DIELECTRIC AND REFRACTIVE INDEX MEASUREMENTS FOR THE SYSTEMS 1-PENTANOL + 2,5,8,11,14-PENTAOXAPENTADECANE, OR FOR 2,5,8,11,14-PENTAOXAPENTADECANE + OCTANE AT (293.15-303.15) K.

VÍCTOR ALONSO, JUAN ANTONIO GONZÁLEZ*, ISAÍAS GARCÍA DE LA FUENTE, JOSÉ CARLOS COBOS

G.E.T.E.F., Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Valladolid, 47071 Valladolid, Spain,
*e-mail: jagl@termo.uva.es; Fax: +34-983-423136; Tel: +34-983-423757

ABSTRACT

Relative permittivities, ε_r , and refractive indices, n_D , have been measured at (293.15-303.15) K, for the mixtures 1-pentanol + 2,5,8,11,14-pentaoxapentadecane (TEGDME) or TEGDME + octane. These data have been used, together with density measurements available in the literature, to calculate the correlation factors, g_K , according to the Kirkwood-Fröhlich equations. The curves of the deviations of ε_r from the ideal behaviour, $\Delta\varepsilon_r$, of the 1-pentanol + TEGDME system are shifted to high mole fractions of the alcohol, and show a rather large minimum. The shape of the $\Delta\varepsilon_r$ curves of methanol + TEGDME or + polyethylene glycol dimethyl ether 250 (PEG-250) mixtures is similar. This reveals that polyethers can break the alcohol self-association even at high alkanol concentrations. The higher $\Delta\varepsilon_r$ values of the methanol solutions are ascribed to large self-association of this alcohol. The $\Delta\varepsilon_r$ curves of the 1-pentanol + dibutyl ether (DBE) system are nearly symmetrical, and the $\Delta\varepsilon_r$ values are higher than those of the corresponding TEGDME mixture. This indicates that effects related to the alcohol self-association are much more relevant in the DBE system. These findings are supported by g_K and molar polarization data. Values of molar refraction of 1-pentanol systems reveal that dispersion forces become more important in the sequence: octane < DBE < TEGDME. Such forces are also more relevant in the 1-pentanol + TEGDME system than in the methanol + TEGDME solution. The comparison of ε_r and g_K data for TEGDME or DBE + octane mixtures shows than the polyether is a more structured liquid.

1. INTRODUCTION

1-Alkanol + ether mixtures are of high interest from both practical and theoretical points of view. For example, mixtures containing oxygenated compounds, such as ethers and/or alkanols are of great importance because they are increasingly used as additives to gasoline owing to their octane-enhancing and pollution-reducing properties [1,2]. Polyethers are important solvents in many chemical reactions such as Grignard reduction, or alkylation or organo-metallic reactions [3]. On the other hand, in a series of recent articles [4-7], we have shown some crucial features of 1-alkanol + ether systems. A short summary follows. (i) Effects related to self-association of 1-alkanols are determinant when considering the thermodynamic properties of mixtures with linear monoethers. (ii) Such effects are weakened if a linear monoether is replaced by a cyclic monoether, in such way that, from 1-hexanol, 1-alkanol + tetrahydrofuran, or + tetrahydropyran mixtures show a structure close to that of random mixing. (iii) The replacement of a linear monoether by a linear polyether also leads to a weakening of the mentioned effects relative to self-association of 1-alkanols, while dipolar interactions are increased. These results have been obtained from measurements on phase equilibria, molar excess enthalpies, molar excess heat capacities at constant pressure or from volumetric measurements and from the application of different theories such ERAS [8], DISQUAC [9], Flory [10], or the Kirkwood-Buff integrals formalism [11]. The investigation of the mixture structure can be also carried out on the basis of ε_r, and n_D, data. These magnitudes together with density data make possible the determination of the Kirkwood´s correlation factor, g_K, [12-15], which provides useful information on the mixture structure. As a part of a general systematic study in which liquid solutions are investigated using g_K, we report here ε_r and n_D measurements for the mixtures 1-pentanol + TEGDME, or TEGDME + octane at (293-15-303.15) K. Previously, we have investigated 1-pentanol + DBE, or + octane mixtures, or the DBE + octane system [16]. ε_r and n_D data at different temperatures for the methanol + TEGDME, or + PEG-250 systems [17-19], or for glyme + alkane mixtures [20-22] are available in the literature.

2. EXPERIMENTAL

2.1 Materials

1-Pentanol, octane and TEGDME were supplied by Fluka, and used without further purification. Their purity in mass fractions was $\geq$ 0.99; $\geq$ 0.99 and $\geq$ 0.98, respectively. Values of the physical properties of pure compounds, density, ρ, (measured with an Anton Paar DMA

602 vibrating-tube densimeter (uncertainty 5 g·cm^{-3}), thermostated within $\pm$ 0.01 K); ε_r, and n_D are listed in Table 1. They are in good agreement with the literature values (Table 1).

2.2 Apparatus and procedures

Binary mixtures were prepared by mass in small flasks of about 10 cm^3. All weighings were corrected for buoyancy effects. The error on the final mole fraction is estimated to be lower than $\pm$ 0.0001. Conversion to molar quantities was done using the relative atomic mass Table of 1995 issued by I.U.P.A.C [23]. All the ε_r and n_D measurements were carried out under static conditions and atmospheric pressure

Permittivity measurements were taken using the Agilent 16452A cell, connected to a precision impedance analyzer model 4294A through a 16048G test lead, both also from Agilent. Temperature is controlled within $\pm$ 0.02 K by means of a thermostatic bath LAUDA RE304 and measurements were taken at 1 MHz. Details on the apparatus configuration and on the calibration procedure can be found elsewhere [16]. The ε_r accuracy is of 3% or less. From the differences between our data and values available in the literature, the uncertainty of ε_r is estimated to be l% or less.

Refractive indices were measured with a refractometer model RMF970 from Bellingham-Stanley. The temperature is controlled by Peltier modulus and the temperature stability is $\pm$ 0.05 K. Prior to the measurement at each temperature, the apparatus must be calibrated with a known reference, usually distilled and deionised water or toluene. The uncertainty of the n_D measurements is 0.02% or better, as it is shown by the differences between our n_D results and those reported in the literature for recommended liquids [24].

3.   RESULTS

Table 2 lists, in the temperature range (293.15-303.15) K, values of ε_r and of deviations of this magnitude from the ideal state, $\Delta\varepsilon_r$, vs. x_1, the mole fraction of the first component for 1-pentanol + TEGDME or for TEGDME + octane systems. For an ideal mixture at the same temperature and pressure than the system under study, the ε_r^{id} values are calculated from the equation [22]:

$$\varepsilon_r^{id} = \phi_1 \varepsilon_{r1} + \phi_2 \varepsilon_{r2} \tag{1}$$

where $\phi_i = x_i V_i / V^{id}$. Deviations from the ideal behaviour are calculated from the expression:

$$\Delta\varepsilon_r = \varepsilon_r - \phi_1\varepsilon_{r1} - \phi_2\varepsilon_{r2} \qquad (2)$$

Table 3 contains, for the same mixtures, n_D values at (293.15-303.15) K, needed for g_K calculations. Results on $\Delta\varepsilon_r$ are shown graphically in Figures 1-2. No data have been found in the literature for comparison. The $\Delta\varepsilon_r$ data have been fitted by unweighted least-squares polynomial regression to the equation:

$$\Delta\varepsilon_r = x_1(1-x_1)\sum_{i=0}^{k-1} A_i(2x_1-1)^i \qquad (3)$$

The number of coefficients used (k) in equation (3) for each mixture was determined by applying an F-test [25] at the 99.5 % confidence level. Table 4 lists the parameters A_i obtained in the regression. The $n_D(x_1)$ measurements were fitted to the function:

$$n_D = \sum_{i=0}^{p} A_i x_1^i \qquad (4)$$

Values of the A_i coefficients are given in Table 4, which also lists the corresponding standard deviations, σ, defined by:

$$\sigma(F) = \left[\frac{1}{N-k}\sum\left(F_{cal} - F_{exp}\right)^2 \right]^{1/2} \qquad (5)$$

where N is the number of direct experimental values and $F = \Delta\varepsilon_r$ or n_D. For the methanol + TEGDME, or + PEG-250 mixtures at 303.15 K, $\Delta\varepsilon_r$ values have been obtained in this work using $\varepsilon_r(x_1)$ measurements reported elsewhere [17,18]. The coefficients of the corresponding Redlich-Kister expansions were also determined. Results are shown graphically in Figure 1.

4.   DISCUSSION

Inspection of the $\Delta\varepsilon_r$ curves allows state some interesting features. (i) The curves of the 1-pentanol + TEGDME system are skewed to high x_1 values, and show a rather large minimum (Figure 1). This indicates that the polyether is a very active breaker of the alcohol structure, in such way that the total number of parallel aligned effective dipoles of 1-pentanol, that contribute

to the dielectric polarization of the system, decreases upon mixing [26]. A similar behaviour is observed for methanol + TEGDME, or + PEG-250 mixtures (Figure 1). (ii) For 1-pentanol systems, larger $|\Delta\varepsilon_r|$ values are encountered for the mixture with TEGDME than for the DBE solution (Figure 1). That is, the linear monoether is a less active compound when breaking the self-association of the 1-alkanol. (iii) In addition, the $\Delta\varepsilon_r$ curve is much more symmetrical for the DBE mixture, which clearly reveals that effects related to the alcohol self-association are here more important than in the corresponding pentaether system, (iv) For mixtures including TEGDME, $\Delta\varepsilon_r$ (methanol) $>\Delta\varepsilon_r$ (1-pentanol), which can be ascribed to the higher self-association of methanol. For example, in terms of the ERAS model, the equilibrium constant of methanol is 986 while that of 1-pentanol is 153 [5,8]. (v) Interestingly, $\Delta\varepsilon_r$ results for methanol + TEGDME or + PEG-250 systems are rather similar (Figure 1), although it seems that PEG-250 breaks more easily the alcohol self-association. A systematic study on effect of the increasing the number of (CH$_2$CH$_2$O) groups on $\Delta\varepsilon_r$ measurements is currently undertaken. (vi) In the case of octane solutions, $\Delta\varepsilon_r$ (TEGDME) $<$ $\Delta\varepsilon_r$ (DBE) (Figure 2). This merely reveals that the polyether is a more structured liquid than DBE.

The temperature dependence of ε_r has been examined from the parameter:

$$\alpha = \frac{1}{\varepsilon_r}\frac{d\varepsilon_r}{d(1/T)} \qquad (6)$$

Figure 3 shows that α is positive at any composition, which is the normal behaviour of dipolar liquids. For 1-pentanol + organic solvent mixtures, at $x_1 > 0.4$, α changes in the sequence: TEGDME < DBE < octane. This suggests that the mixture structure of the TEGDME solution changes in less extent at increased temperature values due to the higher ability of this ether to break the self-association of the alcohol at room temperature. The disappearance of the minimum of the α curve for the octane systems at lower 1-pentanol concentrations can be explained in similar terms as such minimum has been ascribed to the existence of cyclic multimers of 1-pentanol at those concentrations [16]. On the other hand, at low x_1 values, α (methanol + TEGDME) $<$ α (1-pentanol + TEGDME). This indicates that association effects are more relevant for the methanol system. Finally, for octane solutions, α (TEGDME) $>\alpha$ (DBE), in agreement with the higher structure of TEGDME.

We have calculated the Kirkwood correlation factor, g_K, of 1-pentanol or methanol + TEGDME, or PEG-250 mixtures, and of the TEGDME + octane system. Our ε_r and

n_D measurements were used for the systems with 1-pentanol or octane. For methanol solutions, ε_r and n_D data were taken from [17-19]. Density data, needed for calculations are available in the literature [27-30]. Along calculations the molar weight of PEG-250 was taken as 283.33 g [31]. For a system containing one polar compound and one non-polar component, g_K can be determined by the Fröhlich equation [12,13,32,33]

$$g_\mathrm{K} = \frac{9k_\mathrm{B}T\varepsilon_0(2\varepsilon_r + \varepsilon_1^\infty)^2}{N_\mathrm{A}\mu_1^2 x_1(\varepsilon_1^\infty + 2)^2(2\varepsilon_r + 1)}[\frac{V_\mathrm{m}(\varepsilon_\mathrm{r} - 1)}{\varepsilon_\mathrm{r}} - \frac{3V_1 x_1(\varepsilon_1^\infty - 1)}{2\varepsilon_r + \varepsilon_1^\infty} - \frac{3V_2 x_2(n_{\mathrm{D}2}^2 - 1)}{2\varepsilon_r + n_{\mathrm{D}2}^2}] \qquad (7)$$

where the symbols have their usual meaning [16]. The high frequency relative permittivity of the polar compound 1, ε_1^∞, was calculated from the Clausius-Mossotti equation [15], adopting the atomic polarization (P_A), evaluated using the relation $P_\mathrm{A} + P_\mathrm{E} = 1.1P_\mathrm{E}$, where P_E, the electronic polarization, was calculated by the Lorenz-Lorentz equation using the refractive index for the sodium-D line [12,13,33]. For a binary mixture involving two polar compounds, g_K is given by [15,34,35]:

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

Here, $\varepsilon_\mathrm{r}^\infty$ is the high frequency relative permittivity of the system, calculated similarly to ε_1^∞ (see above) [36,37] and μ represents the gas phase dipole moment of the solution, estimated from the equation [34]:

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

where μ_i stands for the dipole moment in the gas phase of component i: 1.65 D for 1-pentanol [38]; 2,47 D for TEGDME [39], and 2.8 for PEG-250 [40] (1 D = 3.3564 10^{-30} C·m).

It is interesting to compare g_K curves of the 1-pentanol + octane, or + DBE, or + TEGDME systems. We note that, at low alcohol concentrations, g_K (octane) < g_K (DBE) < g_K (TEGDME) (Figure 4), and the typical minimum encountered in the g_K curves of 1-alcohol + alkane mixtures [12-14,33,41] vanishes when the non polar compound is replaced by an ether. This minimum has been ascribed to the existence of cyclic species, mainly tetramers [14], characterized, according to the rules of vector addition, by dipole moments equal to zero. Thus,

the observed behaviour confirms that oxaalkanes are more effective breakers of the alcohol structure than alkanes. At higher alcohol concentrations, g_K changes in opposite way to that stated above. If one takes into account that the dipole moment of a linear chain is larger than that of a monomer, such g_K variation indicates that effects related to alcohol self-association decrease in the order: octane > DBE > TEGDME. As conclusion, the polyether is a more active molecule when breaking the linear multimers of alcohol, the dominant species at high alcohol concentrations. The g_K curves for the TEGDME or DBE + octane mixtures are also compared in Figure 4. From these results, it is clear that TEGDME is a more structured liquid than DBE.

It is remarkable that at 303.15 K g_K curves of methanol or 1-pentanol +TEGDME or methanol + PEG-250 systems are rather similar (Figure 5). This suggests that the mixture structure is also similar for such solutions.

Interestingly, the molar excess enthalpies, H_m^E, of 1-pentanol systems at equimolar composition and 298.15 K, changes in the sequence: 614 (octane) [42] < 843 (DBE) [43] < 1956 (TEGDME) [44] (all values in J·mol^{-1}), which clearly remarks that effects due to the alcohol self-association are stronger in alkane solutions, while H_m^E of the 1-pentanol + TEGDME mixture is essentially determined by dipolar interactions between like molecules. This is supported by the concentration dependence of the H_m^E curves, which are progressively skewed, from lower mole fractions of 1-pentanol for the octane solution [42], to higher alcohol concentrations for the pentaether mixture [44].

Let's now examine the temperature dependence of g_K for 1-pentanol solutions. In the dilute alcohol region, g_k increases with the temperature, while the opposite trend is observed at high alkanol concentrations. Thus, for the octane system [16], $(\Delta g_K / \Delta T)_{298.15}(x_1 = 0.05) = 0.026$ K^{-1}; $(\Delta g_K / \Delta T)_{298.15}(x_1 = 0.90) = -0.015$ K^{-1}. The values for the corresponding TEGDME mixture are: $(\Delta g_K / \Delta T)_{298.15}(x_1 = 0.05) = 0.001$ K^{-1}; $(\Delta g_K / \Delta T)_{298.15}(x_1 = 0.90) = -0.008$ K^{-1}. The observed $(\Delta g_K / \Delta T)_{298.15}$ decrease at $x_1 = 0.05$ when octane is replaced by the pentaether merely expresses that a low number of cyclic species can be broken by the ether when temperature is increased. Similarly, the higher $(\Delta g_K / \Delta T)_{298.15}$ value at $x_1 = 0.90$ for this mixture means that a lower number of linear multimers can be broken by the polyether at increased temperatures. That is, oxaalkanes are better breakers of the alcohol structure than alkanes. On the other hand, at equimolar composition: $(\Delta g_K / \Delta T)_{298.15} = -0.013$ K^{-1} (octane) < -0.006 K^{-1} (DBE) < -0.0005 K^{-1} (TEGDME). This is consistent with the higher values of the excess heat capacities at constant pressure, $C_{p,m}^E$, of 1-alkanol + alkane mixtures compared with

those of 1-alkanol + ether solutions. Thus, equimolar composition and 298.15 K, $C_{p,m}^E$ /J·mol^{-1}·K^{-1} = 11.7, for ethanol + heptane [45], and is 7.2 for ethanol + methyl butyl ether [46]. For 1-alkanol + polyether mixtures $C_{p,m}^E$ values are lower, which is a characteristic behavior of mixtures where strong dipolar interactions are present [47]. In the case of the 1-propanol + 2,5,8-trioxanonane mixture, $C_{p,m}^E$ = 4.4 J·mol^{-1}·K^{-1} [46].

The molar polarization of the mixtures (or polarizability volume), P_m, was calculated according to the equation [34]:

$$P_m = \frac{(\varepsilon_r - n_D^2)(2\varepsilon_r + n_D^2)V_m}{9\varepsilon_r} \tag{10}$$

The very different shape of the P_m curves is remarkable (Figures 6,7). We note that P_m of 1-pentanol + octane, or + DBE mixtures increases regularly with the alcohol concentration (Figure 6), which indicates that the alignment of the alcohol dipoles becomes progressively predominant [16]. The P_m curve of the 1-pentanol + TEGDME system shows a minimum at $x_1 \approx 0.6$ (Figure 6). This reveals a decrease of the mixture polarization which can be explained in terms of an increase in the number of alcohol multimers broken by the polyether upon mixing. The larger P_m values of this solution or of the methanol + TEGDME or + PEG-250 systems are due to the higher molar polarizations of polyethers. TEGDME has a P_m value (320 cm^3·mol^{-1}) close to that of 1-pentanol (339 cm^3·mol^{-1}), and much higher than those of DBE (57.5 cm^3·mol^{-1}) or octane (0.7 cm^3·mol^{-1}). At 303.15 K, P_m of PEG-250 is 402.3 cm^3·mol^{-1}. Note the large differences between P_m values of the TEGDME or DBE + octane mixtures (Figure 7). Data on n_D have been used also to calculate molar refractions, R_m, (Figures 8,9) according to the equation [48,49]:

$$R_m = \frac{(n_D^2 - 1)V_m}{(n_D^2 + 2)} \tag{11}$$

This equation is obtained from the Lorentz-Lorenz equation by replacing the refractive index at infinite frequency by the refractive index at optical frequencies (usually, the sodium D line) [15,48,49]. Figure 8 plots R_m results for some 1-alkanol + organic solvent mixtures. R_m decreases with increased alkanol concentrations, and this indicates that the polarization of the

alkane or ethers is higher than that of the alkyl chain of 1-alkanols. For 1-pentanol systems, R_m increases as follows: octane < DBE < TEGDME. Due to R_m is regarded as a measure of dispersion forces within fluids, this means that such forces become more important in the same order as above, that is, when increasing the number of oxygen atoms in the solvent. Consequently, R_m (methanol + PEG-250) > R_m (methanol + TEGDME). The fact that, for TEGDME solutions, R_m (1-pentanol) > R_m (methanol) reveals that dispersion forces are more relevant in the 1-pentanol systems. Comparison of Figures 8 and 9 shows that R_m is higher for the ether + octane mixtures than for the systems including 1-alkanols at large alcohol concentrations, as in this case orientational polarization is much more important. On the other hand, R_m changes linearly with the concentration and does not depend on the temperature. This is the normal behaviour of systems where no complex formation exist [48,50].

5. CONCLUSIONS

The properties ε_r and n_D have been measured at (293.15-303.15) K for the systems 1-pentanol + TEGDME, or TEGMDE + octane. Values of $\Delta\varepsilon_r$ and g_K for 1-alkanol + TEGDME, or + PEG-250 show that polyethers can break the alcohol structure even at high alcohol concentrations, and that DBE is a less active compound when breaking the alcohol self-association. This is supported by P_m values and by the temperature dependence of ε_r. R_m values of 1-pentanol systems reveal that dispersion forces become more important in the order: octane < DBE < TEGDME. Dispersion forces are also more relevant in the 1-pentanol + TEGDME system than in the methanol + TEGDME solution. Comparison of ε_r and g_K data for TEGDME or DBE + octane mixtures shows than the polyether is a more structured liquid.

6. REFERENCES

1. R.W. Reynolds, J.S. Smith, T. Steinmetz, Abstracts of Papers of the American Chemical Society, (1974) 11.

2.   S.S. Dill, A. Tsolakis, J.M. Herreros, A.P.E. York. Diesel emissions improvements through the use of biodiesel or oxygenated components. Fuel, 95 (2012) 578-586.

3.   W.A. Henderson. Glyme-Lithium salt behaviour. J. Phys, Chem. B., 110 (2006) 13177-13183.

4.   J.A. González, I. Mozo, I. García de la Fuente, J.C. Cobos, V.A. Durov. Thermodynamics of 1-alkanol + cyclic ether mixtures. Fluid Phase Equilib., 245 (2006) 168-184.

5.   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) 1495-1598.

6.   J.A. González, N. Riesco, I. Mozo, I. García de la Fuente, J.C. Cobos. Application of the Flory theory and of the Kirkwood-Buff formalism to the study of orientational effects in 1-alkanol + linear o cyclic monoether mixtures. Ind. Eng. Chem. Res., 48 (2009) 7417-7429.

7.   J.A. González, I. García de la Fuente, J.C. Cobos. Application of the Kirkwood-Buff formalismo to $CH_3(CH_2)_{n-1}OH$ + polyether mixtures for $n = 1,2,3$. Thermochim. Acta, 525 (2011) 103-113.

8.   A. Heintz. A new theoretical approach for predicting excess properties of alkanol/alkane mixtures. Ber. Bunsenges. Phys. Chem. 89 (1985) 172-181

9.   H.V. Kehiaian. Thermodynamics of binary liquid organic mixtures Pure Appl. Chem., 57 (1985) 15-30.

10.   P.J. Flory. Statistical thermodynamics of liquid mixtures. J. Am. Chem. Soc., 87 (1965) 1833-1838.

11.   J.G. Kirkwood, F.P. Buff. The statistical mechanical theory of solutions. J. Chem. Phys., 19 (1954) 774-777.

12.   H.T. French, M. Koshla, K.N. Marsh. Dielectric constants and apparent dipole moments of (butan-1-ol or butan-2-ol + cyclohexane) at 298.15 and 318.15 K and of (2-methylpropan-2-ol + cyclohexane) at 299.15 and 318.15 K. J. Chem. Thermodyn., 20 (1988) 1175-1182.

13.   M. El-Hefnawy, K. Shameshima, 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.

14.   T. Vasiltsova, A. Heintz. Application of a new statistical mechanical model for calculating Kirkwood factors in alkanol + heptane mixtures. J. Phys. Chem. B., 112 (2008) 7544-7554.

15.   A. Chelkowski. Dielectric Physics, Elsevier, Warsaw (1980).

16. 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.

17. S.M. Pereira, M.A. Rivas, L. Mosteiro, J.L. Legido, T.P. Iglesias. Relative permittivity increments for the binary mixture (methanol + polyethylene glycol dimethyl ether 250) at several temperatures from 283.15 K to 323.15 K. J. Chem. Thermodyn., 34 (2002) 1751-1759.

18. S.M. Pereira, T.P. Iglesias, J.L. Legido, M.A. Rivas, J.N. Real. Relative permittivity increments for $\{x\mathrm{CH_3OH} + (1\text{-}x)\ \mathrm{CH_3OCH_2(CH_2OCH_2)_3CH_2OCH_3}\}$ from $T = 283.15$ K to 323.15 K. J. Chem. Thermodyn., 33 (2001) 433-440.

19. S.M. Pereira, T.P. Iglesias, J.L. Legido, L. Rodríguez, J. Vijande. Changes of refractive index on mixing for the binary mixtures $\{x\mathrm{CH_3OH} + (1\text{-}x)\ \mathrm{CH_3OCH_2(CH_2OCH_2)_3CH_2 OCH_3}\}$ and $\{x\mathrm{CH_3OH} + (1\text{-}x)\ \mathrm{CH_3OCH_2(CH_2OCH_2)_nCH_2OCH_3}\}$ ($n = 3\text{-}9$) at temperatures from 293.15 K to 333.15 K. J. Chem. Thermodyn., 30 (1998) 1279-1287.

20. C.F. Riadigos, R. Iglesias, M.A. Rivas, T.P. Iglesias. Permittivity and density of the systems (monoglyme, diglyme, triglyme or tetraglyme + n-heptane) at several temperatures. J. Chem. Thermodyn., 43 (2011) 275-283.

21. M.A. Rivas, T.P. Iglesias, S.M. Pereira, N. Banerji. On the permittivity of the systems {tetraglyme + (n-nonane or n-dodecane)} at various temperatures. J. Chem. Thermodyn., 38 (2006) 245-256.

22. J.C. 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.

23. IUPAC: Atomic weights of the elements 1995 (IUPAC technical report). Pure Appl. Chem., 68 (1996) 2339-2359.

24. K. N. Marsh. Recommended Reference Materials for the Realization of Physical Properties. Blackwell Scientific Publications, Oxford, 1987.

25. P.R. Bevington. Data Reduction and Error Analysis for the Physical Sciences, McGraw-Hill, New York, 1969.

26. R.J. Sengwa, V. Khatri. Study of static permittivity and hydrogen bonded structures in amide-alcohol mixed solvents. Thermochim. Acta, 506 (2010) 47-51.

27. M. E. Ferreyra de Ruiz Holgado, C.R. de Schaefer, E.L. Arancibia, Densities and viscosities of binary mixtures of polyethylene glycol 350 monomethyl ether with n-butanol and n-pentanol and tetraethylene glycol dimethyl ether with n-propanol, n-butanol, and n-pentanol from 278.15 K to 318.15 K. J. Chem. Eng. Data, 47 (2002) 144-148

28   X. Esteve, F. Olive, K.R. Patil, S.K. Chaudhari, A. Coronas. Densities and viscosities of the binary mixtures of interest for absorption refrigeration systems and heat pumps. Fluid Phase Equilib., 110 (1995) 369-382.

29.   S.M. Pereira, M.A. Rivas, J.L. Legido, T.P. Iglesias. Speeds of sound, densities, isentropic compressibilities of the system (methanol + polyethylene glycol dimethyl ether 250) at temperatures from 293.15 to 333.15 K. J. Chem. Thermodyn., 35 (2003) 383-391.

30.   T. Treszczanowicz, G.C. Benson, B. C.-Y. Lu, Excess volumes for binary mixtures formed by 2,5,8,11,14-tetraoxadodecane, or 2,5,8,11,14-pentaoxapentadecane with homologous n-alkanes. Thermochim. Acta, 168 (1990) 95-100.

31.   X. Esteve, D. Boer, K.R. Patil, S.K. Chaudhari, A. Coronas. Densities, viscosities and enthalpies of mixing of the binary system methanol + polyethylene glycol 250 dimethyl ether at 303.15 K. J. Chem. Eng. Data, 39 (1994) 767-769.

32.   T. Avraam, G. Moumouzias, G. Ritzolis. A study on excess volumes and dielectric properties in the γ-butyrolactone + p-xylene system at various temperatures. J. Chem. Eng. Data, 43 (1998) 51-54.

33.   M. El-Hefnawy, R. Tanaka. Density and relative permittivity for 1-alkanols + dodecane at 298.15 K. J. Chem. Eng. Data, 50 (2005) 1651-1656.

34.   C. Moreau, G. Douhéret. Thermodynamic and physical behaviour of water + acetonitrile mixtures. Dielectric properties. J. Chem. Thermodyn., 8 (1978) 403-410.

35.   J.C.R. Reis, T.P. Iglesias. Kirkwood correlation factors in liquid mixtures from extended Onsager-Kirkwood-Fröhlich equation. Phys. Chem. Chem. Phys., 13 (2011) 10670-10680.

36.   M.S. Bakshi, J. Singh, H. Kaur, S. T. Ahmad, G. Kaur. Thermodynamic behaviour of mixtures. 3. Mixtures of acetonitrile with dimethylacetamide, dimethyl sulfoxide, nitrobenzene, and methanol at 25 ºC. J. Chem. Eng. Data, 41 (1996) 1459-1461.

37.   M.S. Bakshi, G. Kaur. Thermodynamic behaviour of mixtures. 4. Mixtures of methanol with pyridine and N,N-dimethylformamide. J. Chem. Eng. Data, 42 (1997) 298-300

38.   J.A. Riddick, W.B. Bunger, T.K. Sakano. Organic Solvents, Techniques of Chemistry. Weissberger, A. Ed., Wiley: NewYork, Vol. II, (1986).

39.   A.L. McClellan, Tables of Experimental Dipole Moments, Vols., 1,2,3, Rahara Enterprises, El Cerrito, US, (1974).

40.   A. Kotera, K. Suzuki, K. Matsumura, T. Nakano, T. Oyama, U. Kambayashi. Dipole moments of polyethylene glycol ethers. Bull. Chem, Soc. Jpn., 35 (1962) 797-801.

41.   C. Campbell, G. Brink, L. Glasser. Dielectric studies of molecular association. Concentration dependence of dipole moment of 1-octanol in solution. J. Phys. Chem., 79 (1975) 660-665.

42. P.V. Verdes, M.M. Mato, E. Jíménez, J.L. Legido, M.I. Paz Andrade. Experimental and theoretically estimated excess molar enthalpies for *tert*-butyl methyl ether + 1-pentanol + octane at 298.15 K. J. Therm. Anal. Calorim., 89 (2007) 73-79.

43. I. Mozo, I. García de la Fuente, J.A. González, J.C. Cobos. Molar excess enthalpies at T = 298.15 K for (1-alkanol + dibutylether) systems. J. Chem. Thermodyn., 42 (2010) 17-22.

44. M.E.F. de Ruiz-Holgado, J. Fernández, M.I. Paz Andrade, E.L. Arancibia. Excess molar enthalpies of mixtures of methyl derivatives of polyethylene glycol with 1-alkanol at 298.15 K and 101.3 kPa. Can. J. Chem., 80 (2002) 462-466.

45. R. Tanaka, S. Toyama, S. Murakami. Heat capacitities of $\{x\, C_nH_{2n+1}OH + (1-x)\, C_7H_{16}\}$ for n = 1 to 6 at 298.15 K. J. Chem. Thermodyn., 18 (1986) 63-73.

46. M.A. Villamañán, C. Casanova, G. Roux-Desgranges, J.-P.E. Grolier. Thermochemical behaviour of mixtures of *n*-alcohol + aliphatic ether: heat capacities and volumes at 298.15 K. Thermochim. Acta, 52 (1982) 279-283.

47. J.A. González, J.C. Cobos, I. García de la Fuente. Thermodynamics of liquid mixtures containing a very strongly polar compound. Part 6. DISQUAC characterization of *N,N*-dialkylamides. Fluid Phase Equilib., 224 (2004) 169-183.

48. A. Piñeiro, P. Brocos, A. Amigo, M. Pintos, R. Bravo. Refractive indexes of binary mixtures of tetrahydrofuran with 1-alkanols at 25 ºC and temperature dependence of n and ρ for the pure liquids. J. Solution Chem., 31 (2002) 369-380.

49. 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.

50. M.E. Baur, D.A. Horsma, C.M. Knobler, P. Pérez. Dielectric constant and refractive index of weak complexes in solution. J. Phys. Chem., 73 (1969) 641-650.

51. C. Boned, A. Baylaucq, J.P. Bazile. Liquid density of 1-pentanol at pressures up to 140 Ma and from 293.15 to 403.15 K. Fluid Phase Equilib., 270 (2008) 69-74.

52. L. Segade, J. Jiménez de Llano, M. Domínguez-Pérez, O. Cabeza, M. Cabanas, E. Jiménez. Density, surface tension, and refractive index of octane + 1-alkanol mixtures at T = 298.15 K. J. Chem. Eng. Data, 48 (2003) 1251-1255.

53. D'Aprano, I.D. Donato. Dielectric polarization and polarizability of 1-pentanol + *n*-octane mixtures from static dielectric constant and refractive index data at 0, 25 and 45 ºC. J. Solution Chem., 19 (1990) 883-892.

54. N.V. Sastry, M.K. Valand. Densities, viscosities, and relative permittivities for pentane + 1-alcohols (C_1 to C_{12}) at 298.15 K. J. Chem. Eng. 43 (1998) 152-157.

55. R. Riggio, H.E. Martínez, H.N. Solimo. Densities, viscosities and refractive indexes for the methyl isobutyl ketone + pentanols systems. Measurements and correlations. J. Chem. Eng. Data, 31 (1986) 235-238.

56. I.L. Acevedo, L. Lugo, M.J.P. Comuñas, E.L. Arancibia, J. Fernández. Volumetric properties of binary tetraethylene glycol dimethyl ether + heptane mixtures between (278.15 and 353.15 K) and up to 25 MPa. J. Chem. Eng. Data, 48 (2003)1271-1278.

57. J.N. Real. T.P. Iglesias, S.M. Pereira, M.A. Rivas. Analysis of temperature dependence of some physical properties of (n-nonane + tetraethylene glycol dimethyl ether). J. Chem. Thermodyn., 34 (2002) 1029-1043.

58. H. Iloukhani, M. Rezaei-Sameti. Volumetric properties of methylcyclohexane with n-alkanes (C_5-C_{10}) at 293.15, 298.15 and 303.15 K. Comparison with Prigogine-Flory-Patterson theory. J. Mol. Liq., 126 (2006) 62-68.

59. A.S. Al-Jimaz, J.A. Al-Kandary, A.H.M. Abdul-Latif, A.M. Al-Zanki. Physical properties of {anisole + n-alkanes} at temperatures between (293.15 and 303.15 K). J. Chem. Thermodyn., 37 (2005) 631-642.

60. B. González, A. Domínguez, J. Tojo, Dynamic viscosities of 2-pentanol with alkanes (octane, decane, and dodecane) at three temperatures T = (293.15, 298.15 and 303.15 K). New UNIFAC-VISCO interaction parameters. J. Chem. Eng. Data, 49 (2004) 1225-1230.

TABLE 1

Properties of pure compounds at temperature T: density, ρ, relative permittivity, ε_r, and refractive index, n_D.

Compound	T/K	ρ		ε_r		n_D	
		Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
1-pentanol	293.15	0.81474	0.8147 [51]	15.739	15.736 [16]	1.4100	1.4100[16]
	298.15	0.81106	0.81083 [52]	15.158	15.04 [53]	1.4082	1.4080 [52]
			0.81107 [54]		15.558 [54]		1.40767 [53]
			0.8116 [27]				
	303.15	0.80739	0.8073 [51]	14.579	14.565 [16]	1.4061	1.40573 [55]
TEGDME	293.15	1.01106	1.0111 [56]	7.939	7.90 [18]	1.4326	1.43224 [19]
			1.0114 [57]				1.43268 [57]
	298.15	1.00707	1.00668 [20]	7.816	7.78 [20]	1.4306	1.43039 [57]
			1.0067 [56]				
	303.15	1.00249	1.0021 [56]	7.692	7.65[18]	1.4286	1.42802 [19]
Octane	293.15	0.70277	0.70262 [58]	1.968		1.3976	1.3965 [59]
	298.15	0.69873	0.69850 [52]	1.961	1.96 [53]	1.3952	1.3951 [52]
							1.3947 [59]
	303.15	0.69470	0.69449 [60]	1.954		1.3929	1.3926 [59]

TABLE 2

Relative permittivities, ε_r, and the corresponding deviations form the ideal state, $\Delta\varepsilon_r$, at temperature T for the systems 1-pentanol(1) + 2,5,8,11,14-pentaoxapentadecane(2) or 2,5,8,11,14-pentaoxapentadecane(1) + octane(2).

x_1	ε_r	$\Delta\varepsilon_r$	ε_r	$\Delta\varepsilon_r$	ε_r	$\Delta\varepsilon_r$
	1-pentanol(1) + 2,5,8,11,14-pentaoxapentadecane(2)					
	$T = 293.15$ K		$T = 298.15$ K		$T = 303.15$ K	
0.0505	7.990	-0.148	7.863	-0.140	7.737	-0.131
0.1002	7.970	-0.374	7.843	-0.355	7.715	-0.335
0.1509	8.043	-0.523	7.911	-0.496	7.779	-0.467
0.1919	8.041	-0.714	7.906	-0.679	7.771	-0.642
0.2458	8.132	-0.885	7.993	-0.838	7.854	-0.790
0.2910	8.150	-1.100	8.009	-1.041	7.866	-0.984
0.3384	8.271	-1.236	8.119	-1.174	7.968	-1.109
0.3986	8.344	-1.513	8.186	-1.436	8.029	-1.357
0.4554	8.523	-1.690	8.350	-1.607	8.180	-1.521
0.4930	8.615	-1.848	8.438	-1.755	8.260	-1.662
0.5496	8.857	-2.008	8.662	-1.909	8.469	-1.808
0.5931	9.027	-2.170	8.819	-2.065	8.615	-1.955
0.6455	9.353	-2.272	9.122	-2.165	8.896	-2.052
0.6979	9.710	-2.379	9.454	-2.269	9.203	-2.154
0.7424	10.138	-2.376	9.853	-2.270	9.577	-2.155
0.7959	10.730	-2.337	10.413	-2.230	10.103	-2.117
0.8372	11.351	-2.179	10.992	-2.087	10.643	-1.986
0.8679	11.894	-2.002	11.506	-1.918	11.123	-1.829
0.8987	12.519	-1.766	12.102	-1.688	11.691	-1.605
0.9225	13.119	-1.483	12.665	-1.423	12.217	-1.358
0.9488	13.878	-1.090	13.383	-1.050	12.896	-1.003
0.9793	14.929	-0.489	14.377	-0.479	13.834	-0.462
	2,5,8,11,14-pentaoxapentadecane(1) + octane(2)					
0.0330	2.107	-0.124	2.098	-0.121	2.088	-0.118
0.0659	2.254	-0.234	2.242	-0.228	2.230	-0.222
0.0998	2.413	-0.334	2.398	-0.325	2.382	-0.318
0.1330	2.577	-0.417	2.558	-0.407	2.538	-0.399
0.1645	2.736	-0.488	2.715	-0.476	2.693	-0.465

TABLE 2 (continued)

0.2003	2.922	− 0.557	2.896	− 0.545	2.870	− 0.533
0.2488	3.190	− 0.625	3.158	− 0.612	3.126	− 0.599
0.3002	3.476	− 0.684	3.438	− 0.670	3.400	− 0.657
0.3486	3.762	− 0.713	3.718	− 0.699	3.675	− 0.684
0.3951	4.030	− 0.739	3.981	− 0.724	3.931	− 0.710
0.4461	4.347	− 0.734	4.291	− 0.720	4.234	− 0.707
0.5092	4.738	− 0.716	4.674	− 0.703	4.610	− 0.690
0.5516	5.005	− 0.692	4.937	− 0.679	4.867	− 0.667
0.6003	5.313	− 0.656	5.238	− 0.644	5.163	− 0.632
0.6409	5.578	− 0.612	5.499	− 0.600	5.420	− 0.588
0.6930	5.909	− 0.557	5.823	− 0.546	5.736	− 0.537
0.7072	6.004	− 0.536	5.916	− 0.526	5.827	− 0.517
0.7515	6.298	− 0.468	6.205	− 0.459	6.111	− 0.451
0.8002	6.622	− 0.386	6.523	− 0.379	6.421	− 0.375
0.8461	6.943	− 0.288	6.838	− 0.283	6.732	− 0.278
0.8985	7.279	− 0.199	7.168	− 0.196	7.057	− 0.191
0.9441	7.585	− 0.104	7.469	− 0.101	7.351	− 0.099

TABLE 3

Refractive indices, n_D, at temperature T for the systems 1-pentanol(1) + 2,5,8,11,14-pentaoxapentadecane(2) or 2,5,8,11,14-pentaoxapentadecane(1) + octane(2).

x_1	n_D		
	1-pentanol(1) + 2,5,8,11,14-pentaoxapentadecane(2)		
	T = 293.15 K	T = 298.15 K	T = 303.15 K
0.0505	1.4319	1.4300	1.4279
0.1002	1.4315	1.4294	1.4273
0.1509	1.4305	1.4286	1.4265
0.1919	1.4301	1.4281	1.4259
0.2458	1.4291	1.4272	1.4251
0.2910	1.4285	1.4265	1.4244
0.3384	1.4276	1.4256	1.4236
0.3986	1.4265	1.4246	1.4225
0.4554	1.4256	1.4235	1.4215
0.4930	1.4248	1.4229	1.4207
0.5496	1.4236	1.4217	1.4196
0.5931	1.4227	1.4207	1.4186
0.6455	1.4214	1.4194	1.4174
0.6979	1.4200	1.4181	1.4160
0.7424	1.4188	1.4168	1.4148
0.7959	1.4172	1.4153	1.4133
0.8372	1.4159	1.4141	1.4121
0.8679	1.4149	1.4131	1.4111
0.8987	1.4139	1.4121	1.4100
0.9225	1.4130	1.4112	1.4092
0.9488	1.4120	1.4102	1.4081
0.9793	1.4109	1.4090	1.4070
	2,5,8,11,14-pentaoxapentadecane(1) + octane(2)		
0.0503	1.3993	1.3969	1.3946
0.1003	1.4011	1.3987	1.3965
0.1515	1.4031	1.4007	1.3985
0.2061	1.4052	1.4028	1.4006
0.2450	1.4067	1.4043	1.4021
0.3050	1.4091	1.4067	1.4045

TABLE 3 (continued)

0.3569	1.4111	1.4087	1.4065
0.4054	1.4127	1.4106	1.4084
0.4487	1.4144	1.4122	1.4100
0.5043	1.4163	1.4142	1.4121
0.5537	1.4182	1.4159	1.4138
0.5963	1.4195	1.4173	1.4151
0.6473	1.4213	1.4191	1.4170
0.6930	1.4228	1.4208	1.4186
0.7515	1.4248	1.4227	1.4207
0.8067	1.4268	1.4248	1.4230
0.8475	1.4281	1.4260	1.4239
0.8941	1.4295	1.4275	1.4256
0.9470	1.4310	1.4290	1.4271

TABLE 4

Coefficients A_i and standard deviations, σ (equation 5) for representation of the $\Delta\varepsilon_r$ and n_D properties at temperature T for 1-pentanol(1) + 2,5,8,11,14-pentaoxapentadecane(2) or 2,5,8,11,14-pentaoxapentadecane(1) + octane(2) systems by equation 3 ($\Delta\varepsilon_r$) or by equation 4 (n_D)

Property	T/K	A_1	A_2	A_3	A_4	A_5	σ
		1-pentanol(1) + 2,5,8,11,14-pentaoxapentadecane(2)					
$\Delta\varepsilon_r$	293.15	-7.45	-6.73	-4.82	-4.51	-2.58	0.019
n_D		1.4322	-0.0083	-0.0135			0.0001
$\Delta\varepsilon_r$	298.15	-7.08	-6.43	-4.63	-4.39	-2.59	0.018
n_D		1.4303	-0.0087	-0.013			0.0002
$\Delta\varepsilon_r$	303.15	-6.70	-6.11	-4.39	-4.26	-2.58	0.017
n_D		1.4281	-0.0083	-0.013			0.0002
		2,5,8,11,14-pentaoxapentadecane(1) + octane(2)					
$\Delta\varepsilon_r$	293.15	-2.90	0.78	-0.08	0.32		0.005
n_D		1.3971	0.0405	-0.005			0.0002
$\Delta\varepsilon_r$	293.15	-2.84	0.76	-0.06	0.29		0.004
n_D		1.3947	0.041	-0.005			0.0001
$\Delta\varepsilon_r$	303.15	-2.78	0.73	-0.05	0.29		0.004
n_D		1.3932	0.0365				0.0003

CAPTION TO FIGURES

FIG. 1 $\Delta \varepsilon_r$ at temperature T for some 1-alkanol(1) + ether(2) mixtures. Symbols, experimental values. Full symbols, 1-pentanol(1) + TEGDME(2) mixtures (this work): (▲), $T = 293.15$ K; (■), $T = 298.15$ K; (●), $T = 303.15$ K. Open symbols: (O), 1-pentanol(1) + DBE(2) ($T = 298.15$ K) [16]; (□), methanol(1) + TEGDME(2) ($T = 303.15$ K) [18]; (△), methanol(1) + PEG-250(2) ($T = 303.15$ K) [17]. Solid lines, smoothed values from Redlich-Kister expansions.

FIG. 2 $\Delta \varepsilon_r$ at temperature T for ether(1) + octane(2) mixtures. Symbols, experimental values. Full symbols, TEGDME mixtures (this work): (▲), $T = 293.15$ K; (■), $T = 298.15$ K; (●), $T = 303.15$ K. Open symbols, DBE system at 298.15 K [16]. Solid lines, smoothed values from Redlich-Kister expansions.

FIG. 3 α parameter (equation 6) at 298.15 K. Symbols: (●), 1-pentanol(1) + TEGDME(2); (■), TEGDME(1) + octane(2) (this work). Solid curves: (1) 1-pentanol(1) + octane(2); (2), 1-pentanol(1) + DBE(2); (3), DBE(1) + octane(2) [16]. Dashed line, methanol(1) + TEGDME(2) [18].

FIG. 4 Correlation factor, g_K, at 298.15 K for the systems: (■), 1-pentanol(1) + TEGDME(2) (this work); (□), 1-pentanol(1) + octane(2); (O), 1-pentanol(1) + DBE(2) [16]. Dashed lines: (1), TEGDME(1) + octane (this work); (2), DBE(1) + octane(2) [16]

FIG. 5 Correlation factor, g_K, at 303.15 K for 1-alkanol(1) + polyether(2) systems (this work): (●), 1-pentanol(1) + TEGDME(2); (■), methanol(1) + TEGDME(2); (▲), methanol(1) + PEG-250(2).

FIG. 6 Molar polarization (this work), P_m, at temperature T for the systems: 1-pentanol(1) + TEGDME(2) (●), + DBE(2) (□) or + octane(2) (O) at 298.15 K; and for methanol(1) + TEGDME(2) (■) or + PEG-250 (▼) at 303.15 K.

FIG. 7 Molar polarization, P_m, at 298.15 K for ether(1) + octane(2) systems: (●), TEGDME (this work); (O), DBE [16]

FIG. 8 Molar refraction (this work), R_m, at 298.15 K for the systems: 1-pentanol(1) + TEGDME(2) (●), + DBE(2) (■) or + octane(2) (▲) at 298.15 K; and for methanol(1) + TEGDME(2) (O) or + PEG-250 (□) at 303.15 K.

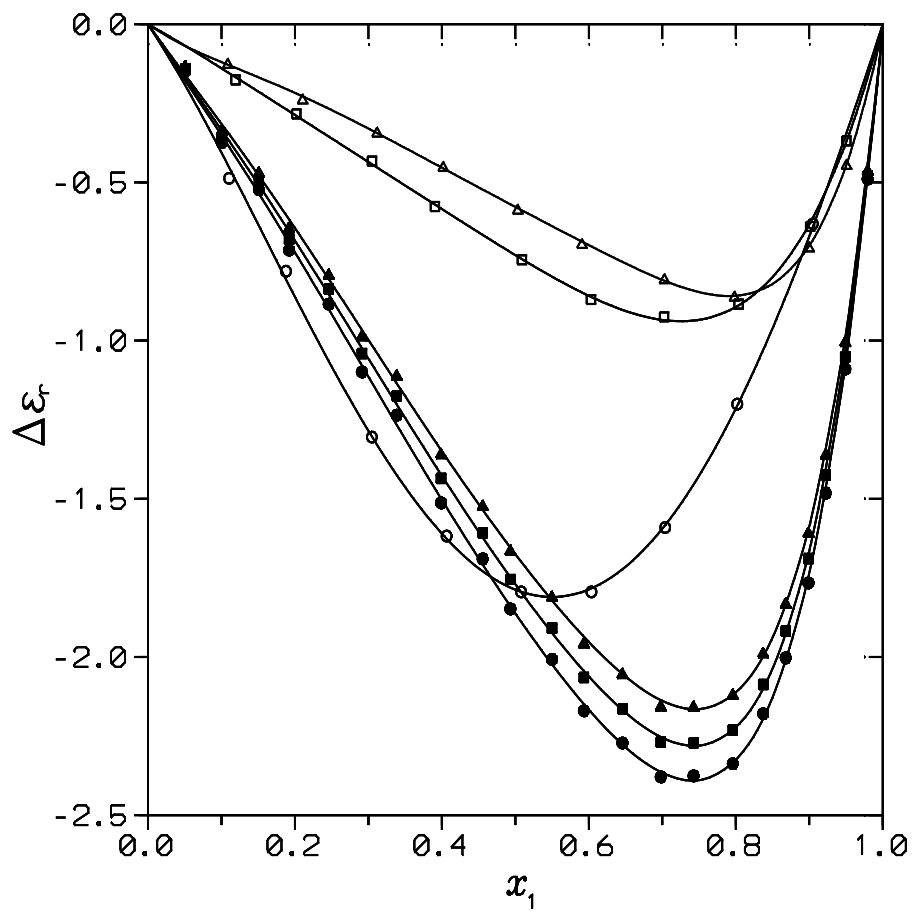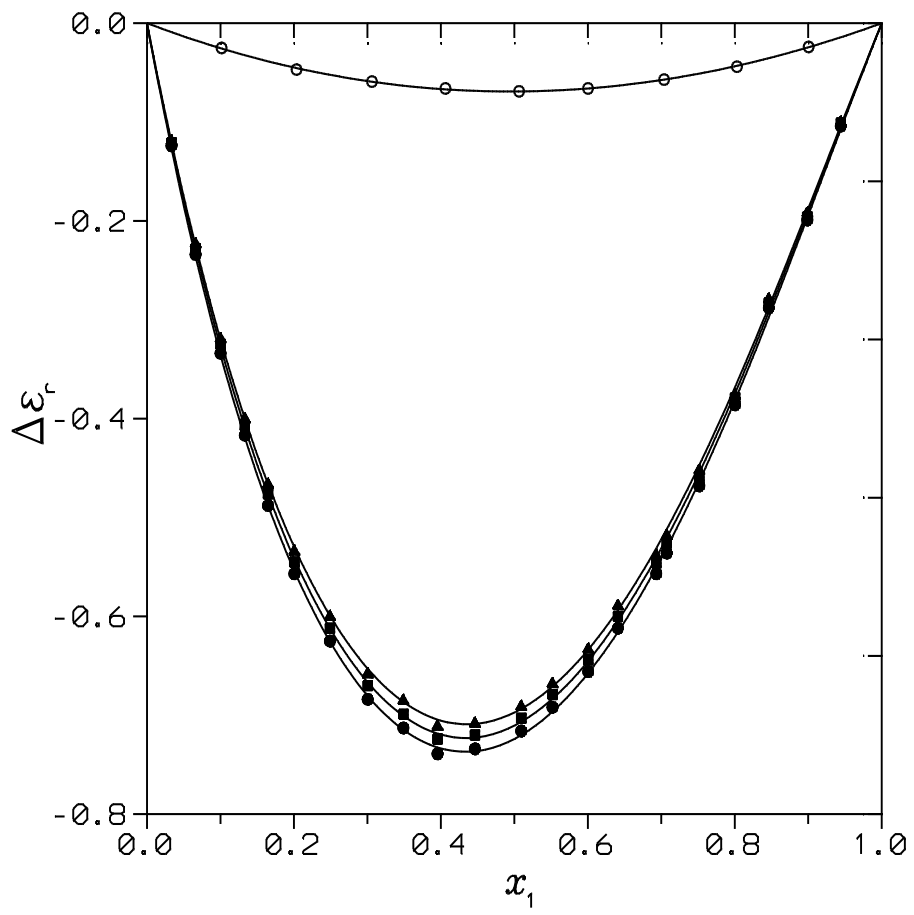**FIG. 9** Molar refraction, R_m, at 298.15 K for ether(1) + octane(2) systems: (●), TEGDME; (O) (this work), DBE [16]
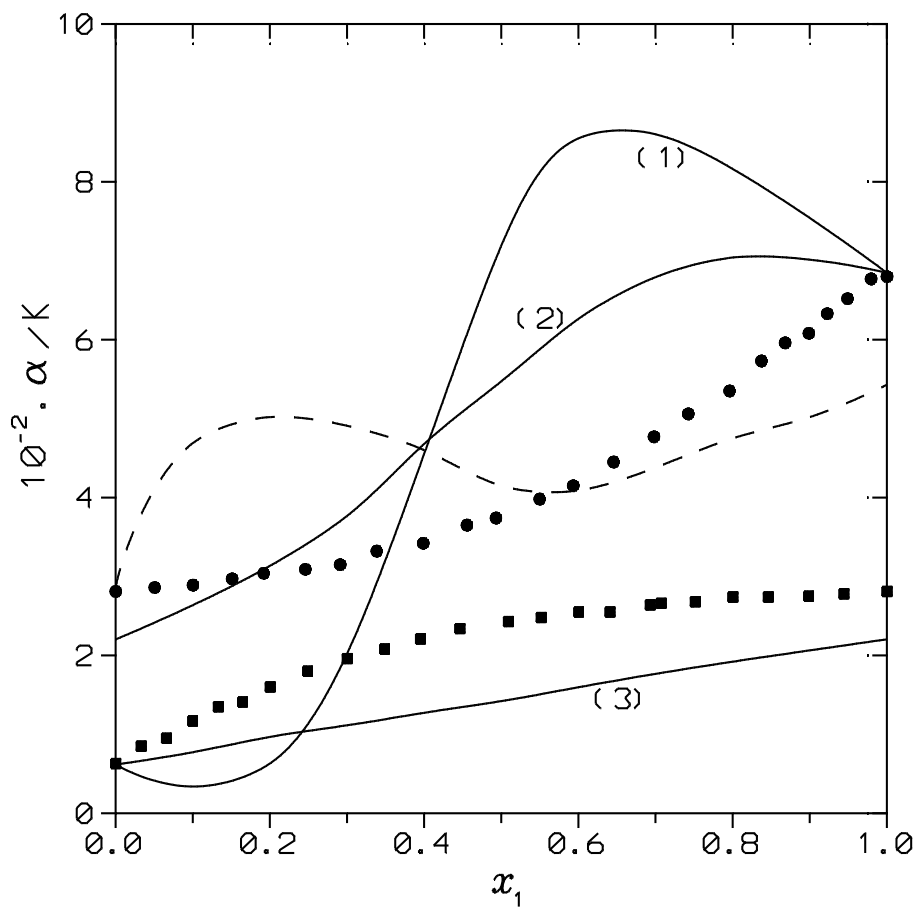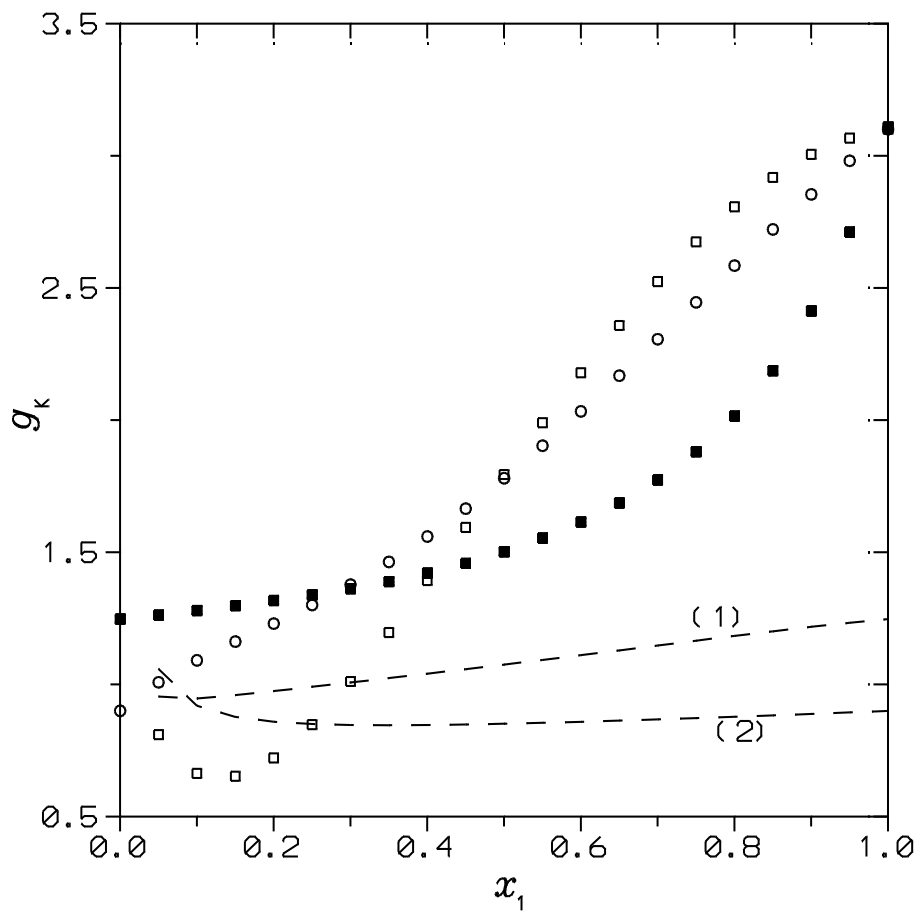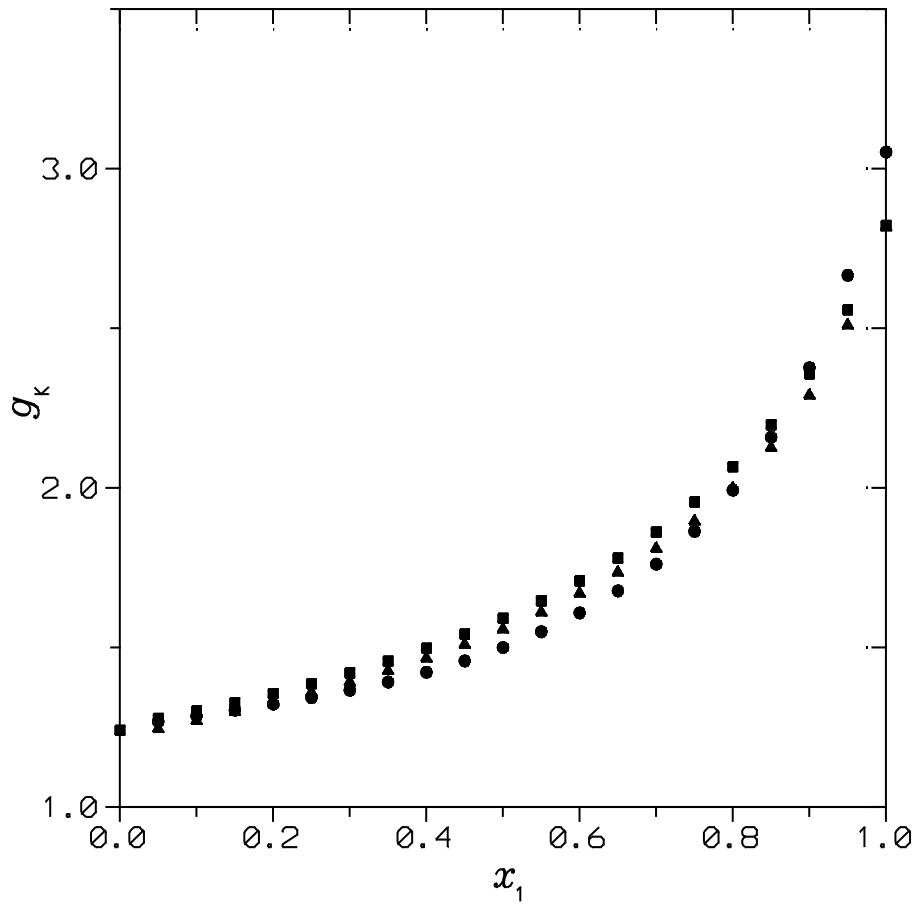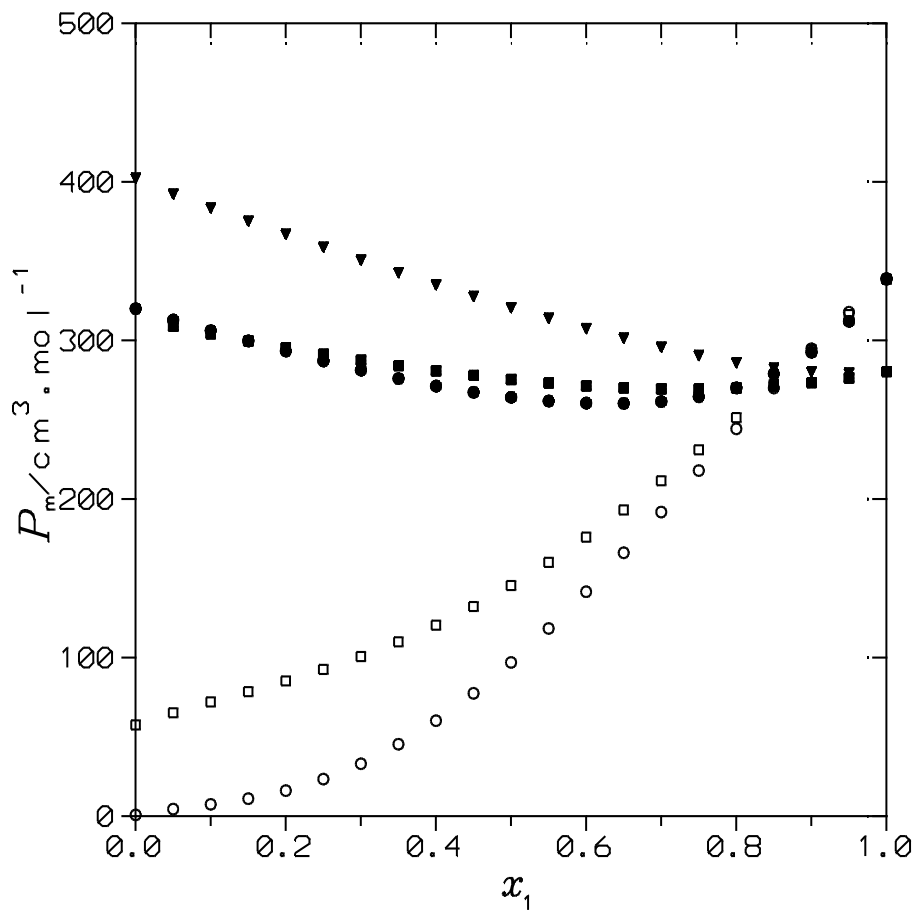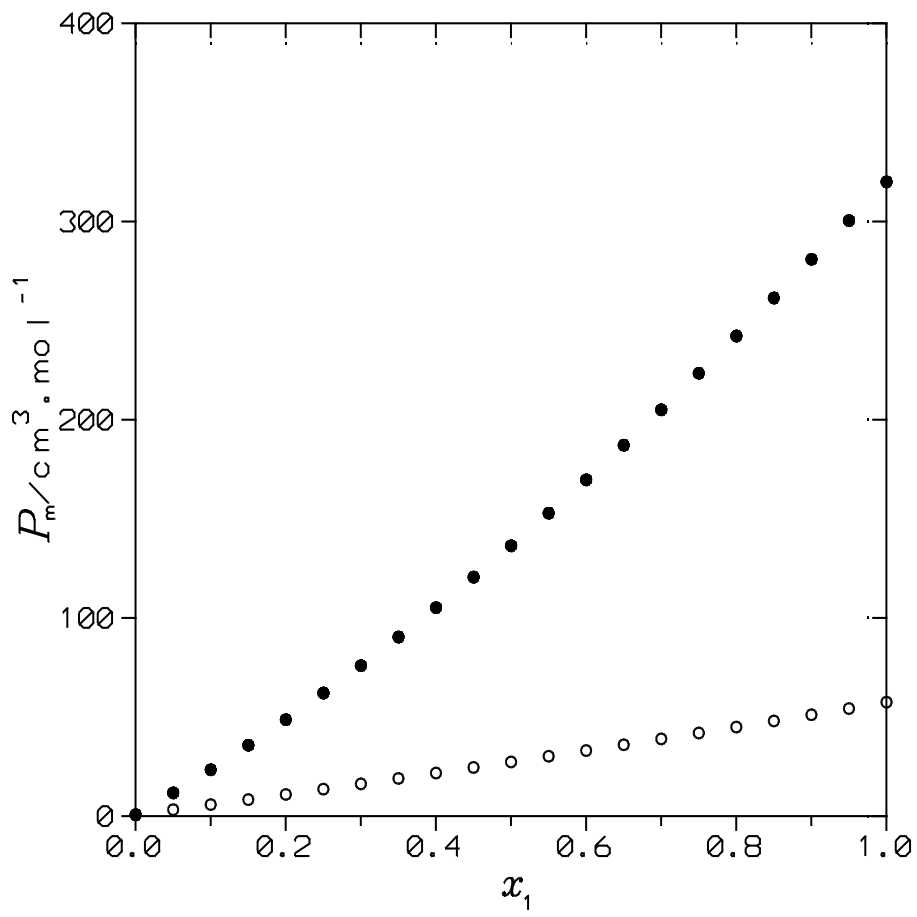
Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9