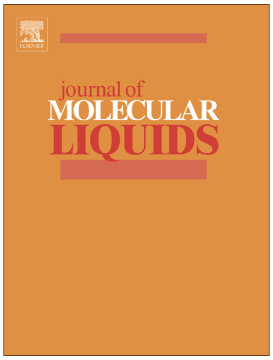

Thermodynamics of mixtures with strongly negative deviations from Raoult's law. XVI. Permittivities and refractive indices for 1-alkanol + di-n-propylamine systems at (293.15–303.15) K. Application of the Kirkwood-Fröhlich model

Fernando Hevia, Ana Cobos, Juan Antonio González, Isaías García de la Fuente, Luis Felipe Sanz

PII: S0167-7322(18)33281-1
DOI: doi:10.1016/j.molliq.2018.09.040
Reference: MOLLIQ 9646

To appear in: *Journal of Molecular Liquids*

Received date: 28 June 2018
Revised date: 5 September 2018
Accepted date: 8 September 2018

Please cite this article as: Fernando Hevia, Ana Cobos, Juan Antonio González, Isaías García de la Fuente, Luis Felipe Sanz , Thermodynamics of mixtures with strongly negative deviations from Raoult's law. XVI. Permittivities and refractive indices for 1-alkanol + di-n-propylamine systems at (293.15–303.15) K. Application of the Kirkwood-Fröhlich model. Molliq (2018), doi:10.1016/j.molliq.2018.09.040

Thermodynamics of mixtures with strongly negative deviations from Raoult's law. XVI. Permittivities and refractive indices for 1-alkanol + di-*n*-propylamine systems at (293.15-303.15) K. Application of the Kirkwood-Fröhlich model

Fernando Hevia, Ana Cobos, Juan Antonio González*, Isaías García de la Fuente, Luis Felipe Sanz

G.E.T.E.F., Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Valladolid. Paseo de Belén, 7, 47011 Valladolid, Spain.

*e-mail: jagl@termo.uva.es; Tel: +34-983-423757

Abstract

Relative permittivities at 1 MHz, ε_r, and refractive indices at the sodium D-line, n_D, are reported at 0.1 MPa and at (293.15-303.15) K for the binary systems 1-alkanol + di-*n*-propylamine (DPA). Their corresponding excess functions are calculated and correlated. For the methanol mixture, positive values of the excess permittivities, $\varepsilon_\mathrm{r}^\mathrm{E}$, are found. Except at high concentrations of the alcohol in the 1-propanol mixture, the remaining systems show negative values of this property. This fact reveals that the creation of (1-alkanol)-DPA interactions contributes positively to $\varepsilon_\mathrm{r}^\mathrm{E}$, being this contribution dominant in the methanol mixture. The negative contributions arising from the disruption of interactions between like molecules are prevalent in the other mixtures. At ϕ_1 (volume fraction) = 0.5, $\varepsilon_\mathrm{r}^\mathrm{E}$ changes in the sequence: methanol > 1-propanol > 1-butanol > 1-pentanol < 1-heptanol. An analogous variation with the chain length of the 1-alkanol is observed in mixtures such as 1-alkanol + heptane, + cyclohexylamine or + *n*-hexylamine (HxA). Moreover, for a given 1-alkanol, $\varepsilon_\mathrm{r}^\mathrm{E}$ is larger for DPA than for HxA mixtures, suggesting that in DPA solutions multimers with parallel alignment of the molecular dipoles are favoured and cyclic multimers are disfavoured when compared to HxA mixtures. The $(\partial\varepsilon_\mathrm{r}/\partial T)_p$ values are higher for the mixtures than for pure 1-alkanols, because (1-alkanol)-DPA interactions are stronger than those between 1-alkanol molecules. Calculations on molar refractions indicate that dispersive interactions in the systems under study increase with the chain length of the 1-alkanol and are practically identical to those in HxA solutions. The considered mixtures are treated by means of the Kirkwood-Fröhlich model, reporting the Kirkwood correlation factors and their excess values.

Keywords: 1-alkanol; di-*n*-propylamine; permittivity; refractive index; Kirkwood correlation factor.

1. Introduction

Amines are found in situations of biological interest. For instance, the breaking of amino acids releases amines and proteins that are usually bound to DNA polymers contain several amine groups [1]. Their low vapour pressure makes them useful in green chemistry. Mixtures containing amines are being investigated to be used in CO_2 capture [2]. On the other hand, many of the ions of the technically important ionic liquids are related to amine groups [3]. Linear primary and secondary amines are weakly self-associated compounds [4-8] with rather low dipole moments. Liquid mixtures formed by 1-alkanol and a linear primary or secondary amine are rather interesting from a theoretical point of view, as they show strongly negative deviations from Raoult's law. In fact, the excess molar Gibbs energies, G_m^E, at x_1 (mole fraction) = 0.5 for methanol systems are: –823 J·mol^{-1} (di-*n*-ethylamine; T = 298.15 K [9]) and –799 J·mol^{-1} (*n*-butylamine, T = 348.15 K [10]). Accordingly, the excess molar enthalpies (H_m^E) values are large and negative. For instance, at 298.15 K and x_1 = 0.5; H_m^E(methanol)/J·mol^{-1} = –3200 (*n*-hexylamine (HxA)) [11]; –4581 (di-*n*-ethylamine) [12]. This has been explained in terms of two different opposing effects. In the pure liquid state, both 1-alkanols and linear amines are self-associated by means of O-H---O and N-H---N bonds, respectively. Such bonds are disrupted along the mixing process, which positively contribute to H_m^E. On the other hand, it is well known that the formation of interactions between unlike molecules upon mixing contribute negatively to H_m^E. Therefore, the large and negative H_m^E values of this type of systems reveal that the new O-H---N bonds created are stronger than the O-H---O and N-H---N bonds. For instance, the values of the enthalpy of the hydrogen bonds between methanol and amine estimated from the application of the ERAS model [13] are: –42.4 kJ·mol^{-1} (*n*-hexylamine) [7]; –45.4 kJ·mol^{-1} (di-*n*-ethylamine) [14]. We remark that such values are much more negative than that used, within this model, for the enthalpy of the H bonds between alkanol molecules, –25.1 kJ·mol^{-1} [7, 13, 14]. As a consequence of the strong interactions between unlike molecules, the systems are highly structured. For example, at T = 298.15 K and x_1 = 0.5, TS_m^E $(= H_\mathrm{m}^\mathrm{E} - G_\mathrm{m}^\mathrm{E})$ is –3758 J·mol^{-1} for the methanol + di-*n*-ethylamine mixture (see above). This result is much more negative than the value for the 1-propanol + hexane system, TS_m^E = (533 $(= H_\mathrm{m}^\mathrm{E})$ – 1295 $(= G_\mathrm{m}^\mathrm{E})$) = –762 J·mol^{-1} [15, 16]. The large and negative excess molar volumes [7, 17-21] and solid-liquid equilibria (SLE) measurements [22] also support the existence of strong interactions between unlike molecules in 1-alkanol + linear amine mixtures. It is to be noted that the SLE phase diagrams show that complex formation is an important feature of these solutions [22]. In addition, $\varepsilon_\mathrm{r}^\mathrm{E}$ values also indicate strong interactions between unlike molecules in 1-alkanol +

linear primary amine systems; e.g. for the methanol + HxA mixture [23] ε_r^E = 1.480 at T = 298.15 K and ϕ_1 (volume fraction) = 0.5.

We have extended the database of 1-alkanol + amine mixtures reporting excess molar volumes [7, 17-21]; dynamic viscosities [19-21]; vapour-liquid equilibria [24]; permittivities (ε_r) and refractive indices (n_D) [19-21, 25]. In addition, these systems have been investigated using different models as DISQUAC or ERAS [6, 7, 14, 17, 18, 20, 26-28]; the formalism of the Kirkwood-Buff integrals [29], or the concentration-concentration structure factor ($S_{CC}(0)$) formalism [30]. More recently [23], we have provided ε_r and n_D data for the 1-alkanol + HxA mixtures over the temperature range (293.15-303.15) K, and analysed them using the Kirkwood-Fröhlich model [31-34], which is a useful approach to gain insight into the mixture structure and interactions. As a continuation, and in order to investigate the effect of replacing a linear primary amine (HxA) by a linear secondary amine (di-*n*-propaylamine, (DPA)), we report similar measurements over the same range of temperature for mixtures formed by the latter amine and methanol, or 1-propanol, or 1-butanol, or 1-pentanol or 1-heptanol. In addition, the systems are also studied by means of Kirkwood-Fröhlich model.

2. Experimental

2.1 Materials

Information about the purity and source of the pure compounds, which were used in the experiments without further purification, is collected in Table 1. Their ε_r values at 1 MHz, densities (ρ) and n_D values at 0.1 MPa and at the working temperatures can be found in Table 2. These results agree well with literature data.

2.2 Apparatus and procedure

Binary mixtures were prepared by mass in small vessels of about 10 cm^3 with the aid of an analytical balance Sartorius MSU125p (weighing accuracy 0.01 mg), taking into account the corresponding corrections on buoyancy effects. The standard uncertainty in the final 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) [35]. In order to minimize the effects of the interaction of the compounds with air components, they were stored with 4 Å molecular sieves (except methanol, because measurements were affected). In addition, the measurement cell (see below) was completely filled with the samples and appropriately closed. Different density measurements of pure compounds, conducted along experiments, showed that this quantity remained unchanged within the experimental uncertainty.

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

The ε_r measurements were performed with the aid of an equipment from Agilent. A 16452A cell, which is a parallel-plate capacitor made of Nickel-plated cobalt (54% Fe, 17% Co, 29% Ni) with a ceramic insulator (alumina, Al_2O_3), is filled with a sample volume of ≈ 4.8 cm^3. The cell is connected by a 16048G test lead to a precision impedance analyser 4294A, and immersed in a thermostatic bath LAUDA RE304, with a temperature stability of 0.02 K. Details about the device configuration and calibration are given elsewhere [36]. 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, 1-propanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol and 1-decanol.

A Bellingham+Stanley RFM970 refractometer was used for the n_D measurements. The technique is based on the optical detection of the critical angle at the wavelength of the sodium D line (589.3 nm). The temperature is controlled by Peltier modules and its stability is $0.02\,\mathrm{K}$. The refractometer has been calibrated using 2,2,4-trimethylpentane and toluene at (293.15-303.15) K, following the recommendations by Marsh [37]. The standard uncertainty of n_D is 0.00008.

Densities were obtained using a vibrating-tube densimeter and sound analyzer Anton Paar DSA5000, which is automatically thermostated within $0.01\,\mathrm{K}$. The calibration procedure has been described elsewhere [38]. The relative standard uncertainty of the ρ measurements is 0.0012.

3. Results

Let us denote by x_i the mole fraction of component i. The corresponding volume fraction, ϕ_i, is given by $\phi_i = x_i V_{\mathrm{m}i}^* / \left(x_1 V_{\mathrm{m}1}^* + x_2 V_{\mathrm{m}2}^* \right)$, where $V_{\mathrm{m}i}^*$ stands for the molar volume of component i. For an ideal mixture at the same temperature and pressure as the mixture under study, the relative permittivity, $\varepsilon_{\rm r}^{\rm id}$, the derivative $\left[\left(\partial\varepsilon_{\rm r}/\partial T\right)_p\right]^{\rm id}$, and the refractive index, $n_{\rm D}^{\rm id}$, are given by [39, 40]:

$$\varepsilon_{\rm r}^{\rm id} = \phi_1\varepsilon_{\rm r1}^{*} + \phi_2\varepsilon_{\rm r2}^{*} \tag{1}$$

$$n_{\rm D}^{\rm id} = \left[\phi_1\left(n_{\rm D1}^{*}\right)^2 + \phi_2\left(n_{\rm D2}^{*}\right)^2\right]^{1/2} \tag{2}$$

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

where $\varepsilon_{{\rm r}i}^{*}$ and $n_{{\rm D}i}^{*}$ denote the relative permittivity and the refractive index of pure species i, and $\left(\partial\varepsilon_{\rm r}^{\rm id}/\partial T\right)_p$ is calculated from linear regressions as indicated above. The corresponding excess functions, $F^{\rm E}$, are obtained as

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

Table 3 lists ϕ_1, ε_r and $\varepsilon_{\rm r}^{\rm E}$ values of 1-alkanol (1) + DPA (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, $n_{\rm D}$ and $n_{\rm D}^{\rm E}$ values.

We calculated the derivative $\left(\partial\varepsilon_{\rm r}/\partial T\right)_p$ at 298.15 K as the slope of a linear regression of experimental $\varepsilon_{\rm r}$ values in the range (293.15 – 303.15) K. The data of $\left[\left(\partial\varepsilon_{\rm r}/\partial T\right)_p\right]^{\rm E} = \left(\partial\varepsilon_{\rm r}^{\rm E}/\partial T\right)_p$ are collected in Table S1 (supplementary material).

The $F^{\rm E}$ data were fitted to a Redlich-Kister equation [41] by unweighted linear least-squares regressions:

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

The number, k, of necessary coefficients for this regression has been determined, for each system and temperature, by applying an F-test of additional term [42] at a 99.5% confidence level. Table 5 includes the parameters A_i obtained, and the standard deviations $\sigma\left(F^{\rm E}\right)$, defined by:

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

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

Values of $\varepsilon_{\mathrm{r}}^{\mathrm{E}}$, $n_{\mathrm{D}}^{\mathrm{E}}$ and $\left(\partial\varepsilon_{\mathrm{r}}^{\mathrm{E}} / \partial T\right)_p$ versus ϕ_1 of 1-alkanol + DPA 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

Unless stated otherwise, the below values of the thermophysical properties and their corresponding excess functions are referred to T = 298.15 K and $\phi_1 = 0.5$. We will denote by n the number of C atoms of the 1-alkanol.

4.1. Excess relative permittivities

It is known that the breaking of interactions between like molecules in the mixing process leads to a negative contribution to $\varepsilon_{\mathrm{r}}^{\mathrm{E}}$. On the other hand, the creation of interactions between molecules of different species can lead to either a positive or to a negative contribution to $\varepsilon_{\mathrm{r}}^{\mathrm{E}}$, depending on the capability of the multimers formed to respond to an external electric field and lead to a macroscopic dipole moment. For instance, 1-alkanol + heptane mixtures show rather large negative values of this quantity, which can be ascribed to the breaking of the 1-alkanol self-association (Figure 4): $\varepsilon_{\mathrm{r}}^{\mathrm{E}}$ = –1.075 (n = 3), –2.225 (n = 4), –2.525 (n = 5), –2.875 (n = 7), –1.775 (n = 10) [20, 43-45]. For methanol, there exists a partial immiscibility region [46]. The corresponding $\varepsilon_{\mathrm{r}}^{\mathrm{E}}$ values of 1-alkanol + DPA systems are higher: 2.406 (n = 1), –0.246 (n = 3), –0.715 (n = 4), –0.883 (n = 5), –0.747 (n = 7) (Figure 4). This reveals that alkanol-amine interactions contribute positively to the mixture polarization. The positive $\varepsilon_{\mathrm{r}}^{\mathrm{E}}$ result for the methanol + DPA system strongly confirms this conclusion. 1-Alkanol + cyclohexylamine [21, 25], or + HxA [23] mixtures behave similarly and also show higher $\varepsilon_{\mathrm{r}}^{\mathrm{E}}$ values than those of 1-alkanol + heptane systems (Figure 4). On the other hand, the $\varepsilon_{\mathrm{r}}^{\mathrm{E}}(n)$ variation for 1-alkanol + DPA, or + cyclohexylamine, or + HxA mixtures follow the sequence: 1-propanol > 1-butanol > 1-pentanol < 1-heptanol (Figure 4), which is similar to that encountered for 1-alkanol + heptane mixtures (see above, Figure 4). For the latter systems, it has been explained in terms of the lower and weaker self-association of longer 1-alkanols [25]. For amine systems, this statement is still valid, but interactions between unlike molecules must be also considered. Studies on 1-alkanol + amine mixtures using the ERAS model show that solvation effects between unlike molecules decrease when the alkanol size is increased [7, 17, 18]. This means that the polarization changes, along the mixing process, in lower extent when longer 1-alkanols are involved, since these alcohols are less self-associated and the corresponding solvation effects are also less important. It is to be noted that $\varepsilon_{\mathrm{r}}^{\mathrm{E}}$ changes more sharply for mixtures with shorter 1-alkanols than for systems involving longer 1-alkanols and that the same occurs for the excess molar volumes and for the excess molar enthalpies [17].

Interestingly, for a given 1-alkanol, say 1-butanol, $\varepsilon_{\mathrm{r}}^{\mathrm{E}}$ (DPA) = –0.715 > $\varepsilon_{\mathrm{r}}^{\mathrm{E}}$ (HxA) = –1.424 [15] (Figure 4). This suggests that in DPA solutions multimers with parallel alignment of the molecular dipoles are favoured and cyclic multimers are disfavoured when compared to HxA mixtures. Furthermore, at $\phi_1 = 0.47$, the 1-butanol + di-*n*-ethylamine mixture [47] shows even a higher value (–0.13), which can be explained by the formation of a higher number and stronger of H bonds between unlike molecules, due to the amine group is less sterically hindered in this amine.

It may be pertinent to compare the dielectric behaviour of mixtures formed by 1-alkanol and DPA or di-*n*-propylether (DPE), as both solvents have similar size and structure. It is well known that the thermodynamic properties of the DPE systems are mainly characterized by the alkanol self-association [48]. Thus, the $H_{\mathrm{m}}^{\mathrm{E}}$ values are moderately positive ($H_{\mathrm{m}}^{\mathrm{E}}$/J·mol^{-1} = 740 for the 1-propanol system [49]); remain nearly constant for mixtures involving the longer 1-alkanols, and the corresponding $H_{\mathrm{m}}^{\mathrm{E}}$ curves are shifted towards low mole fractions of the 1-alkanol [48]. In contrast, as it has been previously mentioned, solvation, i.e. strong interactions between unlike molecules, is the main feature of 1-alkanol + DPA mixtures [14]. This is clearly demonstrated by the large and negative $H_{\mathrm{m}}^{\mathrm{E}}$ values of these systems (-2432 J·mol^{-1} for the 1-butanol solution [50]). For DPE mixtures, the dependence of $\varepsilon_{\mathrm{r}}^{\mathrm{E}}$ with the alcohol size is similar to that encountered for the amine systems examined: –1.03 (ethanol) < –1.24 (1-butanol) < –1.60 (1-hexanol) > –0.80 (1-decanol) [51]. On the other hand, for mixtures with a given 1-alkanol, $\varepsilon_{\mathrm{r}}^{\mathrm{E}}$ changes in the order: heptane < DPE < DPA (see above, Figure 4). This reveals that interactions between unlike molecules contribute more positively to the mixture polarization in the case of DPA systems.

4.2. Molar refraction

The refractive index at optical wavelengths is closely related to dispersion forces, since the molar refraction (or molar refractivity), R_{m} [34, 52]:

$$R_{\mathrm{m}} = \frac{n_{\mathrm{D}}^2 - 1}{n_{\mathrm{D}}^2 + 2} V_{\mathrm{m}} = \frac{N_A \alpha_e}{3\varepsilon_0} \qquad (7)$$

(where N_A and ε_0 stand for Avogadro's constant and the vacuum permittivity, respectively) is proportional to the mean electronic polarizability, α_e [32, 34]. For the investigated systems, the values of R_m / cm^3·mol^{-1} at x_1 = 0.5 are (Figure S2, supplementary material): 20.5 (*n* = 1), 25.2 (*n* = 3), 27.5 (*n* = 4), 29.8 (*n* = 5), 34.4 (*n* = 7). It is clear that dispersive interactions are more important in longer 1-alkanols. Moreover, the values are practically identical to those of 1-alkanol + HxA mixtures [23]. This is to be expected, as DPA and HxA are isomers and both linear, so dispersive interactions cannot differ appreciably. The excess molar refractions, $R_\mathrm{m}^\mathrm{E} = R_\mathrm{m} - R_\mathrm{m}^\mathrm{id}$, have also been calculated, with R_m^id evaluated substituting ideal values in equation (7). Values of R_m^E for 1-alkanol + hexane (*n* = 3, 4, 5, 6, 8 [53, 54]) are positive and small (< 0.04 cm^3·mol^{-1}). The same occurs for DPA + heptane (< 0.07 cm^3·mol^{-1} [45, 55], assuming ideal behaviour of n_D). However, in 1-alkanol + DPA systems the curves are negative; at x_1 = 0.5, R_m^E / cm^3·mol^{-1} –0.45 (*n* = 1), –0.37 (*n* = 3), –0.38 (*n* = 4), –0.39 (*n* = 5), –0.40 (*n* = 7). This loss in dispersive interactions along mixing with respect to the ideal state can then be ascribed to a large number of O-H---N bonds formed in the mixing process, being greater for the methanol mixture.

4.3. Temperature dependence of the permittivity

Firstly, we note that, for pure compounds, $(\partial\varepsilon_\mathrm{r}^*/\partial T)_p$ values are negative (Table 6), which is the typical behaviour of normal liquids. In the case of 1-alkanols, this quantity increases with *n* since the alcohol self-association decreases at this condition and a lower number of interactions between alcohol molecules are broken when the temperature is increased. The higher $(\partial\varepsilon_\mathrm{r}^*/\partial T)_p$ values of DPA or HxA can be explained similarly. Interestingly, results for $(\partial\varepsilon_\mathrm{r}/\partial T)_p$ are larger for the considered systems than for pure 1-alkanols (Table 6), which underlines the existence of (1-alkanol)-amine interactions. It is known that such interactions are stronger than those between alcohol molecules. For example, in the framework of the ERAS model, as already mentioned, the enthalpy of the hydrogen bonds between 1-alkanol molecules is –25 kJ·mol^{-1} [7, 11, 13, 17] while the enthalpies between methanol or 1-heptanol and DPA molecules are, respectively, –42.4 and –34.5 kJ·mol^{-1} [17]. Thus, one can expect that the number of (1-alkanol)-amine interactions broken when the temperature is increased is lower than the number of disrupted interactions between 1-alkanol molecules. This makes ε_r change more smoothly with temperature for the mixtures than for pure 1-alkanols since, as it has been previously indicated, (1-alkanol)-amine interactions contribute positively to the system polarization. On the other hand, $(\partial\varepsilon_\mathrm{r}/\partial T)_p$ also increases in line with *n*. The weaker temperature dependence of ε_r for systems containing longer 1-alkanols can be newly explained as above, i.e., in terms of the lower self-association of these 1-alkanols and of the less important solvation effects involved. We also note that $(\partial\varepsilon_\mathrm{r}^\mathrm{E}/\partial T)_p$ may show either positive or negative values (Table 5). Negative values (systems with *n* = 1-4) mean that ε_r decreases with the increase of temperature more rapidly than $\varepsilon_\mathrm{r}^\mathrm{id}$ does. This behaviour is encountered for solutions where the effects related to the alcohol self-association and solvation effects between unlike molecules are more relevant. They become less important in systems with *n* = 5,7, and the temperature dependence of ε_r is weaker than that of $\varepsilon_\mathrm{r}^\mathrm{id}$, leading to positive $(\partial\varepsilon_\mathrm{r}^\mathrm{E}/\partial T)_p$ values. Finally, the replacement of DPA by HxA in systems with a given 1-alkanol leads to less negative $(\partial\varepsilon_\mathrm{r}/\partial T)_p$ values (Table 6). This newly suggests that cyclic multimers formed by unlike molecules also exist in 1-alkanol + HxA systems, as the disruption of such multimers for increased temperature values positively contributes to the mixture polarization.

4.4. Kirkwood-Fröhlich model

In the Kirkwood-Fröhlich model, the fluctuations of the dipole moment in the absence of the 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 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 neighbours. This is an important parameter, as it provides information about specific interactions in the liquid state. For a mixture, g_K can be determined, in the context of a one-fluid model [31], from macroscopic physical properties according to the expression [31-34]:

$$g_\mathrm{K} = \frac{9k_\mathrm{B}TV_\mathrm{m}\varepsilon_0(\varepsilon_\mathrm{r}-\varepsilon_\mathrm{r}^\infty)(2\varepsilon_\mathrm{r}+\varepsilon_\mathrm{r}^\infty)}{N_\mathrm{A}\mu^2\varepsilon_\mathrm{r}(\varepsilon_\mathrm{r}^\infty+2)^2} \qquad (8)$$

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 $\varepsilon_\mathrm{r}^\infty = 1.1n_\mathrm{D}^2$ [56]. μ represents the dipole moment of the solution, estimated from the equation [31]:

$$\mu^2 = x_1\mu_1^2 + x_2\mu_2^2 \qquad (9)$$

where μ_i stands for the dipole moment of component i (=1,2). Calculations have been performed using smoothed values of V_m^E [17], n_D^E (this work) and ε_r^E (this work) at Δx_1 = 0.01. The source and values of μ_i are collected in Table 2.

Figure 5 shows our calculations on g_K of 1-alkanol + DPA systems, which takes the values: 2.97 (*n* = 1), 2.72 (*n* = 3), 2.60 (*n* = 4), 2.47 (*n* = 5), 2.25 (*n* = 7). These are greater than the corresponding values for 1-alkanol + HxA mixtures [23]: 2.68 (*n* = 1), 2.32 (*n* = 3), 2.16 (*n* = 4), 2.01 (*n* = 5), 1.77 (*n* = 7). This would mean that parallel alignment of the dipoles is more favoured in DPA mixtures, supporting our previous statement inferred from the analysis of ε_r^E. It is interesting to note that for $\phi_1 > 0.4$ the g_K curve for methanol + DPA is practically constant, suggesting that the structure of the mixture in this concentration range is quite similar to that of the pure methanol because the rupture of the methanol self-association is compensated by the methanol-DPA hydrogen bonds created.

We have calculated as well the excess Kirkwood correlation factors, $g_K^E = g_K - g_K^{id}$, where g_K^{id} is calculated substituting the real quantities by ideal ones in equation (8). The values for 1-alkanol + DPA systems are (Figures 6 and 7): 0.317 (*n* = 1), –0.110 (*n* = 3), –0.270 (*n* = 4), –0.366 (*n* = 5), –0.377 (*n* = 7). The trend is parallel to that of 1-alkanol + HxA mixtures [23], being this, as the corresponding ε_r^E, lower (Figure 7): 0.170 (*n* = 1), –0.257 (*n* = 3), –0.421 (*n* = 4), –0.505 (*n* = 5), –0.508 (*n* = 7). The interpretation of this fact is thus similar [23]. For the minimum of the curves, the variation is the same as the one encountered for ε_r^E, but it occurs at lower values of ϕ_1. Then, according to the model, the ε_r^E minima are influenced by other factors different from the variation of the correlations in the orientation of the dipoles in the mixing process.

5. Conclusions

Measurements of ε_r and n_D have been reported for the 1-alkanol + di-*n*-propilamine systems at (293.15-303.15) K. Interactions between unlike molecules form multimers that contribute positively to ε_r^E. Such contribution is dominant for the methanol mixture and ε_r^E is positive. For the remaining systems (except for high ϕ_1 values in the 1-propanol mixture) ε_r^E values are negative, indicating that dominant contributions arise from the breaking of interactions between like molecules. For a given 1-alkanol, ε_r^E is larger for di-*n*-propylamine than for *n*-hexylamine mixtures. This suggests that parallel alignment of the dipoles is more favoured and cyclic multimers disfavoured in the former case. The behaviour of $(\partial\varepsilon_\mathrm{r}/\partial T)_p$ and the application of the Kirkwood-Fröhlich model support these findings. The values of $(\partial\varepsilon_\mathrm{r}/\partial T)_p$ are higher for the mixtures than for pure 1-alkanols, because (1-alkanol)-DPA interactions are stronger than those between 1-alkanol molecules. Calculations on R_m show that dispersive interactions in the studied mixtures increase with the length of the 1-alkanol, and that they have the same importance as in *n*-hexylamine systems.

Acknowledgements

F. Hevia and A. Cobos are grateful to Ministerio de Educación, Cultura y Deporte for the grants FPU14/04104 and FPU15/05456 respectively. The authors gratefully acknowledge the financial support received from the Consejería de Educación y Cultura of Junta de Castilla y León, under Project BU034U16.

References

[1] D.L. Nelson, M.M. Cox, Lehninger Principles of Biochemistry, 3rd ed., Worth Publishing, New York, 2000.

[2] Y. Coulier, A. Lowe, P.R. Tremaine, J.Y. Coxam, K. Ballerat-Busserolles, Absorption of CO2 in aqueous solutions of 2-methylpiperidine: Heats of solution and modeling, Int. J. Greenh. Gas Control, 47 (2016) 322-329. https://doi.org/10.1016/j.ijggc.2016.02.009

[3] M. Götz, R. Reimert, S. Bajohr, H. Schnetzer, J. Wimberg, T.J.S. Schubert, Long-term thermal stability of selected ionic liquids in nitrogen and hydrogen atmosphere, Thermochim. Acta, 600 (2015) 82-88. https://doi.org/10.1016/j.tca.2014.11.005

[4] H. Funke, M. Wetzel, A. Heintz, New applications of the ERAS model. Thermodynamics of amine + alkane and alcohol + amine mixtures, Pure Appl. Chem., 61 (1989) 1429-1439. https://doi.org/10.1351/pac198961081429

[5] S. Villa, J.A. González, I.G. De La Fuente, N. Riesco, J.C. Cobos, Thermodynamics of Organic Mixtures Containing Amines. II. Excess Molar Volumes at 25°C for Methylbutylamine + Alkane Systems and Eras Characterization of Linear Secondary Amine + Alkane Mixtures, J. Solution Chem., 31 (2002) 1019-1038. https://doi.org/10.1023/A:1021881627444

[6] J.A. González, I. Mozo, I. García de la Fuente, J.C. Cobos, Thermodynamics of organic mixtures containing amines. IV. Systems with aniline, Can. J. Chem., 83 (2005) 1812-1825. https://doi.org/10.1139/v05-190

[7] S. Villa, N. Riesco, I. García de la Fuente, J.A. González, J.C. Cobos, Thermodynamics of mixtures with strongly negative deviations from Raoult’s law. Part 8. Excess molar volumes at 298.15 K for 1-alkanol + isomeric amine (C6H15N) systems: Characterization in terms of the ERAS model, Fluid Phase Equilib., 216 (2004) 123-133. https://doi.org/10.1016/j.fluid.2003.10.008

[8] J.A. González, L.F. Sanz, I. García De La Fuente, J.C. Cobos, Thermodynamics of mixtures containing amines: XIII. Application of the ERAS model to cyclic amine + alkane mixtures, Thermochim. Acta, 573 (2013) 229-236. https://doi.org/10.1016/j.tca.2013.09.033

[9] R. Srivastava, B.D. Smith, Total-pressure vapor-liquid equilibrium data for binary systems of diethylamine with acetone, acetonitrile, and methanol, J. Chem. Eng. Data, 30 (1985) 308-313. https://doi.org/10.1021/je00041a022

[10] K. Nakanishi, H. Shirai, T. Minamiyama, Vapor-liquid equilibrium of binary systems containing alcohols. Methanol with aliphatic amines, J. Chem. Eng. Data, 12 (1967) 591-594. https://doi.org/10.1021/je60035a031

[11] A. Heintz, P.K. Naicker, S.P. Verevkin, R. Pfestorf, Thermodynamics of alkanol + amine mixtures. Experimental results and ERAS model calculations of the heat of mixing, Ber. Bunsenges. Phys. Chem., 102 (1998) 953-959. https://doi.org/10.1002/bbpc.19981020707

[12] K. Nakanishi, H. Touhara, N. Watanabe, Studies on Associated Solutions. II. Heat of Mixing of Methanol with Aliphatic Amines, Bull. Chem. Soc. Jpn., 43 (1970) 2671-2676. https://doi.org/10.1246/bcsj.43.2671

[13] A. Heintz, A New Theoretical Approach for Predicting Excess Properties of Alkanol/Alkane Mixtures, Ber. Bunsenges. Phys. Chem., 89 (1985) 172-181. https://doi.org/10.1002/bbpc.19850890217

[14] J.A. González, I. García de la Fuente, J.C. Cobos, Thermodynamics of mixtures with strongly negative deviations from Raoult's Law: Part 4. Application of the DISQUAC model to mixtures of 1-alkanols with primary or secondary linear amines. Comparison with Dortmund UNIFAC and ERAS results, Fluid Phase Equilib., 168 (2000) 31-58. https://doi.org/10.1016/S0378-3812(99)00326-X

[15] L. Wang, G.C. Benson, B.C.Y. Lu, Excess enthalpies of 1-propanol + n-hexane + n-decane or n-dodecane at 298.15 K, J. Chem. Eng. Data, 37 (1992) 403-406. https://doi.org/10.1021/je00008a007

[16] S.-c. Hwang, R.L. Robinson, Vapor-liquid equilibria at 25 ºC for nine alcohol-hydrocarbon binary systems, J. Chem. Eng. Data, 22 (1977) 319-325. https://doi.org/10.1021/je60074a025

[17] S. Villa, N. Riesco, I. García de la Fuente, J.A. González, J.C. Cobos, Thermodynamics of mixtures with strongly negative deviations from Raoult’s law: Part 5. Excess molar volumes at 298.15 K for 1-alkanols+dipropylamine systems: characterization in terms of the ERAS model, Fluid Phase Equilib., 190 (2001) 113-125. https://doi.org/10.1016/S0378-3812(01)00595-7

[18] S. Villa, N. Riesco, I. García de la fuente, J.A. González, J.C. Cobos, Thermodynamics of mixtures with strongly negative deviations from Raoult’s law: Part 6. Excess molar volumes at 298.15 K for 1-alkanols + dibutylamine systems. Characterization in terms of the ERAS model, Fluid Phase Equilib., 198 (2002) 313-329. https://doi.org/10.1016/S0378-3812(01)00808-1

[19] L.F. Sanz, J.A. González, I. García De La Fuente, J.C. Cobos, Thermodynamics of mixtures with strongly negative deviations from Raoult's law. XI. Densities, viscosities and refractives indices at (293.15–303.15) K for cyclohexylamine + 1-propanol, or +1-butanol systems, J. Mol. Liq., 172 (2012) 26-33. https://doi.org/10.1016/j.molliq.2012.05.003

[20] L.F. Sanz, J.A. González, I. García de la Fuente, J.C. Cobos, Thermodynamics of mixtures with strongly negative deviations from Raoult’s law. XII. Densities, viscosities and refractive indices at T = (293.15 to 303.15) K for (1-heptanol, or 1-decanol + cyclohexylamine) systems. Application of the ERAS model to (1-alkanol + cyclohexylamine) mixtures, J. Chem. Thermodyn., 80 (2015) 161-171. https://doi.org/10.1016/j.jct.2014.09.005

[21] L.F. Sanz, J.A. González, I.G. De La Fuente, J.C. Cobos, Thermodynamics of mixtures with strong negative deviations from raoult’s law. XIV. density, permittivity, refractive index and viscosity data for the methanol + cyclohexylamine mixture at (293.15–303.15) K, Thermochim. Acta, 631 (2016) 18-27. https://doi.org/10.1016/j.tca.2016.03.002

[22] U. Domańska, M. Głoskowska, Experimental Solid + Liquid Equilibria and Excess Molar Volume of Alkanol + Octylamine Mixtures. Analysis in Terms of ERAS, DISQUAC, and Modified UNIFAC, J. Chem. Eng. Data, 49 (2004) 101-108. https://doi.org/10.1021/je0301895

[23] F. Hevia, J.A. González, A. Cobos, I. García de la Fuente, C. Alonso-Tristán, Thermodynamics of mixtures with strongly negative deviations from Raoult's law. XV.

Permittivities and refractive indices for 1-alkanol + n-hexylamine systems at (293.15–303.15) K. Application of the Kirkwood-Fröhlich model, Fluid Phase Equilib., 468 (2018) 18-28. https://doi.org/10.1016/j.fluid.2018.04.007

[24] S. Villa, R. Garriga, P. Pérez, M. Gracia, J.A. González, I.G. de la Fuente, J.C. Cobos, Thermodynamics of mixtures with strongly negative deviations from Raoult's law: Part 9. Vapor–liquid equilibria for the system 1-propanol + di-n-propylamine at six temperatures between 293.15 and 318.15 K, Fluid Phase Equilib., 231 (2005) 211-220. https://doi.org/10.1016/j.fluid.2005.01.013

[25] J.A. González, L.F. Sanz, I. García de la Fuente, J.C. Cobos, Thermodynamics of mixtures with strong negative deviations from Raoult’s law. XIII. Relative permittivities for (1-alkanol + cyclohexylamine) systems, and dielectric study of (1-alkanol + polar) compound (amine, amide or ether) mixtures, J. Chem. Thermodyn., 91 (2015) 267-278. https://doi.org/10.1016/j.jct.2015.07.032

[26] J.A. González, I.G. de la Fuente, J.C. Cobos, Thermodynamics of mixtures with strongly negative deviations from Raoult's law. Part 3. Application of the DISQUAC model to mixtures of triethylamine with alkanols. Comparison with Dortmund UNIFAC and ERAS results, Can. J. Chem., 78 (2000) 1272-1284. https://doi.org/10.1139/v00-114

[27] J.A. González, I. Mozo, I.G.d.l. Fuente, J.C. Cobos, Thermodynamics of organic mixtures containing amines: V. Systems with pyridines, Thermochim. Acta, 441 (2006) 53-68. https://doi.org/10.1016/j.tca.2005.11.027

[28] J.A. González, I. Mozo, I.G. de la Fuente, J.C. Cobos, N. Riesco, Thermodynamics of mixtures containing amines: VII. Systems containing dimethyl or trimethylpyridines, Thermochim. Acta, 467 (2008) 30-43. https://doi.org/10.1016/j.tca.2007.10.011

[29] J.A. González, I.G. de la Fuente, I. Mozo, J.C. Cobos, N. Riesco, Thermodynamics of Organic Mixtures Containing Amines. VII. Study of Systems Containing Pyridines in Terms of the Kirkwood−Buff Formalism, Ind. Eng. Chem. Res., 47 (2008) 1729-1737. https://doi.org/10.1021/ie071226e

[30] J.A. González, J.C. Cobos, I. García de la Fuente, I. Mozo, Thermodynamics of mixtures containing amines. IX. Application of the concentration–concentration structure factor to the study of binary mixtures containing pyridines, Thermochim. Acta, 494 (2009) 54-64. https://doi.org/10.1016/j.tca.2009.04.017

[31] J.C.R. Reis, T.P. Iglesias, Kirkwood correlation factors in liquid mixtures from an extended Onsager-Kirkwood-Frohlich equation, Phys. Chem. Chem. Phys., 13 (2011) 10670-10680. https://doi.org/10.1039/C1CP20142E

[32] H. Fröhlich, Theory of Dielectrics, Clarendon Press, Oxford, 1958.

[33] C. Moreau, G. Douhéret, Thermodynamic and physical behaviour of water + acetonitrile mixtures. Dielectric properties, J. Chem. Thermodyn., 8 (1976) 403-410. https://doi.org/10.1016/0021-9614(76)90060-4

[34] A. Chelkowski, Dielectric Physics, Elsevier, Amsterdam, 1980.

[35] CIAAW, Atomic weights of the elements 2015, ciaaw.org/atomic-weights.htm (accessed 2015).

[36] V. Alonso, J.A. González, I. García de la Fuente, J.C. Cobos, Dielectric and refractive index measurements for the systems 1-pentanol + octane, or + dibutyl ether or for dibutyl ether + octane at different temperatures, Thermochim. Acta, 543 (2012) 246-253. https://doi.org/10.1016/j.tca.2012.05.036

[37] K.N. Marsh, Recommended reference materials for the realization of physicochemical properties, Blackwell Scientific Publications, Oxford, UK, 1987.

[38] J.A. González, I. Alonso, I. Mozo, I. García de la Fuente, J.C. Cobos, Thermodynamics of (ketone + amine) mixtures. Part VI. Volumetric and speed of sound data at (293.15, 298.15, and 303.15) K for (2-heptanone + dipropylamine, +dibutylamine, or +triethylamine) systems, J. Chem. Thermodyn., 43 (2011) 1506-1514. https://doi.org/10.1016/j.jct.2011.05.003

[39] J.C.R. Reis, T.P. Iglesias, G. Douhéret, M.I. Davis, The permittivity of thermodynamically ideal liquid mixtures and the excess relative permittivity of binary dielectrics, Phys. Chem. Chem. Phys., 11 (2009) 3977-3986. https://doi.org/10.1039/B820613A

[40] J.C.R. Reis, I.M.S. Lampreia, Â.F.S. Santos, M.L.C.J. Moita, G. Douhéret, Refractive Index of Liquid Mixtures: Theory and Experiment, ChemPhysChem, 11 (2010) 3722-3733. https://doi.org/10.1002/cphc.201000566

[41] O. Redlich, A.T. Kister, Algebraic Representation of Thermodynamic Properties and the Classification of Solutions, Ind. & Eng. Chem., 40 (1948) 345-348. https://doi.org/10.1021/ie50458a036

[42] P.R. Bevington, D.K. Robinson, Data Reduction and Error Analysis for the Physical Sciences, McGraw-Hill, New York, 2000.

[43] N.V. Sastry, M.K. Valand, Densities, Speeds of Sound, Viscosities, and Relative Permittivities for 1-Propanol + and 1-Butanol + Heptane at 298.15 K and 308.15 K, J. Chem. Eng. Data, 41 (1996) 1421-1425. https://doi.org/10.1021/je960135d

[44] N.V. Sastry, M.K. Valand, Dielectric constants, refractive indexes and polarizations for 1-Alcohol +Heptane mixtures at 298.15 and 308.15 K, Ber. Bunsenges. Phys. Chem., 101 (1997) 243-250. https://doi.org/10.1002/bbpc.19971010212

[45] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic solvents: physical properties and methods of purification, Wiley, New York, 1986.

[46] A. Skrzecz, Critical evaluation of solubility data in binary systems formed by methanol with n-hydrocarbons, Thermochim. Acta, 182 (1991) 123-131. https://doi.org/10.1016/0040-6031(91)87013-M

[47] C. Wohlfahrt, Static Dielectric Constants of Pure Liquids and Binary Liquid Mixtures. Landolt-Börnstein - Group IV Physical Chemistry Vol. 6, Springer Berlin Heidelberg, Berlin, 1991.

[48] J.A. González, I. Mozo, I. García de la Fuente, J.C. Cobos, N. Riesco, Thermodynamics of (1-alkanol+linear monoether) systems, J. Chem. Thermodyn., 40 (2008) 1495-1508. https://doi.org/10.1016/j.jct.2008.06.001

[49] R. Garriga, F. Sánchez, P. Pérez, M. Gracia, Isothermal vapour-liquid equilibrium at eight temperatures and excess functions at 298.15 K of di-n-propylether with 1-propanol or 2-propanol, Fluid Phase Equilib., 138 (1997) 131-144. https://doi.org/10.1016/S0378-3812(97)00173-8

[50] F. Sarmiento, M.I. Paz Andrade, J. Fernandez, R. Bravo, M. Pintos, Excess enthalpies of 1-heptanol + n-alkane and di-n-propylamine + normal alcohol mixtures at 298.15 K, J. Chem. Eng. Data, 30 (1985) 321-323. https://doi.org/10.1021/je00041a025

[51] M.C. Mateos, P. Pérez, F.M. Royo, M. Gracia, C. Gutiérrez-Losa, Permitividad estática de mezclas de mono-alcoholes + dipropil-éter, + butanona. + butironitrillo (II), Rev. Acad. Cienc. Exact. Fis. Quim. Nat. Zaragoza, 41 (1986) 73-82.

[52] P. Brocos, A. Piñeiro, R. Bravo, A. Amigo, Refractive indices, molar volumes and molar refractions of binary liquid mixtures: concepts and correlations, Phys. Chem. Chem. Phys., 5 (2003) 550-557. https://doi.org/10.1039/B208765K

[53] E. Jiménez, H. Casas, L. Segade, C. Franjo, Surface Tensions, Refractive Indexes and Excess Molar Volumes of Hexane + 1-Alkanol Mixtures at 298.15 K, J. Chem. Eng. Data, 45 (2000) 862-866. https://doi.org/10.1021/je000060k

[54] A. Heintz, B. Schmittecker, D. Wagner, R.N. Lichtenthaler, Excess volumes of binary 1-alkanol/hexane mixtures at temperatures between 283.15 and 323.15 K, J. Chem. Eng. Data, 31 (1986) 487-492. https://doi.org/10.1021/je00046a030

[55] L. Lepori, P. Gianni, A. Spanedda, E. Matteoli, Thermodynamic study of (heptane + amine) mixtures. III: Excess and partial molar volumes in mixtures with secondary, tertiary, and cyclic amines at 298.15 K, J. Chem. Thermodyn., 43 (2011) 1453-1462. https://doi.org/10.1016/j.jct.2011.04.017

[56] Y. Marcus, The structuredness of solvents, J. Solution Chem., 21 (1992) 1217-1230. https://doi.org/10.1007/bf00667218

[57] M. El-Hefnawy, K. Sameshima, T. Matsushita, R. Tanaka, Apparent Dipole Moments of 1-Alkanols in Cyclohexane and n-Heptane, and Excess Molar Volumes of (1-Alkanol + Cyclohexane or n-Heptane) at 298.15 K, J. Solution Chem., 34 (2005) 43-69. https://doi.org/10.1007/s10953-005-2072-1

[58] R.D. Bezman, E.F. Casassa, R.L. Kay, The temperature dependence of the dielectric constants of alkanols, 73–74 (1997) 397-402. https://doi.org/10.1016/S0167-7322(97)00082-2

[59] J. Canosa, A. Rodríguez, J. Tojo, Binary mixture properties of diethyl ether with alcohols and alkanes from 288.15 K to 298.15 K, Fluid Phase Equilib., 156 (1999) 57-71. https://doi.org/10.1016/S0378-3812(99)00032-1

[60] G.J. Janz, R.P.T. Tomkins, Nonaqueus Electrolytes Handbook, Vol. 1, Academic Press, New York, 1972.

[61] S.P. Serbanovic, M.L. Kijevcanin, I.R. Radovic, B.D. Djordjevic, Effect of temperature on the excess molar volumes of some alcohol + aromatic mixtures and modelling by cubic EOS mixing rules, Fluid Phase Equilib., 239 (2006) 69-82. https://doi.org/10.1016/j.fluid.2005.10.022

[62] C. Wohlfahrt, Optical Constants. Refractive Indices of Pure Liquids and Binary Liquid Mixtures. Landolt-Börnstein - Group III Condensed Matter Vol. 47, Springer Berlin Heidelberg, Berlin, 2008.

[63] S. Chen, Q. Lei, W. Fang, Density and Refractive Index at 298.15 K and Vapor−Liquid Equilibria at 101.3 kPa for Four Binary Systems of Methanol, n-Propanol, n-Butanol, or Isobutanol with N-Methylpiperazine, J. Chem. Eng. Data, 47 (2002) 811-815. https://doi.org/10.1021/je010249b

[64] M.I. Aralaguppi, C.V. Jadar, T.M. Aminabhavi, Density, Viscosity, Refractive Index, and Speed of Sound in Binary Mixtures of Acrylonitrile with Methanol, Ethanol,

Propan-1-ol, Butan-1-ol, Pentan-1-ol, Hexan-1-ol, Heptan-1-ol, and Butan-2-ol, J. Chem. Eng. Data, 44 (1999) 216-221. https://doi.org/10.1021/je9802219

[65] R. Anwar Naushad, S. Yasmeen, Volumetric, compressibility and viscosity studies of binary mixtures of [EMIM][NTf2] with ethylacetate/methanol at (298.15–323.15) K, J. Mol. Liq., 224, Part A (2016) 189-200. https://doi.org/10.1016/j.molliq.2016.09.077

[66] S.M. Pereira, T.P. Iglesias, J.L. Legido, L. Rodríguez, J. Vijande, Changes of refractive index on mixing for the binary mixtures {xCH3OH+(1−x) CH3OCH2(CH2OCH2)3CH2OCH3} and {xCH3OH+(1−x)CH3OCH2(CH2OCH2)nCH2OCH3} (n=3–9) at temperatures from 293.15 K to 333.15 K, J. Chem. Thermodyn., 30 (1998) 1279-1287. https://doi.org/10.1006/jcht.1998.0395

[67] A. Rodríguez, J. Canosa, J. Tojo, Density, Refractive Index, and Speed of Sound of Binary Mixtures (Diethyl Carbonate + Alcohols) at Several Temperatures, J. Chem. Eng. Data, 46 (2001) 1506-1515. https://doi.org/10.1021/je010148d

[68] A.P. Gregory, R.N. Clarke, Traceable measurements of the static permittivity of dielectric reference liquids over the temperature range 5–50 °C, Meas. Sci. Technol., 16 (2005) 1506. https://doi.org/10.1088/0957-0233/16/7/013

[69] M.J. Fontao, M. Iglesias, Effect of Temperature on the Refractive Index of Aliphatic Hydroxilic Mixtures (C2–C3), Int. J. Thermophys., 23 (2002) 513-527. https://doi.org/10.1023/A:1015113604024

[70] J.L. Hales, J.H. Ellender, Liquid densities from 293 to 490 K of nine aliphatic alcohols, J. Chem. Thermodyn., 8 (1976) 1177-1184. https://doi.org/10.1016/0021-9614(76)90126-9

[71] N.G. Tsierkezos, I.E. Molinou, A.C. Filippou, Thermodynamic Properties of Binary Mixtures of Cyclohexanone with n-Alkanols (C1–C5) at 293.15 K, J. Solution Chem., 34 (2005) 1371-1386. https://doi.org/10.1007/s10953-005-8508-9

[72] C. Yang, H. Lai, Z. Liu, P. Ma, Density and Viscosity of Binary Mixtures of Diethyl Carbonate with Alcohols at (293.15 to 363.15) K and Predictive Results by UNIFAC-VISCO Group Contribution Method, J. Chem. Eng. Data, 51 (2006) 1345-1351. https://doi.org/10.1021/je0600808

[73] C.P. Smyth, W.N. Stoops, The dielectric polarization of liquids. VI. Ethyl iodide, ethanol, normal-butanol and normal-octanol, J. Am. Chem. Soc., 51 (1929) 3312-3329. https://doi.org/10.1021/ja01386a019

[74] B. Giner, A. Villares, M.C. López, F.M. Royo, C. Lafuente, Refractive indices and molar refractions for isomeric chlorobutanes with isomeric butanols, Phys. Chem. Liq., 43 (2005) 13-23. https://doi.org/10.1080/00319100420003035 18

[75] E. Jiménez, M. Cabanas, L. Segade, S. García-Garabal, H. Casas, Excess volume, changes of refractive index and surface tension of binary 1,2-ethanediol + 1-propanol or 1-butanol mixtures at several temperatures, Fluid Phase Equilib., 180 (2001) 151-164. https://doi.org/10.1016/S0378-3812(00)00519-7

[76] G.A. Iglesias-Silva, A. Guzmán-López, G. Pérez-Durán, M. Ramos-Estrada, Densities and Viscosities for Binary Liquid Mixtures of n-Undecane + 1-Propanol, + 1-Butanol, + 1-Pentanol, and + 1-Hexanol from 283.15 to 363.15 K at 0.1 MPa, J. Chem. Eng. Data, 61 (2016) 2682-2699. https://doi.org/10.1021/acs.jced.6b00121

[77] T.P. Iglesias, J.L. Legido, S.M. Pereira, B. de Cominges, M.I. Paz Andrade, Relative permittivities and refractive indices on mixing for (n-hexane + 1-pentanol, or 1-hexanol, or 1-heptanol) atT = 298.15 K, J. Chem. Thermodyn., 32 (2000) 923-930. https://doi.org/10.1006/jcht.2000.0661

[78] M.N.M. Al-Hayan, Densities, excess molar volumes, and refractive indices of 1,1,2,2-tetrachloroethane and 1-alkanols binary mixtures, J. Chem. Thermodyn., 38 (2006) 427-433. https://doi.org/10.1016/j.jct.2005.06.015

[79] S.P. Patil, A.S. Chaudhari, M.P. Lokhande, M.K. Lande, A.G. Shankarwar, S.N. Helambe, B.R. Arbad, S.C. Mehrotra, Dielectric Measurements of Aniline and Alcohol Mixtures at 283, 293, 303, and 313 K Using the Time Domain Technique, J. Chem. Eng. Data, 44 (1999) 875-878. https://doi.org/10.1021/je980250j

[80] Á. Piñeiro, P. Brocos, A. Amigo, M. Pintos, R. Bravo, Refractive Indexes of Binary Mixtures of Tetrahydrofuran with 1-Alkanols at 25°C and Temperature Dependence of n and ρ for the Pure Liquids, J. Solution Chem., 31 (2002) 369-380. https://doi.org/10.1023/A:1015807331250

[81] J.J. Cano-Gómez, G.A. Iglesias-Silva, E.O. Castrejón-González, M. Ramos-Estrada, K.R. Hall, Density and Viscosity of Binary Liquid Mixtures of Ethanol + 1-Hexanol and Ethanol + 1-Heptanol from (293.15 to 328.15) K at 0.1 MPa, J. Chem. Eng. Data, 60 (2015) 1945-1955. https://doi.org/10.1021/je501133u

[82] U. Domańska, M. Królikowska, Density and Viscosity of Binary Mixtures of {1-Butyl-3-methylimidazolium Thiocyanate + 1-Heptanol, 1-Octanol, 1-Nonanol, or 1-Decanol}, J. Chem. Eng. Data, 55 (2010) 2994-3004. https://doi.org/10.1021/je901043q

[83] R.C. Reid, J.M. Prausnitz, B.E. Poling, The Properties of Gases and Liquids, McGraw-Hill, New York, US, 1987.

[84] C.M. Kinart, A. Ćwiklińska, W.J. Kinart, A. Bald, Density and Relative Permittivity of 2-Methoxyethanol + Dipropylamine Mixtures at Various Temperatures, J. Chem. Eng. Data, 49 (2004) 1425-1428. https://doi.org/10.1021/je040006u

[85] J.M. Resa, C. González, S. Ortiz de Landaluce, J. Lanz, Vapor−Liquid Equilibrium of Binary Mixtures Containing Diethylamine + Diisopropylamine, Diethylamine + Dipropylamine, and Chloroform + Diisopropylamine at 101.3 kPa, and Vapor Pressures of Dipropylamine, J. Chem. Eng. Data, 45 (2000) 867-871. https://doi.org/10.1021/je000020g

[86] S.L. Oswal, P. Oswal, R.L. Gardas, S.G. Patel, R.G. Shinde, Acoustic, volumetric, compressibility and refractivity properties and reduction parameters for the ERAS and Flory models of some homologous series of amines from 298.15 to 328.15 K, Fluid Phase Equilib., 216 (2004) 33-45. https://doi.org/10.1016/j.fluid.2003.09.007

[87] I. Alonso, I. Mozo, I.G. de la fuente, J.A. González, J.C. Cobos, Thermodynamics of ketone + amine mixtures Part IV. Volumetric and speed of sound data at (293.15; 298.15 and 303.15 K) for 2-butanone +dipropylamine, +dibutylamine or +triethylamine systems, Thermochim. Acta, 512 (2011) 86-92. https://doi.org/10.1016/j.tca.2010.09.004

[88] T. Shinomiya, Dielectric Dispersion and Intermolecular Association for 28 Pure Liquid Alcohols. The Position Dependence of Hydroxyl Group in the Hydrocarbon Chain, Bull. Chem. Soc. Jpn., 62 (1989) 908-914. https://doi.org/10.1246/bcsj.62.908

Table 1

Sample description.

Chemical name	CAS Number	Source	Purification method	Purity[a]
methanol	67-56-1	Sigma-Aldrich	none	99.99%
1-propanol	71-23-8	Sigma-Aldrich	none	99.84%
1-butanol	71-36-3	Sigma-Aldrich	none	99.86%
1-pentanol	71-41-0	Sigma-Aldrich	none	99.9%
1-heptanol	111-70-6	Sigma-Aldrich	none	99.9%
di-*n*-propylamine (DPA)	111-26-2	Aldrich	none	99.9%

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

Table 2

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

Compound	μ / D	*T*/K	ε_r^*		n_D^*		ρ^* / g·cm^{-3}	
			Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
methanol	1.664 [57]	293.15	33.569	33.61 [58]	1.32878	1.32859 [59]	0.79163	0.7916 [60] 0.791400 [61]
		298.15	32.619	32.62 [58]	1.32667	1.3267 [62] 1.32652 [63]	0.78695	0.7869 [64] 0.786884 [65]
		303.15	31.652	31.66 [58]	1.32457	1.32457 [66] 1.32410 [67]	0.78222	0.782158 [65]
1-propanol	1.629 [57]	293.15	21.146	21.15 [68]	1.38505	1.38512 [69]	0.80366	0.80361 [70]
		298.15	20.450	20.42 [68]	1.38304	1.38307 [67]	0.79968	0.79960 [70]
		303.15	19.788	19.75 [68]	1.38100	1.38104 [67]	0.79566	0.79561 [70]
1-butanol	1.614 [57]	293.15	18.198	18.19 [68]	1.39925	1.3993 [71]	0.80985	0.80982 [72] 0.8098 [73]
		298.15	17.548	17.53 [68]	1.39732	1.397336 [74]	0.80606	0.80606 [72]
		303.15	16.927	16.89 [68]	1.39536	1.3953 [75]	0.80222	0.8022 [73]
1-pentanol	1.598 [57]	293.15	15.695	15.63 [58]	1.40992	1.40986 [67]	0.81466	0.81468 [76]
		298.15	15.099	15.08 [77]	1.40796	1.40789 [67]	0.81103	0.81103 [76]
		303.15	14.523	14.44 [58]	1.40603	1.40592 [78]	0.80735	0.81737 [76]
1-heptanol	1.583 [57]	293.15	12.016	11.54 [79]	1.42422	1.42433 [80]	0.82237	0.8223 [81]
		298.15	11.506	11.45 [77]	1.42234	1.42240 [80]	0.81890	0.81881 [82]
		303.15	11.021	11.07 [47]	1.42048	1.42047 [78] 1.42048 [80]	0.81537	0.8153 [81]
di-*n*-propylamine (DPA)	1.1 [83]	293.15	3.130	3.31 [84] 3.068 [45]	1.40417	1.4043 [45]	0.737782	0.7375 [45]
		298.15	3.080	3.24 [84]	1.40154	1.40132 [85]	0.733220	0.73321 [50]
		303.15	3.032	3.18 [84]	1.39890	1.4022 [86]	0.728698	0.729087 [87]

[a] The standard uncertainties are: $u(T) = 0.02\,\mathrm{K}$ (for ρ^* measurements, $u(T) = 0.01\,\mathrm{K}$); $u(p) = 1\,\mathrm{kPa}$; $u(\nu) = 20$ 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 1-alkanol, ϕ_1, relative permittivities, ε_r ,and excess relative permittivities, $\varepsilon_\mathrm{r}^\mathrm{E}$, of 1-alkanol (1) + di-*n*-propylamine (DPA) (2) mixtures as functions of the mole fraction of the 1-alkanol, x_1, at temperature *T*, pressure *p* = 0.1 MPa and frequency $\nu = 1$ MHz. [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) + DPA (2) ; *T*/K = 293.15							
0.0000	0.0000	3.131		0.5940	0.3016	14.249	1.938
0.0664	0.0206	3.698	– 0.060	0.6918	0.3985	17.679	2.418
0.1066	0.0340	4.093	– 0.073	0.7948	0.5334	21.905	2.538
0.1503	0.0496	4.582	– 0.059	0.8492	0.6243	24.438	2.305
0.1990	0.0683	5.201	– 0.009	0.9012	0.7291	27.148	1.825
0.3091	0.1166	6.956	0.276	0.9498	0.8481	30.041	1.096
0.4068	0.1683	8.965	0.711	0.9749	0.9198	31.723	0.595
0.5110	0.2357	11.698	1.393	1.0000	1.0000	33.569	
methanol (1) + DPA (2) ; *T*/K = 298.15							
0.0000	0.0000	3.081		0.5940	0.3015	13.735	1.748
0.0664	0.0206	3.620	– 0.069	0.6918	0.3984	17.081	2.232
0.1066	0.0340	3.998	– 0.087	0.7948	0.5333	21.229	2.395
0.1503	0.0496	4.466	– 0.080	0.8492	0.6243	23.704	2.182
0.1990	0.0683	5.054	– 0.044	0.9012	0.7291	26.354	1.737
0.3091	0.1166	6.725	0.200	0.9498	0.8481	29.179	1.047
0.4068	0.1683	8.641	0.589	0.9749	0.9197	30.817	0.570
0.5110	0.2357	11.261	1.218	1.0000	1.0000	32.619	
methanol (1) + DPA (2) ; *T*/K = 303.15							
0.0000	0.0000	3.035		0.5940	0.3015	13.252	1.589
0.0664	0.0205	3.552	– 0.070	0.6918	0.3984	16.517	2.081
0.1066	0.0340	3.913	– 0.095	0.7948	0.5333	20.583	2.287
0.1503	0.0496	4.357	– 0.097	0.8492	0.6242	22.980	2.082
0.1990	0.0683	4.920	– 0.070	0.9012	0.7290	25.562	1.665
0.3091	0.1166	6.514	0.142	0.9498	0.8481	28.312	1.007
0.4068	0.1683	8.346	0.495	0.9749	0.9197	29.903	0.549
0.5110	0.2356	10.861	1.084	1.0000	1.0000	31.652	
1-propanol (1) + DPA (2) ; *T*/K = 293.15							
0.0000	0.0000	3.130		0.5948	0.4445	10.847	– 0.291
0.0638	0.0358	3.573	– 0.202	0.7018	0.5620	13.243	– 0.012
0.0866	0.0492	3.743	– 0.273	0.7967	0.6812	15.546	0.144
0.1427	0.0832	4.207	– 0.422	0.8431	0.7455	16.741	0.180
0.2045	0.1229	4.789	– 0.555	0.8993	0.8296	18.256	0.180
0.2917	0.1834	5.761	– 0.673	0.9487	0.9098	19.647	0.126

0.3939	0.2616	7.178	– 0.665	1.0000	1.0000	21.146	
0.5012	0.3539	8.988	– 0.518				
1-propanol (1) + DPA (2) ; *T*/K = 298.15							
0.0000	0.0000	3.080		0.5948	0.4442	10.419	– 0.377
0.0638	0.0358	3.501	– 0.201	0.7018	0.5617	12.739	– 0.098
0.0866	0.0491	3.665	– 0.268	0.7967	0.6809	14.969	0.062
0.1427	0.0831	4.108	– 0.415	0.8431	0.7453	16.134	0.108
0.2045	0.1228	4.660	– 0.553	0.8993	0.8294	17.623	0.136
0.2917	0.1832	5.580	– 0.682	0.9487	0.9097	18.987	0.106
0.3939	0.2614	6.929	– 0.692	1.0000	1.0000	20.450	
0.5012	0.3536	8.647	– 0.575				
1-propanol (1) + DPA (2) ; *T*/K = 303.15							
0.0000	0.0000	3.032		0.5948	0.4440	10.029	– 0.443
0.0638	0.0357	3.439	– 0.191	0.7018	0.5614	12.260	– 0.179
0.0866	0.0490	3.593	– 0.260	0.7967	0.6807	14.433	– 0.005
0.1427	0.0830	4.016	– 0.407	0.8431	0.7451	15.567	0.050
0.2045	0.1227	4.540	– 0.548	0.8993	0.8293	17.021	0.093
0.2917	0.1830	5.417	– 0.681	0.9487	0.9096	18.361	0.088
0.3939	0.2612	6.698	– 0.711	1.0000	1.0000	19.788	
0.5012	0.3534	8.331	– 0.623				
1-butanol (1) + DPA (2) ; *T*/K = 293.15							
0.0000	0.0000	3.132		0.5991	0.4993	9.972	– 0.682
0.0484	0.0328	3.455	– 0.171	0.6896	0.5972	11.635	– 0.494
0.1063	0.0735	3.872	– 0.367	0.7484	0.6650	12.765	– 0.386
0.1418	0.0993	4.146	– 0.482	0.8041	0.7326	13.891	– 0.278
0.2157	0.1551	4.788	– 0.681	0.8418	0.7803	14.686	– 0.202
0.3006	0.2229	5.660	– 0.830	0.8890	0.8424	15.681	– 0.143
0.4064	0.3136	6.961	– 0.896	0.9514	0.9289	17.070	– 0.057
0.5030	0.4031	8.373	– 0.832	1.0000	1.0000	18.198	
1-butanol (1) + DPA (2) ; *T*/K = 298.15							
0.0000	0.0000	3.082		0.5991	0.4989	9.580	– 0.719
0.0484	0.0328	3.391	– 0.165	0.6896	0.5968	11.179	– 0.536
0.1063	0.0734	3.786	– 0.358	0.7484	0.6646	12.268	– 0.428
0.1418	0.0992	4.049	– 0.468	0.8041	0.7323	13.368	– 0.307
0.2157	0.1549	4.659	– 0.664	0.8418	0.7800	14.125	– 0.240
0.3006	0.2226	5.486	– 0.816	0.8890	0.8422	15.113	– 0.152
0.4064	0.3133	6.718	– 0.896	0.9514	0.9288	16.455	– 0.063
0.5030	0.4028	8.057	– 0.852	1.0000	1.0000	17.548	
1-butanol (1) + DPA (2) ; *T*/K = 303.15							
0.0000	0.0000	3.036		0.5991	0.4986	9.223	– 0.739
0.0484	0.0327	3.330	– 0.160	0.6896	0.5965	10.738	– 0.584

0.1063	0.0733	3.710	– 0.344	0.7484	0.6643	11.811	– 0.453
0.1418	0.0990	3.961	– 0.450	0.8041	0.7320	12.869	– 0.335
0.2157	0.1547	4.543	– 0.642	0.8418	0.7798	13.609	– 0.259
0.3006	0.2224	5.329	– 0.796	0.8890	0.8420	14.568	– 0.164
0.4064	0.3130	6.497	– 0.887	0.9514	0.9287	15.872	– 0.065
0.5030	0.4024	7.770	– 0.856	1.0000	1.0000	16.927	
1-pentanol (1) + DPA (2) ; *T*/K = 293.15							
0.0000	0.0000	3.130		0.5985	0.5404	9.078	– 0.842
0.0530	0.0423	3.469	– 0.192	0.6570	0.6018	9.926	– 0.766
0.1086	0.0877	3.850	– 0.382	0.6985	0.6464	10.555	– 0.697
0.1497	0.1220	4.157	– 0.506	0.7450	0.6974	11.282	– 0.611
0.2032	0.1675	4.581	– 0.654	0.7921	0.7504	12.039	– 0.520
0.2597	0.2168	5.076	– 0.778	0.8447	0.8110	12.918	– 0.402
0.3006	0.2532	5.461	– 0.850	0.9027	0.8798	13.918	– 0.267
0.4064	0.3507	6.590	– 0.947	0.9435	0.9294	14.657	– 0.151
0.4882	0.4294	7.589	– 0.936	1.0000	1.0000	15.695	
0.5421	0.4829	8.290	– 0.908				
1-pentanol (1) + DPA (2) ; *T*/K = 298.15							
0.0000	0.0000	3.077		0.5985	0.5400	8.729	– 0.840
0.0530	0.0422	3.402	– 0.182	0.6570	0.6014	9.540	– 0.767
0.1086	0.0875	3.767	– 0.362	0.6985	0.6460	10.144	– 0.699
0.1497	0.1218	4.062	– 0.479	0.7450	0.6970	10.849	– 0.607
0.2032	0.1672	4.465	– 0.622	0.7921	0.7500	11.574	– 0.519
0.2597	0.2165	4.935	– 0.745	0.8447	0.8107	12.421	– 0.402
0.3006	0.2529	5.303	– 0.814	0.9027	0.8796	13.397	– 0.255
0.4064	0.3503	6.367	– 0.921	0.9435	0.9293	14.100	– 0.149
0.4882	0.4290	7.316	– 0.918	1.0000	1.0000	15.099	
0.5421	0.4825	7.978	– 0.900				
1-pentanol (1) + DPA (2) ; *T*/K = 303.15							
0.0000	0.0000	3.031		0.5985	0.5396	8.413	– 0.819
0.0530	0.0421	3.342	– 0.173	0.6570	0.6010	9.187	– 0.751
0.1086	0.0874	3.692	– 0.343	0.6985	0.6456	9.765	– 0.685
0.1497	0.1216	3.972	– 0.456	0.7450	0.6967	10.436	– 0.601
0.2032	0.1670	4.357	– 0.593	0.7921	0.7497	11.139	– 0.508
0.2597	0.2162	4.805	– 0.711	0.8447	0.8105	11.962	– 0.383
0.3006	0.2526	5.156	– 0.778	0.9027	0.8794	12.894	– 0.243
0.4064	0.3499	6.167	– 0.885	0.9435	0.9292	13.570	– 0.139
0.4882	0.4286	7.063	– 0.893	1.0000	1.0000	14.523	
0.5421	0.4821	7.695	– 0.876				
1-heptanol (1) + DPA (2) ; *T*/K = 293.15							
0.0000	0.0000	3.131		0.5883	0.5955	7.677	– 0.745

0.0529	0.0544	3.454	– 0.160	0.6378	0.6446	8.154	– 0.704
0.1003	0.1030	3.745	– 0.301	0.6965	0.7028	8.735	– 0.640
0.1474	0.1512	4.050	– 0.424	0.7424	0.7481	9.197	– 0.581
0.1990	0.2038	4.401	– 0.541	0.7892	0.7941	9.687	– 0.500
0.2471	0.2527	4.748	– 0.628	0.8426	0.8465	10.250	– 0.402
0.2924	0.2986	5.083	– 0.701	0.8913	0.8941	10.777	– 0.298
0.3427	0.3494	5.485	– 0.750	0.9395	0.9412	11.325	– 0.169
0.3943	0.4014	5.915	– 0.782	1.0000	1.0000	12.016	
0.4929	0.5003	6.783	– 0.793				
1-heptanol (1) + DPA (2) ; *T*/K = 298.15							
0.0000	0.0000	3.080		0.5883	0.5950	7.390	– 0.703
0.0529	0.0543	3.389	– 0.149	0.6378	0.6442	7.847	– 0.661
0.1003	0.1028	3.669	– 0.277	0.6965	0.7023	8.397	– 0.601
0.1474	0.1509	3.957	– 0.394	0.7424	0.7477	8.837	– 0.543
0.1990	0.2035	4.295	– 0.500	0.7892	0.7938	9.307	– 0.462
0.2471	0.2523	4.626	– 0.580	0.8426	0.8463	9.838	– 0.373
0.2924	0.2982	4.941	– 0.652	0.8913	0.8940	10.344	– 0.269
0.3427	0.3490	5.325	– 0.696	0.9395	0.9411	10.854	– 0.156
0.3943	0.4010	5.728	– 0.731	1.0000	1.0000	11.506	
0.4929	0.4998	6.547	– 0.744				
1-heptanol (1) + DPA (2) ; *T*/K = 303.15							
0.0000	0.0000	3.033		0.5883	0.5946	7.128	– 0.655
0.0529	0.0542	3.329	– 0.137	0.6378	0.6438	7.565	– 0.611
0.1003	0.1027	3.597	– 0.256	0.6965	0.7020	8.086	– 0.555
0.1474	0.1507	3.876	– 0.361	0.7424	0.7473	8.497	– 0.505
0.1990	0.2032	4.196	– 0.460	0.7892	0.7935	8.956	– 0.415
0.2471	0.2520	4.512	– 0.534	0.8426	0.8460	9.459	– 0.332
0.2924	0.2978	4.812	– 0.600	0.8913	0.8938	9.923	– 0.250
0.3427	0.3486	5.177	– 0.641	0.9395	0.9410	10.415	– 0.135
0.3943	0.4005	5.558	– 0.674	1.0000	1.0000	11.021	
0.4929	0.4994	6.334	– 0.688				

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

Table 4

Volume fractions of 1-alkanol, ϕ_1, refractive indices, n_D, and excess refractive indices, n_D^E, of 1-alkanol (1) + di-*n*-propylamine (DPA) (2) mixtures as functions of the mole fraction of the 1-alkanol, 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) + DPA (2) ; *T*/K = 293.15							
0.0000	0.0000	1.40417		0.5900	0.2981	1.39077	884
0.0374	0.0113	1.40406	72	0.6894	0.3958	1.38332	880
0.1111	0.0356	1.40355	199	0.8067	0.5519	1.36969	715
0.1464	0.0482	1.40324	261	0.8492	0.6243	1.36312	611
0.2203	0.0770	1.40238	387	0.8989	0.7241	1.35397	446
0.3034	0.1139	1.40103	524	0.9498	0.8481	1.34258	234
0.4174	0.1745	1.39825	694	0.9829	0.9443	1.33382	82
0.4937	0.2235	1.39553	785	1.0000	1.0000	1.32878	
methanol (1) + DPA (2) ; *T*/K = 298.15							
0.0000	0.0000	1.40154		0.5900	0.2980	1.38830	864
0.0374	0.0113	1.40142	70	0.6894	0.3957	1.38108	849
0.1111	0.0356	1.40093	199	0.8067	0.5518	1.36764	661
0.1464	0.0482	1.40056	254	0.8492	0.6243	1.36109	552
0.2203	0.0769	1.39974	381	0.8989	0.7240	1.35202	397
0.3034	0.1139	1.39844	522	0.9498	0.8481	1.34058	208
0.4174	0.1745	1.39573	696	0.9829	0.9443	1.33174	73
0.4937	0.2234	1.39316	799	1.0000	1.0000	1.32667	
methanol (1) + DPA (2) ; *T*/K = 303.15							
0.0000	0.0000	1.39890		0.5900	0.2980	1.38601	865
0.0374	0.0113	1.39881	73	0.6894	0.3957	1.37877	868
0.1111	0.0356	1.39834	202	0.8067	0.5518	1.36554	690
0.1464	0.0482	1.39800	259	0.8492	0.6242	1.35909	581
0.2203	0.0769	1.39719	387	0.8989	0.7240	1.34996	427
0.3034	0.1139	1.39590	527	0.9498	0.8481	1.33847	227
0.4174	0.1745	1.39317	695	0.9829	0.9443	1.32964	79
0.4937	0.2234	1.39071	807	1.0000	1.0000	1.32457	
1-propanol (1) + DPA (2) ; *T*/K = 293.15							
0.0000	0.0000	1.40417		0.6004	0.4503	1.40172	613
0.0465	0.0259	1.40431	63	0.6962	0.5554	1.39932	574
0.0897	0.0510	1.40448	128	0.7952	0.6792	1.39596	475
0.1524	0.0893	1.40466	219	0.8476	0.7520	1.39367	385
0.2024	0.1215	1.40471	285	0.8965	0.8252	1.39125	284
0.3121	0.1983	1.40456	416	0.9575	0.9247	1.38780	130

0.4059	0.2714	1.40413	512	1.0000	1.0000	1.38505	
0.4936	0.3470	1.40333	577				
1-propanol (1) + DPA (2) ; *T*/K = 298.15							
0.0000	0.0000	1.40159		0.6004	0.4500	1.39924	597
0.0465	0.0259	1.40173	62	0.6962	0.5551	1.39697	565
0.0897	0.0509	1.40191	126	0.7952	0.6789	1.39376	474
0.1524	0.0892	1.40207	212	0.8476	0.7518	1.39153	386
0.2024	0.1214	1.40220	285	0.8965	0.8251	1.38914	284
0.3121	0.1981	1.40205	412	0.9575	0.9246	1.38576	131
0.4059	0.2712	1.40163	505	1.0000	1.0000	1.38304	
0.4936	0.3467	1.40092	573				
1-propanol (1) + DPA (2) ; *T*/K = 303.15							
0.0000	0.0000	1.39890		0.6004	0.4497	1.39684	596
0.0465	0.0258	1.39904	60	0.6962	0.5548	1.39460	560
0.0897	0.0509	1.39921	122	0.7952	0.6786	1.39143	465
0.1524	0.0891	1.39941	210	0.8476	0.7516	1.38929	382
0.2024	0.1213	1.39951	277	0.8965	0.8249	1.38698	283
0.3121	0.1979	1.39942	404	0.9575	0.9245	1.38362	126
0.4059	0.2709	1.39904	497	1.0000	1.0000	1.38100	
0.4936	0.3465	1.39835	563				
1-butanol (1) + DPA (2) ; *T*/K = 293.15							
0.0000	0.0000	1.40409		0.5978	0.4980	1.40746	578
0.0519	0.0352	1.40477	85	0.6903	0.5980	1.40661	541
0.1199	0.0833	1.40556	187	0.7948	0.7210	1.40492	432
0.1581	0.1114	1.40591	236	0.8518	0.7932	1.40366	341
0.2220	0.1600	1.40653	321	0.8875	0.8404	1.40274	272
0.3097	0.2304	1.40713	415	0.9433	0.9174	1.40111	146
0.3936	0.3022	1.40759	496	1.0000	1.0000	1.39925	
0.5007	0.4009	1.40773	558				
1-butanol (1) + DPA (2) ; *T*/K = 298.15							
0.0000	0.0000	1.40147		0.5978	0.4976	1.40506	565
0.0519	0.0352	1.40216	84	0.6903	0.5976	1.40427	528
0.1199	0.0832	1.40293	180	0.7948	0.7207	1.40268	420
0.1581	0.1112	1.40325	224	0.8518	0.7929	1.40148	330
0.2220	0.1598	1.40396	315	0.8875	0.8402	1.40059	261
0.3097	0.2301	1.40458	406	0.9433	0.9173	1.39903	137
0.3936	0.3019	1.40504	482	1.0000	1.0000	1.39732	
0.5007	0.4005	1.40529	548				
1-butanol (1) + DPA (2) ; *T*/K = 303.15							
0.0000	0.0000	1.39888		0.5978	0.4972	1.40264	551
0.0519	0.0351	1.39950	74	0.6903	0.5973	1.40199	521

0.1199	0.0831	1.40031	172	0.7948	0.7204	1.40048	413
0.1581	0.1111	1.40067	218	0.8518	0.7927	1.39930	321
0.2220	0.1596	1.40138	306	0.8875	0.8400	1.39848	256
0.3097	0.2299	1.40206	399	0.9433	0.9171	1.39698	133
0.3936	0.3016	1.40253	471	1.0000	1.0000	1.39536	
0.5007	0.4002	1.40284	537				
1-pentanol (1) + DPA (2) ; *T*/K = 293.15							
0.0000	0.0000	1.40409		0.6080	0.5503	1.41265	535
0.0523	0.0417	1.40515	82	0.7040	0.6523	1.41274	484
0.0950	0.0765	1.40602	148	0.7909	0.7490	1.41238	392
0.1538	0.1254	1.40714	232	0.8562	0.8245	1.41188	298
0.2103	0.1736	1.40815	305	0.8980	0.8741	1.41142	223
0.2984	0.2512	1.40965	409	0.9497	0.9371	1.41074	119
0.4033	0.3478	1.41103	491	1.0000	1.0000	1.40992	
0.5068	0.4477	1.41207	537				
1-pentanol (1) + DPA (2) ; *T*/K = 298.15							
0.0000	0.0000	1.40147		0.6080	0.5498	1.41045	541
0.0523	0.0417	1.40255	81	0.7040	0.6519	1.41065	495
0.0950	0.0764	1.40342	145	0.7909	0.7487	1.41035	402
0.1538	0.1252	1.40462	234	0.8562	0.8242	1.40987	305
0.2103	0.1734	1.40562	302	0.8980	0.8740	1.40943	229
0.2984	0.2509	1.40715	405	0.9497	0.9370	1.40875	120
0.4033	0.3474	1.40861	488	1.0000	1.0000	1.40796	
0.5068	0.4473	1.40974	536				
1-pentanol (1) + DPA (2) ; *T*/K = 303.15							
0.0000	0.0000	1.39888		0.6080	0.5494	1.40811	530
0.0523	0.0416	1.39999	81	0.7040	0.6516	1.40838	484
0.0950	0.0762	1.40087	144	0.7909	0.7484	1.40813	390
0.1538	0.1250	1.40208	230	0.8562	0.8240	1.40777	300
0.2103	0.1731	1.40316	304	0.8980	0.8738	1.40728	215
0.2984	0.2506	1.40468	400	0.9497	0.9369	1.40671	113
0.4033	0.3470	1.40617	480	1.0000	1.0000	1.40603	
0.5068	0.4469	1.40739	531				
1-heptanol (1) + DPA (2) ; *T*/K = 293.15							
0.0000	0.0000	1.40409		0.5988	0.6079	1.42105	469
0.0533	0.0553	1.40617	96	0.6970	0.7050	1.42249	418
0.1009	0.1044	1.40794	173	0.7957	0.8018	1.42346	321
0.1434	0.1482	1.40944	235	0.8458	0.8507	1.42381	258
0.1983	0.2044	1.41129	306	0.8956	0.8991	1.42409	189
0.2939	0.3019	1.41418	398	0.9427	0.9447	1.42420	109
0.3915	0.4006	1.41677	458	1.0000	1.0000	1.42422	

0.4925	0.5021	1.41906	483				
1-heptanol (1) + DPA (2) ; T/K = 298.15							
0.0000	0.0000	1.40147		0.5988	0.6055	1.41883	469
0.0533	0.0547	1.40355	93	0.6970	0.7028	1.42035	422
0.1009	0.1034	1.40532	168	0.7957	0.8002	1.42142	323
0.1434	0.1468	1.40684	229	0.8458	0.8494	1.42180	258
0.1983	0.2028	1.40873	300	0.8956	0.8982	1.42209	186
0.2939	0.2997	1.41170	394	0.9427	0.9442	1.42226	108
0.3915	0.3981	1.41433	451	1.0000	1.0000	1.42234	
0.4925	0.4994	1.41673	480				
1-heptanol (1) + DPA (2) ; T/K = 303.15							
0.0000	0.0000	1.39888		0.5988	0.6030	1.41664	470
0.0533	0.0542	1.40101	95	0.6970	0.7007	1.41822	417
0.1009	0.1025	1.40283	172	0.7957	0.7985	1.41935	320
0.1434	0.1456	1.40436	231	0.8458	0.8481	1.41980	258
0.1983	0.2011	1.40628	303	0.8956	0.8972	1.42012	185
0.2939	0.2975	1.40933	399	0.9427	0.9436	1.42034	107
0.3915	0.3957	1.41205	458	1.0000	1.0000	1.42048	
0.4925	0.4969	1.41451	486				

---

[a] The standard uncertainties are: $u(T) = 0.02\,\mathrm{K}$; $u(p) = 1\,\mathrm{kPa}$; $u(x_1) = 0.0008$; $u(\phi_1) = 0.004$, $u(n_D) =$ 0.00008. The combined expanded uncertainty (0.95 level of confidence) is $U_{rc}(n_D^E) = 0.0002$.

Table 5

Coefficients A_i and standard deviations, $\sigma\left(F^{E}\right)$ (equation (6)), for the representation of F^{E} at temperature T and pressure p = 0.1 MPa for 1-alkanol (1) + di-*n*-propylamine (DPA) (2) systems by equation (5).

Property F^{E}	1-alkanol	T/K	A_0	A_1	A_2	A_3	$\sigma\left(F^{E}\right)$
ε_r^E	methanol	293.15	5.25	13.23	7.18		0.010
		298.15	4.60	12.65	7.4		0.012
		303.15	4.08	12.16	7.6		0.016
	1-propanol	293.15	– 2.03	4.03	2.12	– 1.0	0.008
		298.15	– 2.27	3.48	2.12	– 0.7	0.010
		303.15	– 2.46	2.81	2.1		0.011
	1-butanol	293.15	– 3.32	2.29	1.15	– 1.1	0.006
		298.15	– 3.40	1.89	1.23	– 0.78	0.005
		303.15	– 3.433	1.49	1.29	– 0.39	0.003
	1-pentanol	293.15	– 3.738	1.02	0.43	– 0.71	0.004
		298.15	– 3.680	0.77	0.56	– 0.45	0.004
		303.15	– 3.574	0.59	0.64	– 0.20	0.003
	1-heptanol	293.15	– 3.178	0.51	– 0.05	– 0.53	0.004
		298.15	– 2.982	0.41	0.06	– 0.36	0.004
		303.15	– 2.76	0.35	0.14	– 0.2	0.006
$10^5 n_D^E$	methanol	293.15	3200	2053	24	– 945	5
		298.15	3218	2133	191	– 712	4
		303.15	3247	2236	359	– 712	4
	1-propanol	293.15	2328	970			4
		298.15	2301	970			4
		303.15	2269	977			4
	1-butanol	293.15	2240	810	– 1	– 316	1.7
		298.15	2195	803	– 65	– 356	3
		303.15	2154	782	– 104	– 293	4
	1-pentanol	293.15	2126	459			4
		298.15	2138	520			4
		303.15	2102	470			5
	1-heptanol	293.15	1944	59			1.9
		298.15	1931	96			3
		303.15	1942	61			1.3
$\left(\frac{\partial \varepsilon_r^E}{\partial T}\right)_p$ / K^{-1}	methanol	298.15	– 0.117	– 0.13	0.04	0.05	0.0011
	1-propanol	298.15	– 0.043	– 0.104	0.002	0.056	0.0004
	1-butanol	298.15	– 0.011	– 0.080	0.013	0.08	0.0007
	1-pentanol	298.15	0.0164	– 0.043	0.021	0.051	0.0002
	1-heptanol	298.15	0.0415	– 0.016	0.019	0.032	0.0004

Table 6

Values of the derivative of permittivity with respect to temperature at 298.15 K for pure compounds[a], $\left(\partial \varepsilon_{\mathrm{r}}^{*} / \partial T\right)_p$, and for mixtures, $\left(\partial \varepsilon_{\mathrm{r}} / \partial T\right)_p$, at ϕ_1 = 0.5.

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.	1-alkanol + DPA	1-alkanol + HxA
Methanol	– 0.192	–0.195 [68]	– 0.131	– 0.110
1-propanol	– 0.136	–0.130 [88]	– 0.094	– 0.076
1-butanol	– 0.127	–0.122 [88]	– 0.077	– 0.060
1-pentanol	– 0.117	–0.110 [88]	– 0.062	– 0.044
1-heptanol	– 0.099	–0.096 [88]	– 0.044	– 0.023
DPA	– 0.012			
HXA	– 0.0098			

[a] *n*-hexylamine (HxA), di-*n*-propylamine (DPA).

Figure captions

Figure 1: Excess relative permittivities, $\varepsilon_{\mathrm{r}}^{\mathrm{E}}$, of 1-alkanol (1) + di-*n*-propylamine (2) systems at 0.1 MPa, 298.15 K and 1 MHz. Full symbols, experimental values (this work): (●), methanol; (■), 1-propanol; (▲), 1-butanol; (♦), 1-pentanol; (▼), 1-heptanol. Solid lines, calculations with equation (5) using the coefficients from Table 5.

Figure 2: Derivative of the excess relative permittivity of 1-alkanol (1) + di-*n*-propylamine (2) systems at 0.1 MPa, 298.15 K and 1 MHz. Full symbols, experimental values (this work): (●), methanol; (■), 1-propanol; (▲), 1-butanol; (♦), 1-pentanol; (▼), 1-heptanol. Solid lines, calculations with equation (5) using the coefficients from Table 5.

Figure 3: Excess refractive index, $n_{\mathrm{D}}^{\mathrm{E}}$, of 1-alkanol (1) + di-*n*-propylamine (2) systems at 0.1 MPa, 298.15 K and 1 MHz. Full symbols, experimental values (this work): (●), methanol; (■), 1-propanol; (▲), 1-butanol; (♦), 1-pentanol; (▼), 1-heptanol. Solid lines, calculations with equation (5) using the coefficients from Table 5.

Figure 4: Excess relative permittivities at $\phi_1 = 0.5$ of 1-alkanol (1) + amine (2) or + heptane (2) systems as functions of the number of carbon atoms of the 1-alkanol, at 0.1 MPa, 298.15 K and 1 MHz: (●), *n*-hexylamine [23]; (▲),di-*n*-propylamine (this work); (♦), heptane [20, 43-45]; (■), di-*n*-propylether [51].

Figure 5: Kirkwood correlation factor, g_{K}, of 1-alkanol (1) + di-*n*-propylamine (2) systems at 0.1 MPa, 298.15 K and 1 MHz. Numbers in parentheses indicate the number of atoms of the 1-alkanol.

Figure 6: Excess Kirkwood correlation factor, $g_{\mathrm{K}}^{\mathrm{E}}$, of 1-alkanol (1) + di-*n*-propylamine (2) systems at 0.1 MPa, 298.15 K and 1 MHz. Numbers in parentheses indicate the number of atoms of the 1-alkanol.

Figure 7: Excess Kirkwood correlation factors at $\phi_1 = 0.5$ of 1-alkanol (1) + amine (2) systems as functions of the number of carbon atoms of the 1-alkanol, at 0.1 MPa, 298.15 K and 1 MHz: (●), *n*-hexylamine [23]; (▲), di-*n*-propylamine (this work).

Highlights

- ε_r, n_D and related excess functions are reported at (293.15-303.15) K for 1-alkanol+DPA.
- 1-alkanol-DPA interactions contribute positively to $\varepsilon_\mathrm{r}^\mathrm{E}$, being dominant for methanol.
- $\varepsilon_\mathrm{r}^\mathrm{E}(\phi_1 = 0.5)$ changes in the order: methanol > 1-propanol > 1-butanol > 1-pentanol < 1-heptanol.
- For a given 1-alkanol, $\varepsilon_\mathrm{r}^\mathrm{E}(\phi_1 = 0.5)$ varies in the order: HxA < DPA < DEA.
- The Kirkwood-Fröhlich model is used to study the mixtures.

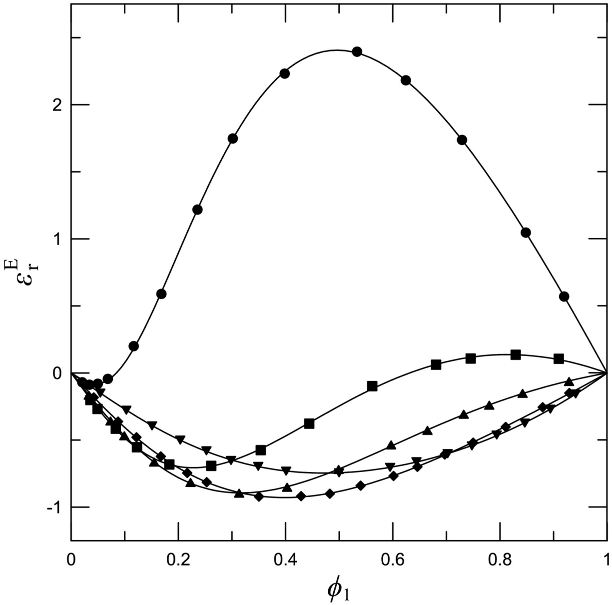

Figure 1

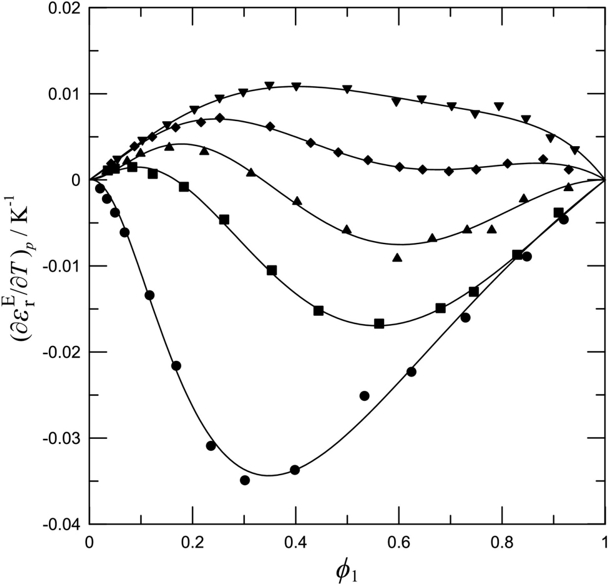
0.02
0.01
0
-0.01
-0.02
-0.03
-0.04
0
0.2
0.4
0.6
0.8
1
$(\partial \varepsilon_r^E / \partial T)_p$ / K^{-1}
ϕ_1

Figure 2

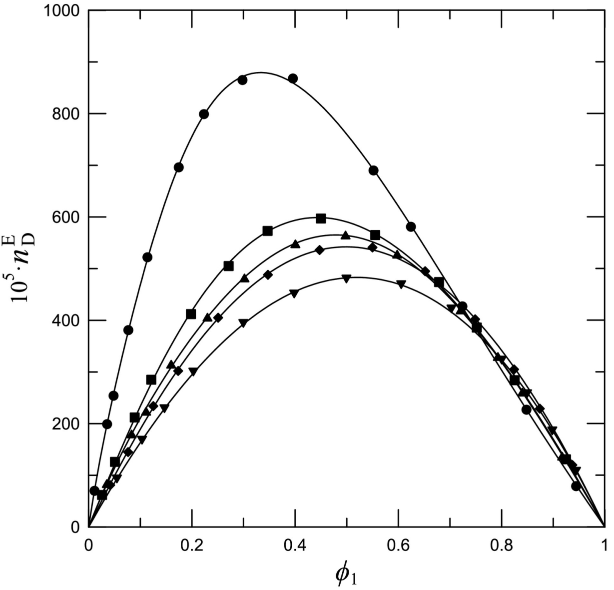

Figure 3

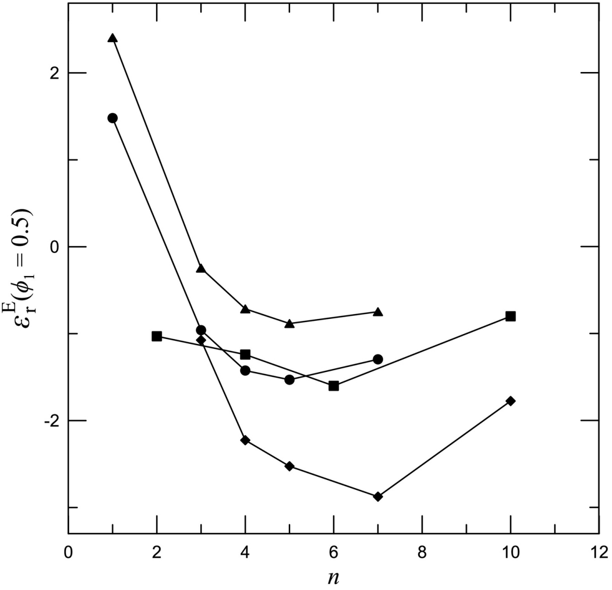

Figure 4

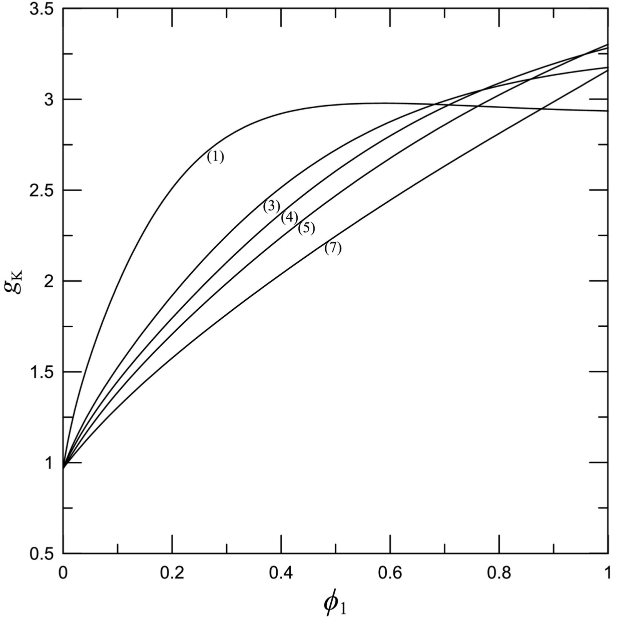

Figure 5

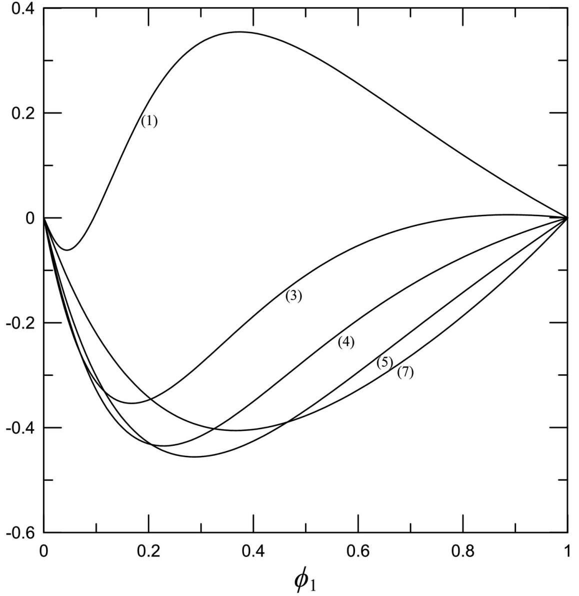

Figure 6

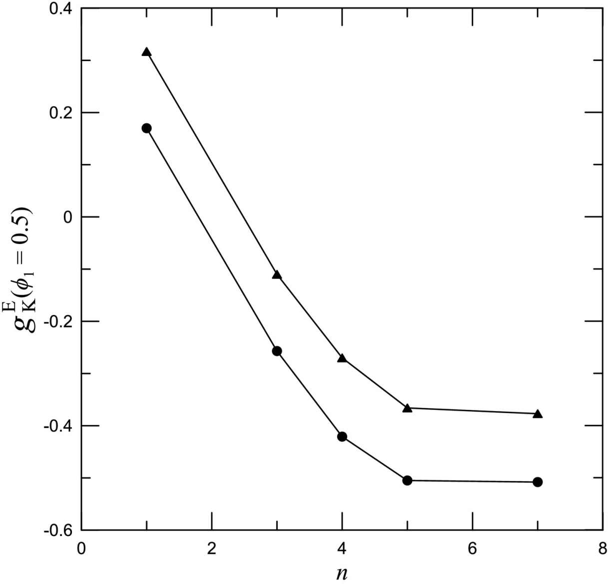

Figure 7