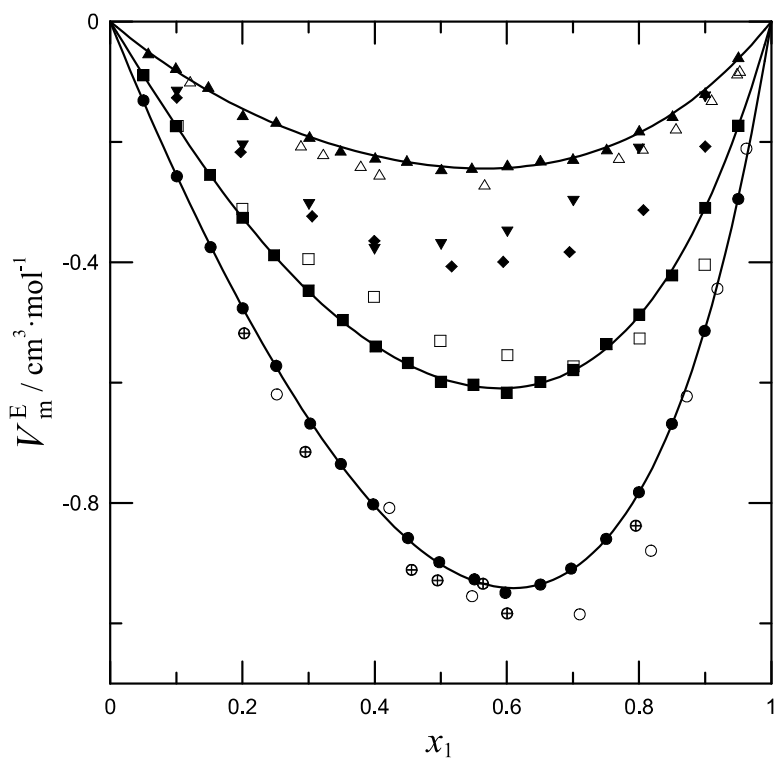


Figure 1. Excess molar volume (V_m^E) of alkan-1-ol (1) + aniline (2) liquid mixtures as a function of the alkan-1-ol mole fraction (x_1) at 298.15 K and 0.1 MPa. Symbols, experimental values: (●), methanol (this work); (■), propan-1-ol (this work); (▲), pentan-1-ol (this work); (○), methanol ([21], $T = 293.15$ K); (⊕), methanol ([22], $T = 308.15$ K); (□), propan-1-ol ([31]); (◆), butan-1-ol ([23]); (▼), butan-1-ol ([33]); (Δ), pentan-1-ol ([30], $T = 293.15$ K). Solid lines, calculations with equation (11) using the coefficients from Table 7.

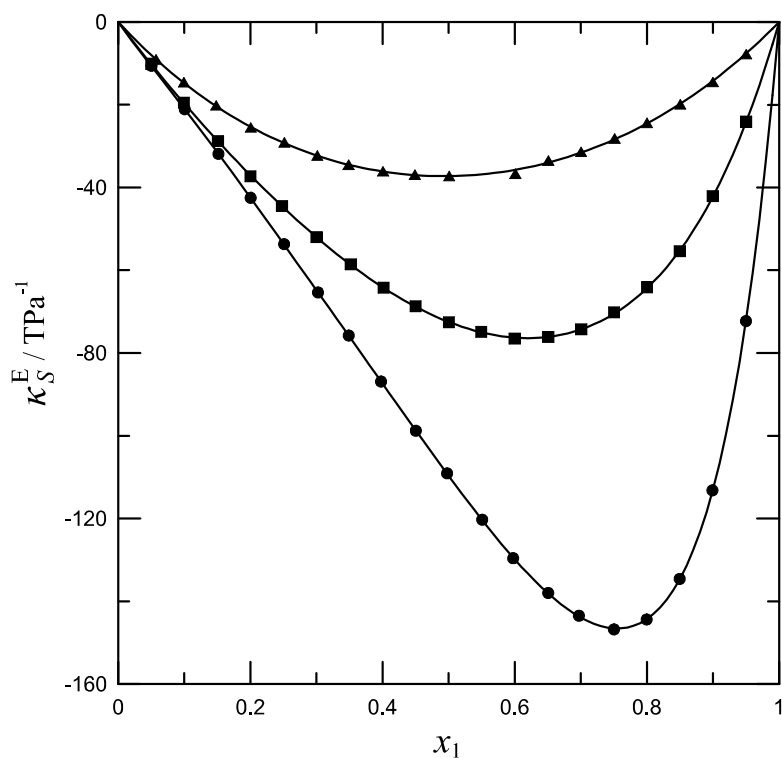


Figure 2. Excess isentropic compressibility (κ_S^E) of alkan-1-ol (1) + aniline (2) liquid mixtures as a function of the alkan-1-ol mole fraction (x_1) at 298.15 K and 0.1 MPa. Full symbols, experimental values (this work): (●), methanol; (■), propan-1-ol; (▲), pentan-1-ol. Solid lines, calculations with equation (11) using the coefficients from Table 7.

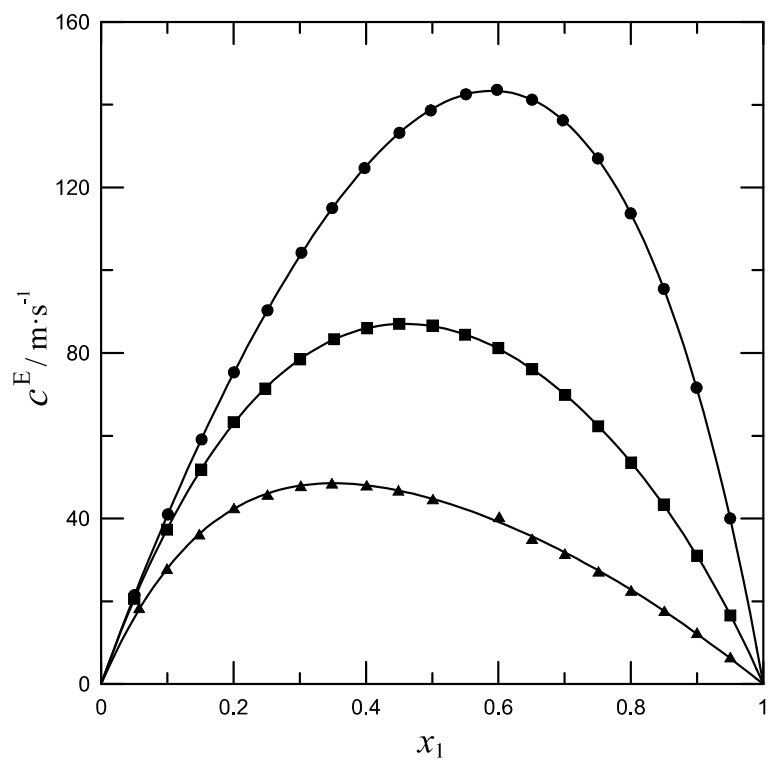


Figure 3. Excess speed of sound (c^E) of alkan-1-ol (1) + aniline (2) liquid mixtures as a function of the alkan-1-ol mole fraction (x_1) at 298.15 K and 0.1 MPa. Full symbols, experimental values (this work): (●), methanol; (■), propan-1-ol; (▲), pentan-1-ol. Solid lines, calculations with equation (11) using the coefficients from Table 7.

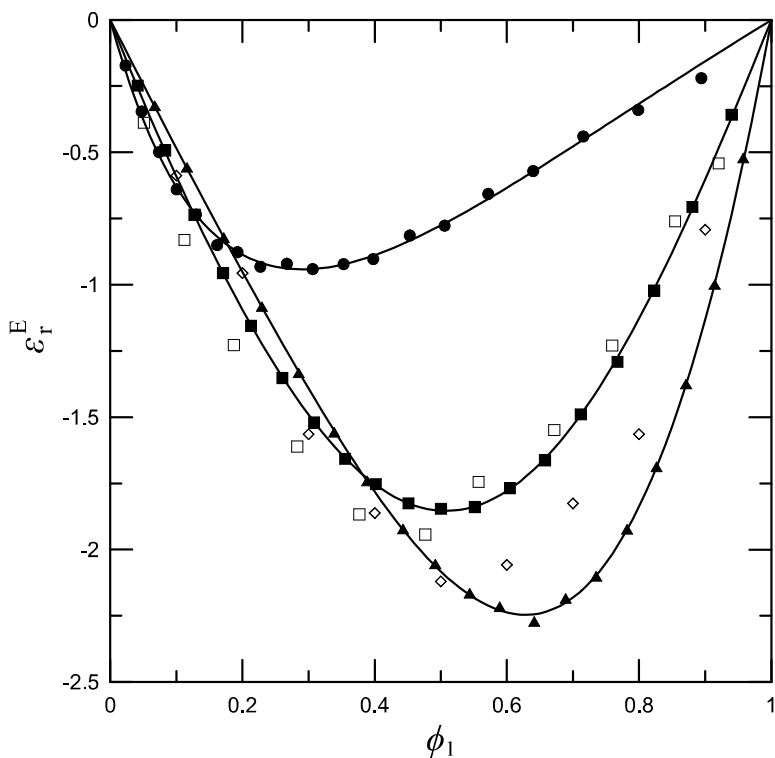


Figure 4. Excess relative permittivity (ϵ_r^E) of alkan-1-ol (1) + aniline (2) liquid mixtures as a function of the alkan-1-ol volume fraction (ϕ_1) at 298.15 K, 0.1 MPa, and 1 MHz. Symbols, experimental values: (●), methanol (this work); (■), propan-1-ol (this work); (▲), pentan-1-ol (this work); (□), propan-1-ol ([24], $T = 307.15$ K); (◇), propan-1-ol ([32], $T = 303.15$ K). Solid lines, calculations with equation (11) using the coefficients from Table 7.

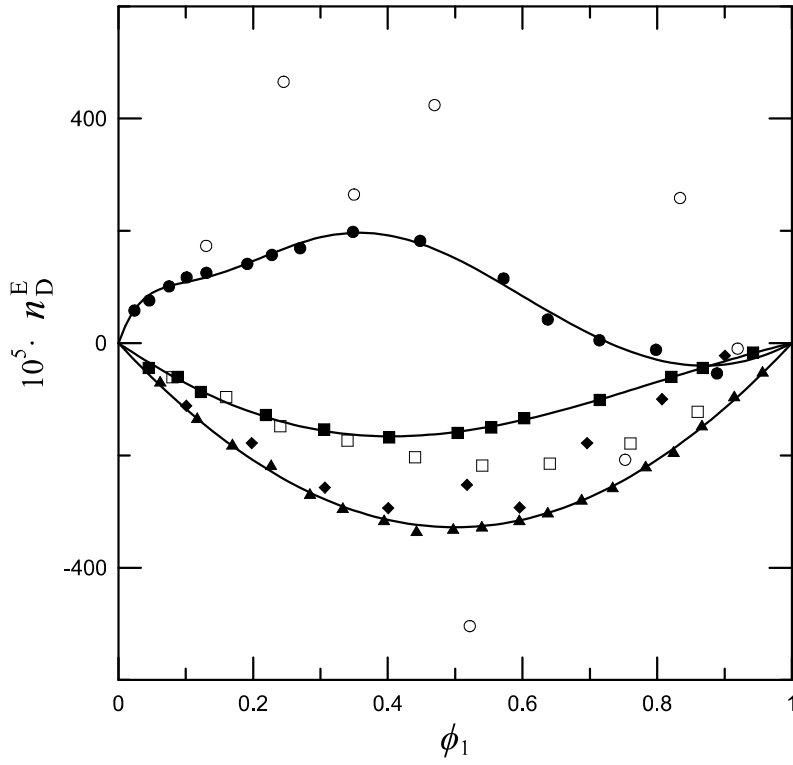


Figure 5. Excess refractive index at the sodium D-line (n_D^E) of alkan-1-ol (1) + aniline (2) liquid mixtures as a function of the alkan-1-ol volume fraction (ϕ_1) at 298.15 K and 0.1 MPa. Full symbols, experimental values: (\bullet), methanol (this work); (\blacksquare), propan-1-ol (this work); (\blacktriangle), pentan-1-ol (this work); (\circ), methanol ([21], $T = 303.15$ K); (\square), propan-1-ol ([37]); (\blacklozenge), butan-1-ol ([23]). Solid lines, calculations with equation (11) using the coefficients from Table 7.

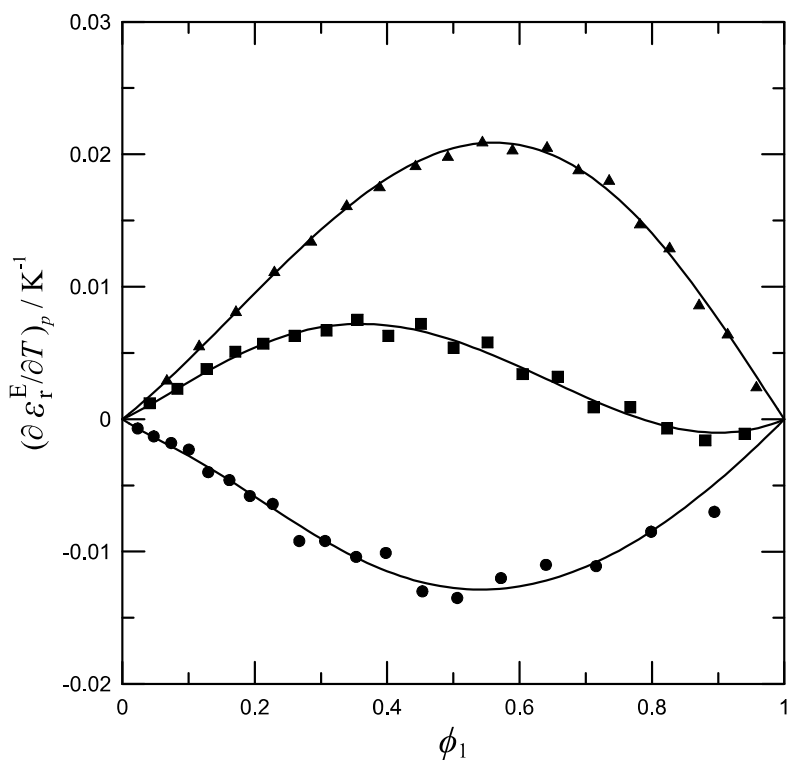


Figure 6. Temperature derivative of the excess relative permittivity $((\partial \epsilon_r^E / \partial T)_p)$ of alkan-1-ol (1) + aniline (2) liquid mixtures as a function of the alkan-1-ol volume fraction (ϕ_1) at 298.15 K, 0.1 MPa, and 1 MHz. Full symbols, experimental values (this work): (●), methanol; (■), propan-1-ol; (▲), pentan-1-ol. Solid lines, calculations with equation (11) using the coefficients from Table 7.

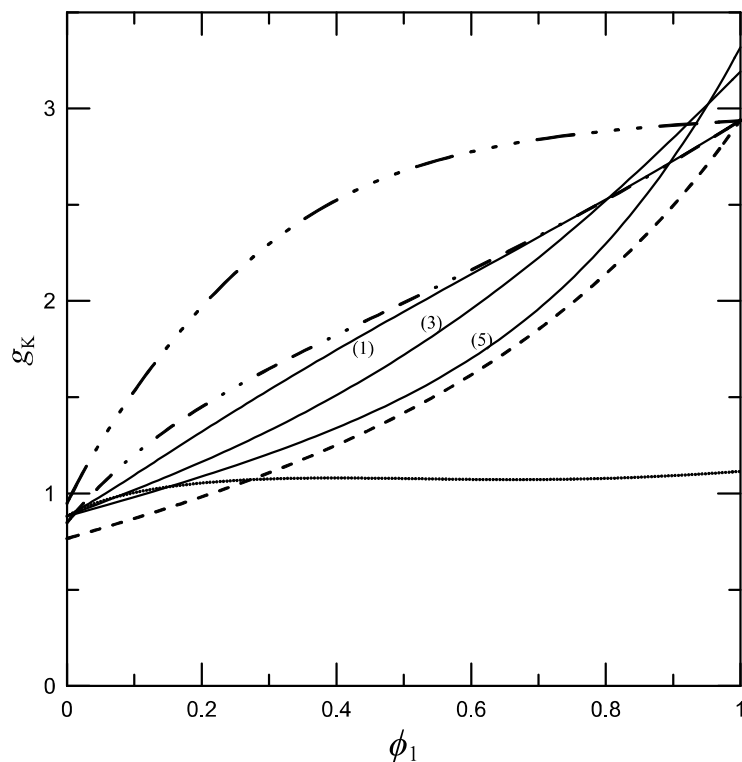


Figure 7. Kirkwood correlation factor (g_K) of several (1) + (2) liquid mixtures as a function of the volume fraction of compound (1), ϕ_1 , at 0.1 MPa and 298.15 K: Solid lines, alkan-1-ol (1) + aniline (2) (this work); the numbers in parentheses indicate the number of carbon atoms of the alkan-1-ol. (— — —), methanol (1) + benzonitrile (2) (293.15 K, [20]). (·····), *N,N*-dimethylformamide (1) + aniline (2) [78]. (— · — · —), methanol (1) + pyridine (2) [68]. (— ··· —), methanol (1) + hexan-1-amine (2) [13].

Alkan-1-ol + aniline liquid mixtures, $T = (293.15 \text{ K to } 303.15) \text{ K}$

Positive
deviations from
Raoult's law

Homocoordination and
structural effects

$$U_{m,V}^E > 0$$

$$V_m^E < 0$$

$$\kappa_S^E < 0$$

$$\varepsilon_r^E < 0$$