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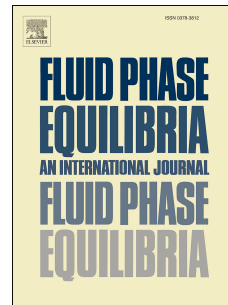
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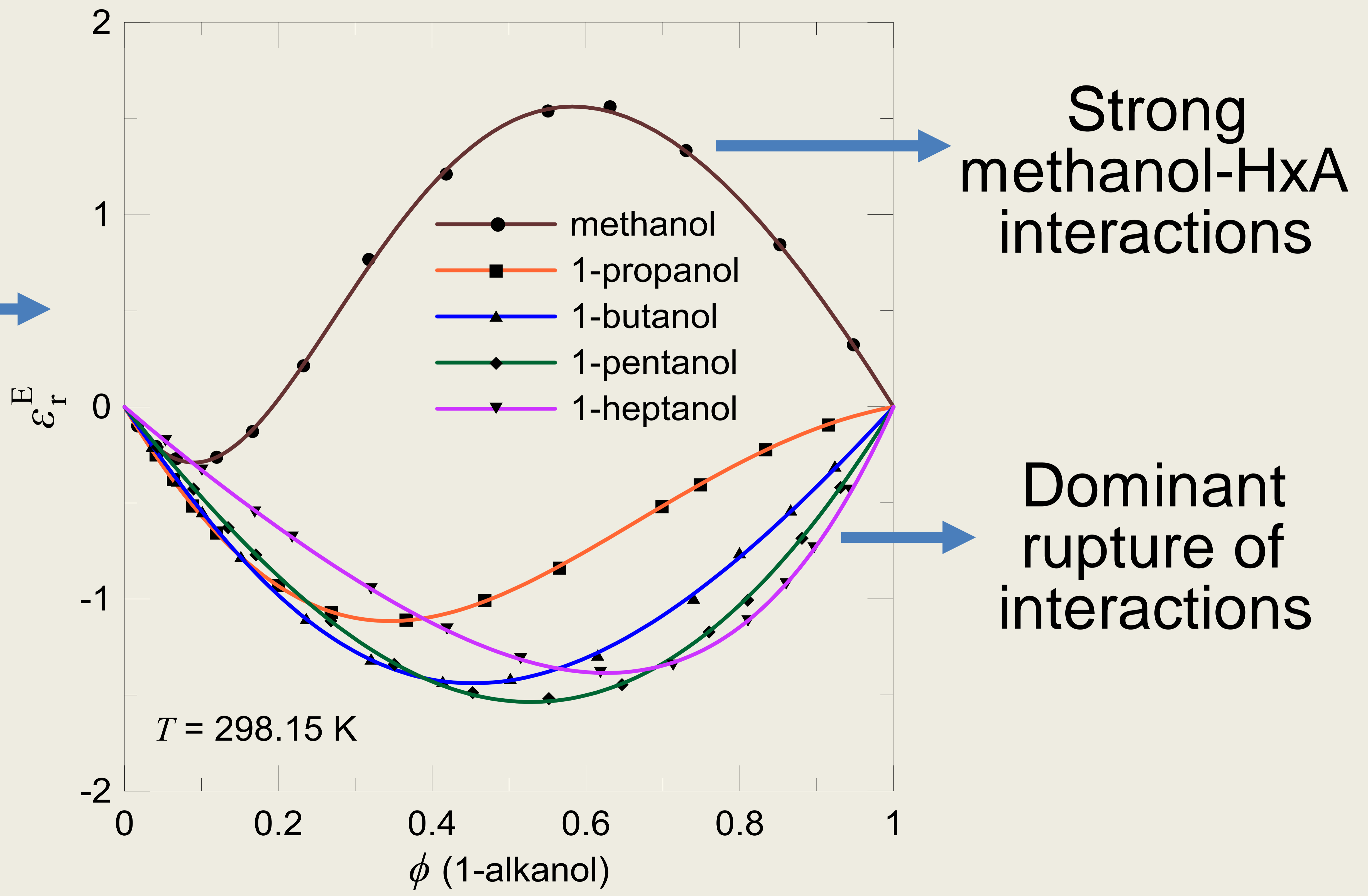
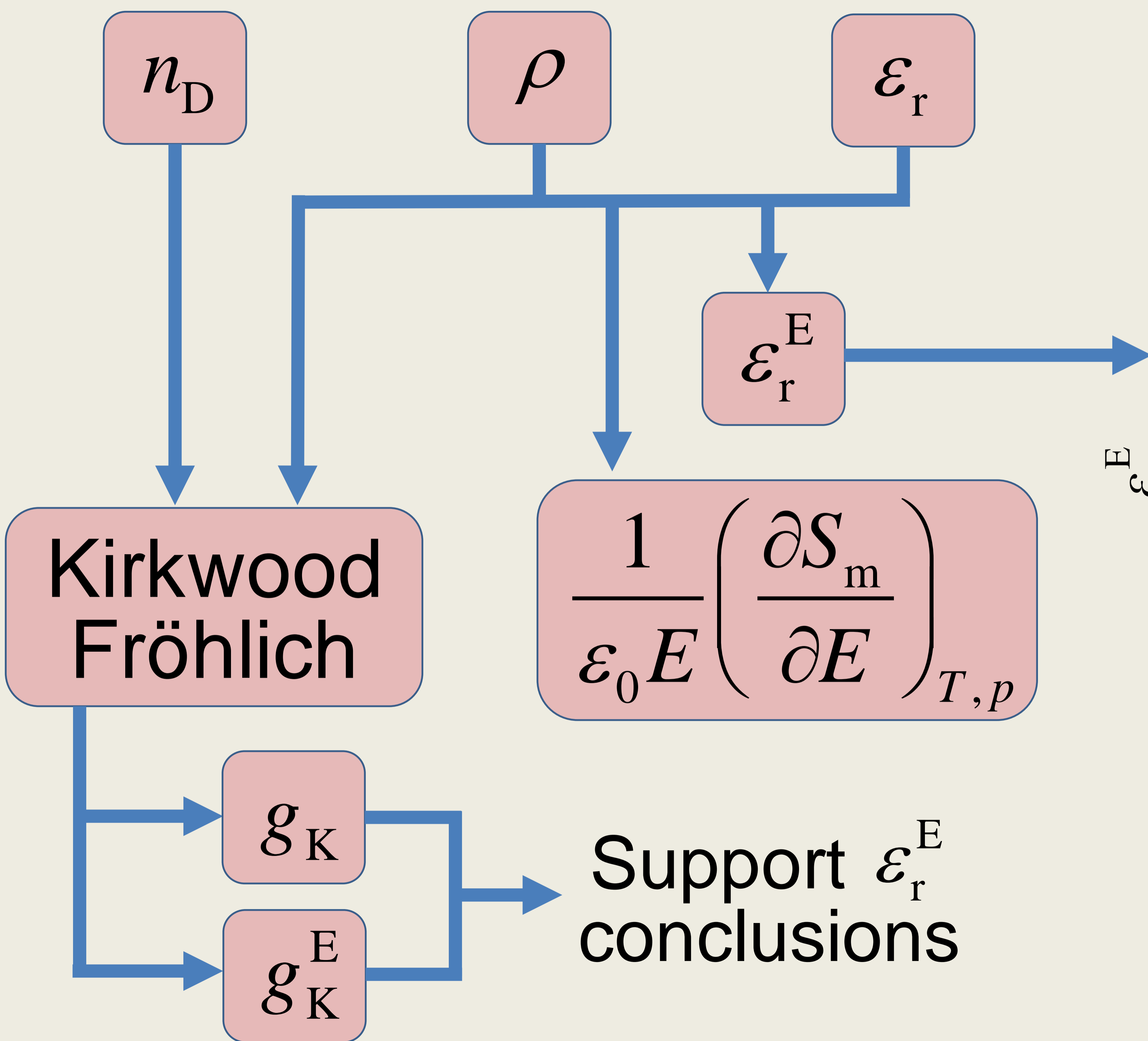
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Thermodynamics of mixtures with strongly negative deviations from Raoult's law. XV. Permittivities and refractive indices for 1-alkanol + *n*-hexylamine systems at (293.15-303.15) K. Application of the Kirkwood-Fröhlich model

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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 + *n*-hexylamine (HxA). Also, their corresponding excess functions are calculated and correlated. Positive values of the excess permittivities, ϵ_r^E , are encountered for the methanol system, whereas the remaining mixtures show negative values. This reveals that interactions between unlike molecules contribute positively to ϵ_r^E . This contribution is dominant for the methanol mixture, while those arising from the breaking of interactions between like molecules are prevalent for the remaining mixtures. At ϕ_1 (volume fraction) = 0.5, ϵ_r^E changes in the order: methanol > 1-propanol > 1-butanol > 1-pentanol < 1-heptanol. Similar variation with the chain length of the 1-alkanol is observed for mixtures such as 1-alkanol + heptane, or + cyclohexylamine, and can be explained in terms of the lower and weaker self-association of longer 1-alkanols. The effect of the replacement of HxA by cyclohexylamine, or by aniline, is also shown. Calculations on molar refractions indicate that dispersive interactions in the systems under study increase with the length of the 1-alkanol. The mixtures are studied by means of the application of the Kirkwood-Fröhlich model, and the Kirkwood correlation factors, including the corresponding excess values, are reported.

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

1. Introduction

Mixtures formed by 1-alkanol and amine are a very interesting class of systems as they show a variety of different behaviours. For example, 1-alkanol + linear primary or secondary amine systems are characterized by strongly negative excess molar enthalpies (H_m^E). Thus, at 298.15 K and equimolar composition, $H_m^E/\text{J}\cdot\text{mol}^{-1} = -3200$ (methanol + *n*-hexylamine (HxA)) [1]; -4581 (methanol + diethylamine) [2]. This has been interpreted as the result of two different opposing effects. In the pure liquid state, both 1-alkanols and amines are self-associated by means of O-H---O and N-H---N bonds, respectively. When the mixing process takes place, such bonds are broken, and this process leads to a positive contribution to H_m^E . However, new interactions between unlike molecules are simultaneously created, which contributes negatively to H_m^E . Therefore, the large and negative H_m^E values reveal that the new O-H---N bonds created are stronger than the O-H---O and N-H---N bonds. Thus, the values of the enthalpy of the hydrogen bonds between methanol and amine estimated from the application of the ERAS model [3] are: $-42.4 \text{ kJ}\cdot\text{mol}^{-1}$ (*n*-hexylamine) [4]; $-45.4 \text{ kJ}\cdot\text{mol}^{-1}$ (diethylamine) [5]. The value used, within this model, for the enthalpy of the H bonds between alkanol molecules is higher: $-25.1 \text{ kJ}\cdot\text{mol}^{-1}$ [3-5]. As a consequence of the strong interactions between unlike molecules, the systems are highly structured. For example, at 298.15 K and $x_1 = 0.5$, $TS_m^E (=H_m^E - G_m^E; G_m^E$ molar excess Gibbs energy) is $-3758 \text{ J}\cdot\text{mol}^{-1}$ for the methanol + diethylamine mixture (value determined using $G_m^E = -823 \text{ J}\cdot\text{mol}^{-1}$ [6]). For comparison, we provide similar results for the 1-propanol + hexane system, $TS_m^E = (533 (=H_m^E) - 1295 (=G_m^E)) = -762 \text{ J}\cdot\text{mol}^{-1}$ [7, 8]. The existence of strong interactions between unlike molecules in this type of solutions is also supported by large and negative excess molar volumes [4, 9-13] and by solid-liquid equilibria measurements, as the corresponding phase diagrams show that complex formation is an important feature of the systems [14]. Interestingly, the replacement of a linear primary amine by aniline leads to very different $H_m^E/\text{J}\cdot\text{mol}^{-1}$ values: -170 (methanol) [15]; 1020 (1-butanol) [16]. This can be explained in terms of a large contribution to H_m^E from the breaking of the strong dipolar interactions between aniline molecules upon mixing. Note that the upper critical solution temperature of the aniline + heptane system is 343.1 K [17].

We have extended the database of 1-alkanol + amine mixtures reporting excess molar volumes [4, 9-13]; dynamic viscosities [11-13]; vapour-liquid equilibria [18]; permittivities (ϵ_r) and refractive indices (n_D) [11-13, 19]. In addition, these systems have been studied by using different models as DISQUAC or ERAS [4, 5, 9, 10, 12, 20-23]; the formalism of the Kirkwood-Buff integrals [24], or the concentration-concentration structure factor ($S_{CC}(0)$)

formalism [25]. As a continuation, we provide now ϵ_r and n_D measurements over the temperature range (293.15-303.15) K for the systems 1-alkanol + HxA. In addition, the data are analyzed in terms of the Kirkwood-Fröhlich model [26-29], which is a useful approach to gain insight into the mixture structure and interactions.

2. Experimental

2.1 Materials

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

2.2 Apparatus and procedure

Binary mixtures were prepared by mass in small vessels of about 10 cm³ 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) [30]. 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.

Densities were obtained using a vibrating-tube densimeter and sound analyser Anton Paar DSA 5000, which is automatically thermostated within 0.01 K. The calibration procedure has been described elsewhere [31]. The relative standard uncertainty of the ρ measurements is 0.0012.

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 K.

The refractometer has been calibrated using 2,2,4-trimethylpentane and toluene at (293.15-303.15) K, following the recommendations by Marsh [32]. The standard uncertainty of n_D is 0.00008.

The ε_r measurements were performed with the aid 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 $\approx 4.8 \text{ cm}^3$. 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 [33]. 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.

3. Results

From the experimental ε_r values at different temperatures, we can also determine the derivative $(\partial\varepsilon_r / \partial T)_p$ at 298.15 K as the slope of a linear regression of experimental ε_r values in the range (293.15 – 303.15) K.

Let us denote by x_i the mole fraction of component i . The corresponding volume fraction, ϕ_i , is given by $\phi_i = x_i V_{mi}^* / (x_1 V_{m1}^* + x_2 V_{m2}^*)$, where V_{mi}^* 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, $\varepsilon_r^{\text{id}}$, the derivative $\left[(\partial\varepsilon_r / \partial T)_p \right]^{\text{id}}$, and the refractive index, n_D^{id} , are given by [34, 35]:

$$\varepsilon_r^{\text{id}} = \phi_1 \varepsilon_{r1}^* + \phi_2 \varepsilon_{r2}^* \quad (1)$$

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

$$\left[\left(\frac{\partial\varepsilon_r}{\partial T} \right)_p \right]^{\text{id}} = \left(\frac{\partial\varepsilon_r^{\text{id}}}{\partial T} \right)_p \quad (3)$$

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

$$F^E = F - F^{\text{id}} \quad , \quad F = \varepsilon_r, n_D, \left(\frac{\partial\varepsilon_r}{\partial T} \right)_p \quad (4)$$

Table 3 lists ϕ_1 , ε_r and ε_r^E values of 1-alkanol (1) + HxA (2) systems as functions of x_1 , in the temperature range (293.15 – 303.15) K. Table 4 contains the corresponding experimental x_1 , ϕ_1 , n_D and n_D^E values. The data of $\left[(\partial\varepsilon_r/\partial T)_p \right]^E = (\partial\varepsilon_r^E/\partial T)_p$ are collected in Table S1 (supplementary material).

The F^E data were fitted to a Redlich-Kister equation [36] by an unweighted linear least-squares regression:

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

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 [37] at 99.5% confidence level. Table 5 includes the parameters A_i obtained, and the standard deviations $\sigma(F^E)$, defined by:

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

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

Values of ε_r^E , n_D^E and $(\partial\varepsilon_r^E/\partial T)_p$ versus ϕ_1 of 1-alkanol + amine 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.

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 $\phi_1 = 0.5$. On the other hand, n stands for the number of C atoms of the 1-alkanol.

4.1. Excess relative permittivities

The rupture of interactions between molecules of the same species along mixing is associated to a negative contribution to ϵ_r^E . The creation of new interactions in the mixture forms multimers, whose total dipole moment can be more or less effective –in its impact on the macroscopic dipole moment under the action of an electric field– than in the ideal mixture. In the first case, the contribution to ϵ_r^E is positive, whereas in the second case it is negative. 1-Alkanol + heptane mixtures show rather large negative values of this quantity (Figure 4): $\epsilon_r^E = -1.075$ ($n = 3$), -2.225 ($n = 4$), -2.525 ($n = 5$), -2.875 ($n = 7$), -1.775 ($n = 10$) [12, 38-40]. These negative values can be attributed to the breaking of 1-alkanol self-association. For methanol, there exists a partial immiscibility region [41]. The $\epsilon_r(n)$ variation follows the sequence: 1-propanol > 1-butanol > 1-pentanol > 1-heptanol < 1-decanol. It can be explained in terms of the lower and weaker self-association of longer 1-alkanols [19]. This statement also applies for the relative variation of ϵ_r^E in the mixtures under study (Figures 1 and 4): 1.480 ($n = 1$), -0.960 ($n = 3$), -1.424 ($n = 4$), -1.530 ($n = 5$), -1.295 ($n = 7$). These results are higher than those of heptane mixtures. This suggests that the formation of (1-alkanol)-HxA interactions yields a positive contribution to ϵ_r^E .

4.1.1. Effect of cyclization

Cyclohexylamine (c-HxA) is a cyclic primary amine with a slightly higher permittivity than HxA ($\epsilon_r^* = 4.53$ [19]). The trend observed in the two series of systems 1-alkanol + heptane and + HxA is the same as for 1-alkanol + c-HxA mixtures (Figure 4), for the same reasons: $\epsilon_r^E = 2.218$ ($n = 1$ [13]), -0.269 ($n = 3$ [19]), -0.848 ($n = 4$ [19]), -0.915 ($n = 7$ [19]) -0.411 ($n = 10$ [19]). Therefore, cyclization of the amine leads to increased ϵ_r^E values compared to those of systems with HxA; i.e., multimers formed by unlike molecules contribute more positively to ϵ_r^E in cyclohexylamine solutions.

4.1.2. Effect of aromaticity

The effect of aromaticity is more dramatic than that of cyclization. In fact, aniline ($\epsilon_r^* = 7.004$ [42]) shows a greater value of the relative permittivity, underlining the importance of aniline-aniline interactions and the polarizability of the aromatic ring. The values of the corresponding excess property are of course negative [42] (Figure 4): -0.775 ($n = 1$), -1.854 ($n = 3$), -2.084 ($n = 5$). In addition, they are lower than those of the mixtures with HxA or c-HxA. This may be explained taking into account that the breaking of the dipolar interactions between aniline molecules contributes more negatively to ϵ_r^E .

4.2. Entropy change with the electric field

ϵ_r is a collective property and its magnitude in a liquid depends on its structure, the permanent dipole moment of its molecules and their polarizability. It must be highlighted that it is also affected by volume effects. In fact, let \vec{B} denote the macroscopic dipole moment and V the volume. The polarization (macroscopic dipole moment per unit volume) of the liquid, \vec{B}/V , is related to the intensity of the electric field, \vec{E} , through the equation $\vec{B}/V = (\epsilon_r - 1)\epsilon_0\vec{E}$ (ϵ_0 = vacuum permittivity). In order to compare the response of different liquids to an electric field, it is desirable to work with the molar susceptibility, $\chi_m = (\epsilon_r - 1)V_m$. This quantity, for a given electric field, is proportional to the macroscopic dipole moment resulting from a fixed amount (1 mol) of molecules. For a linear, isotropic and homogeneous dielectric at constant composition, the molar macroscopic dipole moment B_m is related to χ_m and E by:

$$\frac{1}{\epsilon_0 E} B_m = \chi_m \quad (7)$$

The T -dependence of χ_m is linked to the change of the molar entropy, S_m , with a variation of E through the Schwarz relation (p = pressure):

$$\frac{1}{\epsilon_0 E} \left(\frac{\partial S_m}{\partial E} \right)_{T,p} = \left(\frac{\partial S_m}{\partial (\epsilon_0 E^2 / 2)} \right)_{T,p} = \left(\frac{\partial \chi_m}{\partial T} \right)_p \quad (8)$$

This variation is usually negative in common liquids like the ones considered in this work (Table 6), as it is associated with structure creation (dipolar ordering) by an increase of the electric field and a consequent negative variation of the entropy. It can be calculated from linear regressions of χ_m values in the temperature range (293.15 – 303.15) K. In the following discussion, we will use the notation $\eta_{m,p} = - \left(\frac{\partial \chi_m}{\partial T} \right)_p$.

The values of $\eta_{m,p}^*$ for the pure 1-alkanols increase with n (Table 6). It indicates that a high self-association (in the absence of an electric field) decreases the ability of the electric field to create structure by orientating the dipoles of individual molecules, as the multimers present in the liquid are more stable and the rotational degrees of freedom are more constricted. The lower $\eta_{m,p}^*$ values of the amines seems to be due to their lower μ . As HxA and c-HxA have similar dipole moments (Table 6), the fact that $\eta_{m,p}^*(\text{HxA}) < \eta_{m,p}^*(\text{c-HxA})$ indicates more freedom of rotation of the c-HxA molecules. Also, $\eta_{m,p}^*(\text{c-HxA}) < \eta_{m,p}^*(\text{aniline})$, which can be ascribed to

an extra contribution to the polarizability of the molecules of aniline due to the presence of the aromatic ring.

It is interesting to analyse the $\eta_{m,p}(\phi_1)$ curves for 1-alkanol + HxA systems (Figure 5). The necessary volumetric properties to compute them have been taken from a previous work [4]. Due to the absence of experimental volumetric data in the whole range of temperature necessary for the complete set of studied systems, we have neglected the contribution from the temperature dependence of the excess molar volume; this approximation does not appreciably affect the $\eta_{m,p}$ results, as can be seen by performing the exact calculation for the system 1-butanol + HxA [43]. At low HxA concentrations, $\eta_{m,p}$ varies more rapidly when the 1-alkanol is longer. This shows that, in this region, the difficulty for the electric field to rotate the dipoles decreases more rapidly with concentration when the 1-alkanol self-association is lower and weaker.

4.3. Molar refraction

The refractive index at optical wavelengths is closely related to dispersion forces, since the molar refraction (or molar refractivity), R_m , defined by the Lorentz-Lorenz equation [29, 44]:

$$R_m = \frac{n_D^2 - 1}{n_D^2 + 2} V_m = \frac{N_A \alpha_e}{3\epsilon_0} \quad (9)$$

(where N_A and ϵ_0 stand for Avogadro's constant and the vacuum permittivity, respectively) is proportional to the mean electronic contribution, α_e , to the polarizability, [29]. For the investigated systems, the values of $R_m / \text{cm}^3 \cdot \text{mol}^{-1}$ at $x_1 = 0.5$ are (Figure S2): 20.5 ($n = 1$), 25.2 ($n = 3$), 27.5 ($n = 4$), 29.8 ($n = 5$), 34.5 ($n = 7$). It is clear that dispersive interactions are more important in longer 1-alkanols. We have calculated the corresponding excess values, $R_m^E = R_m - R_m^{\text{id}}$, with R_m^{id} evaluated substituting ideal values in equation (9). The curves are negative, which means a loss in dispersive interactions along mixing with respect to the ideal state, in which dipoles of different components do not interact. The minimum values occur at $x_1 \approx 0.5$; in the same units: -0.37 ($n = 1$), -0.28 ($n \geq 3$). The lower value of the methanol system can be ascribed to a larger number of hydrogen bonds formed by the two species along the mixing process.

4.4. Kirkwood-Fröhlich model

Some relevant hypotheses of the model are: (i) a molecule of a given polar compound is modelled as a dipole moment inside a spherical cavity; (ii) the effect of the induced polarization of the molecules is treated in macroscopic way, assuming that the dipole is rigid (it only rotates)

and the cavity is filled by a continuous medium of relative permittivity ϵ_r^∞ (the value of the permittivity at a high frequency at which only the induced polarizability contributes); (iii) long-range interactions are considered macroscopically by assuming that the outside of the cavity is a continuous dielectric of permittivity ϵ_r ; (iv) short-range interactions are not neglected, and they are brought on stage by means of the so-called Kirkwood correlation factor, g_K , which provides information of 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 [26], from macroscopic physical properties according to the expression [26-29]:

$$g_K = \frac{9k_B T V_m \epsilon_0 (\epsilon_r - \epsilon_r^\infty)(2\epsilon_r + \epsilon_r^\infty)}{N_A \mu^2 \epsilon_r (\epsilon_r^\infty + 2)^2} \quad (10)$$

Here, k_B is Boltzmann's constant; N_A , Avogadro's constant; ϵ_0 , the vacuum permittivity; and V_m , the molar volume of the liquid at the working temperature, T . For polar compounds, ϵ_r^∞ is estimated from the relation $\epsilon_r^\infty = 1.1n_D^2$ [45]. μ represents the dipole moment of the solution, estimated from the equation [26]:

$$\mu^2 = x_1 \mu_1^2 + x_2 \mu_2^2 \quad (11)$$

where μ_i stands for the dipole moment of component i ($=1,2$). Calculations have been conducted using smoothed values of V_m^E [4], n_D^E (this work) and ϵ_r^E (this work) at $\Delta x_1 = 0.01$. The source and values of μ_i are collected in Table 6.

Our calculations on g_K curves for 1-alkanol + HxA systems can be seen in Figure 6. They support the conclusions extracted from the analysis of $\eta_{m,p}$, indicating that the mixture structure varies very rapidly with the HxA concentration for $n = 3, 4, 5, 7$. In contrast, for the methanol system g_K changes slowly from $\phi_1 > 0.6$ approximately, and this indicates that HxA is not able to break effectively the methanol self-association at such concentrations. This phenomenon remarks the strong relationship between the magnitude of the rupture of the 1-alkanol self-association by the amine and the dielectric behaviour of the mixtures.

We have also evaluated the excess Kirkwood correlation factors, $g_K^E = g_K - g_K^{\text{id}}$, where g_K^{id} is calculated substituting the real quantities by ideal ones in equation (10). The values for 1-alkanol + HxA systems are (Figures 7 and 8): 0.170 ($n = 1$), -0.257 ($n = 3$), -0.421 ($n = 4$), -0.505 ($n = 5$), -0.508 ($n = 7$). The positive value for the methanol mixture can be justified by the

formation of strong methanol-HxA interactions, which is consistent with the above analyses. The minima of the g_K^E curves occurs at lower ϕ_1 than in the ε_r^E curves. For the minimum of the curves, $g_K^E(1\text{-pentanol}) > g_K^E(1\text{-heptanol})$, while the opposite behaviour is encountered for ε_r^E . Thus, according to the Kirkwood-Fröhlich model, the destruction of the correlations of the dipoles is not the only responsible for the ε_r^E minima, but there are other effects involved. For c-HxA systems, g_K^E values are higher (Figure 8), indicating that in these mixtures the balance of destruction and creation of correlations is more inclined to the latter than in the case 1-alkanol + HxA. Aniline systems are quite interesting, as $g_K^E(\text{HxA}) < g_K^E(\text{aniline})$ for the 1-pentanol mixtures (Figure 8). This phenomenon may be related to the higher importance of the rupture of interactions between like molecules in 1-alkanol + aniline solutions, as showed by ε_r^E values and also H_m^E (see introduction).

5. Conclusions

ε_r and n_D measurements have been reported for the 1-alkanol + *n*-hexylamine systems at (293.15-303.15) K. The formation of multimers built by unlike molecules contributes positively to ε_r^E . Such contribution is dominant for the methanol mixture and ε_r^E is positive. For the remaining systems, the dominant contributions arise from the breaking of interactions between like molecules, and ε_r^E values are negative. For a given 1-alkanol, ε_r^E changes in the sequence: cyclohexylamine > *n*-hexylamine > aniline. The application of the Kirkwood-Fröhlich model confirms these findings. Calculations on R_m show that dispersive interactions in the studied mixtures increase with the length of the 1-alkanol.

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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	99.8%
<i>n</i> -hexylamine (HxA)	111-26-2	Aldrich	none	99.9%

^a In mole fraction. Provided by the supplier by gas chromatography.

Table 2

Relative permittivity at frequency $\nu = 1$ MHz, ϵ_r^* , refractive index, n_D^* , and density, ρ^* , of pure compounds at temperature T and pressure $p = 0.1$ MPa. ^a

Compound	T/K	ϵ_r^*		n_D^*		$\rho^* / \text{g}\cdot\text{cm}^{-3}$	
		Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
methanol	293.15	33.569	33.61 [46]	1.32862	1.32859 [47]	0.79163	0.7916 [48] 0.791400 [49]
	298.15	32.619	32.62 [46]	1.32654	1.32652 [50]	0.78695	0.7869 [51] 0.786884 [52]
	303.15	31.652	31.66 [46]	1.32439	1.32457 [53] 1.32410 [54]	0.78222	0.782158 [52]
1-propanol	293.15	21.150	21.15 [55]	1.38514	1.38512 [56]	0.80366	0.80361 [57]
	298.15	20.449	20.42 [55]	1.38306	1.38307 [54]	0.79968	0.79960 [57]
	303.15	19.784	19.75 [55]	1.38102	1.38104 [54]	0.79566	0.79561 [57]
1-butanol	293.15	18.192	18.19 [55]	1.39931	1.3993 [58]	0.80985	0.80982 [59] 0.8098 [60]
	298.15	17.545	17.53 [55]	1.39733	1.397336 [61]	0.80606	0.80606 [59]
	303.15	16.933	16.89 [55]	1.39529	1.3953 [62]	0.80222	0.8022 [60]
1-pentanol	293.15	15.701	15.63 [46]	1.40985	1.40986 [54]	0.81466	0.81468 [63]
	298.15	15.102	15.08 [64]	1.40793	1.40789 [54]	0.81103	0.81103 [63]
	303.15	14.536	14.44 [46]	1.40590	1.40592 [65]	0.80735	0.81737 [63]
1-heptanol	293.15	12.019	11.54 [66]	1.42425	1.42433 [67]	0.82237	0.8223 [68]
	298.15	11.504	11.45 [64]	1.42235	1.42240 [67]	0.81890	0.81881 [69]
	303.15	11.014	11.07 [70]	1.42047	1.42047 [65] 1.42048 [67]	0.81537	0.8153 [68]
HxA	293.15	3.964	3.94 [71]	1.41808	1.4180 [72]	0.76443	0.7651 [73]
	298.15	3.904		1.41563	1.41550 [72]	0.76019	0.76013 [74]
	303.15	3.846	3.83 [71]	1.41321	1.4131 [72]	0.75590	0.7562 [73]

^aThe standard uncertainties are: $u(T) = 0.02$ K (for ρ^* measurements, $u(T) = 0.01$ K); $u(p) = 1$ kPa; $u(\nu) = 20$ Hz; $u(n_D^*) = 0.00008$. The relative standard uncertainties are: $u_r(\rho^*) = 0.0012$, $u_r(\epsilon_r^*) = 0.003$.

Table 3

Volume fractions of 1-alkanol, ϕ_1 , relative permittivities, ϵ_r , and excess relative permittivities, ϵ_r^E , of 1-alkanol (1) + HxA (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	ϵ_r^E	x_1	ϕ_1	ϵ_r	ϵ_r^E
methanol (1) + HxA (2) ; $T/K = 293.15$							
0.0000	0.0000	3.964		0.7016	0.4182	17.646	1.301
0.0534	0.0170	4.367	-0.100	0.8002	0.5505	21.864	1.602
0.1220	0.0408	4.964	-0.208	0.8485	0.6313	24.251	1.597
0.1906	0.0672	5.681	-0.272	0.8984	0.7300	26.928	1.352
0.3081	0.1198	7.244	-0.267	0.9496	0.8521	30.037	0.847
0.3950	0.1664	8.783	-0.107	0.9834	0.9477	32.343	0.322
0.4982	0.2329	11.109	0.250	1.0000	1.0000	33.569	
0.6035	0.3176	14.210	0.843				
methanol (1) + HxA (2) ; $T/K = 298.15$							
0.0000	0.0000	3.904		0.7016	0.4183	17.127	1.212
0.0534	0.0170	4.293	-0.099	0.8002	0.5506	21.254	1.540
0.1220	0.0408	4.870	-0.206	0.8485	0.6314	23.597	1.562
0.1906	0.0672	5.564	-0.270	0.8984	0.7301	26.203	1.334
0.3081	0.1199	7.085	-0.262	0.9496	0.8521	29.216	0.844
0.3950	0.1665	8.557	-0.128	0.9834	0.9477	31.440	0.323
0.4982	0.2329	10.806	0.214	1.0000	1.0000	32.619	
0.6035	0.3177	13.794	0.767				
methanol (1) + HxA (2) ; $T/K = 303.15$							
0.0000	0.0000	3.964		0.7016	0.4182	17.646	1.301
0.0534	0.0170	4.367	-0.100	0.8002	0.5505	21.864	1.602
0.1220	0.0408	4.964	-0.208	0.8485	0.6313	24.251	1.597
0.1906	0.0672	5.681	-0.272	0.8984	0.7300	26.928	1.352
0.3081	0.1198	7.244	-0.267	0.9496	0.8521	30.037	0.847
0.3950	0.1664	8.783	-0.107	0.9834	0.9477	32.343	0.322
0.4982	0.2329	11.109	0.250	1.0000	1.0000	33.569	
0.6035	0.3176	14.210	0.843				
1-propanol (1) + HxA (2) ; $T/K = 293.15$							
0.0000	0.0000	3.964		0.6097	0.4688	10.990	-1.031
0.0708	0.0413	4.411	-0.263	0.6977	0.5659	12.847	-0.843
0.1073	0.0636	4.663	-0.394	0.8044	0.6991	15.469	-0.510
0.1470	0.0887	4.953	-0.535	0.8406	0.7487	16.431	-0.400
0.1935	0.1194	5.330	-0.686	0.8989	0.8340	18.080	-0.217
0.3070	0.2002	6.436	-0.969	0.9504	0.9154	19.605	-0.091

0.3941	0.2687	7.471	- 1.111	1.0000	1.0000	21.150	
0.5056	0.3662	9.113	- 1.145				
1-propanol (1) + HxA (2) ; T/K = 298.15							
0.0000	0.0000	3.904		0.6097	0.4686	10.649	- 1.008
0.0708	0.0412	4.336	- 0.250	0.6977	0.5658	12.426	- 0.839
0.1073	0.0635	4.578	- 0.377	0.8044	0.6989	14.948	- 0.519
0.1470	0.0887	4.857	- 0.515	0.8406	0.7486	15.885	- 0.405
0.1935	0.1193	5.222	- 0.656	0.8989	0.8339	17.478	- 0.223
0.3070	0.2001	6.286	- 0.929	0.9504	0.9154	18.955	- 0.094
0.3941	0.2686	7.279	- 1.069	1.0000	1.0000	20.449	
0.5056	0.3660	8.850	- 1.109				
1-propanol (1) + HxA (2) ; T/K = 303.15							
0.0000	0.0000	3.846		0.6097	0.4685	10.324	- 0.989
0.0708	0.0412	4.263	- 0.240	0.6977	0.5656	12.034	- 0.827
0.1073	0.0635	4.499	- 0.359	0.8044	0.6988	14.463	- 0.520
0.1470	0.0886	4.770	- 0.488	0.8406	0.7484	15.354	- 0.420
0.1935	0.1192	5.123	- 0.623	0.8989	0.8338	16.902	- 0.233
0.3070	0.2000	6.148	- 0.886	0.9504	0.9153	18.330	- 0.104
0.3941	0.2685	7.102	- 1.023	1.0000	1.0000	19.784	
0.5056	0.3659	8.605	- 1.073				
1-butanol (1) + HxA (2) ; T/K = 293.15							
0.0000	0.0000	3.965		0.5930	0.5018	9.623	- 1.481
0.0510	0.0358	4.258	- 0.216	0.6983	0.6154	11.376	- 1.344
0.0969	0.0691	4.538	- 0.410	0.8047	0.7402	13.472	- 1.024
0.1402	0.1013	4.828	- 0.578	0.8525	0.7998	14.558	- 0.786
0.2052	0.1515	5.294	- 0.826	0.9035	0.8662	15.741	- 0.547
0.3095	0.2366	6.164	- 1.167	0.9460	0.9237	16.795	- 0.311
0.4059	0.3208	7.139	- 1.390	1.0000	1.0000	18.192	
0.5054	0.4140	8.352	- 1.503				
1-butanol (1) + HxA (2) ; T/K = 298.15							
0.0000	0.0000	3.904		0.5930	0.5016	9.333	- 1.413
0.0510	0.0358	4.186	- 0.206	0.6983	0.6152	11.005	- 1.291
0.0969	0.0690	4.460	- 0.385	0.8047	0.7400	13.003	- 0.995
0.1402	0.1012	4.739	- 0.545	0.8525	0.7997	14.054	- 0.759
0.2052	0.1514	5.190	- 0.779	0.9035	0.8661	15.182	- 0.536
0.3095	0.2364	6.028	- 1.101	0.9460	0.9237	16.197	- 0.307
0.4059	0.3206	6.965	- 1.312	1.0000	1.0000	17.545	
0.5054	0.4138	8.121	- 1.428				
1-butanol (1) + HxA (2) ; T/K = 303.15							
0.0000	0.0000	3.845		0.5930	0.5014	9.058	- 1.349
0.0510	0.0358	4.120	- 0.194	0.6983	0.6150	10.656	- 1.238

0.0969	0.0689	4.385	-0.362	0.8047	0.7398	12.566	-0.962
0.1402	0.1012	4.656	-0.514	0.8525	0.7996	13.565	-0.745
0.2052	0.1512	5.094	-0.730	0.9035	0.8660	14.656	-0.523
0.3095	0.2363	5.898	-1.040	0.9460	0.9236	15.632	-0.301
0.4059	0.3204	6.797	-1.241	1.0000	1.0000	16.933	
0.5054	0.4136	7.905	-1.353				
1-pentanol (1) + HxA (2) ; T/K = 293.15							
0.0000	0.0000	3.967		0.6013	0.5521	8.827	-1.618
0.0520	0.0429	4.248	-0.222	0.6916	0.6470	10.025	-1.534
0.1079	0.0900	4.563	-0.460	0.7952	0.7604	11.649	-1.241
0.1601	0.1348	4.876	-0.673	0.8396	0.8106	12.419	-1.060
0.2014	0.1709	5.146	-0.826	0.9006	0.8810	13.582	-0.723
0.3100	0.2686	5.924	-1.195	0.9431	0.9313	14.457	-0.438
0.3982	0.3510	6.653	-1.433	1.0000	1.0000	15.701	
0.5031	0.4528	7.689	-1.591				
1-pentanol (1) + HxA (2) ; T/K = 298.15							
0.0000	0.0000	3.905		0.6013	0.5519	8.567	-1.518
0.0520	0.0429	4.176	-0.209	0.6916	0.6468	9.702	-1.445
0.1079	0.0899	4.485	-0.427	0.7952	0.7602	11.246	-1.171
0.1601	0.1347	4.785	-0.628	0.8396	0.8104	11.973	-1.006
0.2014	0.1708	5.047	-0.770	0.9006	0.8809	13.084	-0.684
0.3100	0.2684	5.796	-1.114	0.9431	0.9312	13.913	-0.419
0.3982	0.3508	6.494	-1.339	1.0000	1.0000	15.102	
0.5031	0.4526	7.486	-1.487				
1-pentanol (1) + HxA (2) ; T/K = 303.15							
0.0000	0.0000	3.846		0.6013	0.5516	8.319	-1.424
0.0520	0.0428	4.110	-0.194	0.6916	0.6465	9.397	-1.360
0.1079	0.0898	4.408	-0.398	0.7952	0.7600	10.864	-1.106
0.1601	0.1345	4.701	-0.583	0.8396	0.8102	11.555	-0.952
0.2014	0.1706	4.957	-0.713	0.9006	0.8808	12.610	-0.652
0.3100	0.2682	5.675	-1.038	0.9431	0.9311	13.397	-0.402
0.3982	0.3505	6.348	-1.245	1.0000	1.0000	14.536	
0.5031	0.4523	7.298	-1.383				
1-heptanol (1) + HxA (2) ; T/K = 293.15							
0.0000	0.0000	3.963		0.6036	0.6191	7.425	-1.525
0.0503	0.0535	4.202	-0.192	0.7001	0.7136	8.239	-1.473
0.0950	0.1008	4.414	-0.361	0.8007	0.8109	9.272	-1.224
0.1606	0.1696	4.731	-0.598	0.8524	0.8604	9.877	-1.017
0.2073	0.2182	4.970	-0.751	0.8904	0.8966	10.381	-0.805
0.3067	0.3207	5.497	-1.050	0.9402	0.9438	11.091	-0.475
0.4038	0.4196	6.064	-1.279	1.0000	1.0000	12.019	

0.4991	0.5154	6.671	- 1.444				
1-heptanol (1) + HxA (2) ; T/K = 298.15							
0.0000	0.0000	3.903		0.6036	0.6188	7.224	- 1.382
0.0503	0.0534	4.133	- 0.176	0.7001	0.7133	7.981	- 1.344
0.0950	0.1006	4.339	- 0.329	0.8007	0.8107	8.951	- 1.114
0.1606	0.1694	4.644	- 0.547	0.8524	0.8603	9.521	- 0.921
0.2073	0.2180	4.882	- 0.678	0.8904	0.8965	9.983	- 0.734
0.3067	0.3205	5.392	- 0.947	0.9402	0.9437	10.642	- 0.434
0.4038	0.4193	5.934	- 1.156	1.0000	1.0000	11.504	
0.4991	0.5151	6.508	- 1.310				
1-heptanol (1) + HxA (2) ; T/K = 303.15							
0.0000	0.0000	3.848		0.6036	0.6185	7.035	- 1.245
0.0503	0.0534	4.070	- 0.161	0.7001	0.7131	7.746	- 1.212
0.0950	0.1005	4.271	- 0.297	0.8007	0.8105	8.651	- 1.005
0.1606	0.1692	4.567	- 0.493	0.8524	0.8601	9.177	- 0.834
0.2073	0.2178	4.796	- 0.613	0.8904	0.8964	9.607	- 0.665
0.3067	0.3202	5.291	- 0.852	0.9402	0.9436	10.222	- 0.388
0.4038	0.4190	5.811	- 1.040	1.0000	1.0000	11.014	
0.4991	0.5147	6.358	- 1.178				

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

Table 4

Volume fractions of 1-alkanol, ϕ_1 , refractive indices, n_D , and excess refractive indices, n_D^E , of 1-alkanol (1) + HxA (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) + HxA (2) ; $T/K = 293.15$							
0.0000	0.0000	1.41808		0.6997	0.4160	1.38836	679
0.0534	0.0170	1.41741	80	0.7995	0.5494	1.37505	540
0.0942	0.0308	1.41681	140	0.8475	0.6295	1.36685	440
0.1871	0.0657	1.41513	275	0.8978	0.7287	1.35657	309
0.2977	0.1147	1.41250	439	0.9496	0.8521	1.34385	162
0.4039	0.1716	1.40889	576	0.9834	0.9477	1.33399	54
0.4917	0.2283	1.40480	664	1.0000	1.0000	1.32862	
0.5977	0.3124	1.39790	715				
methanol (1) + HxA (2) ; $T/K = 298.15$							
0.0000	0.0000	1.41563		0.6997	0.4161	1.38615	689
0.0534	0.0170	1.41499	83	0.7995	0.5495	1.37296	557
0.0942	0.0308	1.41442	145	0.8475	0.6296	1.36479	457
0.1871	0.0658	1.41282	288	0.8978	0.7288	1.35460	332
0.2977	0.1148	1.41017	448	0.9496	0.8521	1.34182	173
0.4039	0.1717	1.40657	583	0.9834	0.9477	1.33194	59
0.4917	0.2283	1.40243	664	1.0000	1.0000	1.32654	
0.5977	0.3125	1.39550	710				
methanol (1) + HxA (2) ; $T/K = 303.15$							
0.0000	0.0000	1.41321		0.6997	0.4162	1.38372	678
0.0534	0.0170	1.41261	86	0.7995	0.5496	1.37067	556
0.0942	0.0308	1.41204	148	0.8475	0.6297	1.36257	461
0.1871	0.0658	1.41040	286	0.8978	0.7289	1.35240	335
0.2977	0.1148	1.40773	443	0.9496	0.8522	1.33968	179
0.4039	0.1717	1.40412	576	0.9834	0.9477	1.32980	62
0.4917	0.2284	1.40000	658	1.0000	1.0000	1.32439	
0.5977	0.3125	1.39316	709				
1-propanol (1) + HxA (2) ; $T/K = 293.15$							
0.0000	0.0000	1.41808		0.6040	0.4628	1.40784	491
0.0520	0.0301	1.41775	65	0.6965	0.5645	1.40408	450
0.1015	0.0600	1.41735	122	0.8013	0.6949	1.39877	350
0.1475	0.0890	1.41693	175	0.8505	0.7627	1.39588	285

0.2108	0.1311	1.41627	246	0.8953	0.8285	1.39295	211
0.2983	0.1936	1.41509	333	0.9486	0.9125	1.38914	109
0.3967	0.2708	1.41351	427	1.0000	1.0000	1.38514	
0.4998	0.3608	1.41113	485				
1-propanol (1) + HxA (2) ; $T/K = 298.15$							
0.0000	0.0000	1.41563		0.6040	0.4627	1.40551	487
0.0520	0.0300	1.41529	63	0.6965	0.5644	1.40199	466
0.1015	0.0600	1.41492	122	0.8013	0.6948	1.39675	368
0.1475	0.0890	1.41452	176	0.8505	0.7626	1.39373	288
0.2108	0.1310	1.41393	253	0.8953	0.8284	1.39085	216
0.2983	0.1935	1.41276	338	0.9486	0.9124	1.38704	111
0.3967	0.2707	1.41120	432	1.0000	1.0000	1.38306	
0.4998	0.3607	1.40876	480				
1-propanol (1) + HxA (2) ; $T/K = 303.15$							
0.0000	0.0000	1.41321		0.6040	0.4625	1.40323	482
0.0520	0.0300	1.41292	67	0.6965	0.5642	1.39964	450
0.1015	0.0599	1.41258	128	0.8013	0.6947	1.39454	361
0.1475	0.0889	1.41223	185	0.8505	0.7625	1.39168	295
0.2108	0.1310	1.41160	257	0.8953	0.8283	1.38884	224
0.2983	0.1934	1.41049	345	0.9486	0.9124	1.38505	118
0.3967	0.2706	1.40878	421	1.0000	1.0000	1.38102	
0.4998	0.3605	1.40642	473				
1-butanol (1) + HxA (2) ; $T/K = 293.15$							
0.0000	0.0000	1.41810		0.6004	0.5095	1.41298	442
0.0552	0.0388	1.41812	74	0.6977	0.6148	1.41065	407
0.0896	0.0637	1.41800	109	0.7982	0.7322	1.40746	309
0.1588	0.1155	1.41781	187	0.8451	0.7905	1.40577	250
0.1967	0.1448	1.41768	229	0.8996	0.8610	1.40359	165
0.3035	0.2315	1.41702	325	0.9461	0.9239	1.40166	91
0.4077	0.3225	1.41603	396	1.0000	1.0000	1.39931	
0.4984	0.4072	1.41487	439				
1-butanol (1) + HxA (2) ; $T/K = 298.15$							
0.0000	0.0000	1.41565		0.6004	0.5093	1.41079	444
0.0552	0.0388	1.41564	70	0.6977	0.6146	1.40845	403
0.0896	0.0637	1.41556	107	0.7982	0.7321	1.40534	308
0.1588	0.1154	1.41542	187	0.8451	0.7903	1.40368	249
0.1967	0.1447	1.41529	228	0.8996	0.8609	1.40158	169
0.3035	0.2314	1.41470	327	0.9461	0.9238	1.39965	92
0.4077	0.3223	1.41381	404	1.0000	1.0000	1.39733	
0.4984	0.4070	1.41267	445				
1-butanol (1) + HxA (2) ; $T/K = 303.15$							

0.0000	0.0000	1.41322		0.6004	0.5091	1.40852	440
0.0552	0.0388	1.41324	71	0.6977	0.6143	1.40621	398
0.0896	0.0636	1.41319	110	0.7982	0.7319	1.40316	304
0.1588	0.1153	1.41306	190	0.8451	0.7902	1.40155	248
0.1967	0.1446	1.41294	230	0.8996	0.8608	1.39949	169
0.3035	0.2312	1.41240	331	0.9461	0.9238	1.39765	99
0.4077	0.3221	1.41148	401	1.0000	1.0000	1.39529	
0.4984	0.4068	1.41040	445				

1-pentanol (1) + HxA (2) ; $T/K = 293.15$

0.0000	0.0000	1.41813		0.6005	0.5513	1.41756	399
0.0472	0.0389	1.41838	57	0.7122	0.6692	1.41609	350
0.1005	0.0837	1.41862	118	0.7963	0.7616	1.41463	280
0.1648	0.1389	1.41884	186	0.8457	0.8175	1.41364	228
0.2022	0.1716	1.41896	225	0.8982	0.8782	1.41246	160
0.3102	0.2688	1.41908	317	0.9362	0.9230	1.41153	104
0.3982	0.3510	1.41895	372	1.0000	1.0000	1.40985	
0.5002	0.4500	1.41846	405				

1-pentanol (1) + HxA (2) ; $T/K = 298.15$

0.0000	0.0000	1.41563		0.6005	0.5510	1.41543	404
0.0472	0.0389	1.41592	59	0.7122	0.6689	1.41403	355
0.1005	0.0836	1.41622	123	0.7963	0.7614	1.41259	282
0.1648	0.1388	1.41649	193	0.8457	0.8174	1.41164	230
0.2022	0.1715	1.41660	229	0.8982	0.8781	1.41048	161
0.3102	0.2686	1.41679	322	0.9362	0.9230	1.40957	105
0.3982	0.3508	1.41671	378	1.0000	1.0000	1.40793	
0.5002	0.4497	1.41623	406				

1-pentanol (1) + HxA (2) ; $T/K = 303.15$

0.0000	0.0000	1.41324		0.6005	0.5508	1.41329	409
0.0472	0.0388	1.41360	64	0.7122	0.6687	1.41193	359
0.1005	0.0835	1.41392	129	0.7963	0.7612	1.41054	288
0.1648	0.1386	1.41424	202	0.8457	0.8172	1.40958	234
0.2022	0.1713	1.41438	239	0.8982	0.8780	1.40844	164
0.3102	0.2683	1.41458	331	0.9362	0.9229	1.40754	107
0.3982	0.3505	1.41451	384	1.0000	1.0000	1.40590	
0.5002	0.4494	1.41407	412				

1-heptanol (1) + HxA (2) ; $T/K = 293.15$

0.0000	0.0000	1.41807		0.6020	0.6175	1.42550	361
0.0560	0.0596	1.41916	72	0.7029	0.7163	1.42563	313
0.1018	0.1079	1.41999	125	0.7979	0.8082	1.42545	238
0.1463	0.1546	1.42077	174	0.8534	0.8614	1.42521	181
0.2047	0.2155	1.42171	231	0.8986	0.9044	1.42496	130

0.3044	0.3184	1.42310	306	0.9472	0.9504	1.42464	70
0.4059	0.4217	1.42423	355	1.0000	1.0000	1.42425	
0.5044	0.5207	1.42503	374				
1-heptanol (1) + HxA (2) ; $T/K = 298.15$							
0.0000	0.0000	1.41563		0.6020	0.6172	1.42331	353
0.0560	0.0595	1.41674	71	0.7029	0.7161	1.42351	306
0.1018	0.1078	1.41761	125	0.7979	0.8080	1.42339	233
0.1463	0.1545	1.41840	173	0.8534	0.8612	1.42320	178
0.2047	0.2153	1.41937	229	0.8986	0.9043	1.42299	128
0.3044	0.3181	1.42080	303	0.9472	0.9503	1.42271	69
0.4059	0.4214	1.42197	350	1.0000	1.0000	1.42235	
0.5044	0.5204	1.42280	367				
1-heptanol (1) + HxA (2) ; $T/K = 303.15$							
0.0000	0.0000	1.41321		0.6020	0.6169	1.42116	347
0.0560	0.0594	1.41434	70	0.7029	0.7158	1.42142	301
0.1018	0.1077	1.41523	124	0.7979	0.8078	1.42136	228
0.1463	0.1543	1.41604	171	0.8534	0.8611	1.42120	174
0.2047	0.2151	1.41703	226	0.8986	0.9042	1.42103	125
0.3044	0.3178	1.41853	301	0.9472	0.9502	1.42079	68
0.4059	0.4211	1.41974	347	1.0000	1.0000	1.42047	
0.5044	0.5200	1.42062	363				

^aThe standard uncertainties are: $u(T) = 0.02$ K; $u(p) = 1$ 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, $\sigma(F^E)$ (equation (6)), for the representation of F^E at temperature T and pressure $p = 0.1$ MPa for 1-alkanol (1) + HxA (2) systems by equation (5).

Property F^E	System	T/K	A_0	A_1	A_2	A_3	A_3	$\sigma(F^E)$	
ε_r^E	methanol + HxA	293.15	1.12	9.1	8.4	2.2		0.016	
		298.15	0.92	8.4	8.5	3.1		0.017	
		303.15	0.82	8.0	8.6	3.4		0.013	
	1-propanol + HxA	293.15	-4.59	0.66	2.08	0.65		0.004	
		298.15	-4.45	0.44	1.92	0.8		0.005	
		303.15	-4.30	0.23	1.74	0.8		0.005	
	1-butanol + HxA	293.15	-6.00	-1.1	0.8			0.012	
		298.15	-5.70	-1.17	0.6			0.013	
		303.15	-5.41	-1.25	0.49			0.011	
	1-pentanol + HxA	293.15	-6.38	-2.08				0.006	
		298.15	-5.98	-2.02				0.008	
		303.15	-5.55	-1.98	-0.24			0.006	
	1-heptanol + HxA	293.15	-5.81	-2.6	-0.79			0.007	
		298.15	-5.26	-2.38	-0.77			0.007	
		303.15	-4.73	-2.15	-0.73			0.008	
	$10^5 n_D^E$	methanol + HxA	293.15	2694	1518	-255	-670		2
			298.15	2694	1454	-22	-427		4
			303.15	2663	1443	64	-385		0.8
		1-propanol + HxA	293.15	1922	614	-230			5
			298.15	1898	644				8
			303.15	1892	609				1
1-butanol + HxA		293.15	1755	551	-215	-406		3	
		298.15	1772	491	-264	-260		1.5	
		303.15	1761	363	-218			4	
1-pentanol + HxA		293.15	1615	283	-146			0.9	
		298.15	1631	268	-119			1.5	
		303.15	1653	243	-62			1.2	
1-heptanol + HxA		293.15	1495	50	-147			1.5	
		298.15	1468	33	-126			0.9	
		303.15	1451	20	-138			0.6	
$\left(\frac{\partial \varepsilon_r^E}{\partial T}\right)_p / K^{-1}$		methanol + HxA	298.15	-0.028	-0.105	-0.01	0.11	0.05	0.0007
		1-propanol + HxA	298.15	0.0284	-0.038	-0.032			0.0003
		1-butanol + HxA	298.15	0.060	-0.015	-0.034			0.0005
		1-pentanol + HxA	298.15	0.082	0.010	-0.017			0.0005
		1-heptanol + HxA	298.15	0.109	0.045				0.0007

Table 6

Intrinsic dipole moment, μ , and molar dielectric properties of pure liquids at $p = 0.1$ MPa: χ_m^* , molar dielectric susceptibility; $\eta_{m,p}^* = -(\partial\chi_m^*/\partial T)_p$.

Compound	μ / D	$\chi_m^*/\text{cm}^3 \cdot \text{mol}^{-1}$			$\eta_{m,p}^*/\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
		$T = 293.15 \text{ K}$	$T = 298.15 \text{ K}$	$T = 303.15 \text{ K}$	$T = 298.15 \text{ K}$
methanol	1.664 [75]	1318	1287	1256	6.2
1-propanol	1.629 [75]	1507	1462	1419	8.8
1-butanol	1.614 [75]	1574	1521	1472	10.2
1-pentanol	1.598 [75]	1591	1533	1478	11.3
1-heptanol	1.583 [75]	1557	1491	1427	13.0
1-decanol	1.566 [75]	1413 ^a	1342 ^a	1277 ^a	13.6 ^a
HxA	1.3 [76]	392	387	381	1.1
c-HxA	1.26 [77]	418 ^a	409 ^a	401 ^a	1.7 ^a
aniline	1.51 [40]	558 ^b	548 ^b	538 ^b	2.0 ^b

^a Calculated from data of ref. [19].

^b Calculated from data of ref. [78].

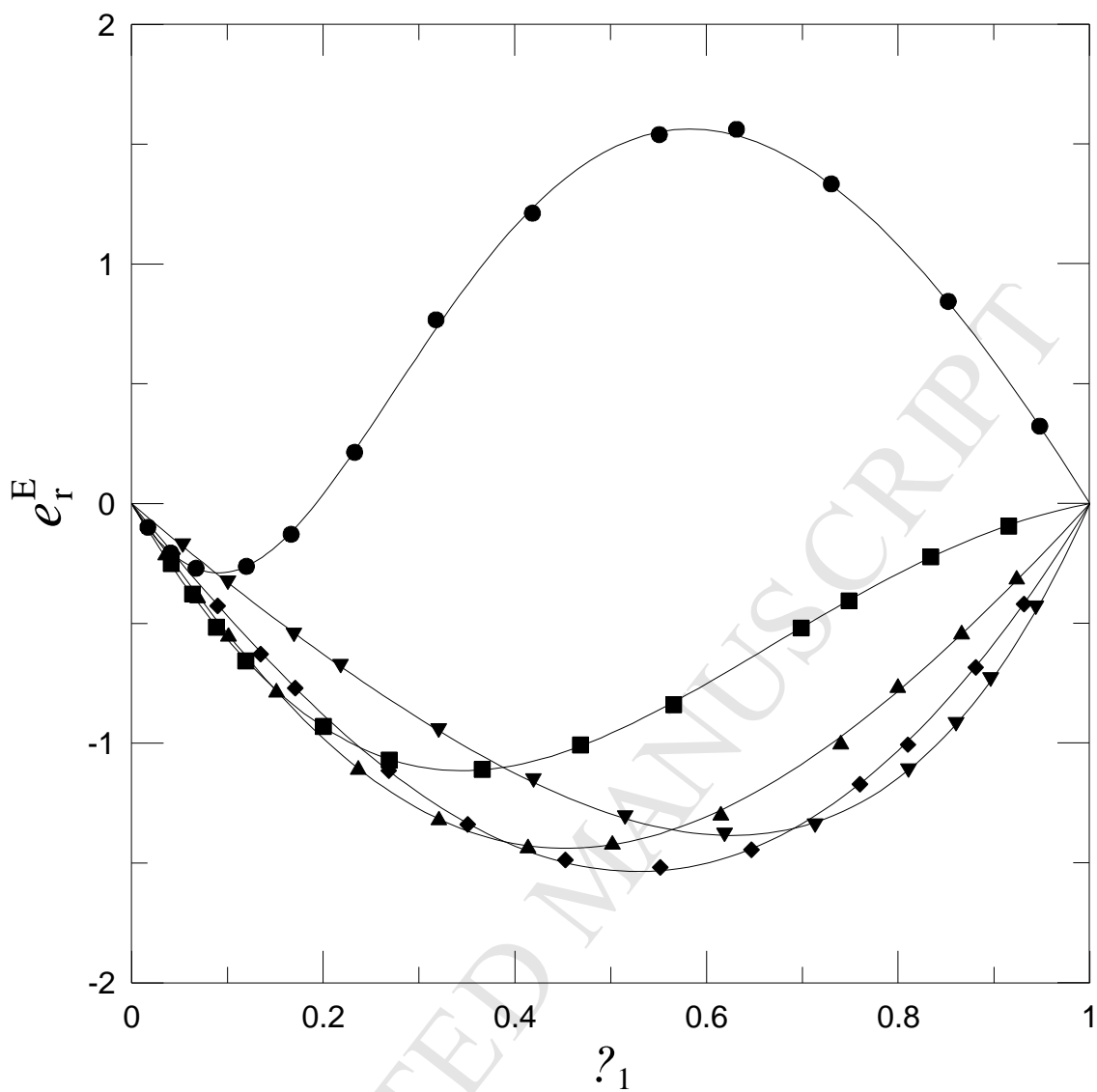


Figure 1

Excess relative permittivities, ϵ_r^E , of 1-alkanol (1) + HxA (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.

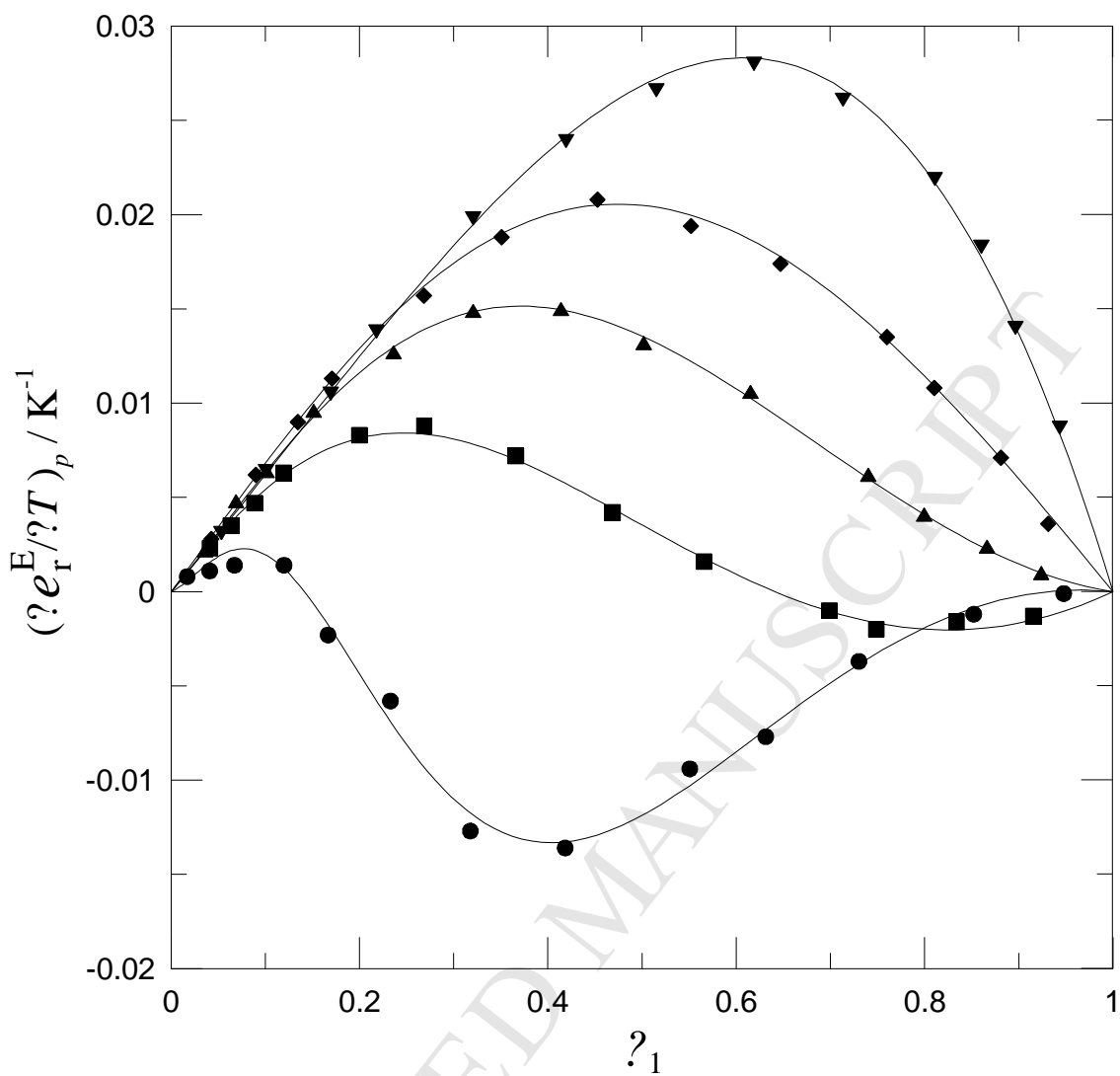


Figure 2

Derivative of the excess relative permittivity of 1-alkanol (1) + HxA (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.

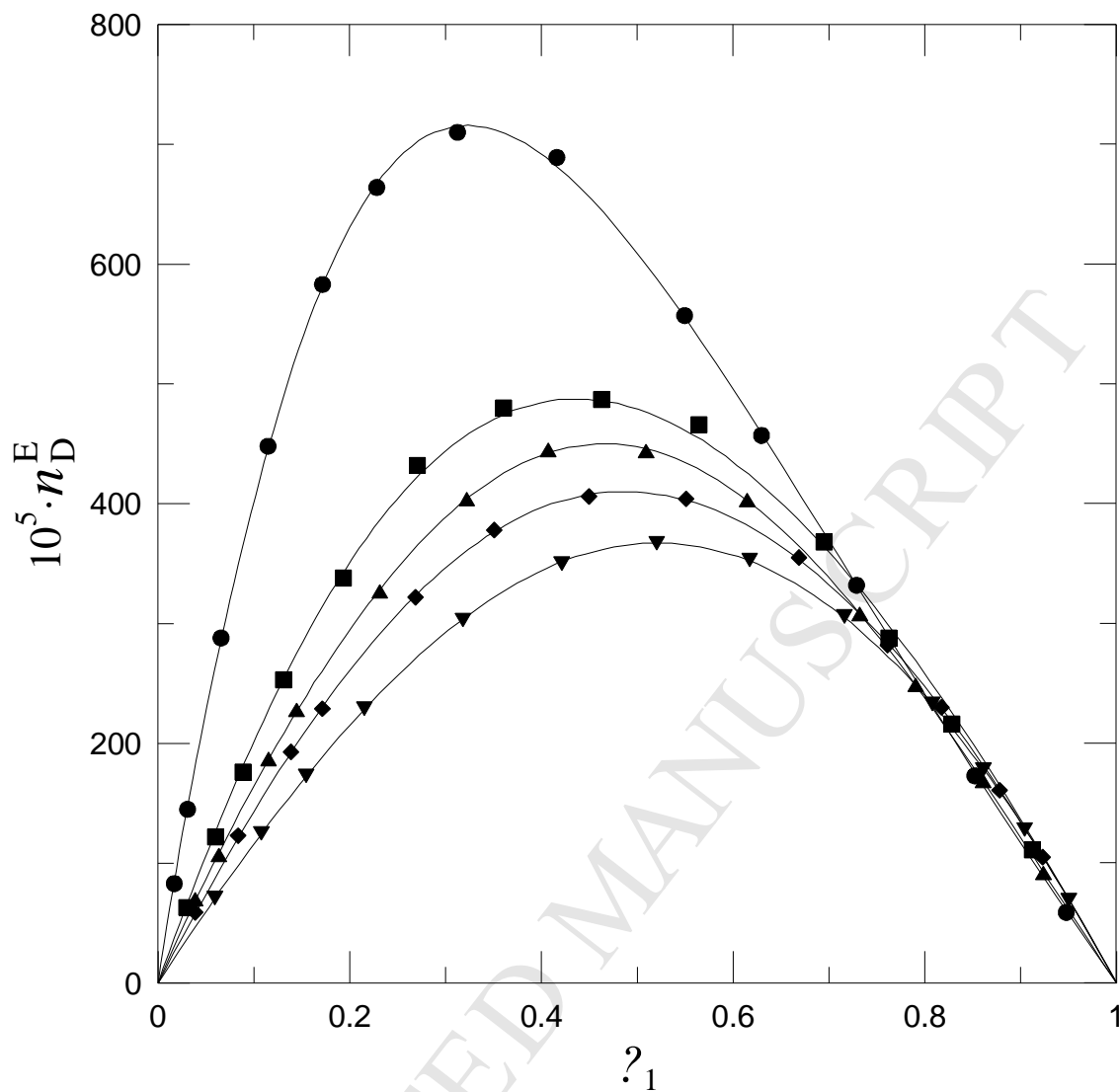


Figure 3

Excess refractive index, n_D^E , of 1-alkanol (1) + HxA (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.

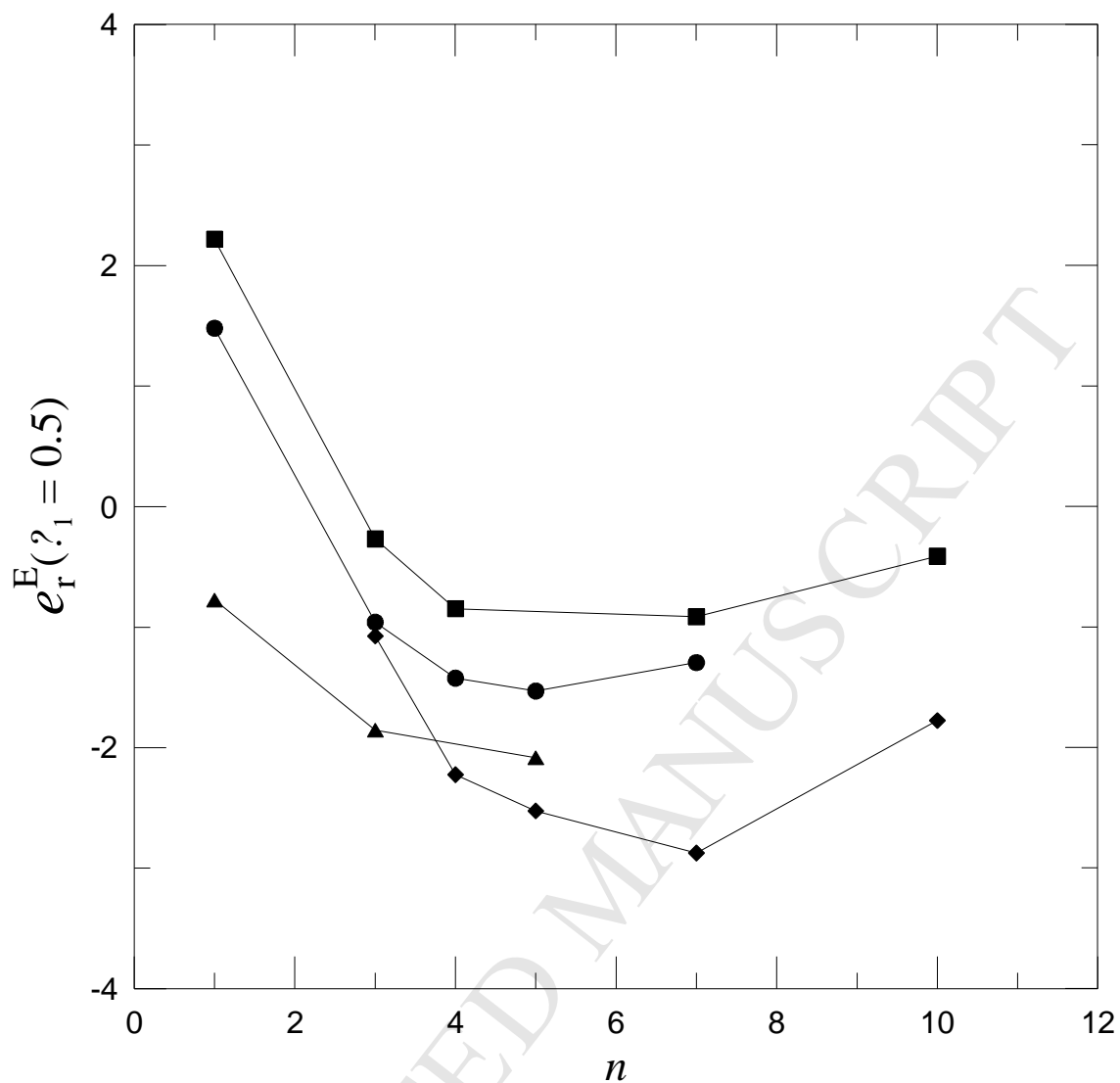


Figure 4

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: (●), HxA (this work); (■), c-HxA [13, 19]; (▲), aniline [42]; (◆), heptane [12, 38-40].

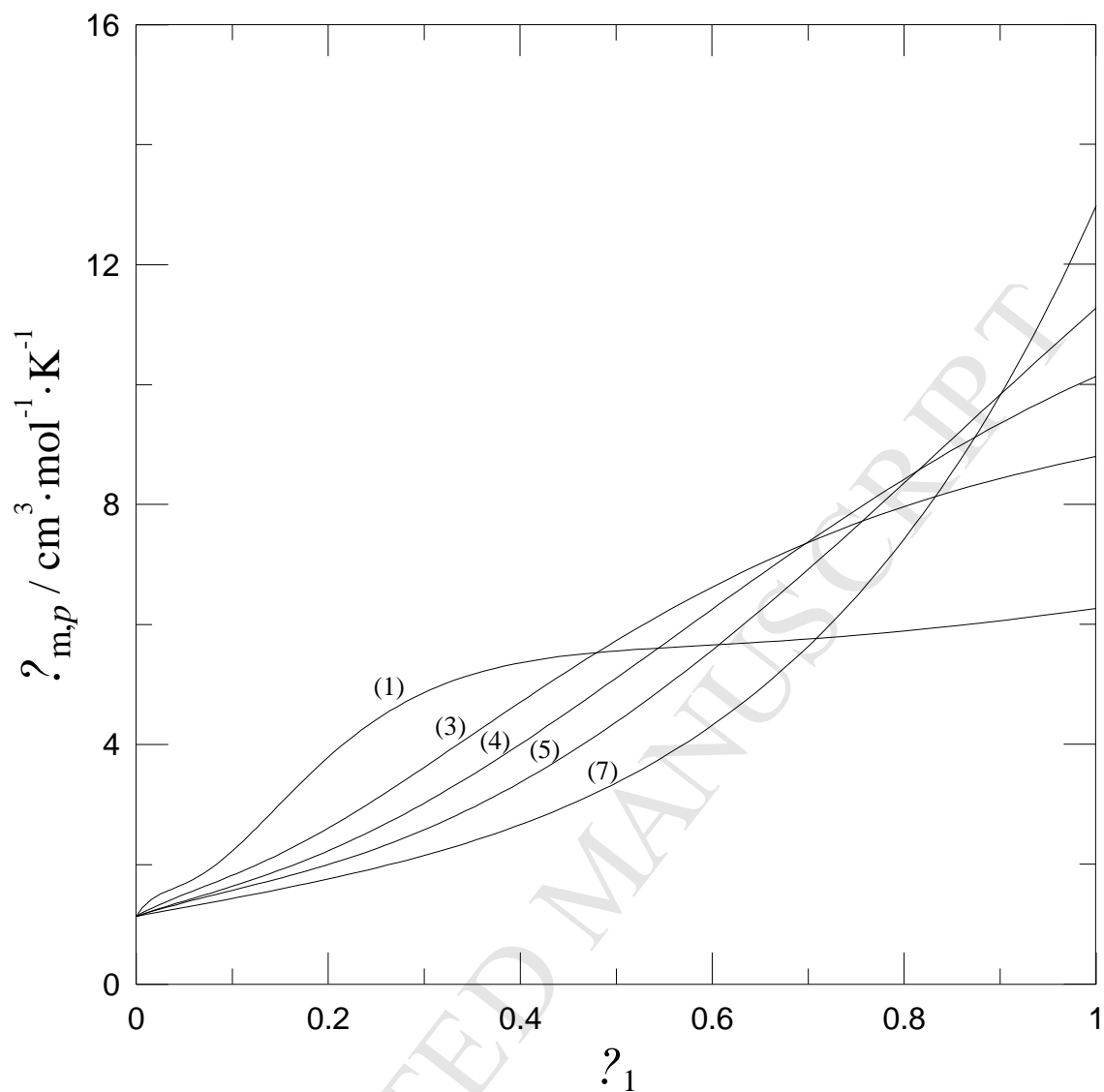


Figure 5

$\eta_{m,p} = -\left(\frac{\partial \chi_m}{\partial T}\right)_p$ of 1-alkanol (1) + HxA (2) systems at 0.1 MPa, 298.15 K and 1 MHz.

Numbers in parentheses indicate the number of atoms of the 1-alkanol.

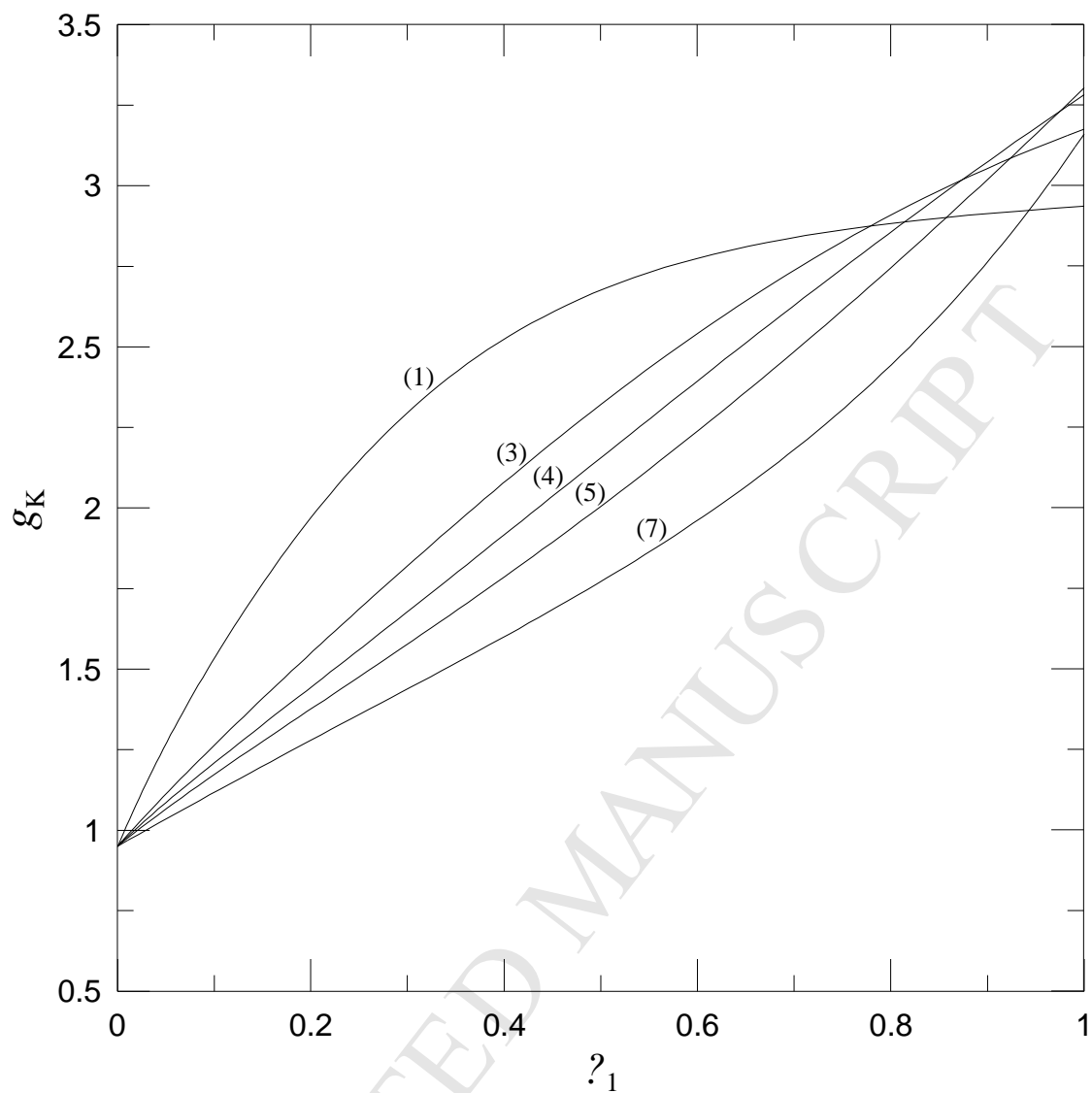


Figure 6

Kirkwood correlation factor, g_K , of 1-alkanol (1) + HxA (2) systems at 0.1 MPa, 298.15 K and 1 MHz. Numbers in parentheses indicate the number of atoms of the 1-alkanol.

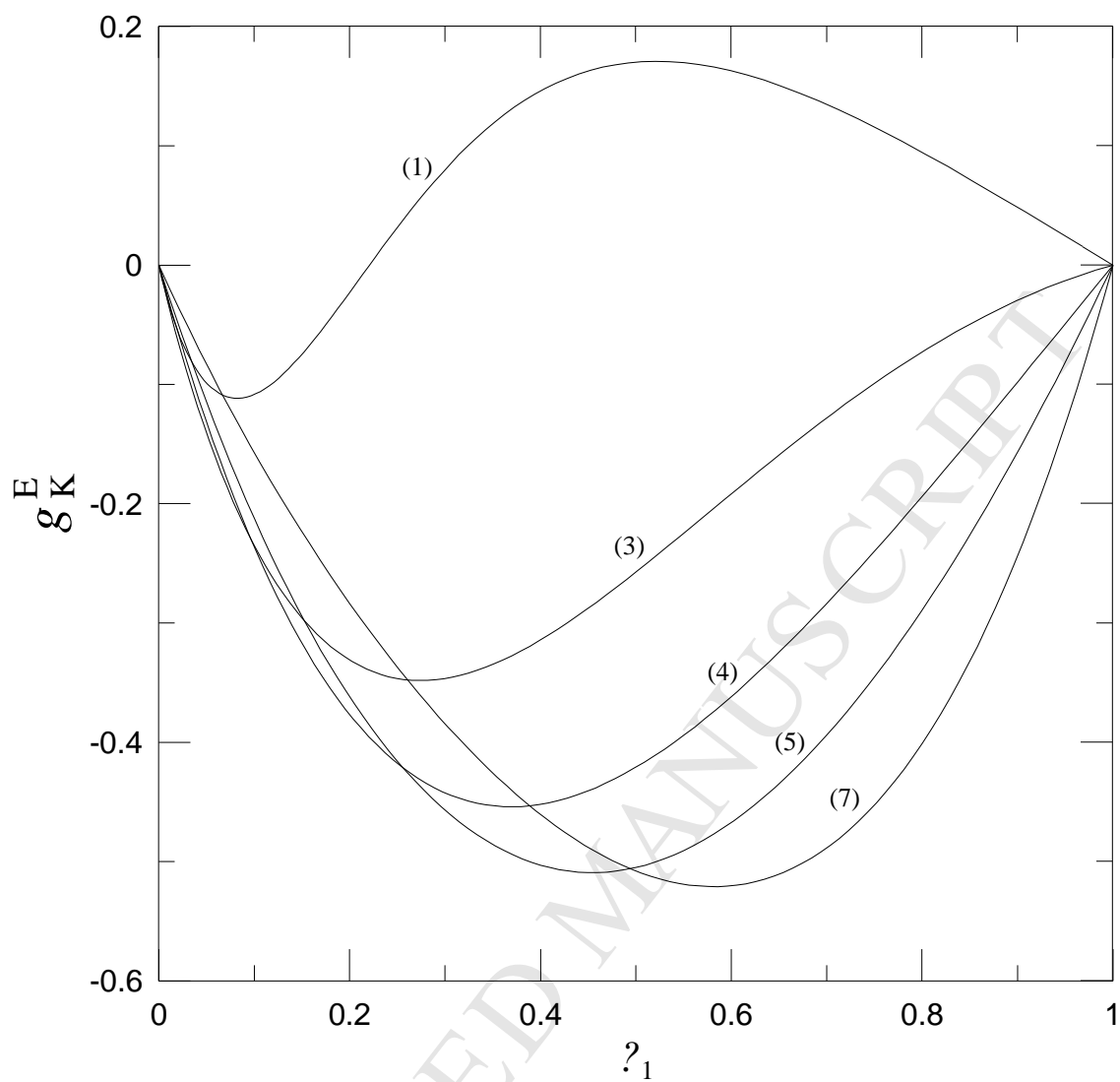


Figure 7

Excess Kirkwood correlation factor, g_K^E , of 1-alkanol (1) + HxA (2) systems at 0.1 MPa, 298.15 K and 1 MHz. Numbers in parentheses indicate the number of atoms of the 1-alkanol.

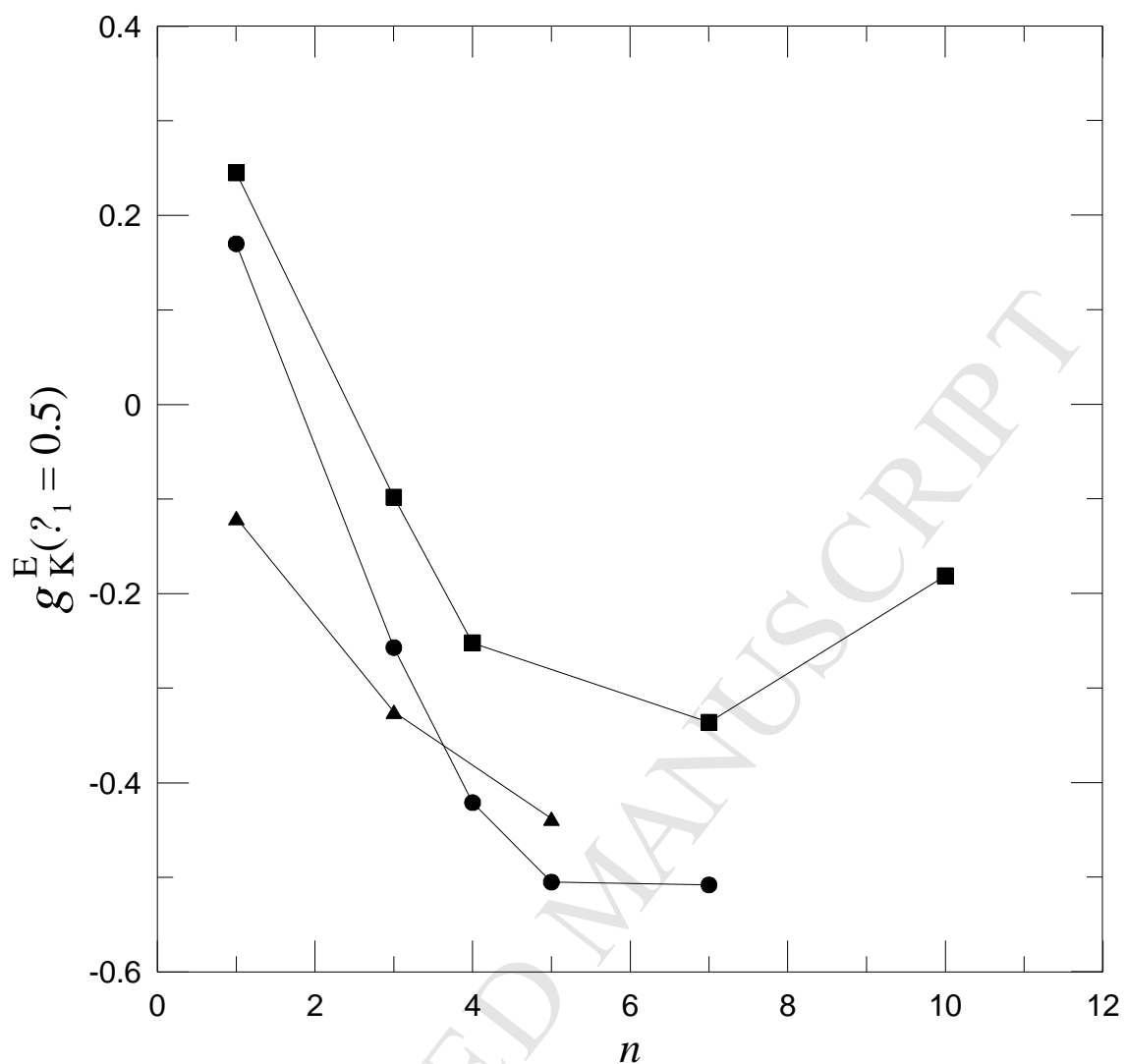


Figure 8

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: (●), HxA (this work); (■), c-HxA [13, 19]; (▲), aniline [42].

Highlights

- ε_r , n_D and their excess functions are reported at (293.15-303.15) K for 1-alkanol+HxA.
- 1-alkanol-HxA interactions contribute positively to ε_r^E , being dominant for methanol.
- $\varepsilon_r^E(\phi_1 = 0.5)$ changes in the order: methanol > 1-propanol > 1-butanol > 1-pentanol < 1-heptanol.
- For a given 1-alkanol, $\varepsilon_r^E(\phi_1 = 0.5)$ varies in the order: aniline < HxA < cyclohexylamine.
- The mixtures are studied using the Kirkwood-Fröhlich model.