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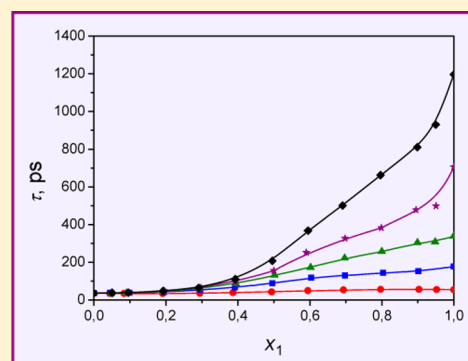
Microwave Dielectric Relaxation Spectroscopy Study of Alkan-1-ol/Alkylbenzoate Binary Solvents

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S Supporting Information

ABSTRACT: The structure and dynamics of alkan-1-ol/alkylbenzoate binary mixtures have been studied by microwave dielectric relaxation spectroscopy in the 200 MHz to 20 GHz frequency range. The binary mixtures of methanol, ethanol, propan-1-ol, butan-1-ol, and pentan-1-ol with methyl, ethyl, propyl, and butyl benzoates were studied at 298.15 K. The relaxational response of the pure alcohols, pure esters, and their binary mixtures over the full composition range is properly described by the Havriliak–Negami model. The alcohol content, alcohol length, and alkyl side-chain effects on the relaxational properties have been studied for these mixtures over the whole composition range. From the experimental readings, the effective and the corrective Kirkwood and Bruggeman correlation factors have been calculated. The data gathered have been interpreted in terms of the alkyl side-chain effect and their reliance on the mixture composition.



1. INTRODUCTION

The need for non-destructive characterization methods of materials has prompted the use of dielectric relaxation spectroscopy (DRS),¹ a powerful technique that contributes to interpret the dynamics and structure of liquids and the nature of the intermolecular interactions.² The effect of the interactions on the dynamics of solvent mixtures revealed by DRS remains an open challenge.³ DRS is ideally suited to monitor changes in sensitive properties when liquids mix up; therefore, dielectric relaxation studies of mixtures have aroused a growing interest.⁴ The dielectric investigation of mixtures containing varying amounts of interacting constituents helps to discern the structure of the complexes formed. H-bonding considerably alters the dielectric properties of liquids; understanding H-bonding remains an intricate task due to the uncertainty to identify the particular bonds and the entities involved.⁵ In this regard, DRS provides a way of connecting its results with those from other techniques.^{3,6} The net dipole moment of the complexes formed also is a key parameter for conformational analyses of liquids.⁷

Alcohols are solvents widely used as reagents and fuels; a lot of effort has gone into interpreting their ability to undergo self-association with manifold internal structures, which rely on the number of C atoms and the location of the OH group.⁸ On the other hand, aromatic esters are an interesting class of solvents with theoretical and technological interest. The polarizable π -electron system, dipolar nature, and ability of alkylbenzoates to separate polar from non-polar compounds turn them into useful tools in many settings; the planarity steadily vanishes with increased side chain, the packing being less efficient as the dipoles move away.⁹ Alcohol–ester interactions play a key role

in biological systems and drug synthesis;⁶ the balance between geometry and dipole–dipole interactions governs the ester features.⁷ The disruption of alkylbenzoate packing upon mixing with alkanols is followed by homo- and heterointeractions.¹⁰

The solvatochromic study of alkan-1-ol/alkylbenzoate mixed solvents has revealed stronger solvation ability of the mixtures than the pure solvents.¹¹ In this work, the binary mixtures of alcohols, from methanol to pentan-1-ol, with methylbenzoate (MB), ethylbenzoate (EB), propylbenzoate (PB), and butylbenzoate (BB) were investigated at 298.15 K by DRS measurements in the 200 MHz to 20 GHz frequency range, pursuing to (i) evaluate the length effect on the structure and dynamics of pure 1-alkanols, (ii) assess the alkyl side-chain effect on the structure and dynamics of pure esters, and (iii) infer the structural features of these alcohol–ester mixed solvents.

2. EXPERIMENTAL SECTION

2.1. Solvents. The pure solvents, of the highest purity commercially available, were used as received; their purity was assessed with a Perkin-Elmer 990 GC. The liquids were degassed with ultrasound and kept out of the light over Fluka Union Carbide 0.3 nm molecular sieves. The binary mixtures, fully miscible over the whole composition range, were prepared by weight ($\pm 10^{-5}$ g) with a Mettler AT 261 Delta Range balance. To avoid preferential evaporation, the samples were

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injected by syringe into suitably stoppered bottles. The uncertainty in the mole fraction was ± 0.0001 .

2.2. Instruments. Microwave DRS measurements were carried out in the 200 MHz to 20 GHz range (± 0.1) with an Agilent 85070E dielectric probe kit and an Agilent N4691B ECal electronic calibration module according to a coaxial reflection technique, and an Agilent N5230A vector network analyzer. The apparatus was calibrated using air, a short circuit, and water. Prior to measurements, calibration refreshment was performed with the ECal module. The temperature, measured to ± 0.01 K with a platinum resistance calibrated according to well-known procedures, was controlled by an external bath.

2.3. Methods. Available methods of dealing with relaxation time distribution patterns have been put forward. Havriliak–Negami described the dielectric dispersion with an asymmetric model for complex dielectric permittivity,¹² combining the Cole–Cole¹³ and Davidson–Cole¹⁴ empirical functions in the form

$$\epsilon^* = \epsilon_\infty + \frac{\Delta\epsilon}{(1 + (j\omega\tau)^\alpha)^\beta} \quad (1)$$

where ϵ^* stands for the dielectric constant (permittivity), τ is the relaxation time, $\Delta\epsilon = \epsilon_s - \epsilon_\infty$ for the dielectric strength, and ϵ_s and ϵ_∞ are the static and high frequency dielectric constants, respectively, with α ($0 < \alpha \leq 1$) and β ($0 < \beta \leq 1$) being fitting parameters. For $\alpha = \beta = 1$, eq 1 yields the Debye function, for $\beta = 1$ the Cole–Cole function, and for $\alpha = 1$ the Davidson–Cole function.^{15,16} Excess permittivity and excess reciprocal relaxation time afford valuable information on interaction dynamics.¹⁷ The formation of dimers and higher oligomers^{18,19} can be concluded from the excess permittivity ϵ^E :

$$\epsilon^E = (\epsilon_s - \epsilon_\infty)_m - [(\epsilon_s - \epsilon_\infty)_1 x_1 + (\epsilon_s - \epsilon_\infty)_2 x_2] \quad (2)$$

where x stands for the mole fraction, m for the mixture, and 1 and 2 alcohol and ester, respectively. The excess reciprocal relaxation time^{6,20} $(1/\tau)^E$, defined as

$$\left(\frac{1}{\tau}\right)^E = \left(\frac{1}{\tau}\right)_m - \left[\left(\frac{1}{\tau}\right)_1 x_1 + \left(\frac{1}{\tau}\right)_2 x_2\right] \quad (3)$$

measures the average broadening of dielectric spectra and informs about the interaction dynamics. A Redlich–Kister polynomial was fitted to the ϵ^E and $(1/\tau)^E$ versus x_1 plots.²¹ The modified Kirkwood–Frohlich model describes polar/non-polar interactions based on short-range forces.²² In polar liquids, the dimensionless g factor informs about dipole orientation.²³ For polar liquid mixtures, the Kirkwood equation (eq 4) applies:²⁴

$$\frac{4\pi N_A}{9kT} \left(\frac{\mu_1^2 \rho_1}{M_1} x_1 + \frac{\mu_2^2 \rho_2}{M_2} x_2 \right) g^{\text{eff}} = \frac{(\epsilon_{\text{sm}} - \epsilon_{\infty\text{m}})(2\epsilon_{\text{sm}} + \epsilon_{\infty\text{m}})}{\epsilon_{\text{sm}}(\epsilon_{\infty\text{m}} + 2)^2} \quad (4)$$

in which the effective Kirkwood correlation factor, g^{eff} , reflects solute–solvent interactions, N_A and k are universal constants, μ is the dipole moment, ρ is the density, T the absolute temperature, and M the molecular weight; the densities and dipole moments of liquids were taken from the literature.^{8,25} If the dipole moments of the two constituents become affected to the same extent, then the Kirkwood equation converts to eq 5:

$$\frac{4\pi N_A}{9kT} \left(\frac{\mu_1^2 \rho_1 g_1}{M_1} x_1 + \frac{\mu_2^2 \rho_2 g_2}{M_2} x_2 \right) g_f = \frac{(\epsilon_{\text{sm}} - \epsilon_{\infty\text{m}})(2\epsilon_{\text{sm}} + \epsilon_{\infty\text{m}})}{\epsilon_{\text{sm}}(\epsilon_{\infty\text{m}} + 2)^2} \quad (5)$$

where g_f is the corrective Kirkwood correlation factor. The g_1 and g_2 factors of 1 and 2 were calculated with eq 4. For associative and non-associative mixtures, the effective g^{eff} factor varies from g_1 ($x_1 = 1$) to g_2 ($x_2 = 1$). The g_i ($i = 1, 2$) factor conveys the association of a reference molecule with its nearest neighbor. Departure of g_i from unity unveils molecular association, with $g_i > 1$ indicating parallel dipole orientation, $g_i < 1$ antiparallel orientation, and $g_i = 1$ non-associating dipoles.²⁶

Bruggeman developed a predictive equation for dilute dispersions of spherical inclusions useful for solute–solvent interactions,²⁷ expressing the f_B factor as

$$f_B = \left(\frac{\epsilon_{\text{sm}} - \epsilon_{s2}}{\epsilon_{s1} - \epsilon_{s2}} \right) \left(\frac{\epsilon_{s1}}{\epsilon_{\text{sm}}} \right)^{1/3} = (1 - \phi_2) \quad (6)$$

with ϕ_2 being the volume fraction of liquid 2. For non-interacting entities, a linear f_B versus ϕ_2 plot holds, whereas, for interacting constituents, f_B varies non-linearly with ϕ_2 . The data measured have served to establish a modified version²⁸ of eq 6 in the form

$$f_B = 1 - [a - (a - 1)\phi_2]\phi_2 \quad (7)$$

The original Bruggeman equation assumes that the orientation of 2 does not interfere with that of 1, which is true only for non-polar solvents.

3. RESULTS AND DISCUSSION

The complex, frequency-dependent, dielectric parameter, ϵ^* , was measured for methanol, ethanol, propan-1-ol, butan-1-ol, and pentan-1-ol with MB, EB, PB, and BB at 298.15 K. Only one relaxation peak was observed for the mixtures. ϵ^* relies on the applied frequency in the form $\epsilon^* = \epsilon' - i\epsilon''$, with ϵ' being the real part (related to the stored energy in the medium) and ϵ'' the imaginary part (related to the energy loss).²⁹

Figure 1 shows a typical Cole–Cole diagram for methanol/MB with the ϵ' and ϵ'' parts evaluated from the experimental readings. The curves resemble arcs with symmetric distribution, semicircles if the data fulfill the Debye model and arcs if the data fulfill the Cole–Cole or Davidson–Cole models. For the two sets of pure constituents and alcohol/alkylbenzoate mixed solvents, the Havriliak–Negami distribution (eq 1) was fitted to the frequency (ν), ϵ' and ϵ'' ; the α , β , ϵ_∞ , ϵ_s , and τ parameters were calculated over the full composition range by non-linear least-squares fitting using the ORIGIN 8.5 program, based on the Levenberg–Marquardt algorithm (Tables 1S and 2S, Supporting Information). The maxima of the relaxation dielectric spectra for propan-1-ol, butan-1-ol, and pentan-1-ol partially fell near the lower frequency limit, and were not included in the range studied. At large, the data fitting fulfilled the Davidson–Cole expression for $\alpha = 1$. For methanol/MB, values of $\alpha \approx \beta \approx 1$ are expected (Figure 1 and Table 2S, Supporting Information); however, as the alcohol size is raised, the deduced β values depart from unity upon increasing the alcohol content.

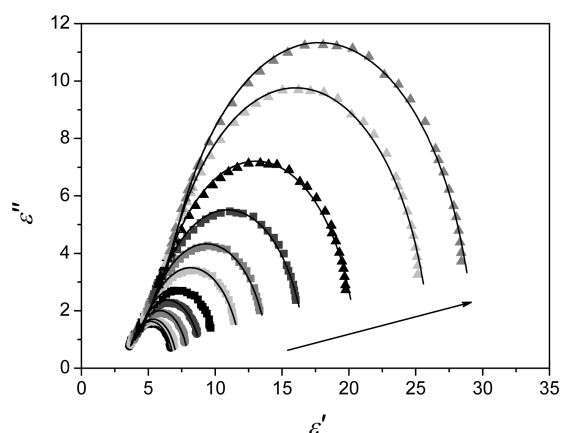


Figure 1. Cole–Cole diagram for methanol/MB at 298.15 K; increasing alcohol mole fraction in the arrow sense: $x_1 = 0.0442, 0.0838, 0.1913, 0.2944, 0.3865, 0.4942, 0.5946, 0.6935, 0.7968, 0.9035, 0.9523$.

Figure 2a shows the composition effect on ϵ_∞ for MB/alkan-1-ols. The ϵ_∞ values diminished with an increase in the alcohol length. Below $x_1 = 0.1$, all systems yielded the same ϵ_∞ values; above this limit, the values at the same composition differed noticeably, with methanol always behaving different. Figure 2b shows the variation of ϵ_∞ with composition for methanol/alkyl benzoate systems. The ϵ_∞ values diminished with an increase in the alkyl side chain. The difference for pure esters with methanol was larger than that with the other alcohols; i.e., the ϵ_∞ difference between the four ester systems became smaller as the alcohol length rose (Figure 2c).

Figure 3 shows the ϵ_s versus x_1 plot; the non-linear variation observed for all mixtures reveals solute–solvent interaction, with the decrease in the dielectric strength, $(\epsilon_s - \epsilon_\infty)_m$, indicating dimer formation.³⁰ For alkanol/MB, the variation of ϵ_s (Figure 3a) was similar to that of ϵ_∞ ; larger values correspond to shorter alcohols, rising with the alcohol content. Up to $x_1 = 0.2$, all five systems displayed nearly the same ϵ_s values, and rose for higher alcohol content, the more so the shorter the alcohol length, tending to the alcohol value. Figure 3b shows the composition effect for methanol–alkylbenzoate systems; the ϵ_s values were smaller the larger the alkyl side chain; these variations correspond to transition from spherical to elongated aggregates, followed by parallel dipole orientation.³⁰ Likewise, the ϵ_s values dropped gradually when the ester and alcohol size were raised, a trend accompanied by a fall in the number of complex dipoles, which entails a decrease in the

molar volume of the rotating entities, consistent with the conclusions drawn from other measurements.³¹

Figure 4 shows the τ versus x_1 plot for alkan-1-ols/MB and methanol/alkylbenzoates. Unlike ϵ_s and ϵ_∞ , the relaxation time increased when the alcohol length rose, the larger the difference, the higher the alcohol content. The increase in τ with the alcohol length (Figure 4a) and ester side chain (Figure 4b) proves hindrance to molecular rotation, concurrent with the reorientation of the OH group, which relies on the ester size and solvent viscosity.³¹ The ϵ_s and τ values obtained, both covered between those of the pure constituents (Tables 1S and 2S, Supporting Information), reveal interaction between the OH and C=O groups.³²

Non-ideal behavior of solvent mixtures can be accounted for by (i) the different size and/or shape of the constituents, (ii) the reorientation of the molecules after mixing, and (iii) the underlying interactions. Deviation of mixtures from the ideal behavior can be interpreted reliably with the derived excess properties, the properties in excess relative to the ideal solution.⁸ Both ϵ^E and $(1/\tau)^E$ are sensitive to the formation of heteroaggregates. Figure 5 shows the ϵ^E (eq 2) versus x_1 plot for alkan-1-ols/MB and methanol/alkylbenzoates. The ϵ^E values obtained (eq 2), always negative, reveal formation of parallel H-bonded alcohol/ester multimers, entailing a diminution of the overall effective dipoles. The sharp minimum for methanol at $x_1 = 0.6$ – 0.7 (Figure 5a) is consistent with the formation of 2:1 aggregates. For ethanol to pentan-1-ol, the minima slightly shifted to $x_1 = 0.5$ (Table 3S, Supporting Information), revealing formation of 1:1 aggregates, in good agreement with the conclusions supported by other thermophysical properties.^{7,10} Also, the deep ϵ^E minima observed when the alkyl side chain was raised (Figure 5b) reveal greater ester ability to break the methanol structure the longer the ester size.³³ The associative role of alcohols inherent to their proton-donor nature cooperates to boost H-bonding with esters, forming linear α -multimer aggregates. When the content of the non-associative esters rises and the alcohol drops, the interactions diminish, even vanishing gradually and forming monomer structures.³⁴

Figure 6 shows the $(1/\tau)^E$ versus x_1 plot (eq 3) for alkanols/MB and methanol/alkylbenzoates. Alkan-1-ol/ester mixtures display positive $(1/\tau)^E$ values for low alcohol content (Figure 6a), revealing that the field created promotes faster rotation of the effective dipoles (Table 4S, Supporting Information).^{6,31} Above $x_1 = 0.2$, the negative values indicate that the field promotes slower rotation; the values became even more negative the larger the alcohol length. The methanol/MB system distinguished its behavior up to $x_1 = 0.5$ relative to the

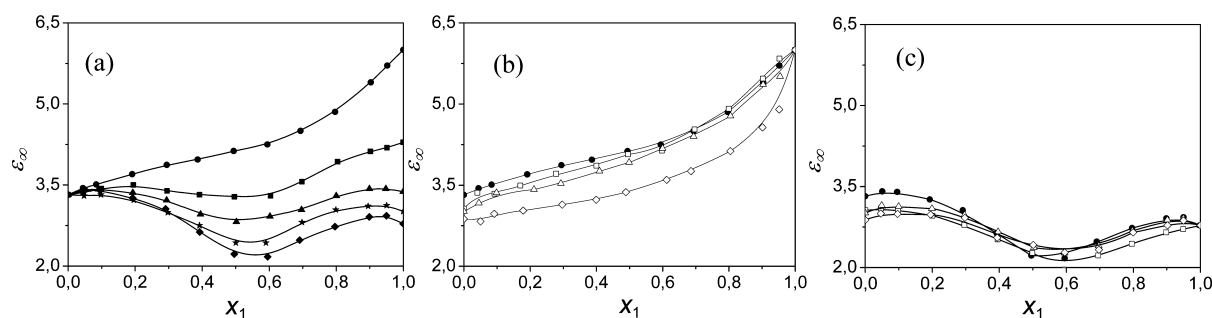


Figure 2. High frequency dielectric constant, ϵ_∞ , for (a) x_1 alkan-1-ol/(1 - x_1) MB, $T = 298.15$ K: ● methanol, ■ ethanol, ▲ propan-1-ol, ★ butan-1-ol, ◆ pentan-1-ol; (b) x_1 methanol/(1 - x_1) alkylbenzoate; (c) x_1 pentan-1-ol + (1 - x_1) alkylbenzoate: ● MB, □ EB, △ PB, ◇ BB.

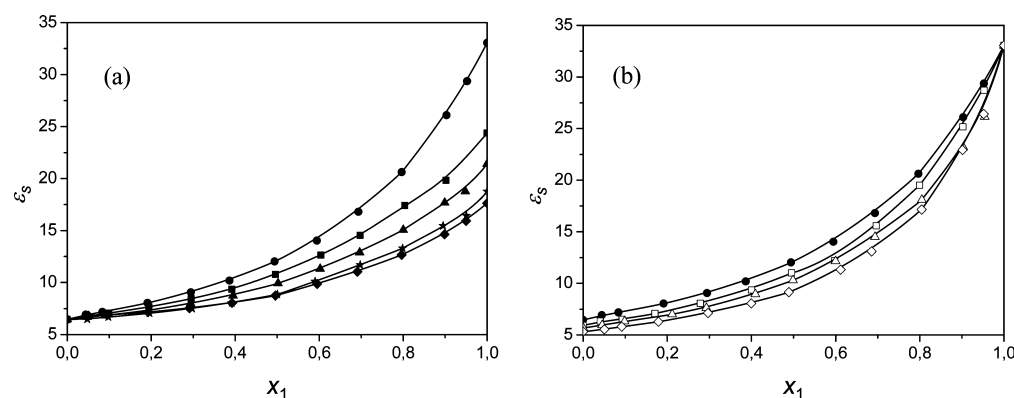


Figure 3. Static dielectric constant ϵ_s for (a) x_1 alkan-1-ol/(1 - x_1) MB: ● methanol, ■ ethanol, ▲ propan-1-ol, ★ butan-1-ol, ◆ pentan-1-ol; (b) x_1 methanol/(1 - x_1) alkylbenzoate: ● MB, □ EB, △ PB, ◇ BB. $T = 298.15$ K.

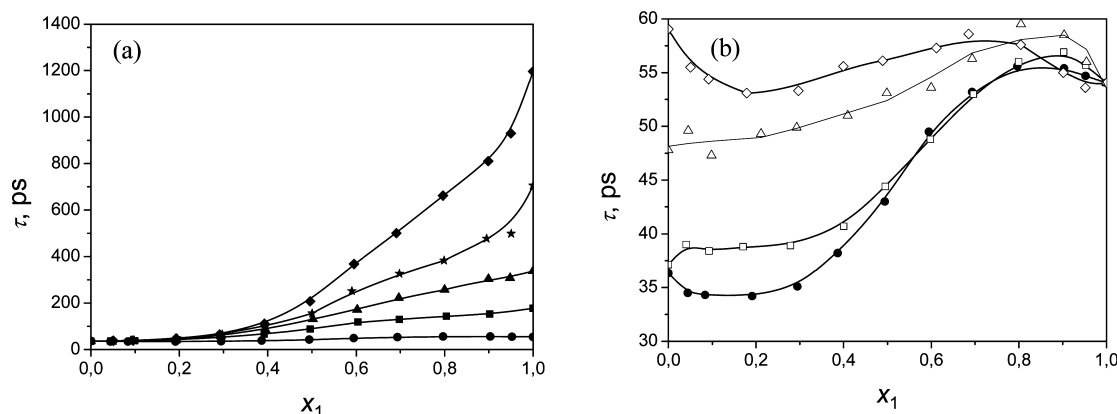


Figure 4. Dielectric relaxation time, τ , for (a) x_1 alkan-1-ol/(1 - x_1) MB: ● methanol, ■ ethanol, ▲ propan-1-ol, ★ butan-1-ol, ◆ pentan-1-ol; (b) x_1 methanol/(1 - x_1) alkylbenzoate: ● MB, □ EB, △ PB, ◇ BB. $T = 298.15$ K.

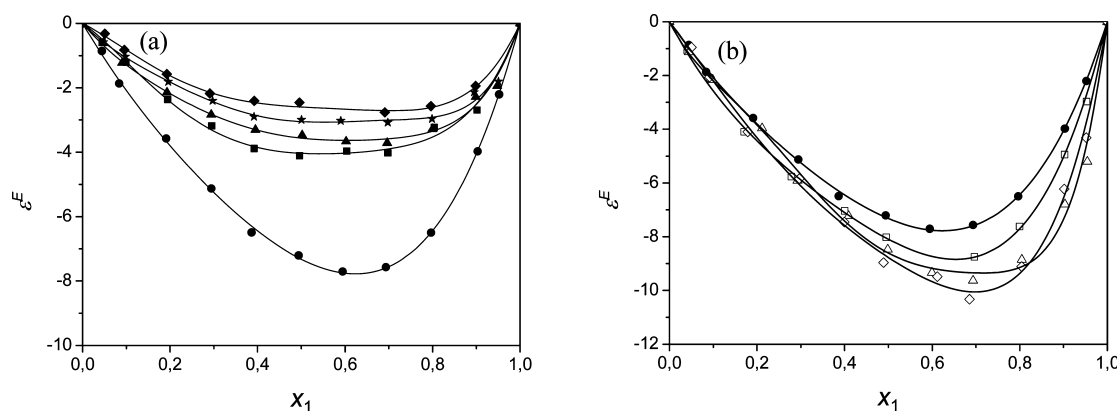


Figure 5. Excess permittivity, ϵ^E , for (a) x_1 alkan-1-ol/(1 - x_1) MB: ● methanol, ■ ethanol, ▲ propan-1-ol, ★ butan-1-ol, ◆ pentan-1-ol; (b) x_1 methanol/(1 - x_1) alkylbenzoate: ● MB, □ EB, △ PB, ◇ BB. $T = 298.15$ K. Continuous lines are Redlich–Kister-type fitting.

other alcohols, with larger positive values that reflect the strongly H-bonded methanol structure and pronounced proton donor ability;⁹ at (roughly) $x_1 = 0.5$, it turns out $(1/\tau)^E = 0$ which, according to eq 3, considers no change in the dynamics of methanol/MB. This feature is reinforced by Figure 6b, showing the same behavior of methanol with all four alkylbenzoates, that is, $(1/\tau)^E = 0$ at (roughly) $x_1 = 0.5$, implying no variation in the rotation velocity of the effective methanol/ester dipoles compared with the sum of rotation rates of the pure constituents. The negative inductive effect followed the sequence methyl < ethyl < propyl < butyl, with the

electron contribution of the butyl group to the CO group being significantly stronger.

The Kirkwood correlation parameter, g_i , informs about dipole orientation and structure. Methanol and pure alkylbenzoates gave similar values, around $g_i = 0.50$, revealing antiparallel dipole orientation, whereas from ethanol to pentan-1-ol it turned out $g_i > 1$, indicating parallel orientation (Table S5, Supporting Information).

Figure 7 shows the composition effect on g^{eff} (eq 4) for methanol/alkylbenzoates and alkan-1-ols/MB (Tables 6S, Supporting Information). For pure alkylbenzoates, the g^{eff}

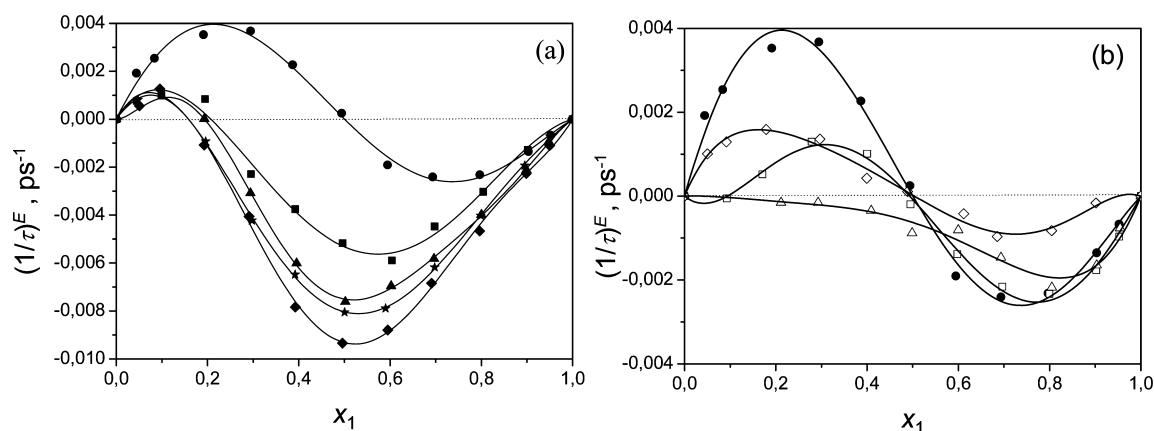


Figure 6. Excess reciprocal relaxation time, $(1/\tau)^E$: (a) x_1 alkan-1-ol/(1 - x_1) MB: ● methanol, ■ ethanol, ▲ propan-1-ol, ★ butan-1-ol, ◆ pentan-1-ol; (b) x_1 methanol/(1 - x_1) alkylbenzoate: ● MB, □ EB, △ PB, ◇ BB. $T = 298.15$ K. Continuous lines are Redlich–Kister-type fitting.

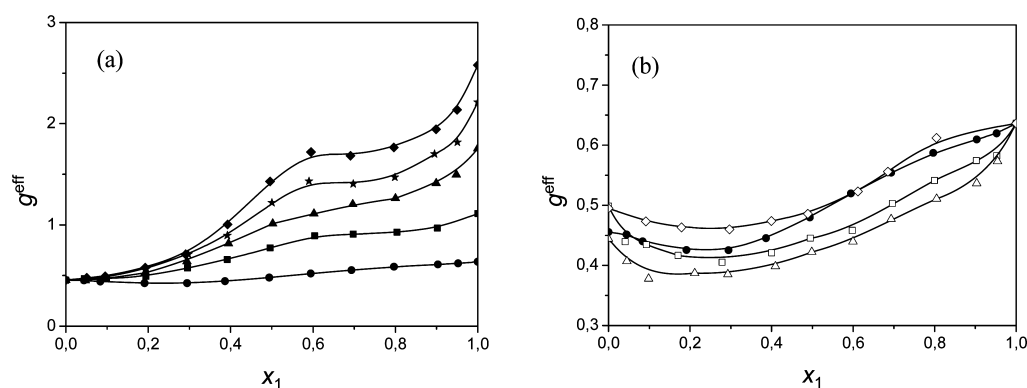


Figure 7. Effective correlation factor, g^{eff} , for (a) x_1 alkan-1-ol/(1 - x_1) MB: ● methanol, ■ ethanol, ▲ propan-1-ol, ★ butan-1-ol, ◆ pentan-1-ol; (b) x_1 methanol/(1 - x_1) alkylbenzoate: ● MB, □ EB, △ PB, ◇ BB. $T = 298.15$ K.

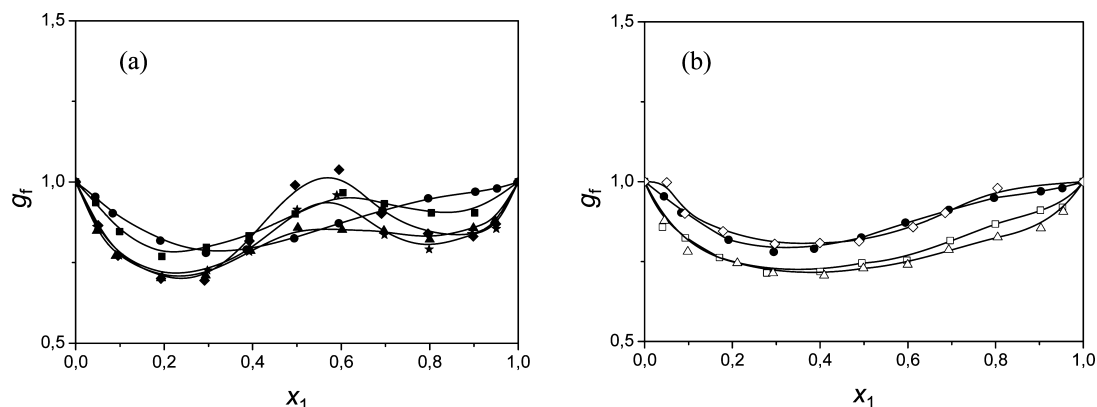


Figure 8. Corrective Kirkwood correlation factor, g_f for (a) x_1 1-alcohol/(1 - x_1) MB: ● methanol, ■ ethanol, ▲ propan-1-ol, ★ butan-1-ol, ◆ pentan-1-ol; (b) x_1 methanol/(1 - x_1) alkylbenzoate: ● MB, □ EB, △ PB, ◇ BB. $T = 298.15$ K.

values were smaller than those for pure alcohols. For the mixtures, the g^{eff} values increased as the alcohol content and alcohol length rose (Figure 7a).

Figure 8 shows the composition effect on the corrective Kirkwood correlation factor, g_f (eq 5), which becomes unity for pure polar liquids and close to unity in the absence of interactions.⁶ Deviation of g_f from unity indicates alcohol/ester interaction. For most systems, the g_f values lay below unity over the full composition range (Tables 6S, Supporting Information), revealing an antiparallel dipole orientation. The rising trend of g_f as the alcohol content was raised indicates

reorientation of adjacent molecules with alignment of parallel dipoles, concurrent with the conclusion drawn from the effect caused on the dielectric relaxation time (Figure 4).

For short alkyl chains, the polar groups are relatively exposed and the dipole interactions stem from associated complexes, thus counteracting the complex coordination.³⁵ For high alcohol content, the central ester is surrounded by a number of alcohol units; for low alcohol content, however, only few are prone to interact with the ester, resulting in weak intermolecular interaction.

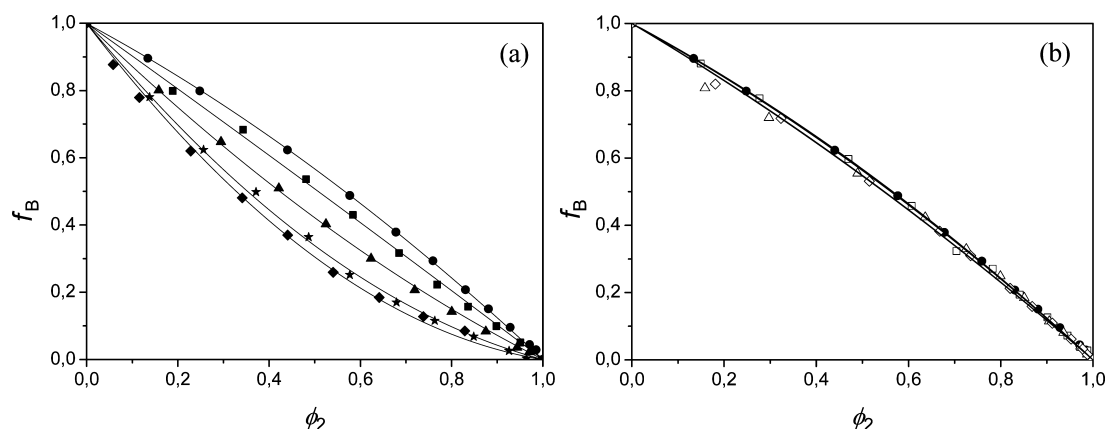


Figure 9. Bruggeman factor, f_B , for (a) x_1 alkan-1-ol/(1 - x_1) MB: ● methanol, ■ ethanol, ▲ propan-1-ol, ★ butan-1-ol, ◆ pentan-1-ol; (b) x_1 methanol/(1 - x_1) alkylbenzoate: ● MB, □ EB, △ PB, ◇ BB. $T = 298.15$ K.

Valuable information is drawn from the Bruggeman factor, f_B (eq 6). The f_B versus ϕ_2 plots (Figure 9) for alcohol–ester mixtures (Table 7S, Supporting Information) displayed a non-linear dependence, the more so the larger the alcohol length, indicating H-bonding interaction through the OH and CO groups.³⁴ Breaking of self-associated alcohols prevails despite the opposite heteroassociating effect of the OH and CO groups, since the larger the alcohol chain, the easier the self-aggregation disruption.³⁶

Values of $a = 1$ (eq 7) correspond to Bruggeman ideal mixtures, the deviations from unity revealing heteroassociation. The a values above/below unity as the solute size was raised reflect the increase/decrease in the effective solvent volume.³⁴ The a values for methanol were below unity with all four esters, and >1 for the other alcohols, and increased with the alcohol length (Table 8S, Supporting Information). Similar a values were deduced for the MB and EB systems and for PB and BB with methanol and ethanol. Propan-1-ol gave similar values with MB and BB and with EB and PB. For butan-1-ol and pentan-1-ol, the a values diminished as the alkyl chain was raised.

4. CONCLUSIONS

The structures of alkan-1-ol/alkylbenzoate binary mixtures have been analyzed on the basis of dielectric constants, relaxation times, and Kirkwood and Bruggeman correlation factors, all revealing formation of solute/solvent aggregates and serving to categorize the interactions on the basis of the H-bond model between the alcohol OH and the ester group. The variation of the static dielectric constant unveils a transition from spherical to elongated aggregates for larger alcohols and larger esters. The negative excess permittivities reveal parallel alcohol/ester multimers with reduced effective dipole moment, with methanol yielding 2:1 aggregates and ethanol to pentan-1-ol 1:1 aggregates. The orientation of neighbor molecules has been deduced from the relaxation time and Kirkwood correlation factors. The excess reciprocal relaxation times calculated emphasize the distinct behavior of methanol relative to the other alcohols as well as its pronounced proton-donor ability.

■ ASSOCIATED CONTENT

Supporting Information

Tables 1S–8S containing relaxation times, static and high frequency dielectric constants for pure constituents and mixed solvents, fitting parameters, excess permittivities, excess

reciprocal relaxation times, Kirkwood and Bruggeman correlation factors for the binary systems. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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