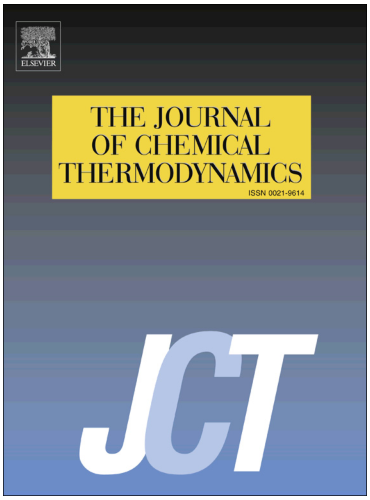

Thermodynamics of mixtures with strongly negative deviations from Raoult's law. XVII. Permittivities and refractive indices for alkan-1-ol + *N,N*-diethylethanamine systems at (293.15-303.15) K. Application of the Kirkwood-Fröhlich model

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Abstract

Relative permittivities at 1 MHz, ε_{r}, at 0.1 MPa and (293.15-303.15) K and refractive indices, n_{D}, at similar conditions have been measured for the alkan-1-ol (methanol, propan-1-ol, butan-1-ol, pentan-1-ol or heptan-1-ol) + *N,N*-diethylethanamine (TEA) systems. Positive values of the excess permittivities, $\varepsilon_{\mathrm{r}}^{\mathrm{E}}$, are encountered for the methanol system at high alcohol concentrations. The remaining mixtures are characterized by negative $\varepsilon_{\mathrm{r}}^{\mathrm{E}}$ values over the whole composition range. At ϕ_1 (volume fraction) = 0.5, $\varepsilon_{\mathrm{r}}^{\mathrm{E}}$ changes in the order: methanol > propan-1-ol > butan-1-ol < pentan-1-ol < heptan-1-ol. Mixtures formed by alkan-1-ol and an isomeric amine, hexan-1-amine (HxA) or *N*-propylpropan-1-amine (DPA) or cyclohexylamine, behave similarly. This has been explained in terms of the lower and weaker self-association of longer alkan-1-ols. From the permittivity data, it is shown that: (i) (alkan-1-ol)-TEA interactions contribute positively to $\varepsilon_{\mathrm{r}}^{\mathrm{E}}$; (ii) TEA is an effective breaker of the network of the alkan-1-ols; (iii) structural effects, which are very important for the volumetric and calorimetric data of alkan-1-ol + TEA systems, are also relevant when evaluating dielectric data. This is confirmed by the comparison of $\varepsilon_{\mathrm{r}}^{\mathrm{E}}$ measurements for alkan-1-ol + aliphatic amine mixtures; (iv) the aromaticity effect (i.e., the replacement of TEA by pyridine in systems with a given alkan-1-ol) leads to an increase of the mixture polarization. Calculations conducted in the framework of the Kirkwood-Fröhlich model are consistent with the previous statements.

Keywords: alkan-1-ol; *N,N*-diethylethanamine; permittivity; refractive index; Kirkwood correlation factor.

1. Introduction

Alkan-1-ol + linear primary or secondary amine mixtures are characterized by showing strongly negative deviations from Raoult's law [1]. As a consequence, their excess molar Gibbs energies, G_m^E, and enthalpies, H_m^E, are both negative, the former even at rather high temperatures. For example, for the methanol + butan-1-amine mixture at equimolar composition, $G_m^E = -799$ J·mol-1 ($T = 348.15$ K) [2] and $H_m^E = -3767$ J.mol-1 ($T = 298.15$ K) [3]. On the other hand, this type of solutions is characterized by large solvation effects. In fact, the equilibrium constants, K_{AB}, related to the formation of linear chains of the type $A_n\text{(alkan-1-ol)} + B_m\text{(linear amine)} \rightleftarrows A_nB_m$, calculated by means of the ERAS model [1,4], are rather large and the corresponding enthalpies of hydrogen bonds between alkan-1-ol and amine, Δh_{AB}^*, are large and negative [1,5-8], and the same occurs for Δv_{AB}^*, the association volume of component A with B. Thus, for the methanol + hexan-1-amine (HxA) system, K_{AB} = 2500 (T = 298.15 K); Δh_{AB}^* = –42.4 kJ·mol^{-1}; Δv_{AB}^*= 9.1 cm^3·mol^{-1} [5]. Interestingly, Δh_{AB}^* values are lower than those related to the H-bonds between alkan-1-ol molecules (–25.1 kJ·mol^{-1} [1,3,4]). That is, (alkan-1-ol)-amine interactions are stronger than those between molecules of alkan-1-ol, which explains the large and negative H_m^E values observed for these systems. Hereafter, we are referring, except when indicated, to excess molar functions at equimolar composition and 298.15 K.

Alkan-1-ol + *N,N*-diethylethanamine (TEA) mixtures are somewhat different. Some of their most relevant features are the following. (i) G_m^E values are usually positive: 284 J·mol^{-1} for the methanol-containing mixture (T = 303.2 K) [9]; (ii) H_m^E values are negative but lower in absolute value than for alkan-1-ol + linear primary or secondary amine systems: –1871 J·mol^{-1} [10], and –1520 J·mol^{-1} [11] for the solutions with methanol, or ethanol, respectively; (iii) Results on V_m^E, excess molar volume, are much more negative than for the systems with the isomeric amines HxA or *N*-propylpropan-1-amine (DPA). For example, V_m^E (propan-1-ol) / 10^{-6} m^3·mol^{-1} = –1.147 (HxA) [5]; –1.550 (DPA) [7]; –1.997 (TEA) [5]. This has been explained in terms of strong structural effects in systems with TEA, which lead to excess molar internal energies at constant volume (–846 J·mol^{-1} for the propan-1-ol + TEA mixture [5]) which largely differ from the corresponding H_m^E results (–1413 J·mol^{-1} [12]).

We have investigated in detail alkan-1-ol + amine systems by means of different models [1,5-8,13-16]: DISQUAC [17,18], ERAS [1,3], the concentration-concentration structure factor, $S_{CC}(0)$ [19,20], or the Kirkwood-Buff formalism [21]. In addition, we have reported data on

V_m^E [5,7,8], vapor-liquid equilibria [22] or viscosity [23-25]. More recently, we have determined permittivities, ε_r, and refractive indices, n_D, for alkan-1-ol + cyclohexylamine [26], or + HxA [27], or + DPA [28] mixtures. As a continuation, and in order to investigate the influence of the shape of TEA molecules on dielectric properties, here we provide ε_r and n_D measurements for methanol, or propan-1-ol, or butan-1-ol, or pentan-1-ol, or heptan-1-ol + TEA systems at (293.15-303.15) K. In addition, and as in previous applications [26-28], the ε_r and n_D results are used to investigate the systems using the Kirkwood-Fröhlich theory [29-32].

This type of studies is relevant for a better understanding of non-covalent interactions, i.e. hydrogen bonding. Hydrogen bonding leads to cooperative effects which are crucial in supramolecular chemistry and biochemistry [33,34]. Thus, such effects are essential for the characterization of association of molecules in the condensed phase [35,36] or of the DNA molecule [37]. Mixtures with amines are of particular interest, since the disruption of amino acids releases amines and proteins that are usually bound to DNA polymers contain several amine groups [38]. They are also used for CO_2 capture [39]. Finally, we remark that many of the ions of the technically important ionic liquids include amine groups [40].

2. Experimental

2.1 Materials

Pure compounds were used in the experiments without further purification. Information about their source and purity is shown in Table 1. Water contents of the employed chemicals was determined using the Karl-Fischer method. The relative standard uncertainty of these measurements is estimated to be 0.025. In the present work, the water contents was ignored along calculations. Values of ε_r at 1 MHz, density (ρ) and n_D at the working temperatures and the dipole moments (μ) of the pure compounds are collected in Table 2. Comparison with literature values reveals a good agreement.

2.2 Apparatus and procedure

Binary mixtures were prepared by mass in small vessels of about 10 cm^3 using an analytical balance Sartorius MSU125p (weighing accuracy 10^{-8} kg), correcting the weighings for buoyancy effects. The standard uncertainty in the mole fraction is 0.0010. Molar quantities were calculated using the relative atomic mass Table of 2015 issued by the Commission on Isotopic Abundances and Atomic Weights (IUPAC) [41]. 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 cell (see below) was completely filled with the samples and appropriately closed to avoid their evaporation. The density of the pure compounds was measured along the experiments, remaining constant within the experimental uncertainty.

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

A RFM970 refractometer from Bellingham + Stanley was used for the experimental n_D determination. This device exploits the optical detection of the critical angle at the wavelength of the sodium D line (589.3 nm). A temperature stability of 0.02 K is guaranteed by Peltier modules. The calibration of the refractometer was performed using 2,2,4-trimethylpentane and toluene at (293.15 – 303.15) K, following the recommendations by Marsh [42]. The standard uncertainty of n_D is 0.00008.

Densities were obtained using a vibrating-tube densimeter and sound analyzer Anton Paar DSA 5000, which is automatically thermostated within 0.01 K. The calibration procedure has been described elsewhere [43]. The relative standard uncertainty of the ρ measurements is 0.0012.

The experimental device to determine ε_r consists of a 16452A cell –parallel-plate capacitor made of Nickel-plated cobalt (54% Fe, 17% Co, 29% Ni) with a ceramic insulator (alumina, Al_2O_3)–, which is filled with a sample volume of ≈ 4.8 cm^3 and connected by a 16048G test lead to a precision impedance analyzer 4294A, all of them from Agilent. The cell is immersed in a thermostatic bath LAUDA RE304, with a temperature stability of 0.02 K. Details about the equipment configuration and calibration are given elsewhere [44]. The relative standard uncertainty of the ε_r measurements (i.e. the repeatability) is 0.0001. The total 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 – 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. Results

The volume fraction of component *i*, ϕ_i, is calculated as $\phi_i = x_i V_{\mathrm{m}i}^* / \left(x_1 V_{\mathrm{m}1}^* + x_2 V_{\mathrm{m}2}^* \right)$, where x_i is the mole fraction of component i and $V_{\mathrm{m}i}^*$ is its molar volume. The derivative $\left(\partial \varepsilon_\mathrm{r} / \partial T \right)_p$ was calculated at 298.15 K as the slope of a linear regression of experimental ε_r values in the range (293.15 – 303.15) K. For an ideal mixture at the same temperature and pressure as the mixture under study, the relative permittivity, $\varepsilon_{\mathrm{r}}^{\mathrm{id}}$, the derivative $\left[\left(\partial\varepsilon_{\mathrm{r}}/\partial T\right)_p\right]^{\mathrm{id}}$, and the refractive index, $n_{\mathrm{D}}^{\mathrm{id}}$, are given by [45,46]:

$$\varepsilon_{\mathrm{r}}^{\mathrm{id}} = \phi_1\varepsilon_{\mathrm{r}1}^{*} + \phi_2\varepsilon_{\mathrm{r}2}^{*} \tag{1}$$

$$n_{\mathrm{D}}^{\mathrm{id}} = \left[\phi_1\left(n_{\mathrm{D}1}^{*}\right)^2 + \phi_2\left(n_{\mathrm{D}2}^{*}\right)^2\right]^{1/2} \tag{2}$$

$$\left[\left(\frac{\partial\varepsilon_{\mathrm{r}}}{\partial T}\right)_p\right]^{\mathrm{id}} = \left(\frac{\partial\varepsilon_{\mathrm{r}}^{\mathrm{id}}}{\partial T}\right)_p \tag{3}$$

where $\varepsilon_{\mathrm{r}i}^{*}$ and $n_{\mathrm{D}i}^{*}$ denote the relative permittivity and the refractive index of pure species i, and $\left(\partial\varepsilon_{\mathrm{r}}^{\mathrm{id}}/\partial T\right)_p$ is calculated from linear regressions as already mentioned. The corresponding excess functions, F^{E}, are calculated from these according to the equation:

$$F^{\mathrm{E}} = F - F^{\mathrm{id}} \quad , \quad F = \varepsilon_{\mathrm{r}},\, n_{\mathrm{D}},\, \left(\frac{\partial\varepsilon_{\mathrm{r}}}{\partial T}\right)_p \tag{4}$$

Table 3 collects ϕ_1, ε_{r} and $\varepsilon_{\mathrm{r}}^{\mathrm{E}}$ values of alkan-1-ol (1) + TEA (2) systems as functions of x_1, in the temperature range (293.15 – 303.15) K. Table 4 contains the experimental x_1, ϕ_1, n_{D} and $n_{\mathrm{D}}^{\mathrm{E}}$ values at the same conditions. The data of $\left[\left(\partial\varepsilon_{\mathrm{r}}/\partial T\right)_p\right]^{\mathrm{E}} = \left(\partial\varepsilon_{\mathrm{r}}^{\mathrm{E}}/\partial T\right)_p$ at 298.15 K are collected in Table S1 (supplementary material).

The F^{E} data were fitted to a Redlich-Kister equation [47] by unweighted linear least-squares regressions:

$$F^{\mathrm{E}} = x_1\left(1-x_1\right)\sum_{i=0}^{k-1} A_i\left(2x_1-1\right)^i \tag{5}$$

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 [48] at a 99.5% confidence level. Table 5 includes the parameters A_i obtained, and the standard deviations, $\sigma\left(F^{\mathrm{E}}\right)$, defined by:

$$\sigma\left(F^{\mathrm{E}}\right) = \left[\frac{1}{N-k}\sum_{j=1}^{N}\left(F_{\mathrm{cal},j}^{\mathrm{E}} - F_{\mathrm{exp},j}^{\mathrm{E}}\right)^2\right]^{1/2} \tag{6}$$

where the index j takes values for each of the N experimental data $F_{\mathrm{exp},j}^{\mathrm{E}}$, and $F_{\mathrm{cal},j}^{\mathrm{E}}$ is the corresponding value of the excess property F^{E} calculated from equation (5).

Values of ε_r^E, $\left(\partial\varepsilon_r^E / \partial T\right)_p$ and n_D^E versus ϕ_1 of alkan-1-ol + TEA systems at 298.15 K are plotted in Figures 1, 2 and 3 respectively with their corresponding Redlich-Kister regressions. Data on n_D are plotted in Figure S1 (supplementary material).

4. Discussion

The present discussion is concerned with binary mixtures including 1-alkanol (component 1, i = 1) and an organic solvent (component 2, usually amine, i = 2). Unless stated otherwise, the below values of the dielectric properties and their corresponding excess functions are referred to T = 298.15 K and $\phi_1 = 0.5$. On the other hand, n will stand for the number of C atoms of the alkan-1-ol.

4.1. Relative permittivities

The magnitude of ε_r for a liquid system is determined by a number of factors, such as the permanent dipole moments and polarizabilities of its molecules, the nature of the liquid structure and collective dynamics. Figure 4 shows our $\varepsilon_r(\phi_1)$ results for systems with methanol or heptan-1-ol and an isomeric amine TEA, HxA [27], or DPA [28]. We note that, at any composition, $\varepsilon_r(\phi_1)$ values for the mixtures with TEA are lower, which indicates that a weakening of the dielectric polarization of the system is produced with regards to that of solutions with linear isomeric amines. This may be ascribed to the dipole moment of TEA ($2.202 \cdot 10^{-30}$ C·m [49]), which is lower than the dipole moments of HxA ($4.336 \cdot 10^{-30}$ C·m [50]) or DPA ($3.669 \cdot 10^{-30}$ C·m [51]). Interestingly, there is a range of concentrations, which depends on the system components, where small negative differences $\varepsilon_r(\phi_1)$(HxA) – $\varepsilon_r(\phi_1)$(DPA) (for a fixed alkan-1-ol) are encountered (Figure 4). Therefore, in those regions, the effective dipole moments of the multimers formed by unlike molecules upon mixing are lower in the case of HxA-containing systems, probably due to the existence of cyclic species. Outside of the mentioned range of compositions, $\varepsilon_r(\phi_1)$(DPA) < $\varepsilon_r(\phi_1)$(HxA), in agreement with the lower dipole moment of DPA. This can be better visualized in Figure 5, where we have eliminated volume effects present in the permittivity by representing the molar susceptibility, $\chi_m = (\varepsilon_r - 1)V_m$ (V_m, molar volume of the mixture), of these mixtures vs ϕ_1. The quantity χ_m is useful to compare the response of different liquids given a value of the equilibrium electric field, because it is proportional to the macroscopic dipole moment resulting from a fixed amount (1 mol) of molecules. The ϕ_1 dependence of χ_m and ε_r are very different for the methanol + DPA or + HxA systems (Figures 4 and 5). In fact, there is a more or less large concentration range where χ_m slowly increases, i.e., where the molar macroscopic dipole moment remains nearly unchanged.

4.2. Excess relative permittivities

It is known that the rupture of interactions between molecules of the same species upon mixing provides a negative contribution to $\varepsilon_\mathrm{r}^\mathrm{E}$. For example, $\varepsilon_\mathrm{r}^\mathrm{E}$(heptane) = –1.075 ($n$ = 3), –2.225 (n = 4), –2.525 (n = 5), –2.875 (n = 7), –1.775 (n = 10) [24,52,53] (Figure 6). For the system methanol + heptane, a partial immiscibility region appears [54]. These rather large and negative values can be ascribed to the disruption of the alcohol network along the mixing process. The creation of new interactions between unlike molecules along this process leads to the formation of multimers whose molecular structure is determinant to provide a more or less effective impact on the macroscopic response to an electric field. If the mentioned multimers are linear chains, the contribution to $\varepsilon_\mathrm{r}^\mathrm{E}$ is positive. In contrast, if cyclic species are created, the contribution to $\varepsilon_\mathrm{r}^\mathrm{E}$ is negative. The $\varepsilon_\mathrm{r}^\mathrm{E}$ values of alkan-1-ol + TEA mixtures are: 0.074 (n = 1), –1.807 (n = 3), –1.980 (n = 4), –1.874 (n = 5), –1.435 (n = 7) (this work), –0.593 (T = 293.15 K) (n = 10); –0.048 (T = 293.15 K) (n = 12); [55] (Figure 6). The comparison of these results for $n \geq 4$ with the lower values given above for alkan-1-ol + heptane systems reveals that the creation of the new (alkan-1-ol)-TEA interactions contributes positively to the $\varepsilon_\mathrm{r}^\mathrm{E}$ of the mixture. In addition, positive $\varepsilon_\mathrm{r}^\mathrm{E}$ values are encountered for the methanol-containing system. An important result is that, for systems with n = 3, $\varepsilon_\mathrm{r}^\mathrm{E}$(TEA) < $\varepsilon_\mathrm{r}^\mathrm{E}$(heptane). This suggests that TEA is an effective breaker of the alkanol self-association, and that the interactions between unlike molecules do not compensate enough the large negative contribution to $\varepsilon_\mathrm{r}^\mathrm{E}$ from the disruption of (propan-1-ol)-(propan-1-ol) interactions. The variation of $\varepsilon_\mathrm{r}^\mathrm{E}$ with the chain length of the alkan-1-ol follows the order: methanol > propan-1-ol > butan-1-ol < pentan-1-ol < heptan-1-ol < decan-1-ol < dodecan-1-ol. In other words, $\varepsilon_\mathrm{r}^\mathrm{E}$ decreases to a minimum and then increases again. Such a trend is similar to those encountered for alkan-1-ol + heptane (see above), + HxA [27], + DPA [28] or + cyclohexylamine [25,26] systems. The observed $\varepsilon_\mathrm{r}^\mathrm{E}$ dependence on n has been explained in terms of a weaker and lower self-association of longer alkanols. In the case of alkan-1-ol + amine systems, one must also take into account that the solvation between molecules of different species decreases when n is increased [1,5,7,8,56]. Thus, the mixture polarization shows a weaker variation with n when longer alkan-1-ols are involved, since they are characterized by a lower self-association and the related solvation effects are also less relevant. Consequently, and as in previous studies, $\varepsilon_\mathrm{r}^\mathrm{E}$ shows a sharper dependence for low n

values [27,28]. Other available data on ε_r^E for the dodecan-1-ol + TEA system at different temperatures [57] should be taken with caution, as they are rather scattered and the corresponding curves are S-shaped, with positive values at higher concentrations of the alkan-1-ol which increase in line with the temperature [57]. This needs further experimental confirmation.

For a given alkan-1-ol, ε_r^E(DPA) [28] > ε_r^E(HxA) [27] > ε_r^E(TEA) (Figure 6). This variation is similar to, although stronger than, the observed change for ε_r. For a better understanding of systems containing TEA, we start examining alkan-1-ol + linear primary or secondary amine systems. A literature survey shows that ε_r^E(propan-1-ol + DPA) = –0.246 [28] > ε_r^E(propan-1-ol + HxA) = –0.96 [27] > ε_r^E(propan-1-ol + propan-1-amine) = –1.99 [58] and that ε_r^E(butan-1-ol + DPA) = –0.715 [28] > ε_r^E (butan-1-ol + HxA) = –1.424 [27] > ε_r^E(butan-1-ol + butan-1-amine) = –2.87 [58]. Since solvation effects are expected to be more relevant in systems involving amines where the amine group is less sterically hindered (propan-1-amine, butan-1-amine), one can conclude that mixtures characterized by larger solvation effects show more negative ε_r^E values. The same trend is observed when comparing, at 303.15 K, ε_r^E results for propan-1-ol + primary aromatic amine, aniline, (–2.07) [59] or + secondary aromatic amine, *N*-methylaniline, (–1.27) [60]. This behavior can be explained taking into account that larger solvation effects imply a decreased number of interactions between like molecules and, therefore, a more negative contribution to ε_r^E from the disruption of interactions between like molecules, particularly between alkanol molecules. In the case of amine mixtures, cyclic species may be more probable in mixtures containing amines with the characteristic group less sterically hindered. We must now remark that systems with TEA deviate from this picture. This can be ascribed to the globular shape of TEA molecules, which makes them better breakers of the alkan-1-ol self-association (see above). In fact, the volume fraction at which minimum ε_r^E values are measured changes in the sequence DPA < HxA < TEA for mixtures with shorter alkan-1-ols. Thus, ϕ_1 (n = 4) = 0.3183 (DPA; ε_r^E = –0.896) [28] < 0.4138 (HxA; ε_r^E = –1.428) [27] < 0.4969 (TEA; ε_r^E = –1.964). For n = 7, the alcohol self-association becomes less relevant, and the minimum ε_r^E values are encountered at similar volume fractions for HxA or TEA mixtures, although these concentrations are still higher than for the DPA solution, e.g. ϕ_1 (n = 7) = 0.5003 (DPA; ε_r^E = –0.793) [28] < 0.5982 (TEA; ε_r^E = –1.455). The fact that the ε_r^E curves of HxA systems are skewed to higher ϕ_1 values than those of mixtures with DPA supports our previous statement about that higher solvation effects lead to a more important breaking of the alcohol network upon mixing. We complete the present analysis as follows. (i) According to the

ERAS model, the equilibrium constants, K_{AB}, change in the order HxA > DPA > TEA in systems with a given alkan-1-ol [5-7]. For example, K_{AB}(methanol) = 2500 (HxA) > 2450 (DPA) > 620 (TEA). That is, solvation effects are less important in mixtures with TEA, in agreement with the fact that the amine group becomes more sterically hindered in the same sequence [56]. (ii) The $S_{CC}(0)$ function is a quantity which allows to study the fluctuations in the number of molecules of a binary mixture regardless of the components, the fluctuations in the mole fraction and the cross fluctuations. It is defined by [19,20]:

$$S_{CC}(0) = \frac{x_1x_2}{1+\frac{x_1x_2}{RT}\left(\frac{\partial^2 G_m^E}{\partial x_1^2}\right)_{T,p}} = \frac{x_1x_2}{D} \tag{7}$$

where $D = 1 + (x_1x_2/RT)\left(\partial^2 G_m^E/\partial x_1^2\right)_{T,p}$. For ideal mixtures, $G_m^{E,id}$ = 0 (excess Gibbs energy of the ideal mixture); D^{id} = 1 and $S_{CC}(0)$ = x_1x_2. From stability conditions, $S_{CC}(0)$ > 0. If a system is close to phase separation, $S_{CC}(0)$ must be large and positive (∞, if the mixture presents a miscibility gap). In the case of compound formation between components, $S_{CC}(0)$ must be very low (0, in the limit). Therefore, $S_{CC}(0) > x_1x_2$ (D < 1) indicates that the dominant trend in the system is homocoordination (separation of the components), and the mixture is then less stable than the ideal. If $0 < S_{CC}(0) < x_1x_2 = S_{CC}(0)^{id}$, ($D$ > 1), the fluctuations in the system have been removed, and the dominant trend in the solution is heterocoordination (compound formation). In such a case, the system is more stable than ideal. We have shortly applied this formalism to methanol + HxA, or + DPA, or + TEA systems at 298.15 K calculating G_m^E by means of the DISQUAC model with interaction parameters for the OH/amine contacts previously determined [1,6]. At equimolar composition, we have obtained: $S_{CC}(0)$ = 0.165 (HxA) < 0.201 (DPA) < 0.341 (TEA). This means that heterocoordination is dominant in the systems with HxA or DPA, while homocoordination is prevalent in the TEA mixture. It is in full agreement with the variation of the K_{AB} constants given above, and with available G_m^E data for methanol + amine mixtures. Thus, G_m^E (methanol)/J·mol^{-1} = –799 (butan-1-amine, 348.15 K) [2], 284 (TEA, 303.15 K) [9]. (iii) Interestingly, viscosity data show that values of $\Delta\eta$ (= $\eta - x_1\eta_1 + x_2\eta_2$; where η is the mixture viscosity and η_i is the viscosity of component i) become more negative in alkan-1-ol mixtures when DPA is replaced by TEA. For example, at 303.15 K and equimolar composition, $\Delta\eta$(DPA)/10^{-3}·Pa·s = –0.142 (propan-1-ol) < –0.259 (butan-1-ol) [61] and $\Delta\eta$(TEA)/10^{-3}·Pa·s = –0.328 (propan-1-ol) [62] < –0.612 (butan-1-ol) [63]. Therefore, the mixture fluidization becomes more relevant in solutions with TEA. This is not only explained by the lower solvation effects present in such systems, but also because a larger number of interactions between alkan-1-ol molecules are broken along the mixing process. Interestingly, at 298.15 K and equimolar composition, $\Delta\eta$ (propan-1-ol)/ $10^{-3}\cdot$Pa·s = –0.305 (propan-1-amine) [64] < –0.253 (butan-1-amine) [65] and $\Delta\eta$ (butan-1-ol)/ $10^{-3}\cdot$Pa·s = –0.460 (propan-1-amine) [64] < –0.280 (butan-1-amine) [65]. It seems that for alkan-1-ol + linear primary amine systems including compounds of similar size and shape, $\Delta\eta$ is lower for the solutions with larger solvation effects. This trend is still valid for mixtures including short chain alkan-1-ols and DPA. For instance, at 303.15 K and $x_1 = 0.5$, the values $\Delta\eta$ (propan-1-amine)/ $10^{-3}\cdot$Pa·s = –0.252 (propan-1-ol); –0.320 (butan-1-ol) [66] are lower than the results given above for alkan-1-ol + DPA systems.

4.3. Temperature dependence of the permittivity

Values of $\left(\partial\varepsilon_\mathrm{r}^*/\partial T\right)_p$ of pure compounds used in this work are negative, as it is usual for normal liquids. Pure TEA shows a very low absolute value of this derivative, $\left(\partial\varepsilon_\mathrm{r}^*/\partial T\right)_p$ = -0.004 K^{-1}, since TEA is not self-associated and has a low ε_r^* value (= 2.419). Thus, the increase of thermal agitation hardly modifies the liquid structure. On the other hand, values of $\left(\partial\varepsilon_\mathrm{r}/\partial T\right)_p$ of TEA systems are higher than for pure alkanols (e.g., for pentan-1-ol $\left(\partial\varepsilon_\mathrm{r}^*/\partial T\right)_p$ = –0.117 K^{-1} < $\left(\partial\varepsilon_\mathrm{r}/\partial T\right)_p$ = –0.034; Figure 7, Table S2). This can be explained as follows. (i) The contribution to $\left(\partial\varepsilon_\mathrm{r}/\partial T\right)_p$ related to the breaking of TEA-TEA interactions when T is increased is practically negligible (see above); (ii) The enthalpy of hydrogen bonds between alkan-1-ol molecules is larger than that corresponding to alkan-1-ol-TEA interactions. Thus, in the framework of the ERAS model, Δh_AB^* (TEA)/ kJ·mol^{-1} = –35.3 (methanol); –30.5 (heptan-1-ol) [5], while the enthalpies between alkan-1-ol molecules are –25 kJ·mol^{-1} [4,5,7,67]. Therefore, one can expect that the number of (alkan-1-ol)-TEA interactions broken when the temperature is increased is lower than the number of disrupted alkanol-alkanol interactions. This leads to a lower ε_r decrease when T is increased in comparison to that produced in pure alkan-1-ols. The variation of $\left(\partial\varepsilon_\mathrm{r}/\partial T\right)_p$ with n can be explained in similar terms. On the other hand, for mixtures with a given alkan-1-ol, $\left(\partial\varepsilon_\mathrm{r}/\partial T\right)_p$ changes in the order TEA > HxA > DPA (Figure 7). The ε_r values vary in the opposite sequence (Figure 4). That is, the structure of mixtures characterized by a higher dielectric polarization is more sensitive to temperature changes. In addition, $\left(\partial\varepsilon_\mathrm{r}^*/\partial T\right)_p$ / K^{-1} = –0.004 (TEA) > –0.0098 (HxA) > –0.012 (DPA). Finally, we note that $\left(\partial\varepsilon_\mathrm{r}^\mathrm{E}/\partial T\right)_p$ / K^{-1} can show negative or positive values (Figures 2 and S2):

–0.003 (n = 1), 0.017 (n = 3), 0.022 (n = 4), 0.025 (n = 5), 0.027 (n = 7). The negative value is encountered only for the methanol solution, for which the effects from alkan-1-ol self-association and solvation between unlike molecules are more relevant, leading to a network that is more difficult to break with the increasing of temperature when compared with the ideal mixture. DPA and HxA systems behave similarly [27,28] but, since association/solvation effects are stronger, the corresponding values are more negative.

4.4. Molar refraction

The molar refraction or molar refractivity is defined by the Lorentz-Lorenz equation [30,32]:

$$R_{\mathrm{m}} = \frac{n_{\mathrm{D}}^2 - 1}{n_{\mathrm{D}}^2 + 2} V_{\mathrm{m}} = \frac{N_A \alpha_e}{3\varepsilon_0} \qquad (8)$$

where N_A is Avogadro's constant and ε_0 denotes the vacuum permittivity. R_{m} is related to dispersive interactions [32,68], since it is proportional to the average electronic contribution to the polarizability, α_e, from one molecule in a macroscopic sphere of liquid [30,32]. The R_{m} / $10^{-6}\cdot\mathrm{m}^3\cdot\mathrm{mol}^{-1}$ values for alkan-1-ol + TEA mixtures are (at equimolar composition): 20.7 (n = 1), 25.4 (n = 3), 27.7 (n = 4), 30.0 (n = 5), 34.7 (n = 7). That is, dispersive interactions are more relevant in mixtures with longer alkan-1-ols. Interestingly, the R_{m} values are very similar to those of alkan-1-ol + HxA or + DPA systems [27,28], and one can conclude that these mixtures differ essentially by solvation effects. The application of the ERAS model [5,7] to alkan-1-ol + HxA, or + DPA, or + TEA systems shows that these mixtures are characterized by the same small physical parameter and that they differ in the parameters K_{AB}, Δh_{AB}^* and Δv_{AB}^*.

4.5. Aromaticity effect

The available $\varepsilon_{\mathrm{r}}^{\mathrm{E}}$ data in the literature for alkan-1-ol + pyridine systems [69,70] indicate that they are higher than those of the TEA solutions. Thus, $\varepsilon_{\mathrm{r}}^{\mathrm{E}}$ (methanol) = 2.85 (pyridine) [69] > 0.074 (TEA, this work); and, at 303.15 K, $\varepsilon_{\mathrm{r}}^{\mathrm{E}}$ (propan-1-ol) = 0.10 [70] (pyridine) > –1.807 (TEA, this work). Therefore, cooperative effects which lead to an increase of the dielectric polarization of the mixture are more relevant in the systems with pyridine, probably because the amine group is less sterically hindered in the aromatic amine and the creation of multimers, formed by unlike molecules, with larger effective dipole moments is favored. This effect predominates over the larger negative contribution to $\varepsilon_{\mathrm{r}}^{\mathrm{E}}$ from the breaking of dipolar interactions between pyridine molecules. Note that the dipole moment of pyridine (2.37 D, [71]) is much higher than the dipole moment of TEA. It is remarkable that the behavior of alkan-1-ol + HxA, or + aniline systems is the opposite, and $\varepsilon_{\mathrm{r}}^{\mathrm{E}}$ values are more negative for the solutions involving aniline [27]. That is, the large negative contribution to $\varepsilon_\mathrm{r}^\mathrm{E}$ from the disruption of aniline-aniline interactions predominates. The mentioned interactions are much stronger than those between pyridine molecules, as it is shown by the upper critical solution temperatures (UCST) of their mixtures with *n*-alkanes. For example. UCST/K= 268.7 (pyridine + dodecane) [72] < 343.1 (aniline + heptane) [73].

4.6. Kirkwood-Fröhlich model

In the Kirkwood-Fröhlich model, the fluctuations of the dipole moment in the absence of electric field are treated as the basis to obtain relations involving the relative permittivity. It is a local-field model in which the molecules are assumed to be in a spherical cavity of an infinitely large piece of dielectric and the induced contribution to the polarizability is treated macroscopically through its relation to $\varepsilon_\mathrm{r}^\infty$ (the value of the permittivity at a high frequency at which only the induced polarizability contributes). The local field takes into account long-range dipolar interactions by considering the outside of the cavity as a continuous medium of permittivity ε_r . Short-range interactions are introduced by the so-called Kirkwood correlation factor, g_K, which provides information about the deviations from randomness of the orientation of a dipole with respect to its neighbors. This is an important parameter, as it provides information about specific interactions in the liquid state. For a mixture of polar liquids, g_K can be determined, in a one-fluid model approach [29], from macroscopic physical properties according to the expression [29-32]:

$$g_\mathrm{K} = \frac{9k_\mathrm{B}TV_\mathrm{m}\varepsilon_0(\varepsilon_\mathrm{r}-\varepsilon_\mathrm{r}^\infty)(2\varepsilon_\mathrm{r}+\varepsilon_\mathrm{r}^\infty)}{N_\mathrm{A}\mu^2\varepsilon_\mathrm{r}(\varepsilon_\mathrm{r}^\infty+2)^2} \tag{9}$$

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, $\varepsilon_\mathrm{r}^\infty$ is estimated from the relation $\varepsilon_\mathrm{r}^\infty = 1.1n_\mathrm{D}^2$ [74]. μ represents the dipole moment of the solution, estimated from the equation [29]:

$$\mu^2 = x_1\mu_1^2 + x_2\mu_2^2 \tag{10}$$

where μ_i stands for the dipole moment of component *i* (= 1,2). Calculations have been performed using smoothed values of V_m^E [5], n_D^E (this work) and $\varepsilon_\mathrm{r}^\mathrm{E}$ (this work) at Δx_1 = 0.01. The source and values of μ_i are collected in Table 2.

We compare the g_K curves obtained from methanol or heptan-1-ol + isomeric amine in Figure 8. Except for values of ϕ_1 very close to zero, where the structure of the mixture is basically that of the pure amine, it is found that g_K(DPA) > g_K(TEA) > g_K(HxA). In order to examine these results, we provide some g_K values for alkan-1-ol + amine mixtures. Thus, g_K (propan-1-ol) = 2.72 (DPA) > 2.32 (HxA) > 1.87 (propan-1-amine), and g_K(butan-1-ol) = 2.60 (DPA) > 2.16 (HxA) > 1.72 (butan-1-amine). In addition, g_K(propan-1-ol, 303.15 K) = 1.54 (aniline) < 1.71 (*N*-methylaniline). This points out that parallel alignment of molecular dipoles has a lower weight in those systems characterized by larger solvation effects and, according to our previous description of ε_r^E, these cooperative effects will lead to lower polarization of the mixture. This underlines the lower contribution to the mixture structure from alkanol-alkanol interactions in systems with larger solvation effects, and suggests the presence of cyclic species in such systems. The g_K results for the methanol + DPA mixture deserve a comment. We note that g_K rapidly increases with ϕ_1, and that it is nearly constant from ϕ_1 = 0.5 and very close to the value of the neat alcohol. This might occur because the contribution to the mixture polarization arising from interactions between alcohol molecules also increases rapidly with ϕ_1 in such a way that interactions between unlike molecules contribute to g_K to a lower extent. It is remarkable that g_K changes more smoothly with ϕ_1 for the methanol + HxA system, in agreement with our analysis of ε_r^E results. For alkan-1-ol + TEA systems, g_K = 2.73 (*n* = 1), 2.47 (*n* = 3), 2.38 (*n* = 4), 2.30 (*n* = 5), 2.13 (*n* = 7) (see Figure S3). For *n* = 1, the g_K curve remains nearly constant from $\phi_1 > 0.7$. It is quite clear that TEA mixtures show an intermediate behavior, which could be due to the existence of a higher proportion of shorter linear-like multimers of alkan-1-ol molecules which are less present in the systems with HxA.

The excess Kirkwood correlation factors ($g_K^E = g_K - g_K^{id}$, where g_K^{id} is obtained replacing real by ideal quantities in equation (9)) of alkan-1-ol + TEA mixtures are: –0.03 (*n* = 1), –0.58 (*n* = 3), –0.76 (*n* = 4), –0.85 (*n* = 5), –0.84 (*n* = 7). Their curves are plotted in Figure S4. The variation of the minimum of the curves as *n* increases is not the same as the one encountered for ε_r^E, and it occurs at lower values of ϕ_1. The model consequently indicates that the variation of the structure of the dipoles in the mixing process is only one of the factors that determine the ε_r^E minima. The g_K^E values are compared with the corresponding ones of alkan-1-ol + HxA or DPA systems in Figure S5. The trend of g_K^E(TEA) is slightly deviated from the parallel behavior of g_K^E(HxA) and g_K^E(DPA). This underlines the stronger structural effects already mentioned in the former mixtures.

5. Conclusions

Measurements of ε_r and n_D have been reported for the alkan-1-ol + TEA mixtures at (293.15-303.15) K. Positive ε_r^E results are encountered only for the methanol system at high ϕ_1 values. ε_r^E changes in the sequence: methanol > propan-1-ol > butan-1-ol < pentan-1-ol < heptan-1-ol. This variation is similar to alkan-1-ol + HxA, or + DPA or + cyclohexylamine. It has been shown that: (i) (alkan-1-ol)-TEA interactions contribute positively to ε_r^E; (ii) TEA is a good breaker of the alkan-1-ol self-association; (iii) structural effects are relevant for ε_r data. (iv) the aromaticity effect leads to an increase of the mixture polarization, and it is opposite to the effect encountered when considering alkan-1-ol + HxA, or + aniline mixtures. The application of the Kirkwood-Fröhlich model supports these statements.

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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	0.9999	10^{-5}
propan-1-ol	71-23-8	Sigma-Aldrich	None	0.9984	10^{-3}
butan-1-ol	71-36-3	Sigma-Aldrich	None	0.9986	10^{-3}
pentan-1-ol	71-41-0	Sigma-Aldrich	None	0.999	$2 \cdot 10^{-4}$
heptan-1-ol	111-70-6	Sigma-Aldrich	None	0.998	$5 \cdot 10^{-4}$
N,N-diethylethanamine (TEA)	121-44-8	Sigma-Aldrich	None	0.9999	10^{-4}

[a] In mole fraction. By gas chromatography. Provided by the supplier.

[b] In mass fraction. By Karl-Fischer titration; the relative standard uncertainty for water content is 0.025

Table 2

Dipole moment, μ, of the pure liquids, and their relative permittivity at frequency $\nu = 1$ MHz, ε_r^*, refractive index at the sodium D-line, n_D^*, and density, ρ^*, at temperature T and pressure p = 0.1 MPa. [a]

Compound	$\mu / 10^{-30}$ C·m	T/K	ε_r^*		n_D^*		ρ^* / kg·m^{-3}	
			Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
methanol	5.551 [75]	293.15	33.576	33.61 [76]	1.32863	1.32859 [77]	791.63	791.6 [78] 791.400 [79]
		298.15	32.624	32.62 [76]	1.32649	1.32652 [80]	786.95	786.9 [81] 786.884 [82]
		303.15	31.684	31.66 [76]	1.32435	1.32457 [83] 1.32410 [84]	782.22	782.158 [82]
propan-1-ol	5.434 [75]	293.15	21.150	21.15 [85]	1.38511	1.38512 [86]	803.66	803.61 [87]
		298.15	20.469	20.42 [85]	1.38306	1.38307 [84]	799.68	799.60 [87]
		303.15	19.799	19.75 [85]	1.38099	1.38104 [84]	795.66	795.61 [87]
butan-1-ol	5.384 [75]	293.15	18.201	18.19 [85]	1.39929	1.3993 [88]	809.85	809.82 [89] 809.8 [90]
		298.15	17.566	17.53 [85]	1.39730	1.397336 [91]	806.06	806.06 [89]
		303.15	16.942	16.89 [85]	1.39529	1.3953 [92]	802.22	802.2 [90]
pentan-1-ol	5.330 [75]	293.15	15.689	15.63 [76]	1.40993	1.40986 [84]	814.66	814.68 [93]
		298.15	15.110	15.08 [94]	1.40794	1.40789 [84]	811.03	811.03 [93]
		303.15	14.537	14.44 [76]	1.40592	1.40592 [95]	807.35	817.37 [93]
heptan-1-ol	5.280 [75]	293.15	12.005	11.54 [96]	1.42433	1.42433 [97]	822.37	822.3 [98]
		298.15	11.504	11.45 [94]	1.42236	1.42240 [97]	818.90	818.81 [99]
		303.15	11.013	11.07 [100]	1.42041	1.42047 [95] 1.42048 [97]	815.37	815.3 [98]
TEA	2.202 [49]	293.15	2.440	2.43 [101] 2.450 [102] 2.46 [103]	1.40044	1.40040 [104] 1.1004 [101] 1.400333 [105]	727.38	726.6 [101] 727.6 [71]
		298.15	2.419	2.42 [103] 2.404 [106]	1.39775	1.39825 [104] 1.3983 [107]	722.76	723.06 [71]
		303.15	2.398	2.387 [106] 2.41 [103]	1.39503	1.39555 [104] 1.3955 [107]	718.11	717.9 [108]

[a] The standard uncertainties are: $u(T)$ = 0.02 K (for ρ^* measurements, $u(T)$ = 0.02 K); $u(p)$ = 1 kPa; $u(\nu)$ = 20 Hz; $u(n_D^*)$ = 0.00008. The relative standard uncertainties are: $u_r(\rho^*)$ = 0.0012, $u_r(\varepsilon_r^*)$ = 0.003.

Table 3

Volume fractions of alkan-1-ol, ϕ_1, relative permittivities at frequency ν = 1 MHz, ε_r, and excess relative permittivities at ν = 1 MHz, $\varepsilon_\mathrm{r}^\mathrm{E}$, of alkan-1-ol (1) + TEA (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	$\varepsilon_\mathrm{r}^\mathrm{E}$	x_1	ϕ_1	ε_r	$\varepsilon_\mathrm{r}^\mathrm{E}$
methanol (1) + TEA (2) ; T/K = 293.15							
0.0000	0.0000	2.442		0.5979	0.3020	11.168	–0.676
0.0580	0.0176	2.801	–0.189	0.7096	0.4155	15.117	–0.261
0.0878	0.0272	3.038	–0.251	0.7992	0.5366	19.374	0.225
0.1593	0.0523	3.575	–0.495	0.8445	0.6124	21.941	0.433
0.1981	0.0671	3.939	–0.592	0.8997	0.7230	25.536	0.584
0.2880	0.1053	4.938	–0.782	0.9515	0.8509	29.454	0.520
0.3971	0.1608	6.538	–0.910	0.9856	0.9522	32.327	0.239
0.4959	0.2225	8.475	–0.894	1.0000	1.0000	33.576	
methanol (1) + TEA (2) ; T/K = 298.15							
0.0000	0.0000	2.422		0.5979	0.3019	10.874	–0.666
0.0580	0.0176	2.769	–0.185	0.7096	0.4154	14.708	–0.260
0.0878	0.0272	2.998	–0.245	0.7992	0.5365	18.829	0.204
0.1593	0.0522	3.518	–0.481	0.8445	0.6123	21.315	0.400
0.1981	0.0670	3.868	–0.578	0.8997	0.7229	24.811	0.556
0.2880	0.1053	4.834	–0.768	0.9515	0.8509	28.615	0.494
0.3971	0.1608	6.387	–0.891	0.9856	0.9522	31.414	0.234
0.4959	0.2224	8.263	–0.876	1.0000	1.0000	32.624	
methanol (1) + TEA (2) ; T/K = 303.15							
0.0000	0.0000	2.402		0.5979	0.3018	10.582	–0.657
0.0580	0.0176	2.736	–0.181	0.7096	0.4153	14.302	–0.261
0.0878	0.0272	2.958	–0.240	0.7992	0.5364	18.293	0.184
0.1593	0.0522	3.461	–0.470	0.8445	0.6122	20.705	0.377
0.1981	0.0670	3.799	–0.565	0.8997	0.7228	24.096	0.529
0.2880	0.1052	4.732	–0.750	0.9515	0.8508	27.792	0.477
0.3971	0.1607	6.236	–0.872	0.9856	0.9521	30.513	0.232
0.4959	0.2224	8.054	–0.860	1.0000	1.0000	31.684	
propan-1-ol (1) + TEA (2) ; T/K = 293.15							
0.0000	0.0000	2.440		0.6027	0.4492	8.889	−1.956
0.0476	0.0262	2.686	−0.244	0.6997	0.5560	11.070	−1.773
0.0932	0.0524	2.954	−0.466	0.7966	0.6780	13.743	−1.382
0.1394	0.0801	3.248	−0.691	0.8455	0.7463	15.298	−1.105
0.2032	0.1206	3.718	−0.978	0.9014	0.8309	17.310	−0.676
0.2896	0.1797	4.459	−1.343	0.9484	0.9081	19.076	−0.355
0.4084	0.2706	5.770	−1.733	1.0000	1.0000	21.150	
0.5043	0.3535	7.131	−1.923				
propan-1-ol (1) + TEA (2) ; T/K = 298.15							

0.0000	0.0000	2.419		0.6027	0.4488	8.651	–1.869
0.0476	0.0261	2.660	–0.230	0.6997	0.5557	10.757	–1.692
0.0932	0.0523	2.916	–0.447	0.7966	0.6776	13.343	–1.307
0.1394	0.0800	3.200	–0.663	0.8455	0.7460	14.842	–1.042
0.2032	0.1204	3.654	–0.938	0.9014	0.8307	16.775	–0.638
0.2896	0.1795	4.368	–1.291	0.9484	0.9080	18.481	–0.327
0.4084	0.2704	5.640	–1.660	1.0000	1.0000	20.469	
0.5043	0.3532	6.954	–1.840				
propan-1-ol (1) + TEA (2) ; *T*/K = 303.15							
0.0000	0.0000	2.398		0.6027	0.4485	8.417	–1.785
0.0476	0.0261	2.631	–0.221	0.6997	0.5553	10.450	–1.611
0.0932	0.0522	2.878	–0.428	0.7966	0.6773	12.945	–1.239
0.1394	0.0799	3.153	–0.635	0.8455	0.7458	14.392	–0.984
0.2032	0.1203	3.592	–0.899	0.9014	0.8305	16.243	–0.607
0.2896	0.1793	4.281	–1.237	0.9484	0.9078	17.887	–0.308
0.4084	0.2701	5.510	–1.588	1.0000	1.0000	19.799	
0.5043	0.3529	6.781	–1.758				
butan-1-ol (1) + TEA (2) ; *T*/K = 293.15							
0.0000	0.0000	2.444		0.6006	0.4973	8.204	–2.076
0.0536	0.0359	2.727	–0.283	0.6985	0.6038	10.001	–1.957
0.1102	0.0753	3.052	–0.579	0.8023	0.7275	12.371	–1.536
0.1536	0.1067	3.335	–0.790	0.8438	0.7804	13.458	–1.283
0.2025	0.1431	3.670	–1.029	0.8910	0.8432	14.801	–0.929
0.2941	0.2151	4.453	–1.380	0.9475	0.9223	16.509	–0.468
0.3957	0.3011	5.409	–1.779	1.0000	1.0000	18.201	
0.5082	0.4047	6.786	–2.035				
butan-1-ol (1) + TEA (2) ; *T*/K = 298.15							
0.0000	0.0000	2.424		0.6006	0.4969	7.984	–1.964
0.0536	0.0359	2.696	–0.272	0.6985	0.6034	9.718	–1.843
0.1102	0.0752	3.010	–0.553	0.8023	0.7272	11.994	–1.441
0.1536	0.1065	3.285	–0.752	0.8438	0.7801	13.032	–1.204
0.2025	0.1429	3.608	–0.980	0.8910	0.8430	14.322	–0.867
0.2941	0.2148	4.365	–1.312	0.9475	0.9222	15.961	–0.427
0.3957	0.3007	5.288	–1.689	1.0000	1.0000	17.566	
0.5082	0.4043	6.618	–1.928				
butan-1-ol (1) + TEA (2) ; *T*/K = 303.15							
0.0000	0.0000	2.403		0.6006	0.4965	7.768	–1.854
0.0536	0.0358	2.666	–0.257	0.6985	0.6030	9.438	–1.732
0.1102	0.0751	2.970	–0.525	0.8023	0.7268	11.621	–1.349
0.1536	0.1063	3.235	–0.713	0.8438	0.7798	12.614	–1.127
0.2025	0.1427	3.547	–0.931	0.8910	0.8428	13.847	–0.809
0.2941	0.2146	4.278	–1.245	0.9475	0.9221	15.415	–0.394
0.3957	0.3004	5.169	–1.602	1.0000	1.0000	16.942	
0.5082	0.4039	6.449	–1.826				
pentan-1-ol (1) + TEA (2) ; *T*/K = 293.15							
0.0000	0.0000	2.437		0.5968	0.5352	7.514	–2.015

0.0588	0.0463	2.743	–0.308	0.7072	0.6526	9.204	–1.881
0.1062	0.0846	3.009	–0.549	0.7960	0.7522	10.867	–1.538
0.1482	0.1192	3.260	–0.757	0.8517	0.8171	12.041	–1.224
0.2159	0.1764	3.708	–1.067	0.8939	0.8676	13.011	–0.923
0.3011	0.2510	4.361	–1.402	0.9465	0.9323	14.330	–0.462
0.4089	0.3498	5.319	–1.754	1.0000	1.0000	15.689	
0.5014	0.4389	6.314	–1.939				
		pentan-1-ol (1) + TEA (2) ; *T*/K = 298.15					
0.0000	0.0000	2.417		0.5968	0.5347	7.316	–1.888
0.0588	0.0463	2.716	–0.289	0.7072	0.6522	8.943	–1.752
0.1062	0.0844	2.969	–0.519	0.7960	0.7518	10.533	–1.427
0.1482	0.1190	3.212	–0.715	0.8517	0.8168	11.652	–1.133
0.2159	0.1761	3.644	–1.008	0.8939	0.8674	12.576	–0.851
0.3011	0.2506	4.276	–1.322	0.9465	0.9321	13.822	–0.426
0.4089	0.3494	5.202	–1.650	1.0000	1.0000	15.110	
0.5014	0.4384	6.162	–1.820				
		pentan-1-ol (1) + TEA (2) ; *T*/K = 303.15					
0.0000	0.0000	2.397		0.5968	0.5342	7.123	–1.759
0.0588	0.0462	2.685	–0.273	0.7072	0.6517	8.683	–1.626
0.1062	0.0843	2.928	–0.492	0.7960	0.7514	10.201	–1.318
0.1482	0.1188	3.164	–0.675	0.8517	0.8165	11.265	–1.044
0.2159	0.1758	3.583	–0.948	0.8939	0.8672	12.144	–0.781
0.3011	0.2503	4.193	–1.243	0.9465	0.9320	13.320	–0.391
0.4089	0.3490	5.087	–1.547	1.0000	1.0000	14.537	
0.5014	0.4379	6.010	–1.703				
		heptan-1-ol (1) + TEA (2) ; *T*/K = 293.15					
0.0000	0.0000	2.438		0.5950	0.5987	6.560	–1.606
0.0451	0.0458	2.663	–0.213	0.6948	0.6981	7.608	–1.509
0.1029	0.1043	2.973	–0.463	0.7925	0.7950	8.806	–1.238
0.1466	0.1486	3.212	–0.648	0.8478	0.8498	9.584	–0.984
0.1997	0.2022	3.527	–0.845	0.8982	0.8996	10.352	–0.692
0.2979	0.3012	4.163	–1.157	0.9465	0.9473	11.135	–0.366
0.3963	0.4000	4.855	–1.410	1.0000	1.0000	12.005	
0.4950	0.4989	5.647	–1.564				
		heptan-1-ol (1) + TEA (2) ; *T*/K = 298.15					
0.0000	0.0000	2.418		0.5950	0.5982	6.398	–1.455
0.0451	0.0457	2.635	–0.198	0.6948	0.6976	7.398	–1.358
0.1029	0.1041	2.933	–0.431	0.7925	0.7947	8.532	–1.107
0.1466	0.1483	3.167	–0.598	0.8478	0.8495	9.268	–0.869
0.1997	0.2019	3.470	–0.782	0.8982	0.8994	9.979	–0.611
0.2979	0.3007	4.086	–1.064	0.9465	0.9472	10.706	–0.318
0.3963	0.3995	4.752	–1.296	1.0000	1.0000	11.504	
0.4950	0.4984	5.518	–1.428				
		heptan-1-ol (1) + TEA (2) ; *T*/K = 303.15					
0.0000	0.0000	2.397		0.5950	0.5977	6.233	–1.314
0.0451	0.0456	2.607	–0.183	0.6948	0.6972	7.187	–1.217

0.1029	0.1039	2.896	–0.396	0.7925	0.7944	8.262	–0.980
0.1466	0.1480	3.122	–0.550	0.8478	0.8493	8.954	–0.761
0.1997	0.2015	3.414	–0.719	0.8982	0.8992	9.611	–0.534
0.2979	0.3003	4.010	–0.974	0.9465	0.9471	10.282	–0.275
0.3963	0.3990	4.652	–1.183	1.0000	1.0000	11.013	
0.4950	0.4978	5.389	–1.297				

[a] The standard uncertainties are: $u\left(T\right)$ = 0.02 K; $u\left(p\right)$ = 1 kPa; $u\left(\nu\right)$= 20 Hz; $u\left(x_1\right)$ = 0.0010; $u\left(\phi_1\right)$ = 0.004. The relative standard uncertainty is: $u_\mathrm{r}\left(\varepsilon_\mathrm{r}\right)$ = 0.003; and the relative combined expanded uncertainty (0.95 level of confidence) is $U_\mathrm{rc}\left(\varepsilon_\mathrm{r}^\mathrm{E}\right) = 0.03$.

Table 4

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) + TEA (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) + TEA (2) ; T/K = 293.15							
0.0000	0.0000	1.40044		0.6002	0.3040	1.38753	852
0.0588	0.0179	1.40013	94	0.6953	0.3990	1.38081	857
0.1072	0.0338	1.39980	173	0.7943	0.5291	1.37056	764
0.1765	0.0587	1.39918	285	0.8504	0.6232	1.36254	641
0.2036	0.0692	1.39890	331	0.9003	0.7243	1.35360	479
0.2989	0.1104	1.39750	481	0.9510	0.8496	1.34215	247
0.4053	0.1655	1.39510	629	0.9851	0.9506	1.33303	76
0.5193	0.2391	1.39143	782	1.0000	1.0000	1.32863	
methanol (1) + TEA (2) ; T/K = 298.15							
0.0000	0.0000	1.39775		0.6002	0.3039	1.38506	858
0.0588	0.0178	1.39752	101	0.6953	0.3989	1.37844	867
0.1072	0.0337	1.39719	178	0.7943	0.5290	1.36825	773
0.1765	0.0587	1.39661	294	0.8504	0.6231	1.36028	649
0.2036	0.0692	1.39635	341	0.9003	0.7242	1.35146	494
0.2989	0.1103	1.39493	486	0.9510	0.8495	1.34008	262
0.4053	0.1654	1.39271	649	0.9851	0.9506	1.33092	82
0.5193	0.2391	1.38891	786	1.0000	1.0000	1.32649	
methanol (1) + TEA (2) ; T/K = 303.15							
0.0000	0.0000	1.39503		0.6002	0.3038	1.38258	864
0.0588	0.0178	1.39482	102	0.6953	0.3988	1.37601	873
0.1072	0.0337	1.39452	181	0.7943	0.5289	1.36595	784
0.1765	0.0586	1.39396	297	0.8504	0.6230	1.35795	652
0.2036	0.0692	1.39371	346	0.9003	0.7241	1.34908	486
0.2989	0.1103	1.39236	495	0.9510	0.8494	1.33782	259
0.4053	0.1654	1.39003	644	0.9851	0.9505	1.32875	81
0.5193	0.2390	1.38631	784	1.0000	1.0000	1.32435	
propan-1-ol (1) + TEA (2) ; T/K = 293.15							
0.0000	0.0000	1.40044		0.6011	0.4475	1.40027	667
0.0476	0.0262	1.40088	84	0.6989	0.5551	1.39836	641
0.0989	0.0557	1.40121	162	0.7959	0.6770	1.39548	540
0.1620	0.0941	1.40154	254	0.8455	0.7463	1.39359	457
0.1967	0.1163	1.40171	304	0.9017	0.8314	1.39090	319
0.2936	0.1826	1.40195	430	0.9484	0.9081	1.38836	183
0.4005	0.2642	1.40203	562	1.0000	1.0000	1.38511	
0.4973	0.3471	1.40153	639				
propan-1-ol (1) + TEA (2) ; T/K = 298.15							
0.0000	0.0000	1.39775		0.6011	0.4472	1.39795	675
0.0476	0.0261	1.39822	85	0.6989	0.5547	1.39615	653

0.0989	0.0556	1.39864	170	0.7959	0.6767	1.39338	555
0.1620	0.0940	1.39904	266	0.8455	0.7460	1.39142	461
0.1967	0.1162	1.39921	316	0.9017	0.8312	1.38887	332
0.2936	0.1824	1.39954	446	0.9484	0.9080	1.38629	187
0.4005	0.2639	1.39949	560	1.0000	1.0000	1.38306	
0.4973	0.3468	1.39902	635				
propan-1-ol (1) + TEA (2) ; T/K = 303.15							
0.0000	0.0000	1.39503		0.6011	0.4468	1.39556	679
0.0476	0.0261	1.39553	86	0.6989	0.5544	1.39378	652
0.0989	0.0556	1.39595	170	0.7959	0.6764	1.39103	548
0.1620	0.0939	1.39642	270	0.8455	0.7458	1.38916	459
0.1967	0.1160	1.39665	324	0.9017	0.8310	1.38667	330
0.2936	0.1822	1.39700	452	0.9484	0.9078	1.38419	190
0.4005	0.2637	1.39705	571	1.0000	1.0000	1.38099	
0.4973	0.3465	1.39662	644				
butan-1-ol (1) + TEA (2) ; T/K = 293.15							
0.0000	0.0000	1.40044		0.6063	0.5033	1.40628	642
0.0556	0.0373	1.40139	99	0.7054	0.6117	1.40572	598
0.1033	0.0705	1.40215	179	0.8013	0.7263	1.40448	488
0.1482	0.1027	1.40284	252	0.8498	0.7882	1.40353	400
0.1992	0.1406	1.40356	328	0.8978	0.8525	1.40241	295
0.2974	0.2178	1.40473	454	0.9530	0.9303	1.40085	148
0.3982	0.3033	1.40566	557	1.0000	1.0000	1.39929	
0.5027	0.3994	1.40624	626				
butan-1-ol (1) + TEA (2) ; T/K = 298.15							
0.0000	0.0000	1.39775		0.6063	0.5029	1.40397	645
0.0556	0.0372	1.39877	104	0.7054	0.6113	1.40352	605
0.1033	0.0703	1.39958	186	0.8013	0.7259	1.40234	492
0.1482	0.1026	1.40029	259	0.8498	0.7880	1.40148	408
0.1992	0.1404	1.40107	338	0.8978	0.8523	1.40036	299
0.2974	0.2175	1.40228	463	0.9530	0.9302	1.39884	151
0.3982	0.3029	1.40324	563	1.0000	1.0000	1.39730	
0.5027	0.3990	1.40385	628				
butan-1-ol (1) + TEA (2) ; T/K = 303.15							
0.0000	0.0000	1.39503		0.6063	0.5024	1.40168	652
0.0556	0.0372	1.39616	112	0.7054	0.6109	1.40125	606
0.1033	0.0702	1.39701	196	0.8013	0.7256	1.40015	493
0.1482	0.1024	1.39776	270	0.8498	0.7877	1.39932	409
0.1992	0.1402	1.39852	345	0.8978	0.8521	1.39827	302
0.2974	0.2172	1.39982	473	0.9530	0.9300	1.39680	153
0.3982	0.3026	1.40078	567	1.0000	1.0000	1.39529	
0.5027	0.3986	1.40150	637				
pentan-1-ol (1) + TEA (2) ; T/K = 293.15							
0.0000	0.0000	1.40044		0.5966	0.5349	1.41188	636
0.0473	0.0372	1.40173	94	0.6985	0.6431	1.41225	570
0.1017	0.0809	1.40321	200	0.8018	0.7588	1.41214	449
0.1483	0.1193	1.40432	274	0.8501	0.8152	1.41197	379
0.2080	0.1696	1.40566	361	0.8985	0.8732	1.41156	283
0.2989	0.2490	1.40765	484	0.9499	0.9365	1.41079	146

0.4002	0.3417	1.40941	572	1.0000	1.0000	1.40993	
0.4963	0.4339	1.41092	635				
pentan-1-ol (1) + TEA (2) ; *T*/K = 298.15							
0.0000	0.0000	1.39775		0.5966	0.5345	1.40966	645
0.0473	0.0371	1.39912	99	0.6985	0.6427	1.41021	590
0.1017	0.0808	1.40057	199	0.8018	0.7585	1.41012	463
0.1483	0.1191	1.40176	279	0.8501	0.8149	1.40986	380
0.2080	0.1693	1.40332	384	0.8985	0.8730	1.40944	279
0.2989	0.2487	1.40516	487	0.9499	0.9364	1.40873	144
0.4002	0.3412	1.40707	583	1.0000	1.0000	1.40794	
0.4963	0.4334	1.40855	637				
pentan-1-ol (1) + TEA (2) ; *T*/K = 303.15							
0.0000	0.0000	1.39503		0.5966	0.5340	1.40737	651
0.0473	0.0370	1.39653	110	0.6985	0.6422	1.40796	593
0.1017	0.0806	1.39806	215	0.8018	0.7581	1.40796	467
0.1483	0.1189	1.39927	294	0.8501	0.8146	1.40777	386
0.2080	0.1691	1.40089	401	0.8985	0.8728	1.40733	279
0.2989	0.2483	1.40272	498	0.9499	0.9363	1.40669	146
0.4002	0.3408	1.40473	598	1.0000	1.0000	1.40592	
0.4963	0.4329	1.40620	645				
heptan-1-ol (1) + TEA (2) ; *T*/K = 293.15							
0.0000	0.0000	1.40044		0.5968	0.6005	1.42052	569
0.0521	0.0529	1.40283	112	0.6945	0.6978	1.42217	502
0.0980	0.0994	1.40484	201	0.7957	0.7982	1.42340	386
0.1540	0.1560	1.40719	300	0.8465	0.8485	1.42384	310
0.2017	0.2042	1.40913	378	0.8935	0.8950	1.42413	229
0.2992	0.3025	1.41266	495	0.9479	0.9487	1.42431	120
0.3958	0.3995	1.41568	565	1.0000	1.0000	1.42433	
0.4951	0.4990	1.41832	591				
heptan-1-ol (1) + TEA (2) ; *T*/K = 298.15							
0.0000	0.0000	1.39775		0.5968	0.6000	1.41831	574
0.0521	0.0528	1.40021	115	0.6945	0.6973	1.42004	508
0.0980	0.0992	1.40230	209	0.7957	0.7979	1.42135	393
0.1540	0.1558	1.40469	308	0.8465	0.8482	1.42183	318
0.2017	0.2039	1.40664	384	0.8935	0.8948	1.42213	234
0.2992	0.3020	1.41026	503	0.9479	0.9486	1.42234	123
0.3958	0.3990	1.41334	572	1.0000	1.0000	1.42236	
0.4951	0.4985	1.41607	600				
heptan-1-ol (1) + TEA (2) ; *T*/K = 303.15							
0.0000	0.0000	1.39503		0.5968	0.5995	1.41611	581
0.0521	0.0527	1.39757	119	0.6945	0.6969	1.41794	517
0.0980	0.0990	1.39971	215	0.7957	0.7975	1.41930	399
0.1540	0.1555	1.40218	317	0.8465	0.8480	1.41980	322
0.2017	0.2035	1.40415	392	0.8935	0.8946	1.42014	238
0.2992	0.3016	1.40783	510	0.9479	0.9485	1.42036	125
0.3958	0.3985	1.41100	580	1.0000	1.0000	1.42041	
0.4951	0.4979	1.41379	607				

[a] The standard uncertainties are: $u\left(T\right)$ = 0.02 K; $u\left(p\right)$ = 1 kPa; $u\left(x_1\right)$ = 0.0010; $u\left(\phi_1\right)$ = 0.004, $u\left(n_\mathrm{D}\right)$ = 0.00008. The combined expanded uncertainty (0.95 level of confidence) is $U_\mathrm{c}\left(n_\mathrm{D}^\mathrm{E}\right)$ = 0.0002.

Table 5

Coefficients A_i and standard deviations, $\sigma\left(F^{\mathrm{E}}\right)$ (equation (6)), for the representation of F^{E} at temperature T and pressure p = 0.1 MPa for alkan-1-ol (1) + TEA liquid mixtures by equation (5).

Property F^{E}	alkan-1-ol	T/K	A_0	A_1	A_2	A_3	A_3	$\sigma\left(F^{\mathrm{E}}\right)$
$\varepsilon_{\mathrm{r}}^{\mathrm{E}}$	methanol	293.15	–3.50	1.8	4.4	7.0	5.7	0.02
		298.15	–3.43	1.8	4.2	6.6	5.5	0.02
		303.15	–3.37	1.7	4.0	6.4	5.4	0.02
	propan-1-ol	293.15	–7.71	–2.7	1.4	2.0		0.018
		298.15	–7.39	–2.5	1.5	2.0		0.017
		303.15	–7.06	–2.4	1.5	1.9		0.014
	butan-1-ol	293.15	–8.09	–3.4	0.4	1.6		0.015
		298.15	–7.67	–3.1	0.5	1.6		0.014
		303.15	–7.26	–2.9	0.6	1.5		0.014
	pentan-1-ol	293.15	–7.81	–2.70				0.019
		298.15	–7.31	–2.43				0.018
		303.15	–6.82	–2.15				0.018
	heptan-1-ol	293.15	–6.33	–1.80				0.018
		298.15	–5.75	–1.46				0.017
		303.15	–5.19	–1.15				0.018
$10^5 n_{\mathrm{D}}^{\mathrm{E}}$	methanol	293.15	3050	2224	809			8
		298.15	3080	2236	918			5
		303.15	3090	2233	945			8
	propan-1-ol	293.15	2547	1161	251			4
		298.15	2557	1164	412			3
		303.15	2587	1120	356			1.4
	butan-1-ol	293.15	2500	832	136			2
		298.15	2515	816	221			3
		303.15	2538	774	269			3
	pentan-1-ol	293.15	2528	551				7
		298.15	2573	545				6
		303.15	2585	475	205			6
	heptan-1-ol	293.15	2366	–16	–30	144		1.1
		298.15	2392	–23	28	148		1.1
		303.15	2422	–16	69	101		0.9
$\left(\partial\varepsilon_{\mathrm{r}}^{\mathrm{E}}/\partial T\right)_p$ / K^{-1}	methanol	298.15	0.014	–0.014	–0.04	–0.06	–0.03	0.0005
	propan-1-ol	298.15	0.0661	0.030				0.0005
	butan-1-ol	298.15	0.0832	0.047	0.014			0.0004
	pentan-1-ol	298.15	0.0953	0.056	0.017			0.0004
	heptan-1-ol	298.15	0.1079	0.065	0.029			0.0004

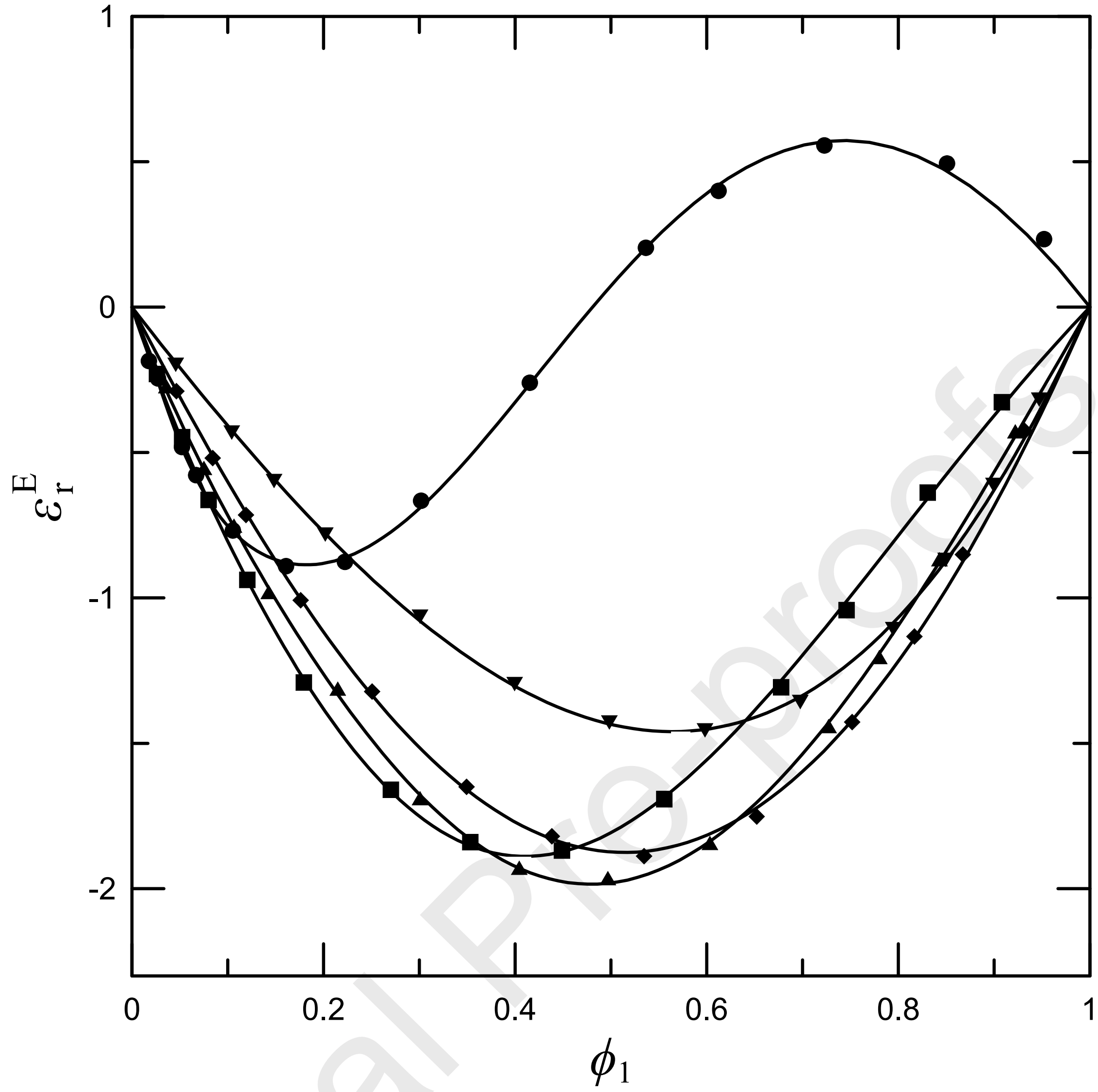


Figure 1

Excess relative permittivity, ε_r^E, of alkan-1-ol (1) + TEA (2) liquid mixtures as a function of the alkan-1-ol volume fraction, ϕ_1, at 0.1 MPa, 298.15 K and 1 MHz. Full symbols, experimental values (this work): (●), methanol; (■), propan-1-ol; (▲), butan-1-ol; (♦), pentan-1-ol; (▼), heptan-1-ol. Solid lines, calculations with equation (5) using the coefficients from Table 5.

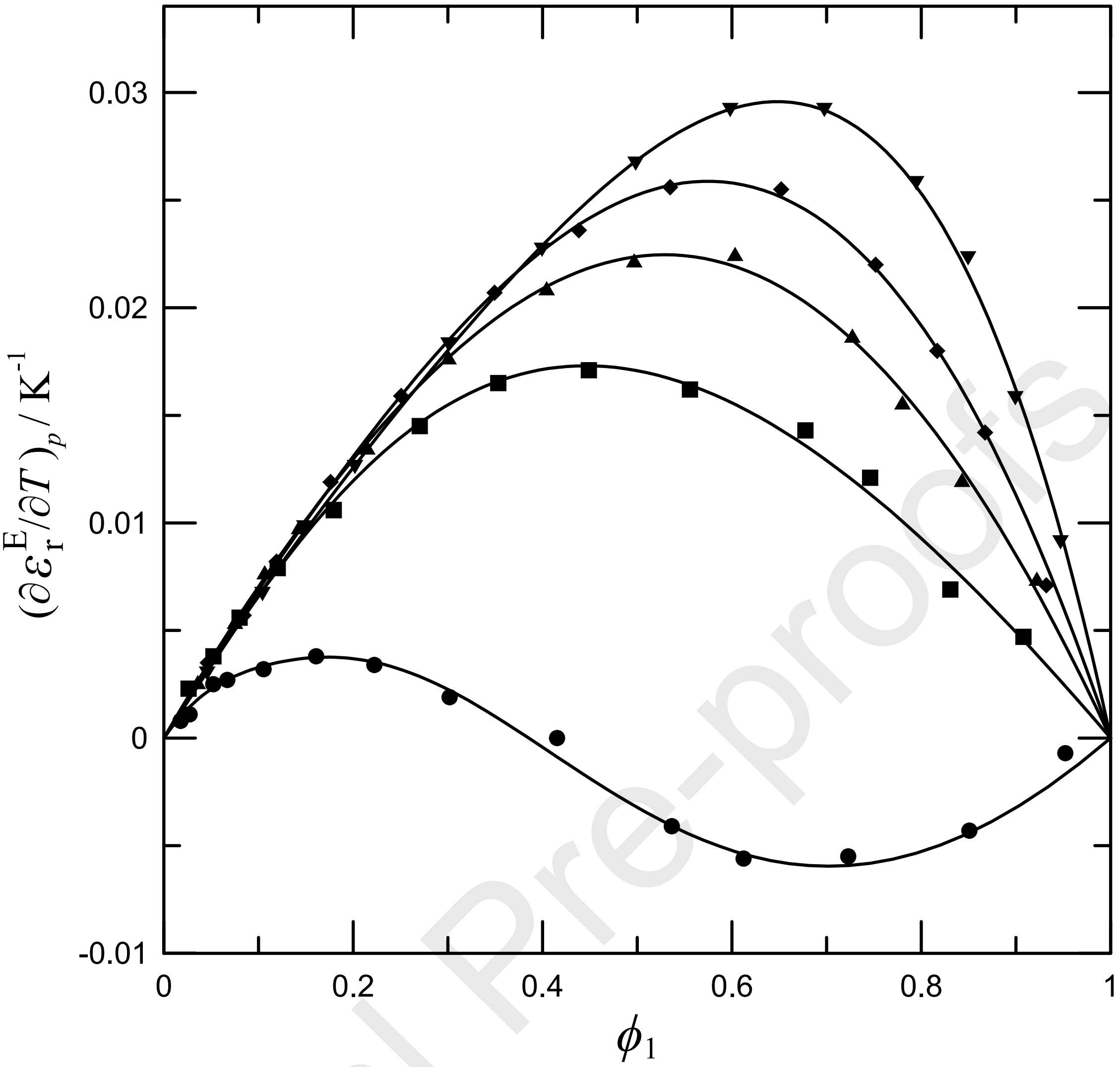


Figure 2

Temperature derivative of the excess relative permittivity, $\left(\partial \varepsilon_r^E / \partial T\right)_p$, of alkan-1-ol (1) + TEA (2) liquid mixtures as a function of the alkan-1-ol volume fraction, ϕ_1, at 0.1 MPa, 298.15 K and 1 MHz. Full symbols, experimental values (this work): (●), methanol; (■), propan-1-ol; (▲), butan-1-ol; (♦), pentan-1-ol; (▼), heptan-1-ol. Solid lines, calculations with equation (5) using the coefficients from Table 5.

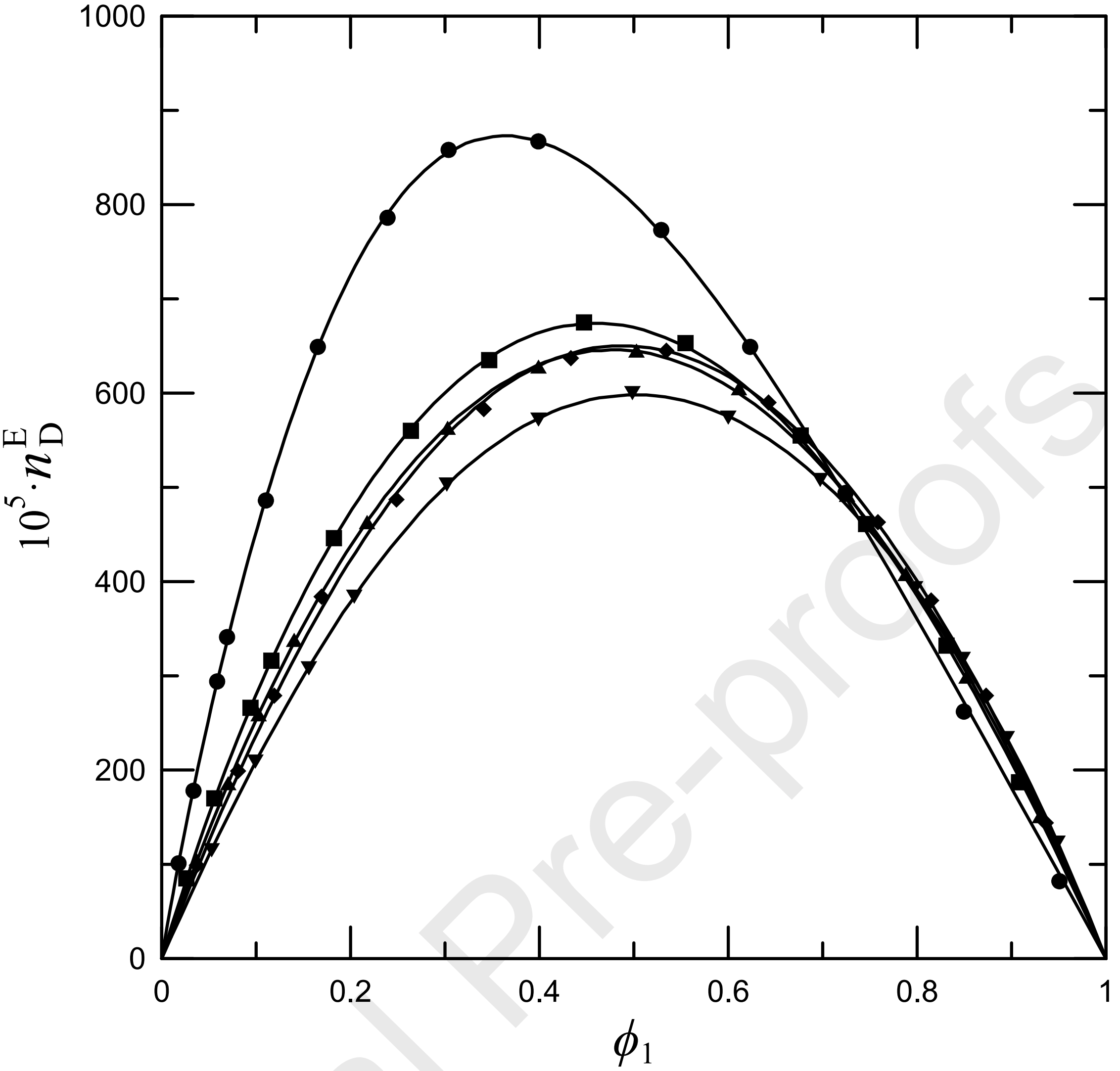


Figure 3

Excess refractive index at the sodium D-line, n_D^E, of alkan-1-ol (1) + TEA (2) liquid mixtures as a function of the alkan-1-ol volume fraction, ϕ_1, at 0.1 MPa, 298.15 K. Full symbols, experimental values (this work): (●), methanol; (■), propan-1-ol; (▲), butan-1-ol; (♦), pentan-1-ol; (▼), heptan-1-ol. Solid lines, calculations with equation (5) using the coefficients from Table 5.

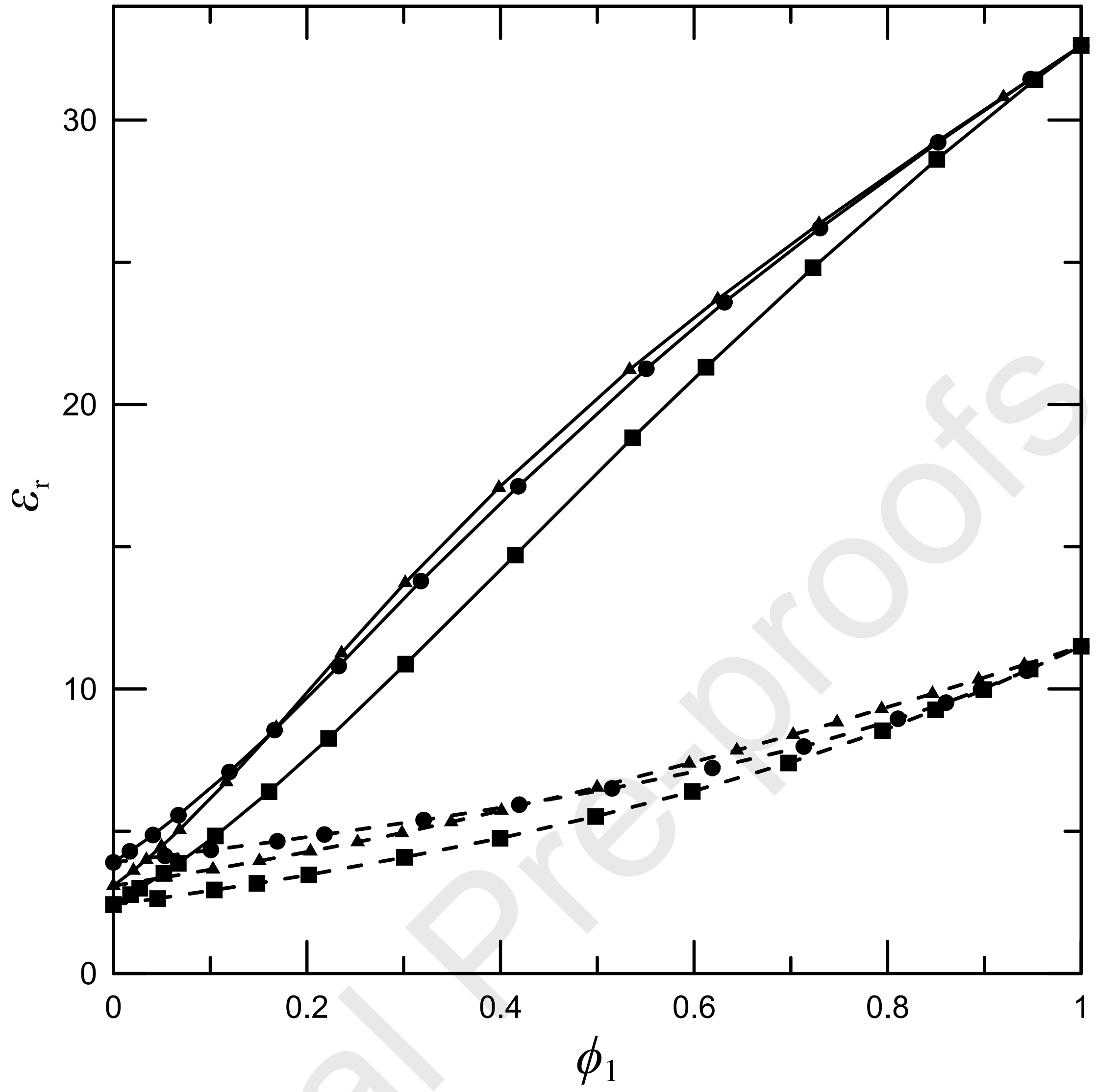


Figure 4

Relative permittivity, ε_r, of alkan-1-ol (1) + amine (2) liquid mixtures as a function of the alkan-1-ol volume fraction, ϕ_1, at 0.1 MPa, 298.15 K and 1 MHz: (●), HxA [27]; (▲), DPA [28]; (■), TEA (this work). Solid lines, methanol; dashed lines, heptan-1-ol.

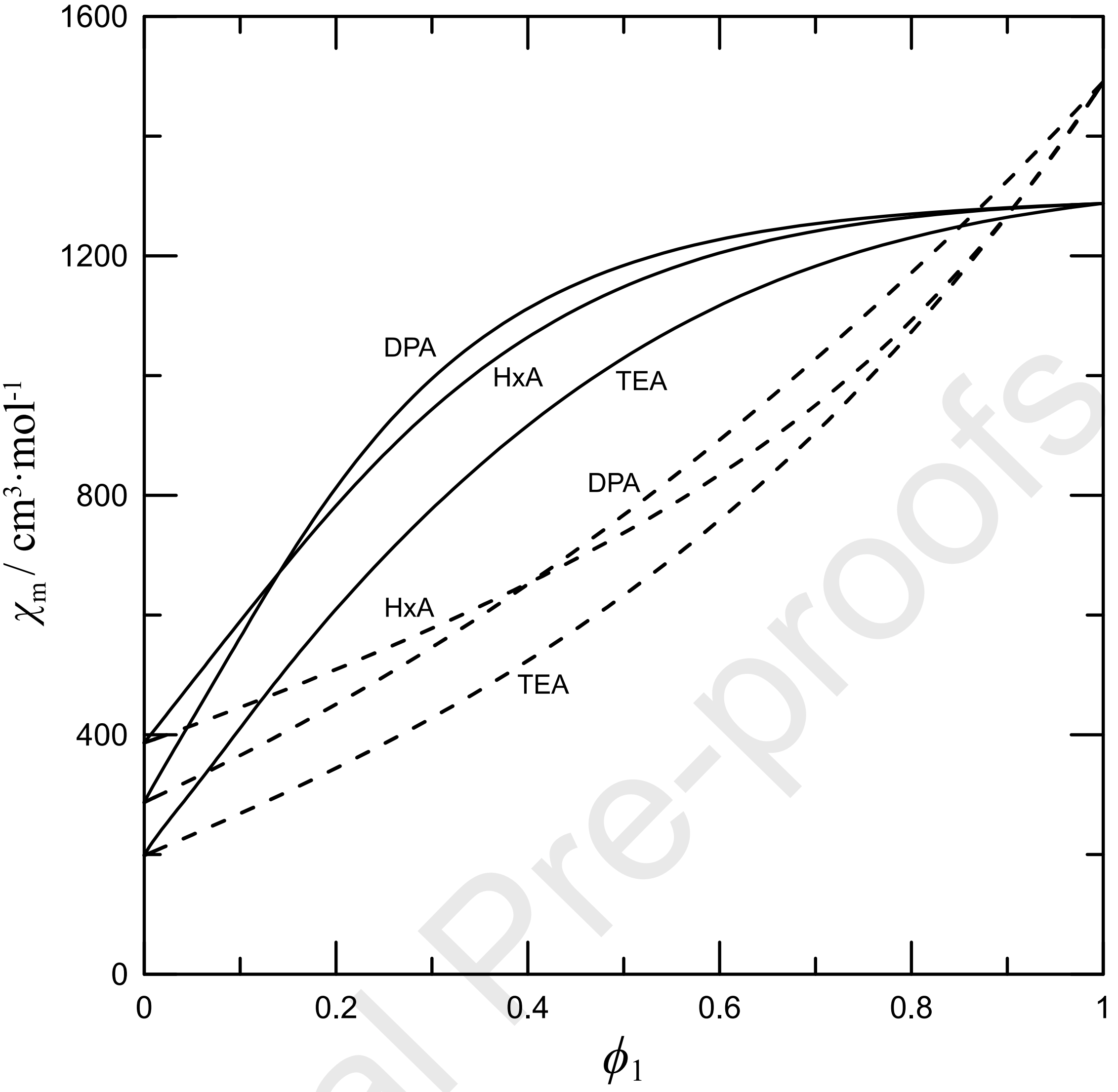


Figure 5

Molar susceptibility, χ_m, of alkan-1-ol (1) + amine (2) liquid mixtures as a function of the alkan-1-ol volume fraction, ϕ_1, at 0.1 MPa, 298.15 K and 1 MHz: HxA [27]; DPA [28]; TEA (this work). Solid lines, methanol; dashed lines, heptan-1-ol.

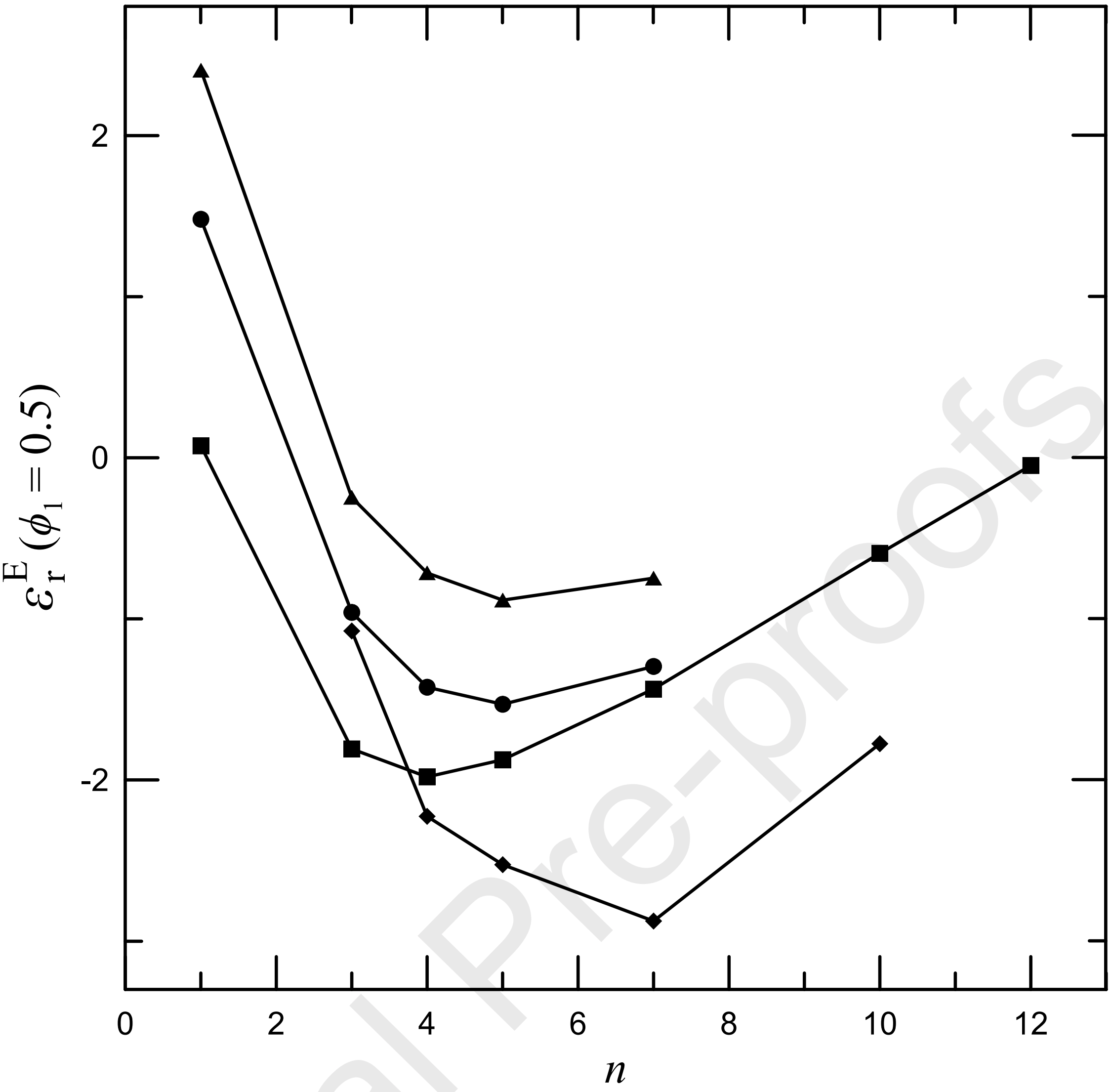


Figure 6

Excess relative permittivity at $\phi_1 = 0.5$ (ϕ_1, alkan-1-ol volume fraction) of alkan-1-ol (1) + amine (2) or + heptane (2) liquid mixtures as a function of the number of carbon atoms of the alkan-1-ol, *n*, at 0.1 MPa, 298.15 K and 1 MHz: (●), HxA [27]; (▲), DPA [28]; (■), TEA (*n* = 1 to 7, this work; *n* = 10,12 are literature values [55] at 293.15 K); (♦), heptane [24,52,53].

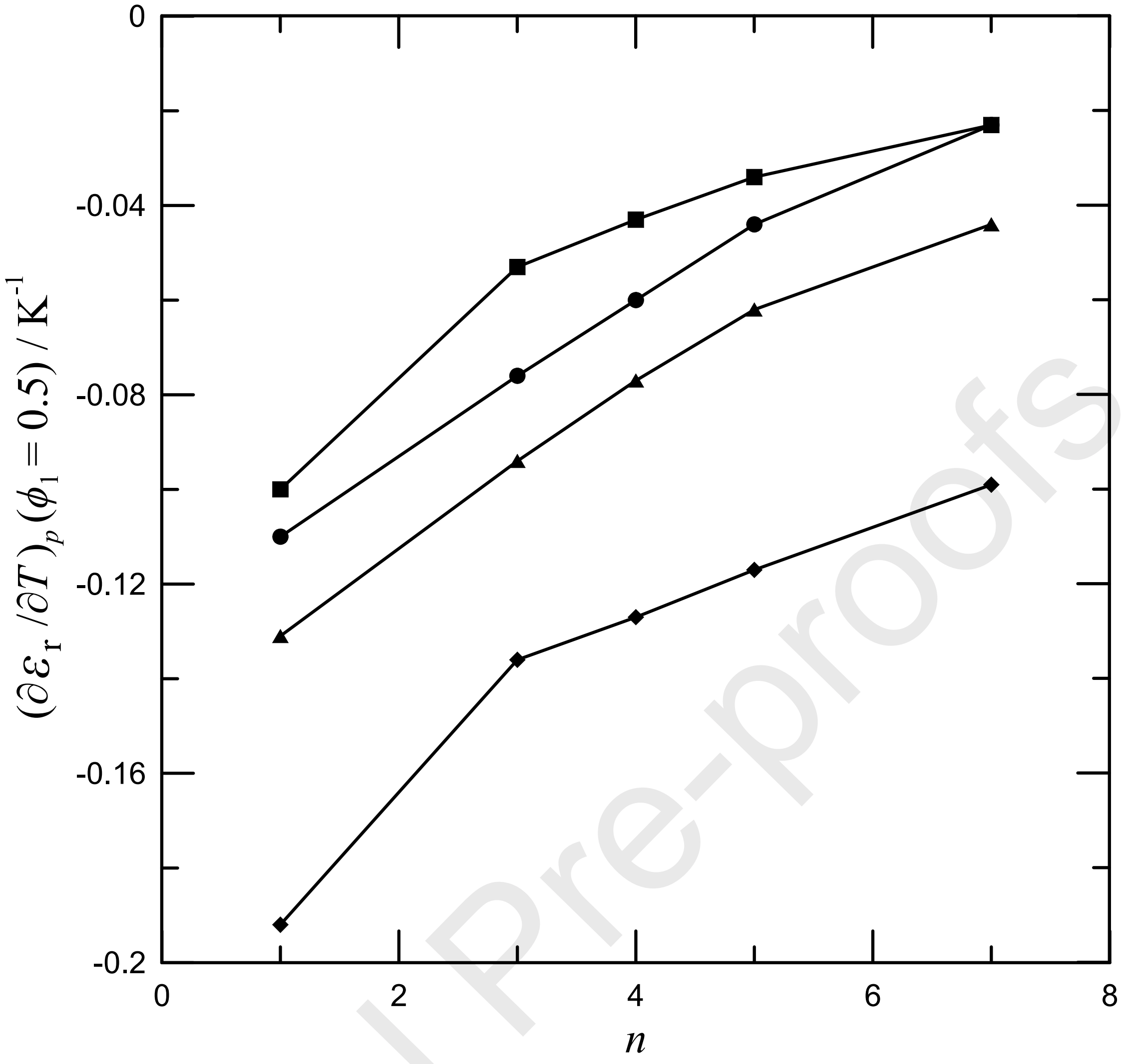


Figure 7

Temperature derivative of the relative permittivity, $\left(\partial\varepsilon_{\mathrm{r}}/\partial T\right)_p$, at $\phi_1 = 0.5$ (ϕ_1, alkan-1-ol volume fraction) of alkan-1-ol (1) + amine (2) liquid mixtures or pure alkan-1-ols as a function of the number of carbon atoms of the alkan-1-ol, *n*, at 0.1 MPa, 298.15 K and 1 MHz: (●), HxA [27]; (▲), DPA [28]; (■), TEA (this work); (♦), pure alkan-1-ols (this work).

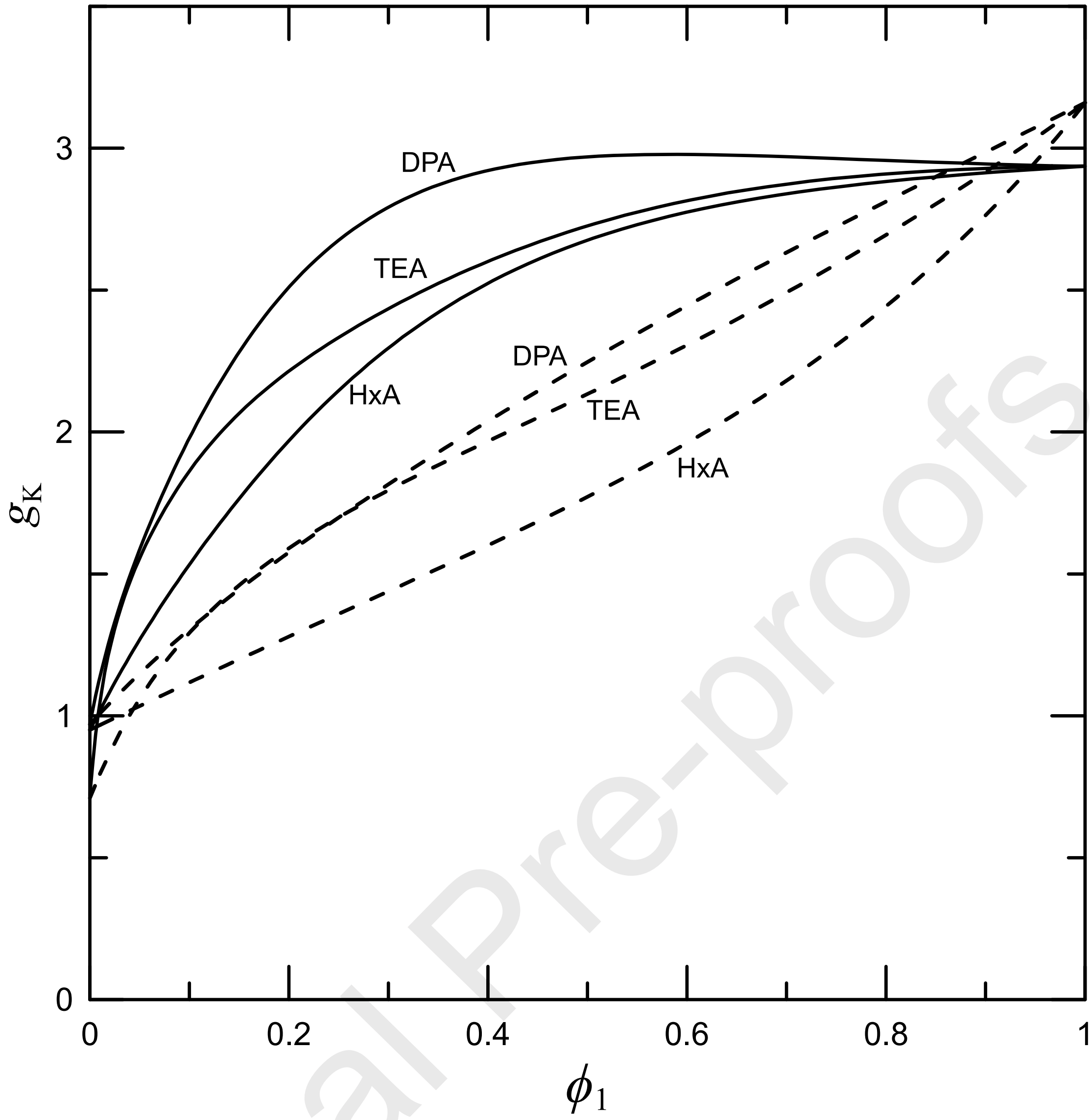


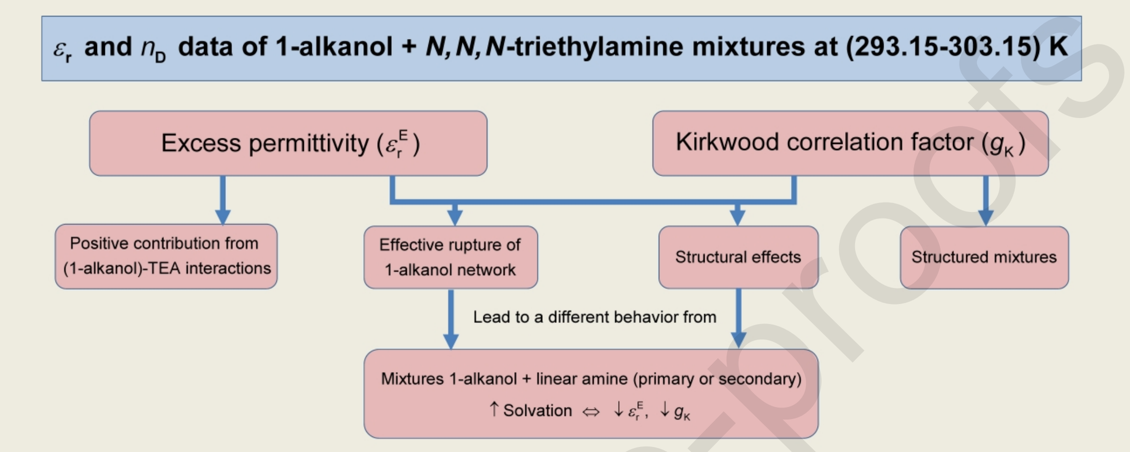
Figure 8

Kirkwood correlation factor, g_K, of alkan-1-ol (1) +amine (2) liquid mixtures as a function of the alkan-1-ol volume fraction, ϕ_1, at 0.1 MPa, 298.15 K: HxA [27]; DPA [28]; TEA (this work). Solid lines, methanol; dashed lines, heptan-1-ol.

Highlights

- ε_r, n_D and excess functions are reported at (293.15-303.15) K for 1-alkanol+TEA.
- (1-alkanol)-TEA interactions contribute positively to ε_r^E.

- $\varepsilon_r^E(\phi_1 = 0.5)$ changes in the order: methanol > 1-propanol > 1-butanol < 1-pentanol < 1-heptanol.
- TEA is a good breaker of 1-alkanol self-association. Structural effects affect ε_r^E.
- The Kirkwood-Fröhlich model is used to study the mixtures.



Thermodynamics of mixtures with strongly negative deviations from Raoult's law. XVII. Permittivities and refractive indices for alkan-1-ol + *N,N*-diethylethanamine systems at (293.15-303.15) K. Application of the Kirkwood-Fröhlich model

Supplementary material

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Table S1

Volume fraction of alkan-1-ol, ϕ_1, and derivative of the excess relative permittivity at frequency ν = 1 MHz, $\left(\partial\varepsilon_{\mathrm{r}}^{\mathrm{E}}/\partial T\right)_p$, of alkan-1-ol (1) + *N,N*-diethylethanamine (TEA) (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	$\left(\partial\varepsilon_{\mathrm{r}}^{\mathrm{E}}/\partial T\right)_p$ / K^{-1}	x_1	ϕ_1	$\left(\partial\varepsilon_{\mathrm{r}}^{\mathrm{E}}/\partial T\right)_p$ / K^{-1}
methanol (1) + TEA (2) ; *T*/K = 298.15					
0.0580	0.0176	0.0008	0.5979	0.3019	0.0019
0.0878	0.0272	0.0011	0.7096	0.4154	0.0000
0.1593	0.0522	0.0025	0.7992	0.5365	–0.0041
0.1981	0.0670	0.0027	0.8445	0.6123	–0.0056
0.2880	0.1053	0.0032	0.8997	0.7229	–0.0055
0.3971	0.1608	0.0038	0.9515	0.8509	–0.0043
0.4959	0.2224	0.0034	0.9856	0.9522	–0.0007
propan-1-ol (1) + TEA (2) ; *T*/K = 298.15					
0.0476	0.0261	0.0023	0.6027	0.4488	0.0171
0.0932	0.0523	0.0038	0.6997	0.5557	0.0162
0.1394	0.0800	0.0056	0.7966	0.6776	0.0143
0.2032	0.1204	0.0079	0.8455	0.7460	0.0121
0.2896	0.1795	0.0106	0.9014	0.8307	0.0069
0.4084	0.2704	0.0145	0.9484	0.9080	0.0047
0.5043	0.3532	0.0165			
butan-1-ol (1) + TEA (2) ; *T*/K = 298.15					
0.0536	0.0359	0.0026	0.6006	0.4969	0.0222
0.1102	0.0752	0.0054	0.6985	0.6034	0.0225
0.1536	0.1065	0.0077	0.8023	0.7272	0.0187
0.2025	0.1429	0.0098	0.8438	0.7801	0.0156
0.2941	0.2148	0.0135	0.8910	0.8430	0.0120
0.3957	0.3007	0.0177	0.9475	0.9222	0.0074
0.5082	0.4043	0.0209			
pentan-1-ol (1) + TEA (2) ; *T*/K = 298.15					
0.0588	0.0463	0.0035	0.5968	0.5347	0.0256
0.1062	0.0844	0.0057	0.7072	0.6522	0.0255
0.1482	0.1190	0.0082	0.7960	0.7518	0.0220
0.2159	0.1761	0.0119	0.8517	0.8168	0.0180
0.3011	0.2506	0.0159	0.8939	0.8674	0.0142
0.4089	0.3494	0.0207	0.9465	0.9321	0.0071
0.5014	0.4384	0.0236			

heptan-1-ol (1) + TEA (2) ; T/K = 298.15					
0.0451	0.0457	0.0030	0.5950	0.5982	0.0292
0.1029	0.1041	0.0067	0.6948	0.6976	0.0292
0.1466	0.1483	0.0098	0.7925	0.7947	0.0258
0.1997	0.2019	0.0126	0.8478	0.8495	0.0223
0.2979	0.3007	0.0183	0.8982	0.8994	0.0158
0.3963	0.3995	0.0227	0.9465	0.9472	0.0091
0.4950	0.4984	0.0267			

[a] The standard uncertainties are: $u(T)$ = 0.02 K; $u(p)$ = 1 kPa; $u(\nu)$ = 20 Hz; $u(x_1)$ = 0.0010; $u(\phi_1)$ = 0.004; $u\left[\left(\partial\varepsilon_{\mathrm{r}}^{\mathrm{E}}/\partial T\right)_p\right]$ = 0.0008 K^{-1}.

Table S2

Values of the derivative of permittivity with respect to temperature for pure compounds, $\left(\partial\varepsilon_{\mathrm{r}}^{*}/\partial T\right)_{p}$, and for mixtures, $\left(\partial\varepsilon_{\mathrm{r}}/\partial T\right)_{p}$, at ϕ_1 = 0.5 (ϕ_1, volume fraction of the alkan-1-ol), temperature T = 298.15 K and pressure p = 0.1 MPa. [a]

Compound	$\left(\partial\varepsilon_{\mathrm{r}}^{*}/\partial T\right)_{p}$/K^{-1}		$\left(\partial\varepsilon_{\mathrm{r}}/\partial T\right)_{p}$/K^{-1}		
	Exp.	Lit.	alkan-1-ol + HxA [1]	alkan-1-ol + DPA [2]	alkan-1-ol + TEA
Methanol	–0.192	–0.195 [3]	–0.110	–0.131	–0.100
propan-1-ol	–0.136	–0.130 [4]	–0.076	–0.094	–0.053
butan-1-ol	–0.127	–0.122 [4]	–0.060	–0.077	–0.043
pentan-1-ol	–0.117	–0.110 [4]	–0.044	–0.062	–0.034
heptan-1-ol	–0.099	–0.096 [4]	–0.023	–0.044	–0.023

[a] hexan-1-amine (HxA), *N*-propylpropan-1-amine (DPA), *N*,*N*-diethylethanamine (TEA).

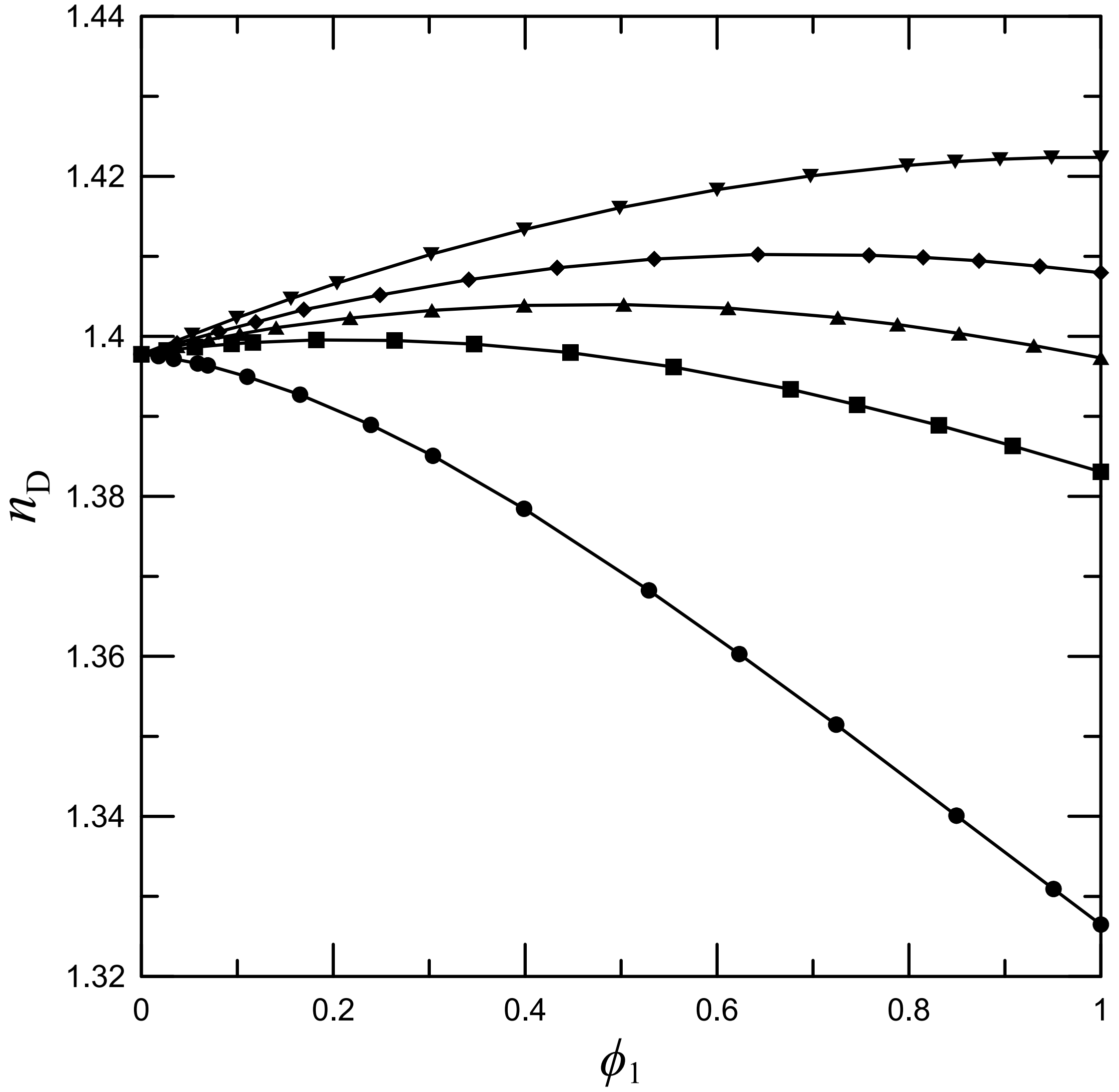

Figure S1

Refractive index at the sodium D-line, n_D, of alkan-1-ol (1) + TEA (2) liquid mixtures as a function of the alkan-1-ol volume fraction, ϕ_1, at 0.1 MPa, 298.15 K. Full symbols, experimental values (this work): (●), methanol; (■), propan-1-ol; (▲), butan-1-ol; (♦), pentan-1-ol; (▼), heptan-1-ol.

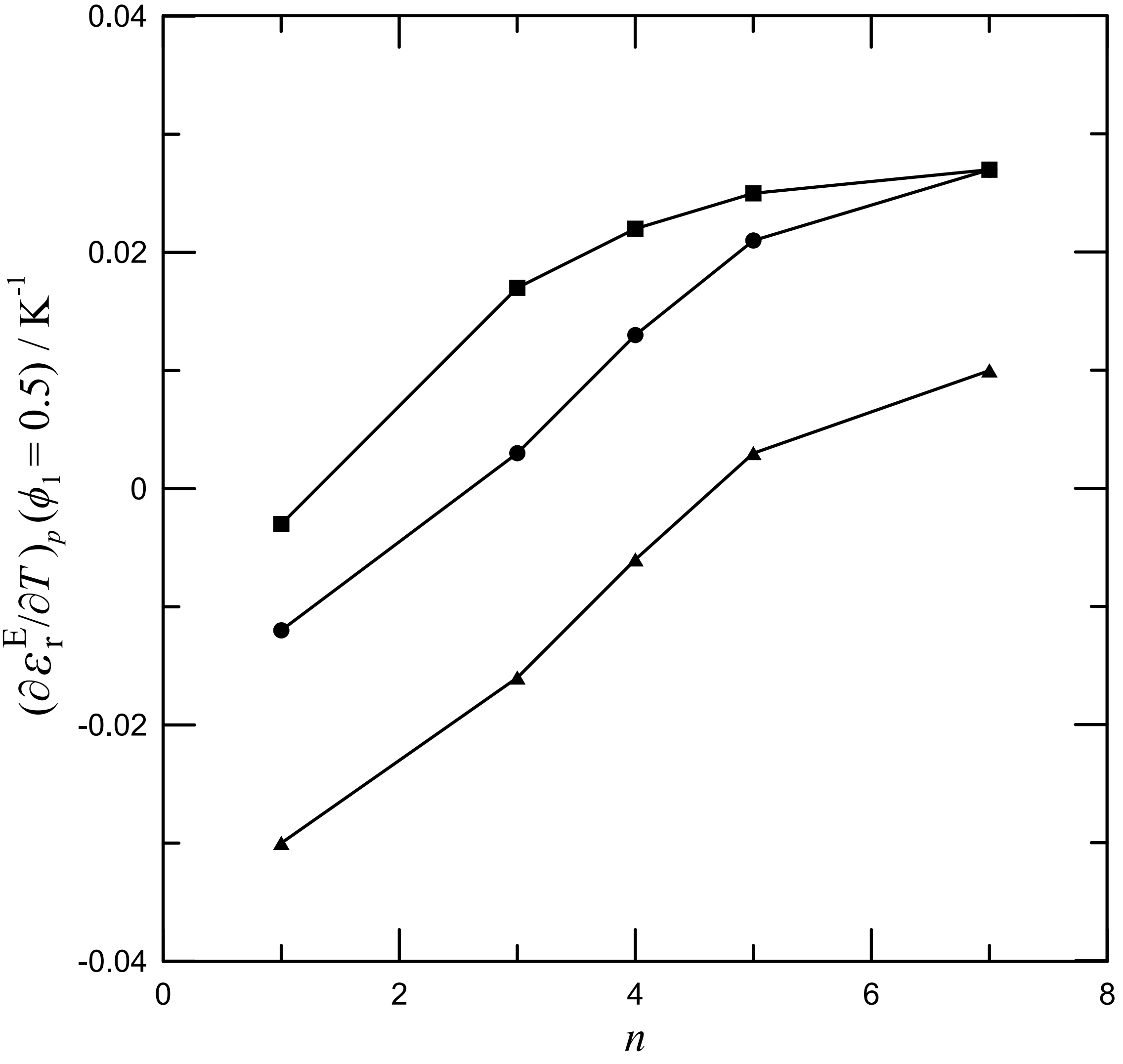

Figure S2

Temperature derivative of the excess relative permittivity, $\left(\partial\varepsilon_r^E / \partial T\right)_p$, at $\phi_1 = 0.5$ of alkan-1-ol (1) + amine (2) liquid mixtures as a function of the number of carbon atoms of the alkan-1-ol, *n*, at 0.1 MPa, 298.15 K and 1 MHz: (●), HxA [1]; (▲), DPA [2]; (■), TEA (this work).

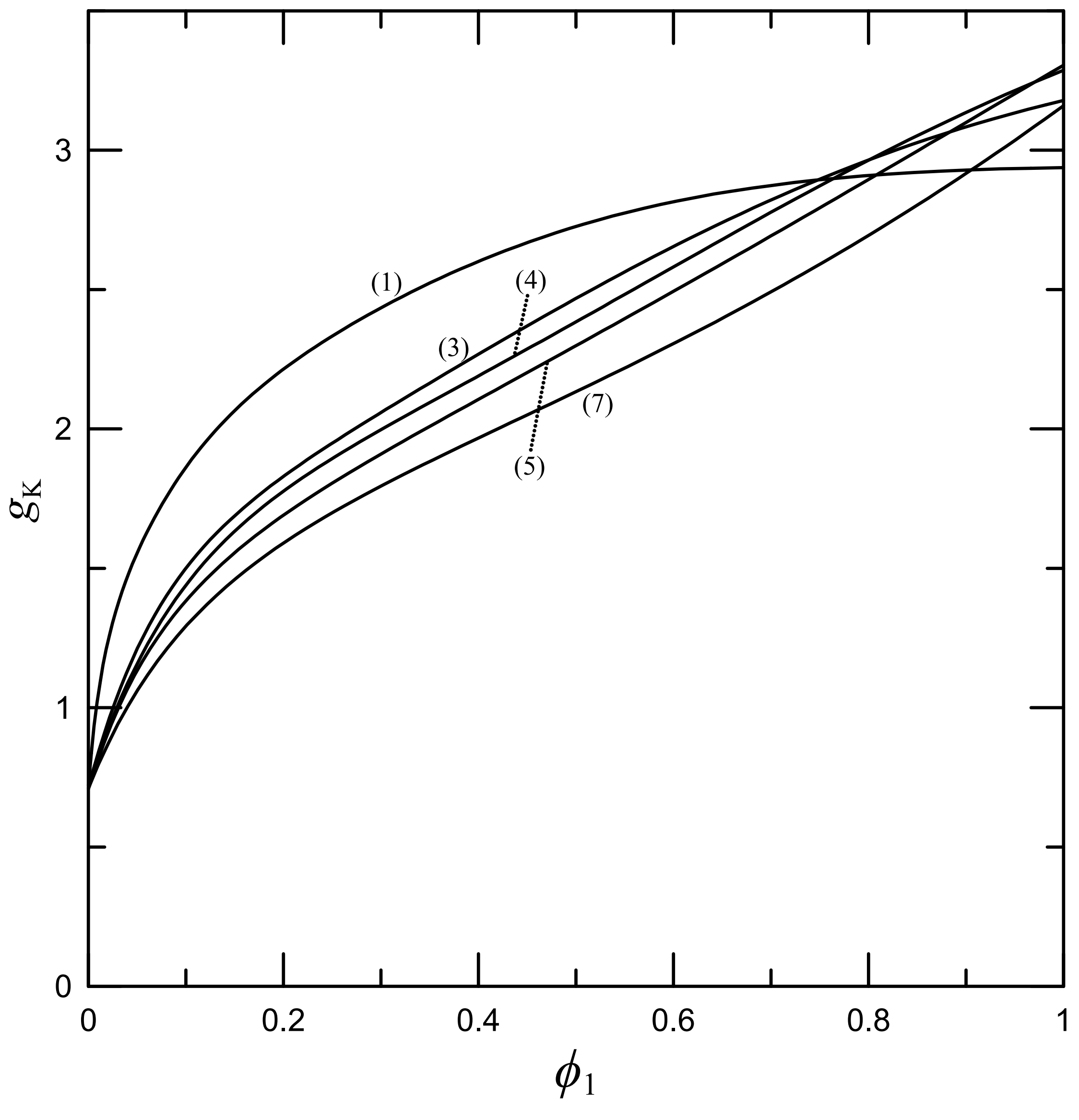

Figure S3

Kirkwood correlation factor, g_K, of alkan-1-ol (1) + TEA (2) liquid mixtures as a function of the alkan-1-ol volume fraction, ϕ_1, at 0.1 MPa, 298.15 K. Numbers in parentheses indicate the number of carbon atoms of the alkan-1-ol.

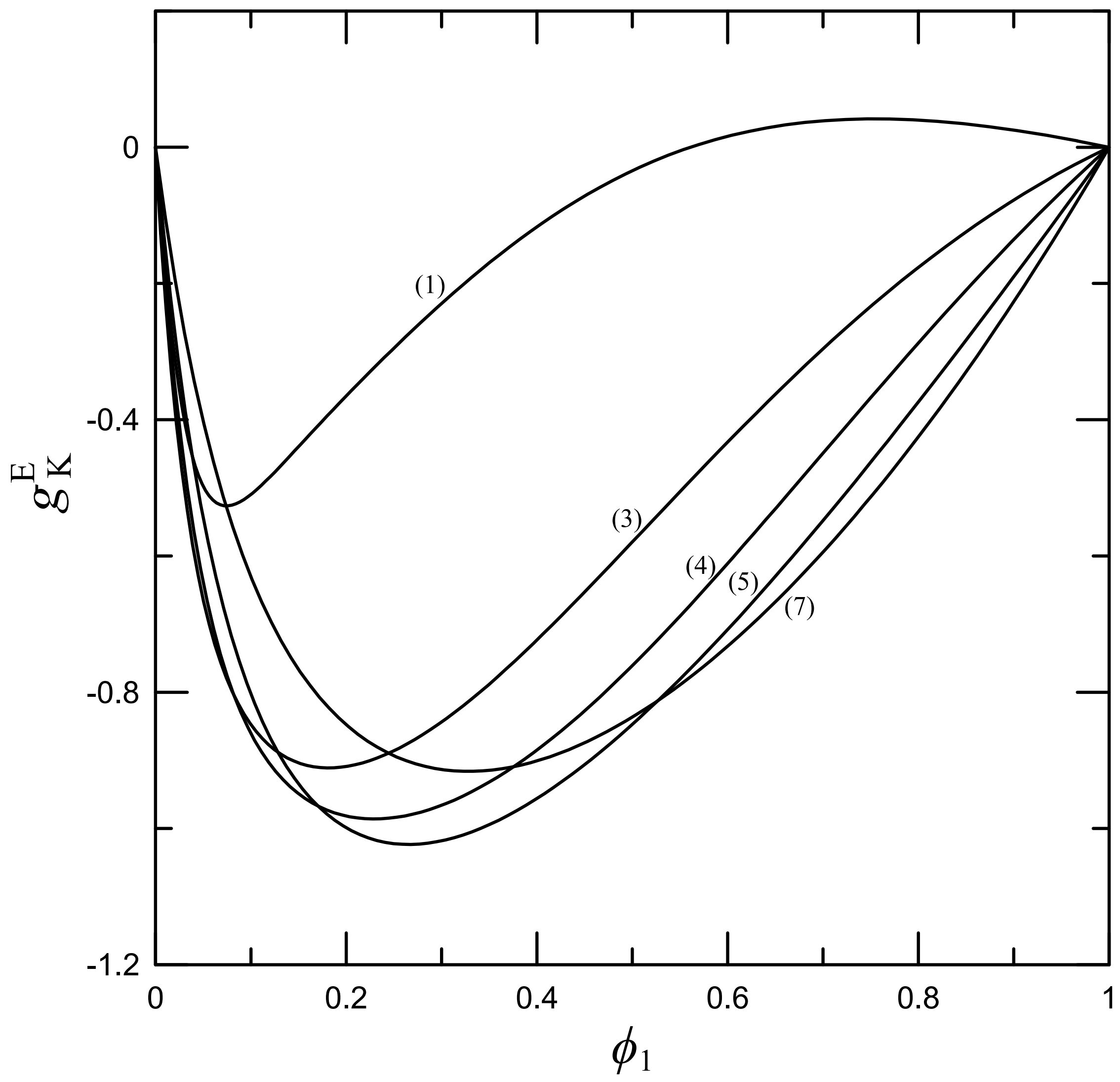

Figure S4

Excess Kirkwood correlation factor, g_K^E, of alkan-1-ol (1) + TEA (2) liquid mixtures as a function of the alkan-1-ol volume fraction, ϕ_1, at 0.1 MPa, 298.15 K. Numbers in parentheses indicate the number of carbon atoms of the alkan-1-ol.

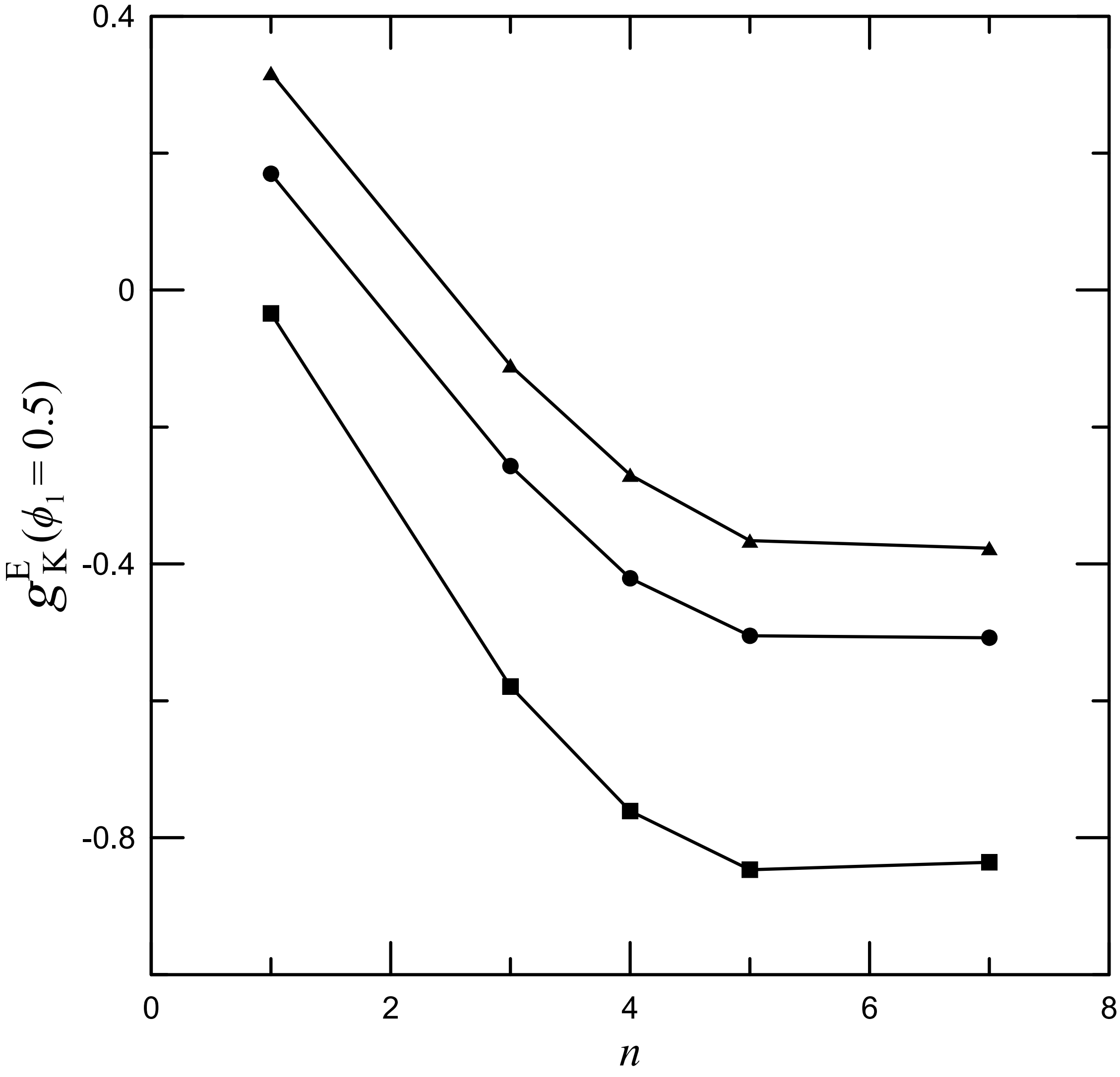

Figure S5

Excess Kirkwood correlation factor at $\phi_1 = 0.5$ (ϕ_1, alkan-1-ol volume fraction) of alkan-1-ol (1) + amine (2) liquid mixtures as a function of the number of carbon atoms of the alkan-1-ol, at 0.1 MPa, 298.15 K: (●), HxA [1]; (▲), DPA [2]; (■), TEA (this work).

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