Molecular Simulation Study of Dielectric Constants of Pure Fluids and Mixtures

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Abstract

The static dielectric constant of fluids is studied with molecular models from the literature. The employed molecular models were developed using only vapor-liquid equilibrium data. No information on the dielectric properties was used, so that the simulation results are predictions. A wide range of different fluids, from slightly to strongly polar, is investigated. Most of the studied models underestimate the dielectric constant, which can be explained by the way the models were developed. For the pure fluids dimethyl ether and acetone, the temperature and pressure dependence of the dielectric constant is also studied. A good agreement with experimental data is found. Additionally, binary mixtures are investigated. Thereby, the validity of several mixing rules for the dielectric constant is assessed.

Keywords: dielectric constant, relative permittivity, dipolar molecules,

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1. Introduction

The dielectric constant ε , also known as the relative permittivity, characterizes how a certain material weakens the electric field compared to vacuum. Obviously, it is an important property in electrical engineering. However, the dielectric constant also plays an important role in several process engineering applications, especially when electrolytes are present. As the dielectric constant directly affects the coulomb potential, it is a key input property for any thermodynamic model for electrolyte solutions, e.g. for G^E -models or equations of state.

Due to its utmost importance as a solvent, the dielectric constant of water has been studied in great detail. Lots of experimental data points are available over a wide range of conditions [1]. However, for many other fluids, only few measurements of the dielectric constant have been reported in the literature. In most cases, only state points at or near ambient conditions for temperature and pressure have been studied. While some reports have been made regarding the temperature dependence of the dielectric constant, its pressure dependence has only been studied for few fluids. For many industrially relevant fluids, no experimental data are available at all.

19 As a consequence, also few data are available for the dielectric properties of
20 mixtures. Hence, several different mixing rules for obtaining the dielectric
21 constants of mixtures from the pure fluid dielectric constants have been pro-
22 posed [2–4], but their range of applicability remains unclear. Thus, a predic-
23 tive method for obtaining dielectric constants, or at least their temperature,
24 pressure and composition dependence (in case of mixtures), is highly desir-
25 able.

26 Molecular modeling and simulation is a versatile tool for predicting proper-
27 ties of fluids. Molecular models trained to only few experimental data usually
28 allow for making reliable predictions, e.g. at conditions at which experiments
29 are cumbersome or unfeasible. In the light of the Onsager-Kirkwood-Fröhlich
30 theory [5–7], the dielectric constant of a fluid depends on the mutual orien-
31 tation of the molecular dipole moments. Thus, on the molecular level, the
32 dielectric constant is a structure-related property and is therefore directly
33 accessible in molecular simulations for a given molecular model. It is usually
34 obtained from sampling Kirkwood’s formula [6]; however, it has been shown
35 recently that a mapped averaging technique is more accurate at low densities
36 [8].

37 At first, molecular simulations of dielectric constants were carried out in the

38 framework of developing long-range corrections for electrostatic interactions
39 such as the reaction field method, e.g. by Neumann and co-workers [9, 10].
40 Later, molecular simulation results were used to assess perturbation theories
41 for the dielectric [11–15] and to study the dielectric virial series [16, 17]. In
42 most of these studies, Stockmayer or Stockmayer-like fluids, i.e. a Lennard-
43 Jones (LJ) site with a superimposed point dipole, were considered.

44 Regarding molecular models of real fluids, again water has been studied in
45 detail [18–20]. In addition, also some systematic benchmarks of transferable
46 force fields covering wide ranges of different fluids are available. Coleman et
47 al. [21] presented an evaluation of the OPLS/AA and GAFF force fields and
48 found that most of the models underestimate the dielectric constant. Núñez-
49 Rojas et al. [22] carried out a similar study on the TraPPE/UA force field and
50 also found that the dielectric constant is typically underestimated, with an
51 average deviation of about 37%. Zangi [23] investigated the OPLS/AA force
52 field for alcohols, and found an average underestimation of the dielectric con-
53 stant of about 33%. Including experimental data on the dielectric constant
54 in the model parametrization has been suggested only recently [24, 25].

55 As all previous systematic benchmarks dealt with transferable force fields, an
56 additional study of essentially independent molecular models for real fluids

57 of different polarity is worthwhile. That study is carried out in the present
58 work using the models available in the MolMod database [26]. To this end,
59 molecular models for a wide range of industrially-relevant fluids are taken
60 from the literature and the dielectric constant of the fluid is predicted. The
61 investigated models were developed based on a fit to the experimental vapor-
62 liquid equilibrium data (VLE) of the fluid. A comparison to experimental
63 data is carried out to assess how reliable the obtained predictions for the
64 dielectric constant are. In a similar manner, three binary mixtures are con-
65 sidered. This allows to study the physical basis behind mixing rules that
66 have been proposed for the dielectric constant of mixtures.

67 The paper is structured as follows: In Section 2, the employed molecular
68 models and simulation methods as well as the mixing rules for the dielectric
69 constant are introduced. The results are presented and discussed in Section
70 3, before summarizing the main conclusions in Section 4.

71 **2. Methods**

72 *2.1. Molecular Models*

73 The MolMod database [26] was searched for molecular models containing
74 either point dipole moments or a partial charge distribution resulting in a

75 permanent dipole moment of the entire molecule. 43 models were found.
76 However, for only 25 of these models at least one experimental data point for
77 the dielectric constant was found in the Dortmund Data Bank [27]. Thus,
78 only those 25 models are considered in the present work. Nevertheless, still a
79 variety of fluids, ranging from slightly to strongly polar, is investigated here.
80 These 25 molecular models were optimized in previous work of our group
81 by a fit to the pure component VLE, hence the dielectric constants studied
82 in the present work are strict predictions obtained from these models. The
83 models are rigid and follow the united-atom approach. The models comprise
84 Lennard-Jones (LJ) sites, point charges, point dipole moments, and point
85 quadrupole moments, so that the total potential energy U in a system of N
86 particles is given by:

$$\begin{aligned}
U &= U_{\text{LJ}} + U_{qq} + U_{q\mu} + U_{qQ} + U_{\mu\mu} + U_{\mu Q} + U_{QQ} \\
&= \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left\{ \sum_{a=1}^{n_i^{\text{LJ}}} \sum_{b=1}^{n_j^{\text{LJ}}} 4\epsilon_{ijab} \left[\left(\frac{\sigma_{ijab}}{r_{ijab}} \right)^{12} - \left(\frac{\sigma_{ijab}}{r_{ijab}} \right)^6 \right] \right. \\
&\quad + \sum_{c=1}^{n_i^e} \sum_{d=1}^{n_j^e} \frac{1}{4\pi\epsilon_0} \left[\frac{q_{ic}q_{jd}}{r_{ijcd}} + \frac{q_{ic}\mu_{jd} + q_{jd}\mu_{ic}}{r_{ijcd}^2} f_1(\omega_i, \omega_j) \right. \\
&\quad + \frac{q_{ic}Q_{jd} + q_{jd}Q_{ic}}{r_{ijcd}^3} f_2(\omega_i, \omega_j) + \frac{\mu_{ic}\mu_{jd}}{r_{ijcd}^3} f_3(\omega_i, \omega_j) \\
&\quad \left. \left. + \frac{\mu_{ic}Q_{jd} + \mu_{jd}Q_{ic}}{r_{ijcd}^4} f_4(\omega_i, \omega_j) + \frac{Q_{ic}Q_{jd}}{r_{ijcd}^5} f_5(\omega_i, \omega_j) \right] \right\} \quad (1)
\end{aligned}$$

87 Here, the indices a, b, c , and d refer to model interaction sites and i and j
 88 refer to molecules, ϵ_0 is the vacuum permittivity, ϵ_{ijab} and σ_{ijab} are the LJ
 89 energy and size parameters, r_{ijab} and r_{ijcd} are site-site distances, q_{ic} and q_{jd}
 90 are the magnitudes of the point charges, μ_{ic} and μ_{jd} are the magnitudes of
 91 the point dipoles, Q_{ic} and Q_{jd} are the magnitudes of the point quadrupole
 92 moments, and the f_k are functions that depend only on the angles ω_i and ω_j
 93 that describe the mutual orientation of the molecules i and j .

94 2.2. Molecular Simulation

95 The dielectric constant ϵ of pure fluids and mixtures is determined with
 96 molecular dynamics (MD) simulations by sampling Kirkwood's formula [6]
 97 in the NpT ensemble:

$$\varepsilon = 1 + \frac{\langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2}{3\varepsilon_0 k_B T \langle V \rangle} \quad (2)$$

Herein, $\mathbf{M}$ is the total dipole moment of the simulation box, which is obtained by summing up the individual molecular dipole moments $\boldsymbol{\mu}_i$:

$$\mathbf{M} = \sum_i \boldsymbol{\mu}_i$$

The other symbols in Eq. (2) have their usual meaning: k_B is Boltzmann's constant, T is the temperature, and $\langle V \rangle$ is the NpT ensemble average of the volume. As only isotropic, non-ferroelectric fluids are studied in the present work, the term $\langle \mathbf{M} \rangle^2$ in Eq. (2) vanishes.

All MD simulations of the present work were carried out using an extended version of the program *ms2* [28]. Further simulation details are documented in the Appendix.

2.3. Mixing Rules for the Dielectric Constant

Looyenga [3] presented a simple empirical mixing rule that directly yields the dielectric constant of the mixture:

$$\varepsilon = \left(\sum_k \phi_k \varepsilon_k^{1/3} \right)^3 \quad (3)$$

110 Here and in all following equations, the sum runs over all components k in
 111 the mixture, ε_k is the dielectric constant of pure k , and ϕ_j is the volume
 112 fraction of j in the mixture, defined as

$$\phi_j = \frac{x_j v_j}{\sum_k x_k v_k}, \quad (4)$$

113 where v_k is the molar volume of pure k . Oster [2] and Wang and Anderko
 114 [4] developed mixing rules based on the polarisation of the mixture. In both
 115 cases, first the polarisation P_k of all pure components is evaluated as

$$P_k = \frac{(\varepsilon_k - 1)(2\varepsilon_k + 1)}{9\varepsilon_k}. \quad (5)$$

116 Then, the polarisation of the mixture P is computed. In the case of Oster's
 117 rule it is given by

$$P = \rho \sum_k x_k v_k P_k, \quad (6)$$

118 where ρ is the density of the mixture. In the case of Wang and Anderko's
 119 rule, the polarisation of the mixture is computed as

$$P = \sum_k \phi_k P_k. \quad (7)$$

120 The only difference between Eqs. (6) and (7) is that the rule by Wang and
 121 Anderko neglects the excess volume and therefore relies solely on pure com-
 122 ponent data. Oster’s rule considers the excess volume, meaning that e.g. the
 123 density ρ of the mixture must be known. Finally, for both rules the di-
 124 electric constant of the mixture is evaluated by solving the equation for the
 125 polarisation of the mixture

$$P = \frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} \quad (8)$$

126 for ε .

127 2.4. Objectives

128 In the present work, the dielectric constants of pure fluids and mixtures
 129 are obtained from molecular simulations. For pure fluids, for each of the
 130 studied molecular models, the relative deviation

$$\Delta\varepsilon = \frac{\varepsilon^{\text{Sim}} - \varepsilon^{\text{Exp}}}{\varepsilon^{\text{Exp}}} \quad (9)$$

131 between the molecular simulation prediction of the dielectric constant ε^{Sim}
 132 and the experimental data from the literature ε^{Exp} is assessed. For each
 133 fluid, one statepoint close to ambient temperature and pressure is consid-

134 ered, as experimental data are available only at such conditions for many of
135 the studied fluids. All statepoints correspond to liquids. For several fluids,
136 the pressure was not reported with the experimental data. In these cases, a
137 pressure somewhat larger than the vapor pressure of the fluid at the inves-
138 tigated temperature was chosen for the simulations. For two fluids, namely
139 dimethyl ether and acetone, experimental data are available for a wide range
140 of temperatures and pressures, so that these two fluids are studied in more
141 detail.

142 Also binary mixtures are considered in the present work. All three binary
143 systems comprising the components water, methanol and acetone are inves-
144 tigated. This choice is again mainly motivated by the availability of exper-
145 imental data. Moreover, these systems are interesting as highly non-ideal
146 dielectric mixing effects are observed. As before, the employed molecular
147 models are taken from the literature, namely SPC/E for water [29], the
148 methanol model by Schnabel et al. [30], and the acetone model by Wind-
149 mann et al. [31]. The interactions between unlike LJ sites are described by
150 the Lorentz-Berthelot combining rules

$$\sigma_{ijab} = \frac{\sigma_{iiaa} + \sigma_{jjbb}}{2}, \quad (10)$$

$$\epsilon_{ijab} = \sqrt{\epsilon_{iiaa}\epsilon_{jjbb}}. \quad (11)$$

151 In addition to the comparison of molecular simulation predictions to exper-
 152 imental data, also the mixing rules introduced in the previous section are
 153 assessed in the present work.

154 3. Results and Discussion

155 3.1. *Pure Fluids*

156 The results of the systematic study of 25 molecular models are com-
 157 piled in Table 1 and are shown as a histogram of deviations in Figure 1.

158 [Table 1 about here.]

159

160 [Figure 1 about here.]

161 The histogram shows that the molecular models typically underestimate the
 162 dielectric constant. The majority of the models underestimate the dielectric
 163 constant by 25 to 75 %. The absolute average deviation is about 50 %. One
 164 likely reason is the model parametrization: The models were trained to VLE

165 data only. Typically, in that adjustment the magnitude of the point dipole
166 or the charge distribution, respectively, are used as adjustable parameters.
167 Training the model to VLE data means that a trade-off between liquid and
168 gas phase properties must be made. Consequently, the magnitude of the
169 resulting dipole moment of the molecule is somewhat lower than might be
170 expected for a liquid state. As the dipole moment enters quadratically in
171 the Kirkwood equation (2), a slightly too low dipole moment automatically
172 results in a large underestimation of the dielectric constant. This hypothesis
173 is supported by the results obtained for acetonitrile. For this fluid, two dif-
174 ferent molecular models are available. Still, both were trained to the same
175 VLE data, and their deviation of the dielectric constant is similar.

176 The present simulation results also allow for a discussion if an assignment of
177 partial charges or the use of a point dipole is more appropriate for describ-
178 ing the dielectric constant. From the 25 models, 17 employ a point dipole,
179 and 8 employ a distribution of partial charges (cf. last column of Table 1).
180 When comparing their deviations to experimental data, however, no system-
181 atic trend is observed, i.e. the models using partial charges do not outperform
182 the ones using point dipole moments (or vice versa). Hence, the general choice
183 whether to use a point dipole or a partial charge distribution does not affect

184 the ability of the molecular model to predict the dielectric constant.
185 Another likely reason for the underestimation of the dielectric constant is the
186 neglect of polarizability, which is common to most molecular models available
187 to date. This hypothesis is supported by the fact that several transferable
188 force fields also underestimate the dielectric constant [21–23].

189 The systematic study shows that molecular models trained to VLE data can
190 usually not be used for accurate quantitative predictions of dielectric con-
191 stants. However, as has already been demonstrated for water [32], dedicated
192 molecular models can of course be adjusted with respect to the dielectric
193 constant. If adjusted to data at only one statepoint, these models are po-
194 tentially useful for predicting e.g. the temperature and pressure dependence
195 of the dielectric constant. To test this hypothesis, fortunately, for two of
196 the fluids studied here experimental data are available over a wide range of
197 temperatures and pressures. These fluids are dimethyl ether and acetone. At
198 the statepoint investigated thus far the deviations for these two fluids were
199 26 % and only 1 %, respectively. This should be kept in mind when looking
200 at the predictions for other conditions.

201 Figure 2 shows the dielectric constant of dimethyl ether for several isotherms
202 as a function of the pressure. The numerical simulation results are docu-

203 mented in Table 2.

204 [Figure 2 about here.]

205 [Table 2 about here.]

206 The molecular model for dimethyl ether overestimates the dielectric constant
207 at all temperatures, but the deviations decrease with increasing temperature.
208 Thus, the influence of temperature on the dielectric constant is underes-
209 timated by the model. However, the pressure dependence is predicted in
210 excellent agreement with the experimental data as the deviations are inde-
211 pendent of the pressure.

212 Figure 3 shows one isobar and one isotherm of the dielectric constant of
213 acetone. The numerical simulation results are documented in Table 3.

214 [Figure 3 about here.]

215 [Table 3 about here.]

216 The molecular model of acetone, which already showed excellent agreement
217 with the experimental data at the single state point considered above, per-
218 forms excellently for both the temperature and the pressure dependence of
219 the dielectric constant. The model yields reliable predictions even at very

high pressures, where experimental investigations are difficult. Thus, in this case molecular modeling and simulation is an excellent tool for obtaining thermodynamic properties at extreme conditions.

Altogether, the results of the present study suggest that a molecular model that captures dielectric constant at one statepoint accurately can also be used to describe the pressure and temperature dependence of the dielectric constant accurately.

3.2. Mixtures

Figure 4 shows the dielectric constants of the three binary mixtures of the components water, methanol and acetone as a function of the composition. In addition to the experimental and molecular simulation data, also values obtained from the mixing rules introduced in Section 2.4 are included. To stress the deviation from ‘ideal’ dielectric mixing behavior, also the excess dielectric constant ε^E , defined as

$$\varepsilon^E = \varepsilon - \sum_k x_k \varepsilon_k \quad (12)$$

is shown. The numerical simulation results are compiled in Table 4.

[Figure 4 about here.]

[Table 4 about here.]

The molecular simulation predictions for the dielectric constants in the studied binary mixtures are not perfect. However, this is mainly due to the inaccurate description of the dielectric constants of pure water and methanol: The excess dielectric constants are in good agreement with the experimental data. This is a remarkable finding as the dielectric mixing in the investigated systems is highly non-ideal: The excess dielectric constant has a large contribution; it is on the order of 50 % of the total value in the water-acetone system and about 10 % for the other systems. Thus, molecular simulations can serve as a predictive tool to study dielectric constants of mixtures quantitatively if models are available that capture the pure fluids' dielectric constants quantitatively.

As the molecular models intrinsically capture the unlike electrostatics in a physical way, the obtained simulation results can be used as an excellent benchmark for assessing mixing rules for the dielectric constant. Thus, the simulation results for the pure fluids were used to evaluate the mixing rules by Looyenga, Oster, and Wang and Anderko for all three binary systems. For the evaluation of Oster's rule, additionally the densities of the mixtures are needed, which are, however, readily available from the NpT simulations.

255 For the system water-methanol, the mixing rules by Oster and by Wang and
256 Anderko, which have some physical reasoning, perform much better than
257 the rather empirical correlation by Looyenga. Surprisingly, this is not the
258 case for the water-acetone system, for which Looyenga’s rule is in best agree-
259 ment with the molecular simulation data. For the system methanol-acetone,
260 clearly all three mixing rules fail to describe the dielectric mixing excess that
261 is found in the molecular simulation data. The simulations are able to pre-
262 dict the non-ideality, even though the dielectric constants of the two pure
263 fluids are predicted to be almost equal. For the systems investigated here,
264 this comparison shows that molecular simulation is a much more reliable tool
265 for studying dielectric constants of mixtures than the use of mixing rules.

266 4. Conclusions

267 Dielectric constants of pure fluids and binary mixtures are computed with
268 molecular dynamics simulations. A comprehensive study of molecular mod-
269 els from the literature that were optimized to VLE properties is carried out,
270 considering one statepoint for each fluid. The majority of the investigated
271 molecular models underpredicts the dielectric constant, with an average devi-
272 ation of about 50 %. However, this disagreement with experimental data can

273 be attributed to the model parametrization. When developing a model to
274 describe the entire fluid region, compromises must be made between proper-
275 ties of liquid, gaseous, and supercritical states. The resulting dipole moments
276 are typically somewhat lower than expected for a liquid, which automatically
277 leads to an underestimation of the dielectric constant in the light of Kirk-
278 wood’s theory. Nevertheless, for the two fluids acetone and dimethyl ether,
279 for which more experimental data are available for comparison, a study of
280 other statepoints reveals that the temperature and pressure dependence is
281 predicted in good agreement with the experimental trends. Thus, molecular
282 models can serve as a reliable tool to extrapolate the dielectric behavior to
283 state conditions that are difficult or even impossible to investigate experi-
284 mentally.

285 An application to binary mixtures of water, methanol and acetone shows that
286 molecular models, although they might disagree with experimental data for
287 the dielectric constants of the pure components, predict the excess dielectric
288 constant, i.e. the effect of mixing, well. They are thus reliable predictive
289 tools for obtaining dielectric properties e.g. of mixed solvents in electrolyte
290 systems. Furthermore, although giving the correct trends for some systems,
291 all the investigated empirical mixing rules for the dielectric constant have a

292 less sound physical basis than the molecular models.

293 **Acknowledgments**

294 The present work was conducted under the auspices of the Boltzmann-
295 Zuse Society of Computational Molecular Engineering (BZS) and the simula-
296 tions were carried out on the Regional University Computing Center Kaisers-
297 lautern (RHRK) under the grant TUK-TLMV, the High Performance Com-
298 puting Center Stuttgart (HLRS) under the grant MMHBF2 as well as the
299 Leibniz Supercomputing Centre (LRZ) under the grant (AMSEL)² (pn56mo).
300 I thank Jadran Vrabec, Kai Langenbach and Hans Hasse for fruitful discus-
301 sions.

302 **Appendix A. Simulation Details**

303 In the present work, MD simulations were carried out with the molecular
304 simulation program *ms2* [28]. Equilibration and production took 500,000
305 and 10,000,000 time steps of length 1.2 fs, respectively. The simulations
306 were run with a total of 1000 particles in the NpT ensemble, employing the
307 velocity scaling thermostat, Andersen’s barostat, and a LJ cutoff radius of
308 17.5 Å for the simulations of pure components and 15.0 Å for the simulations

of mixtures. Statistical simulation uncertainties were estimated with the
block average method by Flyvbjerg and Petersen [33]. Long-range corrections
to the LJ interactions were considered by the angle-averaging approach by
Lustig [34]. Electrostatic long-range interactions were calculated using the
reaction field method with conducting boundary conditions, i.e. assuming
an infinite dielectric constant of the continuum outside the reaction field
sphere. This choice has no influence on the simulation result for the dielectric
constant of the fluid under investigation [10]. Additionally, for two models,
namely the SPC/E water model and the methanol model by Schnabel et al.,
the simulations of the dielectric constants at the statepoint investigated in
the main text were repeated using Ewald summation instead. The results
using these two independent methods were in mutual agreement.

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Figure 1: Histogram of deviations $\Delta\epsilon$ between experiment and molecular simulations for the 25 investigated molecular models.

Figure 2: Isotherms of the dielectric constant of dimethyl ether over the pressure. Left: ($\times$) Experimental data [35], ($\circ$) molecular simulation predictions using the model by Eckl et al. [36]. Right: Deviation in the dielectric constant. Dotted lines are guides to the eye.

Figure 3: 10 MPa isobar (left) and 298.15 K isotherm (right) of the dielectric constant of acetone. ($\times$) Experimental data [37, 38], ($\circ$) molecular simulation predictions using the model by Windmann et al. [31]. Dotted lines are guides to the eye.

Figure 4: Dielectric constants (left panels) and excess dielectric constants (right panels) of binary mixtures at 298.15 K and 1 bar. Top row: water-methanol, middle row: water-acetone, bottom row: methanol-acetone. (x) Experimental data [38–40], (o) molecular simulation predictions. Predictions from mixing rules evaluated with the dielectric constants of the pure fluids from simulation: (□) Oster [2], (△) Wang-Anderko [4], (◇) Looyenga [3].

Table 1: Dielectric constant of 25 pure fluids at the indicated statepoints from experiment and molecular simulation. The entries are sorted by ascending deviation $\Delta\epsilon$ between simulation and experiment. The experimental data were retrieved from the Dortmund Data Bank [27]. For the simulation results, statistical uncertainties for the last significant digit are given in parentheses. The last column indicates if the model uses a distribution of partial charges (entry q) or a point dipole moment (entry μ).

Fluid	Model Ref.	T / K	p / MPa	ϵ^{Exp}	Exp. Ref.	ϵ^{Sim}	$\Delta\epsilon$	Model Type
Hydrogen Cyanide	[36]	295.85	1.0	111.000	[41]	31.5(3)	-0.72	μ
Cyclohexanone	[42]	303.15	0.1	17.950	[43]	5.0(1)	-0.72	μ
Formic Acid	[44]	298.15	0.1	51.100	[45]	14.7(4)	-0.71	q
Acetonitrile	[36]	298.15	0.1	35.990	[46]	12.5(2)	-0.65	μ
Acetonitrile	[47]	298.15	0.1	35.990	[46]	13.9(2)	-0.61	μ
Toluene	[48]	298.15	0.1	2.408	[49]	1.109(2)	-0.54	μ
Phosgene	[48]	295.15	1.0	4.368	[50]	2.04(1)	-0.53	μ
Cyclohexanol	[51]	298.00	0.1	16.400	[52]	8.4(4)	-0.49	q
Nitromethane	[36]	298.15	0.1	36.700	[53]	20.8(4)	-0.43	μ
Isobutane	[36]	296.00	1.0	1.727	[54]	1.01(1)	-0.42	μ
Sulfur Dioxide	[36]	296.15	1.0	14.800	[55]	8.91(5)	-0.40	μ
Methanol	[30]	298.15	0.1	32.730	[56]	21.2(7)	-0.35	q
<i>o</i> -Dichlorobenzene	[48]	293.24	0.1	10.177	[57]	7.40(2)	-0.27	μ
Methylamine	[58]	298.15	1.0	9.400	[59]	8.09(6)	-0.14	q
Hydrazine	[60]	298.15	0.1	51.700	[61]	45(2)	-0.13	q
Ethanol	[62]	298.15	0.1	24.350	[63]	21.6(8)	-0.11	q
Acetone	[31]	298.15	0.1	20.740	[38]	21.0(3)	0.01	μ
Chlorobenzene	[48]	298.15	0.1	5.698	[64]	7.0(3)	0.23	μ
Dimethyl Ether	[36]	303.70	6.3	5.340	[35]	6.71(4)	0.26	μ
R227ea ^{a)}	[65]	293.14	1.0	4.097	[66]	5.50(8)	0.34	μ
Dimethyl Sulfide	[36]	296.30	0.1	6.511	[67]	9.7(1)	0.49	μ
Thiophene	[36]	293.15	0.1	2.769	[68]	4.27(3)	0.54	μ
Ammonia	[69]	298.15	2.0	16.030	[70]	24.7(1)	0.54	q
Hydrogen Chloride	[48]	288.15	10.0	4.960	[71]	9.84(3)	0.98	q
Ethylene Oxide	[72]	272.15	0.1	13.900	[73]	35.5(4)	1.55	μ

^{a)} 1,1,1,2,3,3,3-Heptafluoropropane

Table 2: Molecular simulation results for the dielectric constant of dimethyl ether using the model by Eckl et al. [36]. Statistical uncertainties for the last significant digit are given in parentheses.

p / MPa	ε	p / MPa	ε	p / MPa	ε
$T = 303$ K		$T = 323$ K		$T = 343$ K	
6.3	6.73(4)	1.3	5.62(3)	2.6	4.79(2)
12.2	6.84(4)	10.4	5.72(3)	10.2	5.07(2)
20.2	7.04(4)	22.0	6.18(3)	20.2	5.33(3)
27.5	7.18(4)	31.2	6.28(3)	33.2	5.59(3)
$T = 353$ K		$T = 372$ K		$T = 393$ K	
2.2	4.37(2)	3.4	3.68(1)	6.2	3.21(1)
10.2	4.73(2)	10.2	4.07(2)	12.3	3.60(1)
20.0	4.98(2)	20.0	4.36(2)	20.0	3.88(1)
29.8	5.21(3)	29.2	4.60(2)	29.5	4.08(2)

Table 3: Molecular simulation results for the dielectric constant of acetone using the model by Windmann et al. [31]. Statistical uncertainties for the last significant digit are given in parentheses.

$p = 10 \text{ MPa}$		$T = 298.15 \text{ K}$	
T / K	ε	p / MPa	ε
294	21.6(3)	0.1	21.0(3)
355	15.9(2)	50	22.1(3)
398	12.8(1)	100	23.2(4)
440	10.16(8)	150	25.1(4)
474	8.34(6)	200	25.2(5)
		250	24.8(5)
		300	27.3(6)

Table 4: Molecular simulation results for the dielectric constant of binary mixtures of water (W), methanol (MeOH), and Acetone (AC) at 298.15 K and 1 bar. The composition is given as the mole fraction of component 2. Statistical uncertainties for the last significant digit are given in parentheses.

x_2 / mol mol ⁻¹	W(1)-MeOH(2)	W(1)-AC(2)	MeOH(1)-AC(2)
0	70(2)	70(2)	21.2(7)
0.25	55(2)	37.0(8)	20.5(4)
0.5	39(1)	27.4(5)	19.7(3)
0.75	28.2(9)	22.8(3)	20.6(3)
1	21.2(7)	21.0(3)	21.0(3)