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ARTICLE

Separating the contributions of volume change on mixing, permittivity contrast and molecular interactions for the excess relative permittivity of liquid mixtures

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The excess relative permittivity of binary systems is separated into three parts. The excess molar volume is the basis for estimating the volume-change contribution. It is proposed to evaluate the part from electric permittivity of liquid mixtures that is solely due to the composition and pure-component relative permittivities, named permittivity-contrast contribution, with the classic local field approach in the case of point-dipoles contained in Lorentz's spherical cavities embedded in the corresponding ideal mixture. The effect of molecular interactions is simply estimated by the difference required to make up experimental excess relative permittivities. This analysis has been applied to 16 binary aqueous organic and organic–organic systems and the estimated values for the contribution of molecular interactions provide interesting insights into the molecular arrangement of these liquid mixtures and on the suitability of solvents for determining solute dipole moments.

1. Introduction

The permittivity of liquid mixtures, ε_r, is a measurable electric property which may provide important insights into molecular interactions in solution. A substantial theoretical and experimental effort is being made in order to obtain information from this thermophysical property. With this goal a bridge has been established with the well-founded thermodynamic formalism to the study of mixtures that is based on the interpretation of excess quantities, which are obtained by subtracting the corresponding ideal value from the experimentally determined property of interest. Here the ideal mixture in the sense of Raoult's law is adopted as reference system. This law takes the pure liquid constituents as standard states. All thermodynamic properties of an ideal mixture so designed can be expressed as a combination of pure component properties. This approach led to introducing the excess relative permittivity, ε_r^E, defined as[1,2]

$$\varepsilon_r^E = \varepsilon_r - \varepsilon_r^{id} \tag{1}$$

As previously demonstrated,[1] from a microscopic point of view and considering a sample in a parallel plate capacitor, the relative permittivity of a thermodynamically ideal binary mixture, ε_r^{id}, formed by substances A and B, is given by

$$\varepsilon_r^{id} = \phi_A \varepsilon_{r,A}^* + \phi_B \varepsilon_{r,B}^* = \varepsilon_{r,B}^* \left[1 + \phi_A \left(r_{A/B} - 1 \right) \right] \tag{2}$$

where ϕ_i (i = A, B) is the volume fraction of component i defined as

$$\phi_i = \frac{x_i V_i^*}{x_A V_A^* + x_B V_B^*} \tag{3}$$

and $r_{A/B} = \varepsilon_{r,A}^* / \varepsilon_{r,B}^*$ is the permittivity contrast of the mixture. Here an asterisk indicates a pure-substance property, x_i are mole fractions and V_i^* are molar volumes, all these quantities being referred to the same temperature T and pressure p. Eqn (2), which has been also demonstrated from a thermodynamic point of view,[2,3] shows that the relative permittivity of an ideal mixture in the sense of Raoult's law is a linear function of the volume fraction. In this respect ε_r^{id} behaves like other thermodynamic intensive properties such as the ideal isothermal compressibility.[4] Furthermore, eqn (2) can be easily generalised to multicomponent mixtures.

The above expression for ε_r^{id} is formally identical with Wiener's upper bound limit for the effective permittivity of a diphasic material when measured in a parallel plate capacitor, the components of the mixture being placed normal to the plates of the capacitor, that is when the capacitor is "filled with mixed fibres stretching from plate to plate".[5]

Although the dielectric behaviour of many binary mixtures has been studied on the basis of entire ε_r^E values, in this work we propose splitting up these values into three separate contributions, namely from the volume change on mixing, ε_r^E(volume), the

permittivity contrast, ε_r^E(contrast), and molecular interactions, ε_r^E(interactions). Hence

$$\varepsilon_r^E = \varepsilon_r^E(\text{volume}) + \varepsilon_r^E(\text{contrast}) + \varepsilon_r^E(\text{interactions}) \tag{4}$$

These contributions will be evaluated considering the binary mixture placed in a parallel plate capacitor, as follows.

Disregarding other effects, ε_r^E(volume) is assumed to be given the ideal permittivity of a ternary system, the third component being some empty volume or void space.

Values of ε_r^E(contrast) will be obtained from the local field theory. In terms of the classic electromagnetic theory to relate the local field to the applied electric field, which is on the basis of the Clausius–Mossotti or Lorentz–Lorenz equation, for a two-component mixture it is obtained[6]

$$\frac{\varepsilon_r - \varepsilon_r^0}{\varepsilon_r + 2\varepsilon_r^0} = \phi_A \frac{\varepsilon_{r,A}^* - \varepsilon_r^0}{\varepsilon_{r,A}^* + 2\varepsilon_r^0} + \phi_B \frac{\varepsilon_{r,B}^* - \varepsilon_r^0}{\varepsilon_{r,B}^* + 2\varepsilon_r^0} \tag{5}$$

Here ε_r stands for the effective relative permittivity of the mixture and ε_r^0 for the relative permittivity of a region outside the vicinity of molecules A and B, where the dielectric can be considered a continuum environment and where it is not necessary to take into account the individual effect of each molecule.

Interestingly, rearranging eqn (5) gives the basic Hashin–Shtrikman (HS) equation: [7]

$$\varepsilon_r(\text{HS}) = \varepsilon_{r,B}^* + \frac{\phi_A(\varepsilon_{r,A}^* - \varepsilon_{r,B}^*)(\varepsilon_{r,B}^* + 2\varepsilon_r^0)}{\varepsilon_{r,A}^* + 2\varepsilon_r^0 - \phi_A(\varepsilon_{r,A}^* - \varepsilon_{r,B}^*)} \tag{6}$$

In this equation ε_r^0 is as an unspecified relative permittivity and the components have been labelled so that $\varepsilon_{r,A}^* > \varepsilon_{r,B}^*$. Eqn (6) was derived using a variational approach for predicting the effective permittivity of a diphasic material that is macroscopically homogeneous and isotropic, disregarding volume effects and electric interactions among the different constituents.

It is known that, if $\varepsilon_r^0 = \varepsilon_{r,B}^*$, then eqn (5) yields the famous Maxwell Garnett (MG) expression[8,9]

$$\frac{\varepsilon_r(\text{MG}) - \varepsilon_{r,B}^*}{\varepsilon_r(\text{MG}) + 2\varepsilon_{r,B}^*} = \phi_A \frac{\varepsilon_{r,A}^* - \varepsilon_{r,B}^*}{\varepsilon_{r,A}^* + 2\varepsilon_{r,B}^*} \tag{7}$$

Eqn (7) gives HS lower bound values. In turn, HS upper bound values arise from setting $\varepsilon_r^0 = \varepsilon_{r,A}^*$ in eqn (5). Sihvola[9] has established this equivalence of HS bounds with the classic MG mixing equation.

If, differently, the "homogenized medium itself is considered as the background against which polarizations are measured",[9] that is, $\varepsilon_r^0 = \varepsilon_r$, then eqn (5) gives the Bruggeman symmetric (BS) equation[9,10]

$$0 = \phi_A \frac{\varepsilon_{r,A}^* - \varepsilon_r(\text{BS})}{\varepsilon_{r,A}^* + 2\varepsilon_r(\text{BS})} + \phi_B \frac{\varepsilon_{r,B}^* - \varepsilon_r(\text{BS})}{\varepsilon_{r,B}^* + 2\varepsilon_r(\text{BS})} \tag{8}$$

It is well known that the MG equation is non-symmetric, that is different values are obtained for ε_r(MG) upon exchanging component labelling. And that the BS equation is a non-explicit expression for ε_r(BS); indeed, it gives the macroscopic relative permittivity of a mixture as the solution of a quadratic equation on the composition.

However, for our purpose is it necessary to have a symmetric equation that predicts the relative permittivity of homogenous mixtures where there are neither change of volume on mixing nor molecular interactions among dissimilar components. In Section 2.2 we accomplish this goal by using eqn (5) with $\varepsilon_r^0 = \varepsilon_r^{id}$.

Finally, the remaining contribution, ε_r^E(interactions), will be obtained by difference in relation to the experimentally determined ε_r^E values.

We performed the partitioning of experimental ε_r^E values for sixteen binary systems at ambient temperatures and spanning all the composition range. The values of ε_r^E(interactions) so obtained give a substantially different view of molecular interactions in relation to conventional analyses based on entire ε_r^E values.

2. Separation of contributions

2.1 Effect of excess molar volume

Different volume fractions have been defined[11] to measure a component contribution to a given property of the mixture. Here we assume that, in the absence of additional effects, relative permittivities are weighed by volume fractions defined by[11,12]

$$\varphi_i = \frac{x_i V_i^*}{V_m} \tag{9}$$

where V_m is the molar volume of the real mixture.

However, for a non-ideal binary mixture $\varphi_A + \varphi_B \neq 1$; instead,

$$\varphi_A + \varphi_B + \frac{V_m^E}{V_m} = 1 \tag{10}$$

where the excess molar volume $V_m^E = V_m - V_m^{id}$ (and $V_m^{id} = x_A V_A^* + x_B V_B^*$ is a linear combination in mole fraction). It is the change in volume when x_A moles of A are mixed with x_B moles of B at constant T and p. Excess molar volumes arise from molecular interactions between constituents of a mixture and from different molecular packing after mixing. They can be regarded as changes in empty (or void) volume, without any commitment to molecular models for estimating the free volume of liquids. In these terms we interpret the quantity V_m^E/V_m as the empty-volume fraction corresponding to changes in free space to which we ascribe relative permittivity $\varepsilon_{r,V}^*$. Hence we can treat the binary system as if it were an ideal ternary system[1] of components A, B and empty volume. Thus we write

$$\varepsilon_r(\text{volume}) = \varphi_A \varepsilon_{r,A}^* + \varphi_B \varepsilon_{r,B}^* + \frac{V_m^E}{V_m}\varepsilon_{r,V}^* \tag{11}$$

Equating $\varepsilon_{r,V}^*$ to the vacuum relative permittivity leads to the following proposal for estimating the excess relative permittivity due to volume changes:

$$\varepsilon_r^E(\text{volume}) = \varepsilon_r(\text{volume}) - \varepsilon_r^{id} = (\varphi_A - \phi_A)\varepsilon_{r,A}^* + (\varphi_B - \phi_B)\varepsilon_{r,B}^* + \frac{V_m^E}{V_m} \tag{12}$$

or

$$\varepsilon_r^E (\text{volume}) = -\frac{V_m^E}{V_m}(\varepsilon_r^{id} - 1) \qquad (13)$$

In principle, provided eqn (13) is taken as a model for ε_r(volume), then a positive/negative V_m^E entails a negative/positive contribution to ε_r^E. This behaviour may be understood in terms of (volume) polarization. If $V_m^E > 0$, then there would be fewer molecular dipoles per unit volume in relation to the ideal mixture, so that the polarization and hence the permittivity would decrease. Conversely, a mixing with $V_m^E < 0$ would be accompanied by an increase in the permittivity. This is a general reasoning for any molecular mixture, independently of component molecular sizes. We note that, in eqn (11) for ε_r^E(volume), the term containing V_m^E will include the effect of molecular interactions that translate concurrently in volume and permittivity changes of the mixture. Therefore, in view of eqn (4) these common interactions will not be accounted for into ε_r^E(interactions).

2.2 Effect of permittivity contrast

The non-symmetric effective permittivity of composite, micro-heterogeneous materials is theoretically well understood.[9,13] Albeit macroscopically homogeneous and isotropic, in a diphasic system the dispersed phase (inclusions) is spatially localised. This is not the case of a homogenous liquid mixture because the thermal agitation does not allow to locate host and inclusion. Indeed, we are interested in estimating the effect of electric interactions arising from the mixing of two liquids of different permittivity without change in volume. To this end we remark that eqn (2) for ε_r^{id} was derived[1] considering point-molecules subjected to an applied electric field in the absence of interactions between dissimilar molecules. In order to evaluate the effect of permittivity contrast, we apply the local field theory for liquid mixtures in the case of molecules that are immersed in a medium having the ideal permittivity. For a point-dipole of A centred in a Lorentz's spherical cavity surrounded by a homogeneous space with permittivity ε_r^{id}, the local electric field, $\vec{E}_{loc,A}$, acting on the dipole is

$$\vec{E}_{loc,A} = \frac{2\varepsilon_r^{id} + \varepsilon_{r,A}^*}{3\varepsilon_r^{id}}\vec{E} = \frac{2(\phi_A r_{A/B} + \phi_B) + r_{A/B}}{3(\phi_A r_{A/B} + \phi_B)}\vec{E} \qquad (14)$$

in which $\vec{E}$ is the average macroscopic field, and analogously for component B. We note that $\vec{E}_{loc} \neq \vec{E}$ and depends only on the permittivity contrast and composition of the mixture. Following the local field theory and working out the expression for the effective relative permittivity due to what we have named the contrast effect, we obtain

$$\frac{\varepsilon_r(\text{contrast}) - \varepsilon_r^{id}}{\varepsilon_r(\text{contrast}) + 2\varepsilon_r^{id}} = \phi_A \frac{\varepsilon_{r,A}^* - \varepsilon_r^{id}}{\varepsilon_{r,A}^* + 2\varepsilon_r^{id}} + \phi_B \frac{\varepsilon_{r,B}^* - \varepsilon_r^{id}}{\varepsilon_{r,B}^* + 2\varepsilon_r^{id}} \qquad (15)$$

It is easy to see that eqn (15) is the same as eqn (5) with $\varepsilon_r^0 = \varepsilon_r^{id}$.

Recalling eqn (2) for ε_r^{id} and bearing in mind the definition of permittivity contrast, eqn (15) is readily transformed into

$$\varepsilon_r(\text{contrast}) = \varepsilon_{r,B}^* \frac{r_{A/B} + 2[1 + \phi_A(r_{A/B} - 1)]^2}{r_{A/B} + 2 + \phi_A(r_{A/B} - 1)} \qquad (16)$$

We have confirmed that the expression (16) is symmetric upon index change and therefore suited for estimating the permittivity of molecular liquid mixtures disregarding volume and molecular interactions. In other words, under these circumstances eqn (16) predicts the normalized permittivity of a binary mixture, that is $\varepsilon_r/\varepsilon_{r,B}^*$, on the knowledge of only two parameters, namely the permittivity contrast $r_{A/B}$ and the composition ϕ_A. Hence

$$\varepsilon_r^E(\text{contrast}) = \varepsilon_r(\text{contrast}) - \varepsilon_r^{id} = -\varepsilon_{r,B}^* \frac{\phi_A(1-\phi_A)(r_{A/B}-1)^2}{r_{A/B} + 2 + \phi_A(r_{A/B}-1)} \qquad (17)$$

Analysis of eqn (17) shows that ε_r^E(contrast) is negative at any intermediate composition. From its differentiation with respect to ϕ_A at fixed $r_{A/B}$ we obtain the volume fraction at which ε_r^E(contrast) is a minimum, $\phi_{A,min}$, according to

$$\frac{(\phi_{A,min})^2}{(1-2\phi_{A,min})} = \frac{(r_{A/B}+2)}{(r_{A/B}-1)} \qquad (18)$$

Consequently, with increasing permittivity contrast, $\phi_{A,min}$ decreases from 0.5 when $r_{A/B} = 1$ down to $\sqrt{2} - 1 = 0.414$ when $r_{A/B}$ is infinitely large.

Given the significance we confer to the permittivity-contrast effect, a final comment is in order. We stress that eqn (16) for ε_r(contrast) arises both from the local field formalism in terms of eqn (14) and from the Hashin–Shtrikman treatment leading to eqn (5) in which the unspecified parameter ε_r^0 is equated to ε_r^{id}. This notwithstanding, only the local field approach explicitly reveals the influence of the permittivity contrast on the effective permittivity of liquid mixtures in the absence of molecular interactions and volume effects. Also theoretically relevant is that the thermodynamic ideal mixture does not make provision for a local electric field different from the average macroscopic electric field, as explicitly assumed in a previous demonstration of this ideal law.[1]

3. Application to selected liquid mixtures

3.1 Polar–polar binary systems

3.1.1 Physical properties

From the literature we selected dielectric and density measurements at ambient temperatures for two sets of binary systems. The first set comprises eight organic–organic and two aqueous organic systems formed by 13 different polar molecular liquids, both protic and aprotic solvents, and spanning a wide range of permittivity contrast values, namely: (a) ethylene carbonate (or 1,3-dioxolan-2-one)(A)–dimethyl carbonate(B) at 313.15 K, $r_{A/B} = 28.22$;[14] (b) water(A)–2-butoxyethanol(B) at 298.15 K, $r_{A/B} = 8.31$;[15] (c) water(A)–2-methoxyethanol(B) at 298.15 K, $r_{A/B} = 4.58$;[15] (d) methanol(A)–tetraglyme (or tetraethylene glycol dimethyl ether or 2,5,8,11,14-pentaoxapentadecane or TEGDME)(B) at 293.15 K, $r_{A/B} = 4.27$;[12,16] (e) 2,2,2-trifluoroethanol(A)–tetraglyme(B) at 288.15 K, $r_{A/B} = 3.56$;[17] (f) 1,1,2,2-tetrachloroethane (A)–1,4-dioxane (B) at 303.15 K, $r_{A/B} = 3.39$;[18] (g) tetraglyme(A)–diethyl carbonate(B) at 298.15 K, $r_{A/B} = 2.74$;[19] (h) tetraglyme(A)–dimethyl carbonate(B) at 298.15 K, $r_{A/B} = 2.49$;[19] (i) butanone (or methyl ethyl ketone) (A)–1,1,2,2-tetrachloroethane (B) at 303.15 K, $r_{A/B} = 2.37$;[18] and (j) dimethyl

carbonate(A)–dodecane(B) at 308.15 K, $r_{A/B}$ = 1.56.[20] By convention, the label A is used for the constituent with largest relative permittivity. The properties of interest of these 13 liquid substances are given in Table 1.

3.1.2 Partitioning the excess relative permittivity

The experimental excess relative permittivity for these 10 binary systems was decomposed according to eqn (4) and the resulting contributions to ε_r^E are graphically shown in Fig. 1.

Globally, the volume-change contribution ε_r^E(volume) estimated with eqn (13) is small and generally unimportant. In turn, the necessarily negative values of ε_r^E(contrast) are often determinative of the observed ε_r^E values, even for mixtures with small permittivity contrast.

Table 1 Relative permittivity, $\varepsilon_{r,i}^*$, and molar volume, V_i^*, of pure liquid components at experimental temperatures

Component	Molecular Formula	T/K	$\varepsilon_{r,i}^*$	V_i^* /cm^3 mol^{-1}
Water	H_2O	298.15	78.35[a]	18.07[a]
Dodecane	$C_{12}H_{26}$	308.15	2.01[b]	230.83[b]
1,1,2,2-Tetra-chloroethane	$C_2H_2Cl_4$	303.15	7.460[c]	106.33[c]
Methanol	CH_4O	293.15	33.71[d]	40.48[e]
2,2,2-Trifluor-ethanol	$C_2H_3OF_3$	288.15	28.64[f]	71.48[f]
2-Methoxy-ethanol	$C_3H_8O_2$	298.15	17.10[a]	79.26[a]
2-Butoxy-ethanol	$C_6H_{14}O_2$	298.15	9.43[a]	31.82[a]
Ethylene carbonate	$C_3H_4O_3$	313.15	90.03[g]	66.61[g]
Dimethyl carbonate	$C_3H_6O_3$	298.15	3.13[h]	84.72[h]
		308.15	3.14[b]	85.79[b]
		313.15	3.19[g]	86.53[g]
Butanone	C_4H_8O	303.15	17.664[c]	90.76[c]
Diethyl carbonate	$C_5H_{10}O_3$	298.15	2.84[h]	121.90[h]
1,4-Dioxane	$C_4H_8O_2$	303.15	2.200[c]	86.17[c]
Tetraglyme	$C_{10}H_{20}O_5$	288.15	8.04[f]	218.79[f]
		293.15	7.90[d]	219.88[e]
		298.15	7.79[h]	220.70[h]

[a] Ref. 15. [b] Ref. 20. [c] Ref. 18. [d] Ref. 12. [e] Ref. 16. [f] Ref. 17. [g] Ref. 14. [h] Ref. 19.

3.1.3 Analysis of ε_r^E(interactions)

Stripping experimental ε_r^E values of volume-change and permittivity-contrast effects, the latter depending only on pure-component properties, should leave amounts that can be ascribed to molecular interactions between the components. These translate into ε_r^E(interactions) > 0 for the majority of the examined systems (Figs. 1a–1e and 1i). The remarkable finding is that, in the instances of

Figs. 1a, 1b, 1d and 1f, ε_r^E(experimental) and ε_r^E(interactions) bear opposite sign and hence endangers the conventional approach that uses the sign of ε_r^E(experimental) as a guide for discussing molecular interactions. Also interesting is the case of Fig. 1b where the experimental S-shaped curve for ε_r^E can be interpreted as arising from the balance of different contributions, even though ε_r^E(interactions) is consistently positive at all compositions.

In the case of Figs. 1a and 1i the binary systems are formed by molecules of similar chemical nature and approximately the same size. However, the much more polar ethylene carbonate molecules and, to a lesser extent, butanone molecules are likely to effectively orientate the weaker dipoles in dimethyl carbonate and 1,1,2,2-tetrachloroethane molecules, respectively, giving rise to the estimated positive ε_r^E(interactions). Both binary systems are chemically akin in that all constituents are aprotic solvents, albeit with very different permittivity contrast. In accordance with these characters our dissection method leads to positive, hence qualitatively similar, ε_r^E(interactions) values and to widely different negative ε_r^E(contrast) values, the balance of these contributions showing opposite-sign values for the experimentally determined excess relative permittivity. In aqueous alkoxyethanol mixtures (Figs. 1b and 1c), the presence of hydrogen bonds between dissimilar molecules should facilitate the orientation of non-bonded molecules along the applied electric field and hence a permittivity increase. This effect is more pronounced with the smaller molecules of 2-methoxyethanol than with the bigger 2-butoxyethanol molecules. In mixtures alcohol–polyether, as are the cases of Figs. 1d and 1e, the disruption of hydrogen-bonded networks in the pure alcohol component due to specific interactions with tetraglyme molecules should help to bring about increased effective polarization of mixtures and hence positive ε_r^E(interactions) values. Since this contribution is larger with strongly polar 2,2,2-trifluorethanol molecules, coupled with the lower magnitude for the negative permittivity-contrast effect, the observed experimental ε_r^E values are positive in opposition to the negative values for the similar methanol–tetraglyme system.

Fig. 1f depicts an interesting example of S-shaped curve for ε_r^E(interactions) in a system formed by two low permittivity aprotic solvents. Although the molecules of 1,4-dioxane do not have a permanent dipole moment in the more stable chair conformation, they can exhibit local polarity around the two oxygen atoms. Moreover, they are in thermodynamic equilibrium with molecules in the less stable boat conformation, which are slightly dipolar. Adding 1,1,2,2-tetrachloroethane to liquid 1,4-dioxane may perturb that conformational equilibrium giving rise to the apparently anomalous curve for ε_r^E(interactions).

It remains to discuss the systems in Figs. 1g, 1h and 1j for which we found ε_r^E(interactions) < 0. For the first two, a magnitude of less than 0.6 has been estimated for the various contributions to the small, negative experimental excess relative permittivities. These three systems are mixtures of long-chain and globular molecules. Both alkyl carbonates do not exhibit preferential orientation under an applied electric field. However, these weakly polar and globular molecules are likely to become anti-parallel to the field under the influence of long-chain tetraglyme molecules. It is interesting to note that the system in Fig. 1j is the only one among the ten binaries
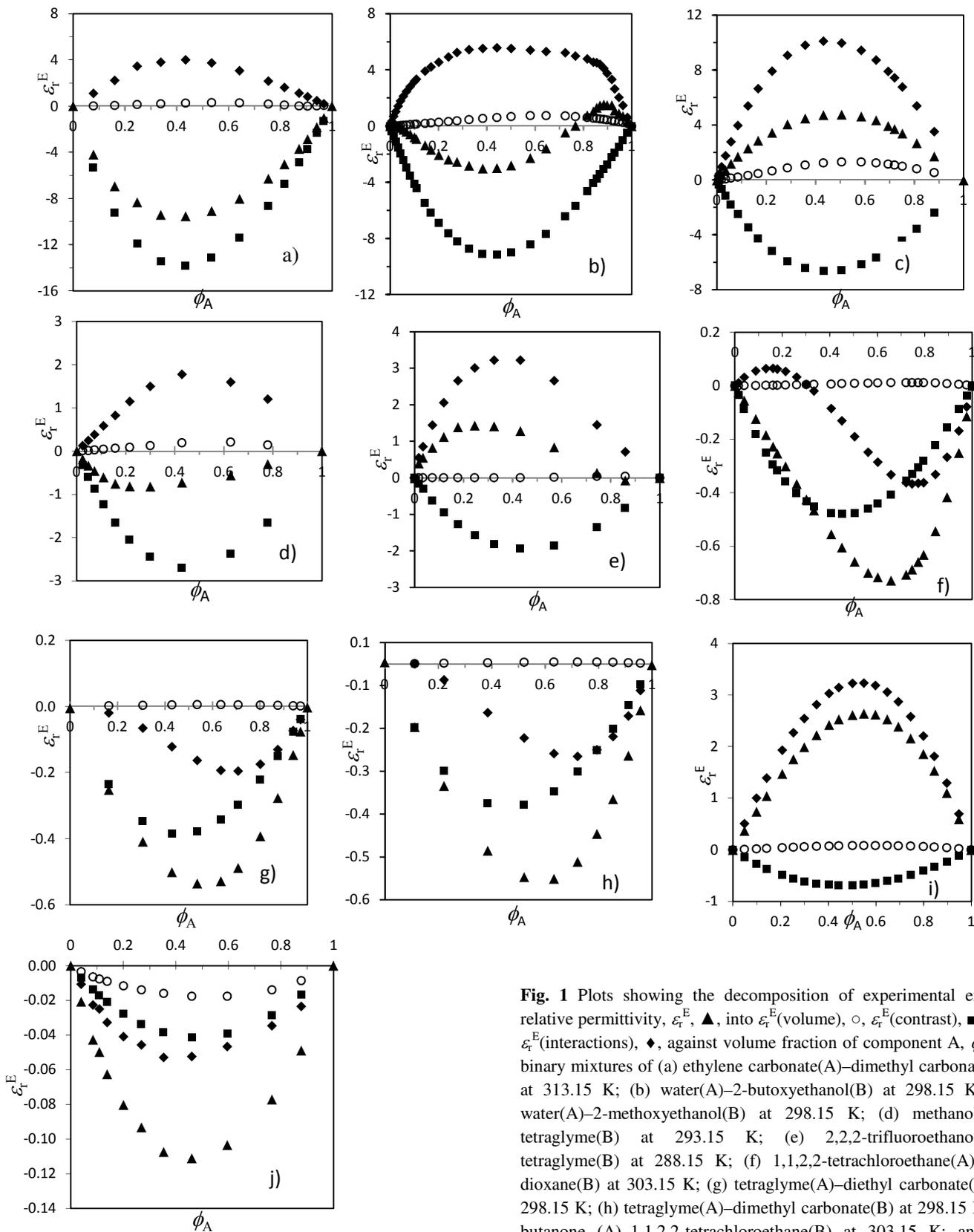
Fig. 1 Plots showing the decomposition of experimental excess relative permittivity, ε_r^E, ▲, into ε_r^E(volume), ○, ε_r^E(contrast), ■, and ε_r^E(interactions), ◆, against volume fraction of component A, ϕ_A, in binary mixtures of (a) ethylene carbonate(A)–dimethyl carbonate(B) at 313.15 K; (b) water(A)–2-butoxyethanol(B) at 298.15 K; (c) water(A)–2-methoxyethanol(B) at 298.15 K; (d) methanol(A)–tetraglyme(B) at 293.15 K; (e) 2,2,2-trifluoroethanol(A)–tetraglyme(B) at 288.15 K; (f) 1,1,2,2-tetrachloroethane(A)–1,4-dioxane(B) at 303.15 K; (g) tetraglyme(A)–diethyl carbonate(B) at 298.15 K; (h) tetraglyme(A)–dimethyl carbonate(B) at 298.15 K; (i) butanone (A)–1,1,2,2-tetrachloroethane(B) at 303.15 K; and (j) dimethyl carbonate(A)–dodecane(B) at 308.15 K.

examined for which all contribution types are negative. Since the long-chain molecules in pure liquid dodecane are aligned with the applied field, some disruption of this order upon adding the globular carbonate molecules should explain the small negative ε_r^E(interactions)-values for this system.

To close, we note that the signs of ε_r^E(interactions) and ε_r^E(volume) are not correlated with each other.

3.2 Polar–non-polar binary systems

3.2.1 Physical properties

The selected set consists of six mixtures formed by a polar liquid and a non-polar solvent used for the experimental determination of dipole moments in solution,[21] namely: (a) monoglyme (or ethylene glycol dimethyl ether or 2-methoxyethyl methyl ether or 3,5,8-trioxanonane)(A)–heptane(B) at 298.15 K, $r_{A/B} = 3.66$;[22] (b) tetraglyme(A)–heptane(B) at 298.15 K, $r_{A/B} = 4.06$;[22] (c) hexan-1-ol(A)–cyclohexane(B) at 298.15 K, $r_{A/B} = 6.42$;[23] (d) hexan-1-ol(A)–hexane(B) at 298.15 K, $r_{A/B} = 6.89$;[23] (e) tetraglyme(A)–cyclohexane(B) at 288.15 K, $r_{A/B} = 3.92$;[2] and (f) tetraglyme(A)–hexane(B) at 288.15 K, $r_{A/B} = 4.21$.[2] Additional density measurements were performed in these two last systems to calculate excess molar volumes. Using the same experimental setup and chemicals as reported elsewhere,[2] the following results were obtained: for tetraglyme(A)–cyclohexane(B) at 288.15 K, V_m/cm^3 mol^{-1} = 107.69 + 115.40 × x_A − 4.4362 × x_A^2 (σ = 0.13); and for tetraglyme(A)–hexane(B) at 288.15 K, V_m/cm^3 mol^{-1} = 130.03 + 88.821 × x_A (σ = 0.09). The relevant properties of these 6 liquid substances are given in table 2.

3.2.2 Partitioning the excess relative permittivity

Fig. 2 shows the result of the proposed decomposition of contributions to ε_r^E for the second set of six binary systems.

As before, the volume-change contribution ε_r^E(volume) is the smallest one, being now negative for 5 out of 6 systems because $V_m^E > 0$ for those systems. Also, for the most part ε_r^E(contrast) values are the largest contribution to the experimental ε_r^E values, except for the system hexan-1-ol–hexane ($V_m^E < 0$) in which case it is slightly surpassed by ε_r^E(interactions) values.

Table 2 Relative permittivity, $\varepsilon_{r,i}^*$, and molar volume, V_i^*, of pure liquid components at experimental temperatures

Component Formula	Molecular	T/K	$\varepsilon_{r,i}^*$	V_i^*/cm^3 mol^{-1}
Cyclohexane	C_6H_{12}	288.15	2.049[a]	107.44[a]
		298.15	2.030[b]	108.76[b]
Hexane	C_6H_{14}	288.15	1.909[a]	129.81[a]
		298.15	1.890[b]	131.53[b]
Heptane	C_7H_{16}	298.15	1.93[c]	147.44[c]
Hexan-1-ol	$C_6H_{14}O$	298.15	13.03[b]	125.36[b]
Monoglime	$C_4H_{10}O_2$	298.15	7.07[c]	104.65[c]
Tetraglyme	$C_{10}H_{20}O_5$	288.15	8.04[a]	218.81[a]
		298.15	7.78[c]	220.81[c]

[a] Ref. 2. [b] Ref. 23. [c] Ref. 22.

3.2.3 Analysis of ε_r^E(interactions)

Hedestrand[24,25] developed a method for obtaining the dipole moment of a solute at infinite dilution in a non-polar solvent from density and relative permittivity measurements. This method is based on Debye's model for polar solutions which assumes negligible interactions between solute and solvent at high dilution. In this context we re-examine previous researches participated with one of us.[22,26] Thus, the dipole moment of tetraglyme (A) in heptane was calculated[22] by applying Hedestrand's procedure to relative permittivities determined at $x_A < 0.1$ ($\phi_A < 0.07$). This range was indeed a good choice because Fig. 1b shows that ε_r^E(interactions) values are there very small. However, in the system monoglyme(A)–heptane(B) only data points for $x_A \geq 0.1$ ($\phi_A \geq 0.17$) were available at that time.[22] Once again, Fig. 2a lends support to the previous conclusion[22] that the conditions for applying Hedestrand's method were not met in this instance, a conclusion reached at from a laborious study of the effect of temperature on this system.[22]

The exam of Fig. 2c for hexan-1-ol–cyclohexane and Fig. 2d for hexan-1-ol–hexane tells us that molecular interactions solute–solvent operate at very low concentrations. Therefore, none of these solvents is appropriate for the determination of hexan-1-ol dipole moment. Moreover, this analysis supports the prediction of an anti-parallel correlation of dipoles suggested by estimates of Kirkwood correlation factors in the dilute range.[26]

Returning to the choice of a solvent for determining tetraglyme dipole moment, in Figs. 2e and 2f we compare cyclohexane and hexane, respectively. Clearly, hexane should be the best choice. The less good performance of cyclohexane may be ascribed to the relatively large excess molar volumes in this solvent. Extending this comparison to heptane as solvent (Fig. 2b), we suggest that linear alkanes are the prime choice for solvents of long straight-chain polar organic molecules in the experimental determination of their dipole moments.

4. Conclusions

We have partitioned the experimental excess relative permittivity, ε_r^E, of binary mixtures of molecular liquids into contributions from the excess molar volume, V_m^E, (cf. eqn (13)), the excess permittivity contrast interactions (cf. eqn (17)) and molecular interactions, the latter being estimated by difference. As a consequence of the approximations made to obtain estimates of ε_r^E(volume), a negative/positive V_m^E gives a positive/negative contribution to ε_r^E. In turn, the permittivity contrast appears as a decisive electric property to describe the relative permittivity of a homogenous liquid mixture in terms of the electromagnetic theory. We applied the classic local field theory of dielectrics to a binary mixture considering the molecules immersed in the ideal permittivity medium of the two components. In this way we obtained a new, symmetric equation (cf. eqn (15) and (16)) for predicting the relative permittivity of binary mixtures in the absence of volume effects and molecular interactions. Assuming these values as an expression of the permittivity contrast, we can estimate the corresponding contribution to ε_r^E. We have calculated the three types of contributions for a variety of binary liquid systems from which we draw information
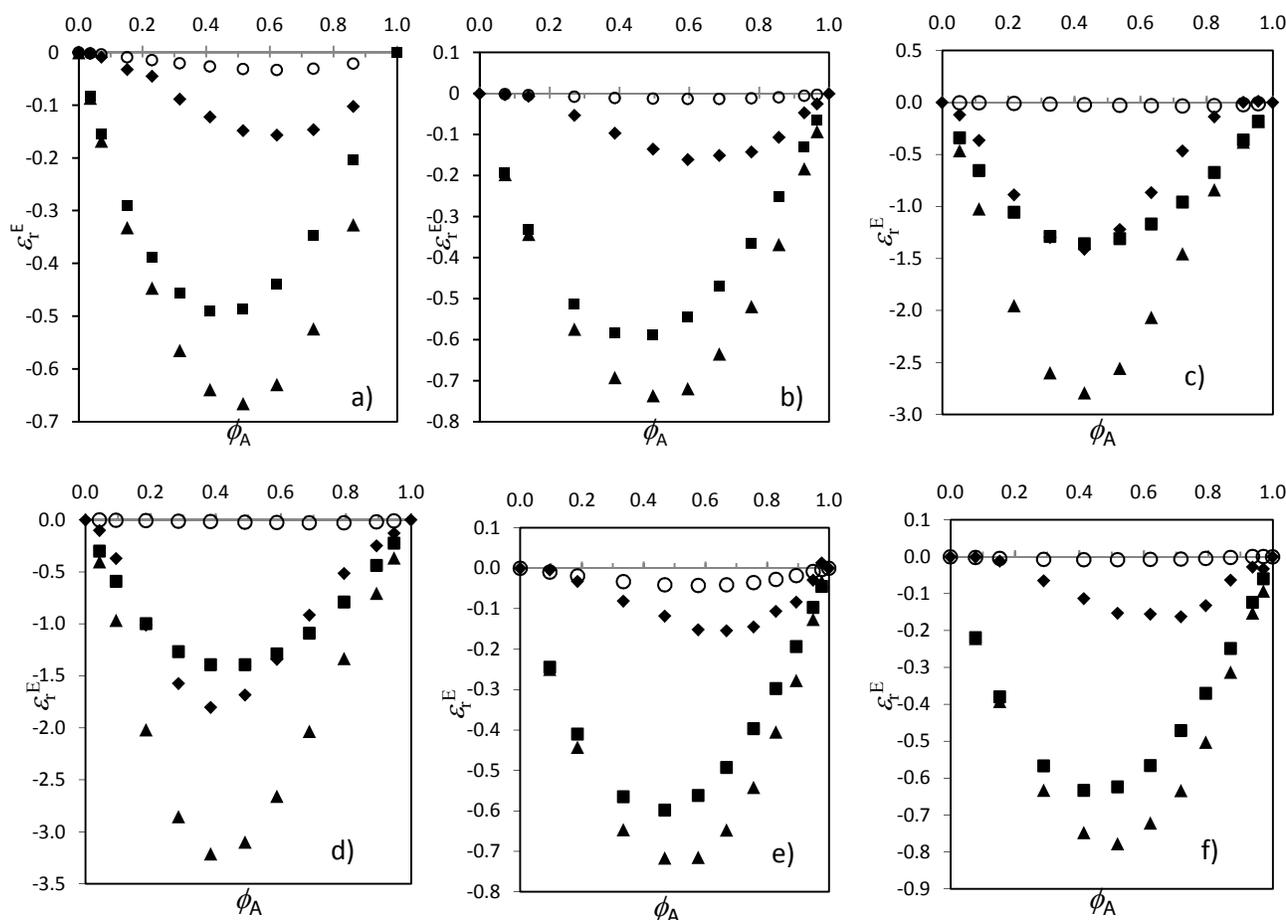
Fig. 2 Plots showing the decomposition of experimental excess relative permittivity, ε_r^E, ▲, into ε_r^E(volume), ○, ε_r^E(contrast), ■, and ε_r^E(interactions), ♦, against volume fraction of component A, ϕ_A, in binary mixtures of (a) monoglyme(A)–heptane(B) at 298.15 K; b) tetraglyme(A)–heptane(B) at 298.15 K; c) hexan-1-ol(A)–cyclohexane(B) at 298.15 K; d) hexan-1-ol(A)–hexane(B) at 298.15 K; e) tetraglyme(A)–cyclohexane(B) at 288.15 K; and f) tetraglyme(A)–hexane(B) at 288.15 K. For the sake of clarity, some data points for ε_r^E(volume) have been omitted in Figs. 2a and 2b at low ϕ_A.

concerning interactions between dissimilar molecules. We underline the finding that, in four out of the sixteen binaries examined, the sign of estimated interaction contributions could be opposite to the sign of the experimentally determined excess relative permittivity on which conventional analyses are based. In fact, the sign of ε_r^E indicates solely how the mixture polarization deviates in relation to the corresponding ideal value. We discuss the proper conditions for determining dipole moments at infinite dilution on the basis ε_r^E(interactions) values for three different polar solutes dissolved in hexane, heptane or cyclohexane. Finally, in view of the small magnitude of ε_r^E(volume) values for both polar–polar and polar–non-polar liquid mixtures, we now correct past attempts[20,27–29] to explain the temperature effect on the relative permittivity of liquid mixtures in terms of changes in molar volume.

Acknowledgements

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