

Composition and temperature dependence of the dielectric constant of 1-propanol/water mixtures: Experiment and molecular dynamics simulations



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ABSTRACT

The dielectric constant of pure 1-propanol, as well as of its mixtures with water, has been determined experimentally, as a function of temperature and composition. In parallel, molecular dynamics simulations, using united atom (UA) and all atom (AA) model potentials for the alcohol, have been performed, in order to calculate the same quantity for the same mixtures and at identical temperatures. Two water models were used, SPC/E and TIP4P/ε. The calculations were able to capture the trends of changes for the dielectric constant with temperature and composition. It has been shown that as water concentration grows, the actual values of calculated static dielectric constant get somewhat farther from the measured data when the SPCE water model is applied. Targeted modifications of the UA interatomic potentials of the alcohol, in combination with the TIP4P/ε water model, provide quantitative reproduction of the measured dielectric constant values over the entire composition and temperature ranges.

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1. Introduction

1-Propanol, $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—OH}$, is one of the most important members of the family of aliphatic alcohols, and one of the few 'lower alcohols' that (at room temperature) are miscible with water in the entire composition region (the others being methanol, ethanol, 2-propanol and *t*-butanol). Although related publications of general interest are available for alcohols and alcohol water mixtures [1–6], to our best knowledge, a systematic study of the temperature dependent static dielectric constant, ϵ , is missing for this particular alcohol and its mixtures with water. This is the reason why we have set out to determine this quantity experimentally, as a function of composition (i.e., of 1-propanol concentration). In order to interpret the measurements, molecular dynamics (MD) computer simulations [7] have been performed. The main question was whether the simulations were able to get close enough to the experimental values, i.e. if the interatomic potential models applied may be called as 'adequate'.

2. Experimental

Apart from the pure alcohol, mixtures with water were prepared, so that the concentration of 1-propanol was 10, 25, 50, 75 and 100 wt%. All materials were analytical grade and supplied by Reanal Ltd. (Hungary).

Water used for the measurements was ultrapure, deionized by a TKA GenPure UV water purification system. The components were measured by mass with an accuracy of ± 0.1 mg.

For the measurement of the dielectric permittivity we used an Agilent 16452A liquid test fixture connected to a precision LCR meter (Agilent 4284A). The fixture has a two electrode parallel plate geometry, where the electrode gap is adjustable with spacer rings. The measurements were carried out with a 0.3 mm electrode gap. The fixture was immersed into the inner bath of a Huber K6-cc-NR thermostat filled with ethylene glycol, and the temperature of the bath was controlled with an accuracy of 0.01 °C. The permittivity measurements have an accuracy of 0.5%. Further technical details can be found in Ref. [8].

The measurements were carried out between temperatures of +25.0 and –25.0 °C (from 248 to 298 K) with 5 degree steps. The capacitance of the cell was measured by the LCR meter at each temperature point at a frequency of 100 kHz three times and the obtained values were averaged. Using the measured capacitance values (C_p) the ϵ' relative permittivity of the mixtures was calculated by the following equation:

$$\epsilon' = X_{\text{cell}} \cdot \frac{C_p}{\epsilon_0},$$

where X_{cell} is the cell constant at the specified temperature and ϵ_0 is the dielectric permittivity of vacuum.

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Table 1
Properties resulting from the parametrization for the 1-propanol UA force field at T = 298 K.

Optimized parameters	Original model [12]	Parametrized	Experimental
Dielectric constant, ϵ	15.68 (23.14%)	19.98 (2.06%)	20.40 [This work]
Surface tension, γ (mN/m ²)	42.04 (9.63%)	46.59 (0.15%)	46.52 [16]
Density, ρ (Kg/m ³)	783.95 (2.03%)	797.39 (0.35%)	800.21 [17]

Since the value of cell constant depends on temperature, it was not calculated from the geometric properties of the cell but was validated by a well-known dielectric material (water) at each temperature point.

Experimental values of the static dielectric constant are reported in Figs. 3–7. Note that all the mixtures started to freeze above 248 K, so that experimental data (black markers) are reported only for the liquid region.

3. Molecular dynamics simulations

MD computer simulations have been performed by using the GROMACS package (version 4.5) [9]. For water, the rigid, non-polarizable SPC/E potential model of Berendsen et al. [10] and the rigid, non-polarizable TIP4P/ε potential model developed by Fuentes-Azcatl et al. [11] have been chosen. For 1-propanol molecules two different models were tested: the first one was the ‘united atom’ (UA) version of the ‘primary alcohols and alcohol-alkane mixture’ (NERD) [12] potential set. In this framework, the methylene (—CH₂—) and methyl (CH₃—) groups of the 1-propanol molecules are treated as single entities (‘super-atoms’), whereas the oxygen and hydrogen atoms of the alcohol-hydroxyl (—OH) group remain distinct. The main advantage of this type of potential functions is that for a molecule of size of 1-propanol, significant speed-up of the simulations may be achieved: instead of the 12 atomic sites, only 5 interaction sites are taken into account. The second model, called all-atom (AA) [13], considered all explicit sites in the 1-propanol molecule, i.e. the complete structure of the molecule was used in the simulation. It is worth mentioning that the TIP4P/ε water model was originally constructed in order to reproduce better the experimental dielectric constant of water.

MD simulations were conducted in the NPT ensemble for several temperatures (in accordance with the experimental points) with pressure P = 1 bar, using the Berendsen thermostat and Berendsen barostat [14] with temperature and pressure relaxation time constants of $\tau_T = 0.1$ ps and $\tau_P = 2.0$ ps, respectively. Periodic boundary conditions were considered in all directions. The time-step was 2 fs and a cutoff radius of 1.5 nm for the dispersion part of the potentials was also employed. To obtain the dielectric constant of pure 1-propanol and pure water, we used 1500 and 3001 molecules, respectively. In the case of the mixtures, 3101 (100 molecules of 1-propanol and 3001 water molecules), 2750 (250 molecules of 1-propanol and 2500 water molecules), 2600 (600 molecules of 1-propanol and 2000 water molecules) and 2849 (1349 1-propanol and 1500 water molecules) were used for the mixtures containing 10, 25, 50 and 75 wt% of alcohol, respectively.

In order to provide a more adequate reproduction of the measured values of the static dielectric constant, ϵ , the NERD-UA potential

parameters for 1-propanol molecules [12] have been further optimized: the partial charges and Lennard-Jones (L-J) parameters were parametrized in a similar fashion as described very recently by Salas et al. [15]. The simulations to obtain the best parametrized parameters were conducted at a temperature of T = 298 K. The essence of the optimization method is as follows:

- 1) All partial charges were scaled to obtain the experimental ϵ of pure 1-propanol.
- 2) With the new charges, all the L-J energy values (potential well depths) were scaled to determine the surface tension.
- 3) With the new charges and new L-J well depths, all the L-J ‘diameter’ values were scaled to obtain the density.

Re-parametrization cycles were performed when it was necessary for obtaining less than 5% deviations from the corresponding experimental values. The values of dielectric constant, ϵ , surface tension, γ and density, ρ for the original and parametrized 1-propanol UA force field are summarized in Table 1 (the values in parentheses are the errors in percentages). Values for the partial charges and the L-J parameters are given in Table 2 for the original and parametrized UA force fields. The L-J ‘diameter’ parameter was not modified since the original set lead to densities within 5% of the experimental values. Note also that the modified values are still rather close to the original ones, i.e., no drastic changes were needed; re-parametrization may be considered as a ‘refinement’ only to the potential model suggested at the first place [12].

As a further characterization of the modified potential parameters (see Table 2), liquid densities (Fig. 1) and self diffusion constants of the propanol molecules (Fig. 2) have been calculated for the mixtures, too, using both the original and the re-parametrized potentials. Densities in Fig. 1 are also compared to available experimental data [17] (unfortunately, for the self diffusion coefficients of the alcohol species, no experimental values could be found). The overall agreement with experiment is rather satisfactory. Differences originating from the modifications are noticeable (of the order of ca. 2 to 3%) for the pure alcohol; on the other hand, for the mixtures the changes are negligible.

The effects of altering the potential parameters are much more apparent when the self diffusion constant of the 1-propanol molecules is considered (see Fig. 2). Essentially, molecules appear to become less mobile due to the new potential; whether this is appropriate may only be decided via comparison to experimental data (whenever they are available). As expected, the influence of the modified parameters decreases rapidly with the decreasing alcohol concentration.

The OPLS-AA simulations were conducted without any re-parametrization, i.e. partial charges and L-J parameters are taken as in reference [13].

Experimental and simulated values for the static dielectric constant, using both the original and optimized partial charges and L-J parameters for 1-propanol, are compared in Figs. 1 to 5. MD simulations were performed at temperature intervals of 10 K; that is, for one composition, 6 calculations spanned the entire temperature region. The static dielectric constant values have been determined from MD trajectories extending to as long as 200 ns, using tools provided by the GROMACS software package [9].

Table 2
Original and parametrized values for partial charges and L-J parameters.

1-Propanol sites	Original model [12] partial charge (e)	Parametrized partial charge (e)	Original model [12] ε L-J parameter (kJ/mol)	Parametrized ε L-J parameter (kJ/mol)
H(—OH)	0.42	0.4494	0.0324	0.033696
O(—OH)	−0.71	−0.7597	0.8979	0.933816
C(CH ₂ —OH)	0.29	0.3103	0.3808	0.396032
C(CH ₂ —R)	0	0	0.3808	0.396032
C(CH ₃ —R)	0	0	0.8647	0.899299

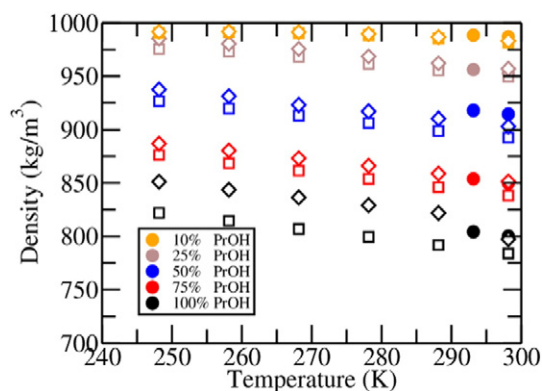


Fig. 1. Densities of different mixtures of 1-ProOH and water. Square symbols are from the original potential model, whereas diamonds denote results from the re-parametrized model for 1-propanol. The solid symbols are the experimental values [17].

4. Results and discussions

In the figures plots of the experimental values over the temperature range of 248 to 298 K and data for SPCE and TIP4P/ε models are shown for different compositions. Both water force fields are used to calculate the dielectric constant, keeping in mind that TIP4P/ε was built to reproduce the dielectric constant of liquid water at room temperature [11].

Fig. 3 concerns pure 1-propanol, for which values of ε are reported over the entire temperature range (248 to 298 K).

The experimentally observed temperature dependence is strictly monotonous and linear, whereas simulation results tend to scatter somewhat. It is obvious that the optimized NERD-UA parameters for the alcohol result in a very close match with experiment, so much that only below 270 K can any difference be spotted between measured and simulated values. Obviously, the optimization of partial charges, that took place at 298 K, is extremely successful. It is interesting to note that the ‘all atom’ type alcohol potential [13] provides the least satisfactory results; still, the trend with temperature could be captured.

In Fig. 4, similar plots for the composition of 75 wt% 1-propanol are provided (corresponding to ca. 47 M% of the alcohol). As mentioned earlier, at the lowest temperature, the mixture started to freeze and therefore

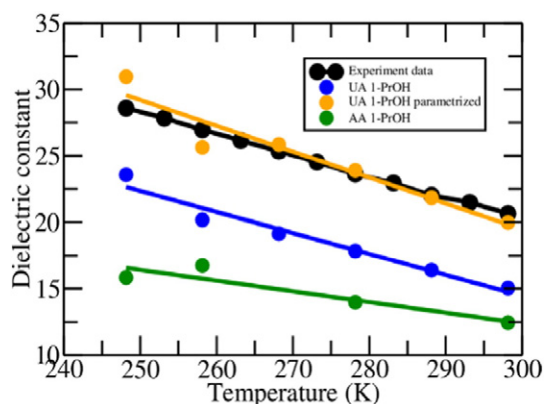


Fig. 3. Dielectric constant of pure 1-propanol calculated for two (+1 optimized) potential models: Khare et al. [12] UA force field (blue dots), the parametrized UA model (orange dots) and the AA force field of Jørgensen et al. [13]. Experimental data are marked by black dots. (The lines in the figure are only guides to the eye.)

the lower boundary of the experimental temperature range was 253 K. Between 253 and 298 K, experimental values of ε decrease, again, linearly and monotonously; this is approximately true for the MD results, too. The optimized 1-propanol potential with TIP4P/ε water provided the closest match to measured data; in fact, the reproduction is perfect. Non-parametrized UA and AA potentials for the alcohol, in combination with TIP4P/ε water, predict a faster decrease of the value of the dielectric constant than measured experimentally. Application of SPC/E water seems to be unfavorable if the actual values are needed, although the slope (with T) is in agreement with the measurement.

Fig. 5 concerns the 50 wt% 1-propanol containing mixture (corresponding roughly to about 23 M%), for which the experimentally reachable temperature range is, again, between 253 and 298 K. The overall behavior of the four curves is similar to what we have seen for the mixtures with higher alcohol contents (75 wt%). The SPC/E water model provides the least favorable agreement with measurement: only the linearly decreasing trend is reproduced. The TIP4P/ε model, on the other hand, matches better the experimental values. The optimized 1-

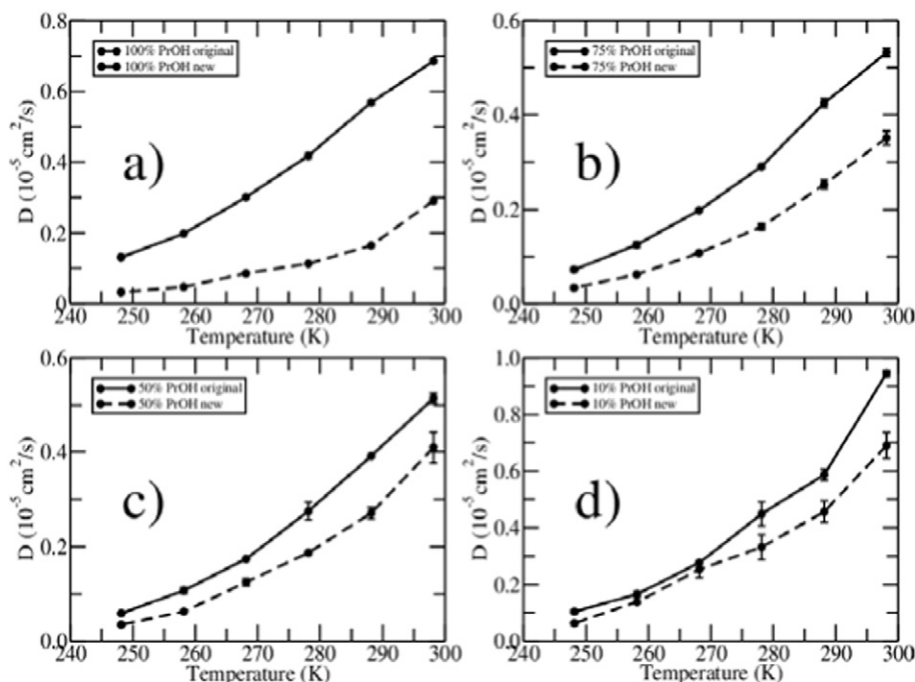


Fig. 2. 1-Propanol self diffusion coefficients for alcohol concentrations of a) 100%; b) 75%; c) 50% and d) 10%.

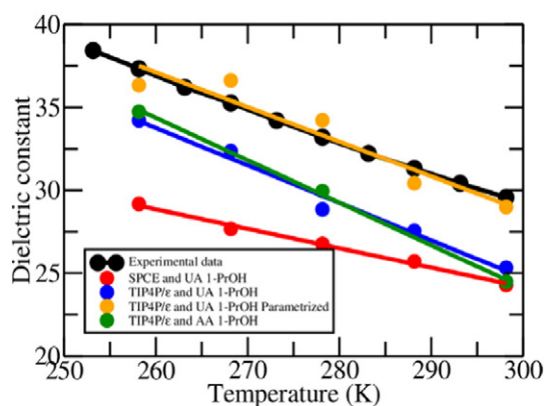


Fig. 4. Dielectric constant values for the 75 wt% 1-propanol mixture with SPCE/E water (red dots), with TIP4P/ε water (blue dots), for the parametrized UA 1-propanol with TIP4P/ε water (orange dots), as well as for the original all-atom potential with TIP4P/ε water (green dots). Experimental data points are shown as black dots.

propanol UA model is significantly more successful than the original one. Above 280 K, the optimized 1-propanol potential with TIP4P/ε provided the closest match to measured data, whereas below that temperature, the AA potential for the alcohol proved to be ideal.

It is instructive to notice that this is the only composition (among the ones considered in this work) where the re-parametrized UA potential set for 1-propanol does not yield exact reproduction of the experimental static dielectric constant. At the same time, the non-optimized AA potential leads to an agreement whose quality is comparable with that obtained for the optimized UA model. A probable explanation may be that this is the concentration region where mixing properties of 1-propanol and water are highly non-ideal, so that the more refined all-atom description of the alcohol molecules is necessary. A more detailed investigation, focusing on compositions with 10 to 30 M% 1-propanol, is therefore planned, involving properties other than the dielectric ones (e.g., structure).

Static dielectric constant values for the mixture with 25 wt% of 1-propanol (corresponding to about 9 M%) are reported in Fig. 6. The tendency observed for the 50 wt% mixture has matured for this solution: the TIP4P/ε model with the optimized 1-propanol UA model yields perfect fit to the experimental points, whereas the application of the all-

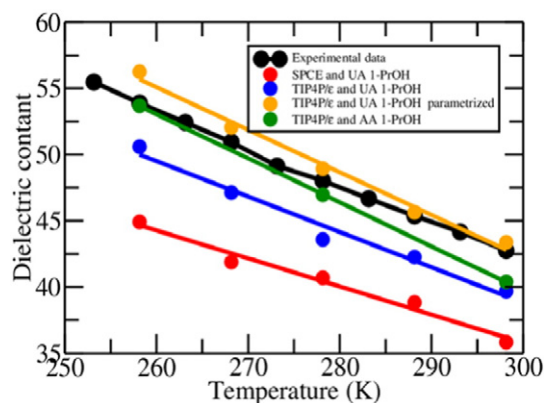


Fig. 5. Dielectric constant for the 50 wt% 1-propanol mixture with SPCE water (red dots), TIP4P/ε water (blue dots) and for the 1-propanol parametrized UA with TIP4P/ε water (orange dots). The all atom representation of 1-propanol, in combination with TIP4P/ε water, appears as green dots. Experimental data are shown as black dots.

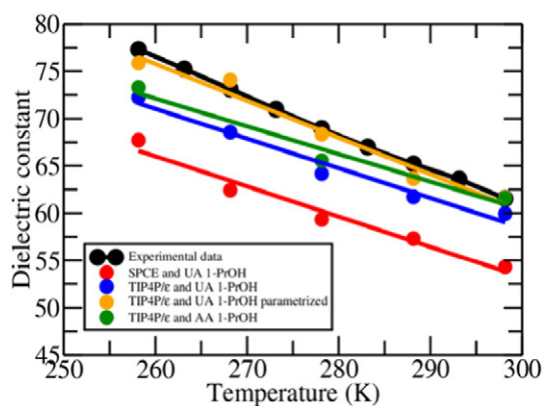


Fig. 6. Dielectric constant for the 25 wt% 1-propanol mixture with SPCE water (red dots), TIP4P/ε water (blue dots) and for the 1-propanol parametrized UA with TIP4P/ε (orange dots). The all atom representation of 1-propanol, in combination with TIP4P/ε water, appears as green dots. Experimental data are shown as black dots.

atom alcohol model is second best over the entire temperature region (between 258 and 298 K) considered.

A similar behavior is seen in Fig. 7 (10 wt%, corresponding to about 3 M%): the best match, again, belongs to the re-parametrized UA 1-propanol + TIP4P/ε mixture. It is also notable that for the mixture with the lowest alcohol content the AA potential of 1-propanol provides equally good results as the parametrized UA one, just as it occurred for the 50 wt% mixture. Here, however, the reason is well understandable: the dielectric constant of the mixture is determined mainly by water molecules, and (as it has been pointed out above) TIP4P/ε was invented to reproduce the dielectric constant of liquid water. For the same reason, naturally, the non-optimized UA potential, combined with the same water representation, also provides an equally good agreement with experiment. When SPCE/E water is used, on the other hand, only the trend of change with temperature could be captured.

5. Summary and conclusions

A fairly extensive series of experiments has been accompanied by detailed molecular dynamics calculations, aiming at the determination of the static dielectric constant of 1-propanol/water mixtures, as a function of composition and temperature. The measured data constitute the most extensive set of available experimental data for the mixtures considered.

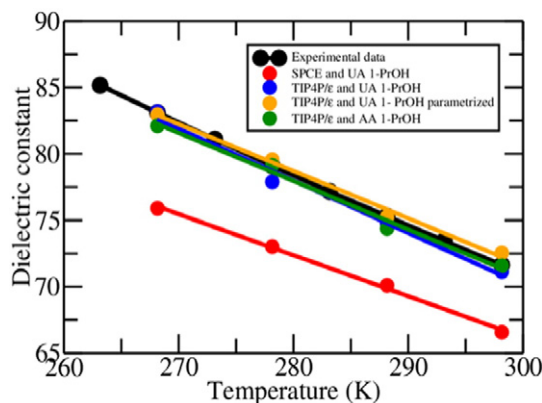


Fig. 7. Dielectric constant for the 10 wt% 1-propanol mixture with SPCE water (red dots), TIP4P/ε (blue dots) and the 1-propanol parametrized with TIP4P/ε (orange dots). The all atom representation of 1-propanol, in combination with TIP4P/ε water, appears as green dots. Experimental data are shown as black dots.

The optimization procedure [15] for the united atom type alcohol potentials [12] has resulted in a rather close (to our best knowledge, unprecedented) match between measurement and simulation at most alcohol concentrations considered in this work. At high alcohol concentrations, down to at least 75 wt% (ca. 50 M%), the parametrized 1-propanol model seems to influence the behavior of the dielectric constant strongly over the temperature region investigated. As the molar ratio of 1-propanol decreases to about 10 wt%, the influence of the improved alcohol potential parameters becomes marginal since the dielectric constant is mainly driven by the actual water potential applied. The only composition region that needs further attention is that of around 50 wt% (ca. 25 M%) where visible deviations were detected between simulation and experiment. For this composition region, optimization of the all atom type potential parameters may prove to be necessary.

As a final note, it is fair to mention that even the un-optimized NERD-UA potential provides acceptable reproduction of the behavior of the dielectric constant of 1-propanol/water mixtures, particularly as the temperature dependence is concerned. The use of TIP4P/ ϵ water model [11], estimates the experimental values better than the SPC/E potential [10]. SPC/E, without any optimization, seems to capture the slope of decrease with temperature for each mixture.

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