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Huib J. Bakker (iD)

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Huib J. Bakker[a] (ID)

AFFILIATIONS

AMOLF, Science Park 104, 1098 XG Amsterdam, The Netherlands

[a]Author to whom correspondence should be addressed: bakker@amolf.nl

ABSTRACT

We present a new effective medium theory for the dielectric response of mixtures of molecules with molecular polarizability and a permanent dipole moment. This model includes the interaction of each local dipole moment with the dipolar reaction fields of neighboring dipolar molecules. This interaction leads to an enhancement of the dielectric response of the mixture and constitutes an alternative method to describe the correlated motion of dipoles in liquids compared to the models of Fröhlich and Kirkwood. The model requires as input parameters the volume fractions of the components contained in the mixture and the dielectric parameters of the pure components. The results of the model are compared with experimental data and with the results of previous effective-medium theories.

INTRODUCTION

The dielectric response of a mixture is not a weighted average of the dielectric responses of its constituting pure components and often shows a nonlinear dependence on the volume fractions of its components. Examples are ice and snow particles in air,[1,2] glass beads and quartz sand in water,[3] micelles in water,[4] and mixtures of organic liquids and water.[5,6] The nonlinear dependence of the dielectric response on the volume fractions of the components is a consequence of the so-called local electric field. Application of an electric field to a medium leads to the polarization of the molecules or particles that together create an additional electric (Lorentz) field at each molecule/particle. Molecules/particles with a high dielectric constant can, thus, mutually amplify each other's dielectric response, which leads to a nonlinear dependence of the overall dielectric response on their volume fraction in case the molecules/particles are embedded in a medium with a lower dielectric constant.

Ideally, the dielectric response of liquids, including liquid mixtures, is described with a microscopic theory that includes all the interactions of the constituting molecules. Such microscopic theories have been developed by Nienhuis and Deutsch,[7] Høye and Stell,[8] and Chandler.[9] In these studies, it was demonstrated that the

dielectric response of a liquid can be expressed as a sum of all the local interactions of the molecules contained in the liquid. Potentially, these theories provide a complete description of the dielectric response of liquids including mixtures, accounting for all dipolar interactions and local structuring effects. However, for practical applications, it is often useful to describe the dielectric response of a mixture in terms of the dielectric properties of the pure constituting components and their volume fractions, using an effective medium approach.

An essential element of all effective medium models is the local electric field E_L that in a medium of dielectric constant ϵ equals $(\epsilon + 2)E/3$, where E is the macroscopic applied electric field. For a system of molecules with polarizability α and no permanent dipole moment, the enhancement of the dielectric response through the local-electric field leads to the well-known Clausius–Mosotti relation between ϵ and α,[10]

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{N\alpha}{3\epsilon_0}, \qquad (1)$$

with N being the number density and ϵ_0 being the vacuum permittivity ($=\sim 8.854 \times 10^{-12}$ C^2 s^2 kg^{-1} m^{-3}). The Clausius–Mosotti relation forms the basis of several effective-medium models for the dielectric response of mixtures, including those of Maxwell–Garnett and

Wagner,[11,12] Bruggeman,[13] Hanai,[14] and Landau–Lifshitz–Looyenga.[15] These models differ in their description of the mixture. The models of Wagner,[11,12] Hanai,[14] and Looyenga[15] consider the mixture as spherical inclusions in a medium with a different dielectric constant than inclusions, whereas Bruggeman described the mixture as a composition of equivalent small spheres with different dielectric constants.[13]

In case the molecules also possess a permanent dipole moment $\mathbf{p}$, the polarization induced by the applied electric field results both from the polarizability α of the molecules and from the rotation of the molecular dipoles in the direction of the field. For liquid water, this latter contribution dominates. Debye proposed that for polar molecules, Eq. (1) can be extended by replacing α with $\alpha + p^2/3kT$.[16] Later, Onsager showed that this approach is not correct because the part of the local electric field $\mathbf{E_L}$ that results from the orientation of the molecular dipoles is not effective in enhancing the dielectric response.[17–19] As a consequence, for mixtures of polar molecules, the local electric field enhancement is expected to be smaller than that predicted by the Debye equation. Nevertheless, the dielectric response of polar liquids is often observed to be substantially larger than one would expect from the number density and individual molecular dipole moments, a result that is also found in molecular dynamics simulations. In these simulations, it is found that the fluctuating dipole moment of large clusters of water molecules is substantially larger than the sum of the uncorrelated dipole moments of the individual water molecules.[20–22]

Kirkwood and Fröhlich accounted for the enhanced dielectric response of polar liquids by considering the interaction between neighboring (water) dipoles. This interaction leads to a correlated motion of the water dipoles in the applied electric field, thereby enhancing the dielectric response.[23,24] This effect can be accounted for by extending the Onsager model with a multiplicative (Kirkwood) factor. For pure liquid water at 300 K, the Kirkwood factor was found to be ~2.7. If the Kirkwood factor is assumed to be the same in aqueous mixtures as in bulk water, the Kirkwood model yields a near-linear dependence of the dielectric response on the water/ice volume fraction, which does not agree with experimental observations.[1–6] These systems are, thus, often described with the approaches of Bruggeman and Wagner that do predict a nonlinear dependence on the water/ice volume fraction, but for an incorrect reason, being that the part of the local electric field resulting from the orientation of the molecular dipoles would be fully effective in enhancing the dielectric response. We, thus, conclude that the existing effective medium theories for the dielectric response of mixture are either not applicable to liquids containing dipolar molecules (Wagner,[11,12] Bruggeman,[13] Hanai,[14] and Looyenga[15]) or not applicable to mixtures (Kirkwood[23,24]). Here, we present an effective medium theory that can be used to describe the dielectric response of liquid mixtures containing polar molecules. We derive a new equation for the dielectric response of mixtures of polar and nonpolar components, and we compare this approach with previous effective-medium models and experimental results.

REACTION-FIELD MODEL

We consider a liquid consisting of molecules k with vacuum dipole moment $\mathbf{p_{k0}}$ and polarizability α_k. Each molecule forms a (mathematical) cavity within the dielectric medium with an effective dielectric constant $\epsilon\epsilon_0$.[17–19] The back reaction of the surrounding medium to the dipole in the cavity creates a reaction field $\mathbf{E_{R,p_{k0}}}$ of the dipole $\mathbf{p_{k0}}$, which is given by (see the supplementary material)

$$\mathbf{E_{R,p_{k0}}} = \frac{2(\epsilon - 1)}{2\epsilon + 1} \frac{\mathbf{p_{k0}}}{4\pi\epsilon_0 a_k^3}, \qquad (2)$$

with a_k being the radius of the cavity. This reaction field of $\mathbf{p_{k0}}$ polarizes the molecule due to its polarizability α_k, which leads to an enhancement of the molecular dipole moment. Onsager derived the following expression for the resulting dipole moment $\mathbf{p_k}$ of the molecule in the cavity (see the supplementary material),

$$\mathbf{p_k} = \frac{(2\epsilon + 1)(n_k^2 + 2)}{6\epsilon + 3n_k^2} \mathbf{p_{k0}}, \qquad (3)$$

with n_k being the refractive index of the molecule in case there would be no dipolar contribution to the dielectric function.

The application of an electric field $\mathbf{E}$ to the above described system results in an electric field $\mathbf{E_C}$ within the cavity of which the magnitude can be calculated from the Laplace equation with the appropriate boundary conditions,[10]

$$\mathbf{E_C} = \frac{3\epsilon}{2\epsilon + 1} \mathbf{E}. \qquad (4)$$

The application of an electric field $\mathbf{E}$ also leads to a change in the reaction field resulting from the electric-field induced change in the dipole moment $\Delta\mathbf{p}_k$, which represents both the change due to the orientation of the permanent dipole $\mathbf{p_k}$ and the induced dipole moment due to the polarizability α_k. The magnitude of this change in the reaction field $E_{R,\Delta p_k}$ follows from Eq. (2),

$$\mathbf{E_{R,\Delta p_k}} = \frac{2(\epsilon - 1)}{2\epsilon + 1} \frac{\Delta\mathbf{p}_k}{4\pi\epsilon_0 a_k^3}. \qquad (5)$$

The sum of the change in the reaction field $\mathbf{E_{R,\Delta p_k}}$ averaged over the liquid, and the cavity field $\mathbf{E_C}$ equals the local field $\mathbf{E_L}$ (see the supplementary material). For systems with a large dielectric constant ϵ_k such as liquid water, $\mathbf{E_{R,\Delta p_k}}$ is much larger than $\mathbf{E_C}$.

For polar molecules, the dielectric response results, in part, from the rotation of the dipoles toward the direction of $\mathbf{E}$, following a torque $\mathbf{W_k} = \mathbf{E_{T,k}} \times \mathbf{p_k}$, with $\mathbf{E_{T,k}}$ being the electric field that is effective in inducing a reorientation of the dipole $\mathbf{p_k}$. The torque field $\mathbf{E_{T,k}}$ consists of the cavity electric field and part of the reaction field. As pointed out by Onsager, the component of the change in the reaction field that results from the rotation of the local dipole $\mathbf{p_{k,i}}$ does not contribute to the torque field. The rotation of the dipole in the applied field induces a change in its reaction field that adds to the already present reaction field of dipole and leads to a dipolar reaction field that remains always perfectly parallel with the rotated dipole $\mathbf{p}'_{k,i}$. This means that the change in the reaction field due to the rotation of the dipole is ineffective in further rotating this dipole and does not contribute to the torque field. The electric field $\mathbf{E_{T,k}}$ that torques the dipole moments is, thus, usually much smaller than the local electric field $\mathbf{E_L}$.

In the original formulation by Onsager, the torque electric field $\mathbf{E}_{T,k}$ was taken equal to the cavity field $\mathbf{E}_C$,[17] but later, it was shown that $\mathbf{E}_{T,k}$ also contains the reaction field component that results from the polarizability α_k of the molecules.[24,25] For polar molecules such as water, this component of the reaction field is usually much smaller than the reaction field of the dipole moment, but due to its orientation along $\mathbf{E}$, this part of the reaction field does contribute to the torque field. The torque field, thus, becomes $\epsilon(n_k^2+2)/(2\epsilon+n_k^2)\mathbf{E}$ (see the supplementary material), which is larger than the cavity field $\mathbf{E}_C$.

Here, we include another reaction-field contribution to the torque field. We consider that molecules outside the considered cavity together yield a net nonzero reaction field component along the applied electric field within the cavity. As discussed above, the change in the reaction field $\mathbf{E}_{R,\Delta\mathbf{p}k,i}$ of each individual $\mathbf{p}_{k,i}$ is ineffective in rotating $\mathbf{p}_{k,i}$ because it leads to a total reaction field that remains always perfectly parallel with $\mathbf{p}_{k,i}$.[17–19] However, the changes in the reaction fields $\mathbf{E}_R, \Delta\mathbf{p}_{k,j\neq i}$ of all the other molecules will have a net orientation along the applied electric field $\mathbf{E}$ and, thus, together create an electric field $\mathbf{E}_B$ that exerts a torque on the local $\mathbf{p}_{k,i}$. The electric field $\mathbf{E}_B$ adds to the electric field $\mathbf{E}$. The torque field $\mathbf{E}_{T,k}$, thus, becomes

$$\mathbf{E}_{T,k} = \frac{\epsilon(n_k^2 + 2)}{2\epsilon + n_k^2}(\mathbf{E} + \mathbf{E}_B). \tag{6}$$

The different electric field components of the reaction-field model are schematically illustrated in Fig. 1.

The polarization due to the dipolar orientation of all the dipoles is equal to $N_k p_k \overline{\cos\theta_k}$, where N_k is the number density and θ_k represents the angle between the dipole moment $\mathbf{p}_k$ and the direction of the electric field. The ensemble average $\overline{\cos\theta_k}$ can be calculated by considering the potential energy V_k of the dipole in the field $\mathbf{E}_{T,k}$: $V_k = -E_{T,k}p_k\cos\theta_k$. The value of $\overline{\cos\theta_k}$ can be calculated using a Boltzmann distribution of the orientation of the different dipoles in the torque field $\mathbf{E}_{T,k}$,

$$\overline{\cos\theta_k} = \int \cos\theta_k e^{-V_k/k_BT}\sin\theta_k d\theta_k / \int e^{-V_k/k_BT}\sin\theta_k d\theta_k$$
$$\simeq E_{T,k}p_k/3k_BT, \quad E_{T,k}p_k \ll k_BT, \tag{7}$$

with k_B being Boltzmann's constant and T being the temperature. The total polarization $\mathbf{P}$ due to the dipolar reorientation and the polarizability of the molecules of a mixture consisting of components k is, thus, given by

$$\mathbf{P} = \sum_k f_k N_k \left(p_k \overline{\cos\theta_k} + \frac{\epsilon(n_k^2+2)}{2\epsilon+n_k^2}\alpha_k(\mathbf{E}+\mathbf{E}_B) \right)$$
$$= \sum_k \frac{f_k N_k \epsilon(n_k^2+2)}{2\epsilon+n_k^2}\left(\frac{p_k^2}{3k_BT} + \alpha_k \right)(\mathbf{E}+\mathbf{E}_B), \tag{8}$$

where the summation runs over the different components k of the mixture and f_k is the volume fraction of component k.
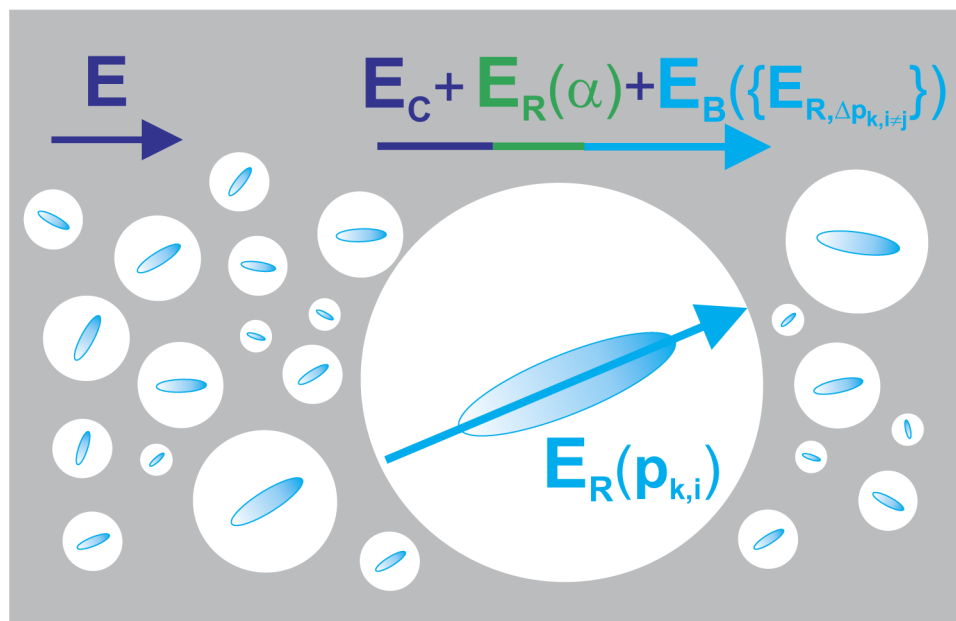
FIG. 1. Schematic representation of the electric fields in the reaction-field model for the dielectric response of liquids. The electric field $\mathbf{E}_T$ that torques the dipole $\mathbf{p}_{k,i}$ consists of the cavity electric field $\mathbf{E}_C$, the reaction field resulting from the polarizability of the molecules $\mathbf{E}_R(\alpha)$, and the background reaction field $\mathbf{E}_B(\{\mathbf{E}_{R,\Delta\mathbf{p}_{j\neq i}}\})$, which is determined by the electric-field induced changes in the dipolar reaction fields of all the other dipoles $\mathbf{p}_{k,j\neq i}$.

We take the background field $\mathbf{E_B}$ proportional to the polarization resulting from the dipolar orientation of the different components in the mixture,

$$\mathbf{E_B} = \sum_k \frac{\epsilon(n_k^2 + 2)}{2\epsilon + n_k^2} \frac{b_k f_k N_k p_k^2}{3k_B T\epsilon_0}(\mathbf{E} + \mathbf{E_B}), \quad (9)$$

where b_k is a parameter of the pure component k that we will determine later. b_k does not depend on the volume fraction f_k and is assumed to be independent of the nature and volume fractions of the other components in the mixture. Equation (9) has important characteristics that $\mathbf{E_B}$ scales with the volume fractions of the polar molecules present in the mixture and that $\mathbf{E_B}$ has a self-amplifying effect, i.e., the applied field $\mathbf{E}$ aligns the dipoles leading to a non-zero $\mathbf{E_B}$ that adds to $\mathbf{E}$, thereby increasing the alignment of the dipoles and, thus, the magnitude of $\mathbf{E_B}$. This self-amplifying effect will lead to a nonlinear dependence of the dielectric constant ϵ on the volume fractions of the components of the mixture. This nonlinear dependence on the volume fraction should not be confused with a potential nonlinear dependence of ϵ on the strength of the applied electric field, i.e., the nonlinear dielectric effect.[18]

Equation (9) can be solved for $\mathbf{E_B}$, yielding

$$\mathbf{E_B} = h(\{f_k\}, \epsilon)\mathbf{E}, \quad (10)$$

with

$$h(\{f_k\}, \epsilon) = \frac{\sum_k \frac{\epsilon(n_k^2 + 2)}{(2\epsilon + n_k^2)} \frac{b_k f_k N_{k,0} p_k^2}{3k_B T\epsilon_0}}{1 - \sum_k \frac{\epsilon(n_k^2 + 2)}{(2\epsilon + n_k^2)} \frac{b_k f_k N_k p_k^2}{3k_B T\epsilon_0}}. \quad (11)$$

Using $\mathbf{P} = \epsilon_0(\epsilon - 1)\mathbf{E}$, Eq. (8) for $\mathbf{P}$, and Eq. (10) for $\mathbf{E_B}$, we obtain

$$\epsilon_0(\epsilon - 1) = \sum_k f_k N_k \frac{\epsilon(n_k^2 + 2)}{2\epsilon + n_k^2}\left(\frac{p_k^2}{3kT} + \alpha_k\right)(1 + h(\{f_k\}, \epsilon)). \quad (12)$$

From Eq. (11), it follows that

$$\frac{1}{1 + h(\{f_k\}, \epsilon)} = 1 - \sum_k \frac{\epsilon(n_k^2 + 2)}{(2\epsilon + n_k^2)} \frac{b_k f_k N_k p_k^2}{3k_B T\epsilon_0}. \quad (13)$$

Following the Clausius–Mossotti relation of Eq. (1), we can write

$$N_k \alpha_k = 3\epsilon_0(n_k^2 - 1)/(n_k^2 + 2). \quad (14)$$

Substitution of Eqs. (13) and (14) in Eq. (12) yields

$$\sum_k \frac{f_k(\epsilon - 1)(2\epsilon + n_k^2)}{2\epsilon + n_k^2} - \frac{3f_k\epsilon(n_k^2 - 1)}{2\epsilon + n_k^2}$$
$$= \sum_k \frac{f_k N_k p_k^2}{3k_B T\epsilon_0} \frac{\epsilon(n_k^2 + 2)(1 + (\epsilon - 1)b_k)}{(2\epsilon + n_k^2)}. \quad (15)$$

Using $(\epsilon - 1)(2\epsilon + n_k^2) - 3\epsilon(n_k^2 - 1) = (2\epsilon + 1)(\epsilon - n_k^2)$ and Eq. (3) to substitute p_k by p_{k0}, the last expression can be written as

$$\sum_k \frac{f_k(\epsilon - n_k^2)}{2\epsilon + n_k^2} = \sum_k \frac{f_k N_k p_{k0}^2}{27k_B T\epsilon_0} \frac{\epsilon(2\epsilon + 1)(n_k^2 + 2)^3(1 + (\epsilon - 1)b_k)}{(2\epsilon + n_k^2)^3}. \quad (16)$$

For a pure component k, we have

$$\epsilon_k - n_k^2 = \frac{N_k p_{k,0}^2}{27k_B T\epsilon_0} \frac{\epsilon_k(2\epsilon_k + 1)(n_k^2 + 2)^3(1 + (\epsilon_k - 1)b_k)}{(2\epsilon_k + n_k^2)^2}, \quad (17)$$

which can be solved for b_k,

$$b_k = \frac{27k_B T\epsilon_0}{N_k p_{k0}^2} \frac{(\epsilon_k - n_k^2)(2\epsilon_k + n_k^2)^2}{\epsilon_k(\epsilon_k - 1)(2\epsilon_k + 1)(n_k^2 + 2)^3} - \frac{1}{\epsilon_k - 1}. \quad (18)$$

The value of b_k is, thus, determined by several parameters of the pure component k that are usually well known, i.e., the pure dielectric constant ϵ_k, the pure number density N_k, the vacuum dipole moment p_{k0}, and the high-frequency limit n_k^2 of its dielectric function. Hence, the value of b_k is not an adjustable parameter, but follows directly from the properties of the pure component k. It is useful to tabulate these values as b_k is supposed to be the same for any mixture containing component k. The value of b_k is assumed to depend only on physical parameters such as the pressure and the temperature. Table I presents the values of b_k for several pure components and the corresponding values of h_k ($=\mathbf{E_B}/\mathbf{E}$), which follow from Eq. (11).

For practical applications, it is useful to transfer Eq. (16) to a form that relates the dielectric response ϵ of a mixture to the volume fractions f_k, the dielectric constants ϵ_k and n_k^2 of the pure components, and the new parameters b_k. To arrive at such an expression, we eliminate $N_k p_{k,0}^2/(27k_B T\epsilon_0)$ from Eqs. (16) and (17),

$$\sum_k \frac{f_k(\epsilon - n_k^2)}{2\epsilon + n_k^2} = \sum_k \frac{f_k(\epsilon_k - n_k^2)(2\epsilon_k + n_k^2)^2\epsilon(2\epsilon + 1)(1 + (\epsilon - 1)b_k)}{(2\epsilon + n_k^2)^3\epsilon_k(2\epsilon_k + 1)(1 + (\epsilon_k - 1)b_k)}. \quad (19)$$

Equation (19) can be used to calculate the dielectric response ϵ of any mixture, using the dielectric parameters of the pure components and tabulated values of b_k as input. In case the mixture only contains apolar components, $\epsilon_k(\epsilon) = n_k^2$ for all components k, and Eq. (19) reduces to the well-known Bruggeman expression for the dielectric response of mixtures: $\sum_k(\epsilon - n_k^2)/(2\epsilon + n_k^2) = 0$.

Equation (19) constitutes a higher-order expression in ϵ, and thus, in general, this equation needs to be solved numerically. The evaluation can be simplified in the following manner. We define

$$g_k(\epsilon) = \frac{\epsilon(n_k^2 + 2)}{2\epsilon + n_k^2} \frac{N_k p_k^2}{3k_B T}. \quad (20)$$

Using this expression and Eqs. (10) and (11), we can write $\mathbf{E_B} + \mathbf{E}$ as

TABLE I. Parameters of the pure dipolar liquids that are used in the calculations. The dielectric constants ϵ_k are obtained from Refs. 30, 31, 32, and 35. The temperature-dependent density of water, methanol, and ethanol are obtained from Refs. 31, 33, and 34, respectively.

	Temperature	ϵ_k	n_k^2	N_k (m^{-3})	p_{k0} (debye)	b_k	h_k (=$\mathbf{E_B}$/$\mathbf{E}$)
Water	248 K	98.8	2.0	3.306×10^{28}	1.85	0.0102	0.985
	273 K	87.9	2.0	3.342×10^{28}	1.85	0.0107	0.921
	293 K	80.4	2.0	3.337×10^{28}	1.85	0.0113	0.886
	303 K	76.6	2.0	3.328×10^{28}	1.85	0.0116	0.863
	333 K	66.8	2.0	3.288×10^{28}	1.85	0.0124	0.805
Methanol	248 K	44.4	1.8	1.566×10^{28}	1.69	0.0375	1.604
	273 K	38.0	1.8	1.523×10^{28}	1.69	0.0414	1.500
	293 K	32.5	1.8	1.487×10^{28}	1.69	0.0438	1.355
	303 K	31.7	1.8	1.470×10^{28}	1.69	0.0465	1.400
Ethanol	273 K	28.4	2.2	1.056×10^{28}	1.69	0.0370	0.952
	293 K	25.0	2.2	1.032×10^{28}	1.69	0.0391	0.876
	303 K	23.9	2.2	1.022×10^{28}	1.69	0.0407	0.868
	333 K	19.8	2.2	0.990×10^{28}	1.69	0.0427	0.739
Isopropanol	293 K	16.6	2.2	7.88×10^{27}	1.66	0.0313	0.437
tert-Butanol	293 K	9.7	2.2	6.35×10^{27}	1.66	0.0213	0.163

$$\mathbf{E_B} + \mathbf{E} = \left(\frac{\sum_k f_k b_k g_k(\epsilon)/\epsilon_0}{1 - \sum_k f_k b_k g_k(\epsilon)/\epsilon_0} + 1 \right)\mathbf{E}$$
$$= \frac{\mathbf{E}}{1 - \sum_k f_k b_k g_k(\epsilon)/\epsilon_0}. \tag{21}$$

Using the Clausius–Mosotti expression (14), we can write the contribution of the polarizability of component k to the polarization [Eq. (8)] in the following way:

$$\frac{\epsilon(n_k^2 + 2)}{2\epsilon + n_k^2} N_k \alpha_k = \epsilon_0 \frac{3\epsilon(n_k^2 - 1)}{2\epsilon + n_k^2} = \epsilon_0 c_k(\epsilon), \tag{22}$$

which defines the polarizability response $c_k(\epsilon)$ of component k. Using this expression, we can write Eq. (8) in the following way:

$$\mathbf{P} = \epsilon_0(\epsilon - 1) = \sum_k \frac{f_k[g_k(\epsilon) + \epsilon_0 c_k(\epsilon)]\mathbf{E}}{1 - \sum_k f_k b_k g_k(\epsilon)/\epsilon_0}. \tag{23}$$

For a single pure component k, Eq. (23) yields

$$\epsilon_0(\epsilon_k - 1) = \frac{g_k(\epsilon_k) + \epsilon_0 c_k(\epsilon_k)(\epsilon)}{1 - b_k g_k(\epsilon_k)/\epsilon_0}. \tag{24}$$

This equation can be solved for $g_k(\epsilon_k)/\epsilon_0$,

$$g_k(\epsilon_k)/\epsilon_0 = \frac{\epsilon_k - 1 - c_k(\epsilon_k)}{b_k(\epsilon_k - 1) + 1}. \tag{25}$$

Now, we replace $g_k(\epsilon)$ by $g_k(\epsilon_k)$ and $c_k(\epsilon)$) by $c_k(\epsilon_k)$, which are good approximations if ϵ and ϵ_k are larger than n_k^2. The denominator of Eq. (23) can then be written as

$$1 - \sum_k f_k b_k g_k(\epsilon)/\epsilon_0 \simeq 1 - \sum_k \frac{f_k[\epsilon_k - 1 - c_k(\epsilon_k)]}{b_k(\epsilon_k - 1) + 1}$$
$$= \sum_k \frac{f_k[1 + b_k c_k(\epsilon_k)]}{b_k(\epsilon_k - 1) + 1}. \tag{26}$$

When substituting this expression and Eq. (25) in Eq. (23) and replacing $g_k(\epsilon)$ by $g_k(\epsilon_k)$ and $c_k(\epsilon)$ by $c_k(\epsilon_k)$, we obtain

$$\epsilon - 1 = \frac{\sum_k f_k[(\epsilon_k - 1 - c_k(\epsilon_k)) + c_k(\epsilon_k)(b_k(\epsilon_k - 1) + 1)]/(b_k(\epsilon_k - 1) + 1)}{\sum_k f_k[1 + b_k c_k(\epsilon_k)])/(b_k(\epsilon_k - 1) + 1)}. \tag{27}$$

In the case of a mixture consisting of an apolar component and a single polar component with a large dielectric constant, e.g., water, Eq. (27) can be further simplified to

$$\epsilon - 1 = \frac{f_w(\epsilon_w - 1)[1 + \frac{3}{2}b_w(n_w^2 - 1)] + (1 - f_w)(n_a^2 - 1)][b_w(\epsilon_w - 1) + 1]}{1 + \frac{3}{2}f_w b_w(n_w^2 - 1) + (1 - f_w)b_w(\epsilon_w - 1)}, \tag{28}$$

where the subscript w refers to the polar component and the subscript a refers to the apolar component for which the dipolar reaction field parameter b_a equals zero. In this expression, the contribution of the polarizability of the polar component, represented by $c_w(\epsilon_w)$, is approximated as $\frac{3}{2}(n_w^2 - 1)$, which is a good approximation if $\epsilon_w > n_w^2$.

RESULTS AND DISCUSSION

In Fig. 2, we present experimental and calculated results for the static dielectric constant as a function of volume fraction f of water for a mixture of water and an apolar liquid [Fig. 2(a)] and for mixtures of water with different alcohols as a function of
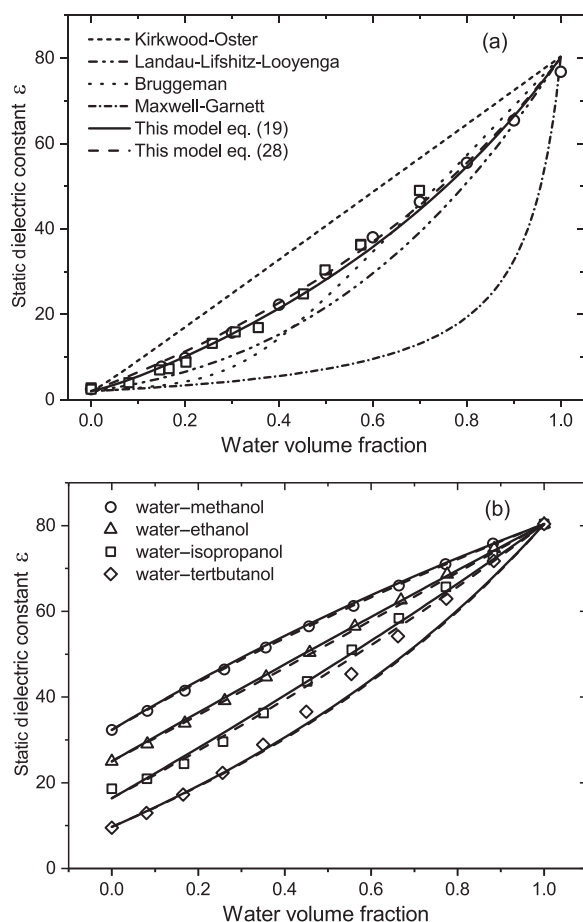
FIG. 2. Static dielectric constant of the water volume fraction f_w. (a) Comparison of five effective medium theories and three experimental systems. The open circles represent data measured for a mixture of Nujol, CCl$_4$ (oil phase), water and Tween 20 and Span 20 as the surfactants,[28] and the open squares represent data of a mixture of n-dodecane, water, and H–(CH$_2$)$_8$(–O–CH$_2$CH$_2$)$_3$–OH and a mixture of n-decane, water, and H–(CH$_2$)$_{10}$(–O–CH$_2$CH$_2$)$_4$–OH.[29] (b) Static dielectric constant of mixtures of water and four different alcohols. The symbols represent data from Ref. 30 (all water–alcohol mixtures) and Ref. 31 (water–ethanol mixtures). The solid curves are calculated with Eq. (19), and the dashed curves are calculated with Eq. (27).

water volume fraction [Fig. 2(b)]. For the apolar liquid, we take $\epsilon_k = n_k^2 = 2.0$. It is seen in Fig. 2(a) that the Wagner, Landau–Lifshitz–Looyenga, and Bruggeman models all yield a too strong nonlinear dependence of ϵ on the water volume fraction. This too strong nonlinear dependence results from the fact that in these models, the part of the reaction field that results from the orientation of the water dipoles is assumed to be fully effective in enhancing the dielectric response. The curve denoted as Kirkwood–Oster is obtained by applying the theory of Kirkwood[23,24] to mixtures using an Oster rule approach.[26,27] In this approach, it is assumed that the Kirkwood factors of the pure components retain their values in the mixture. This approach predicts a nearly linear dependence of the dielectric constant on the water volume fraction, which is again in poor agreement with the experimental observations. In the present model, we do not describe the correlated motion of the dipoles with a Kirkwood factor, but as the result of the background reaction field of the water dipoles of which the strength increases with an increase in the water volume fraction, and that possesses a self-amplifying effect, as expressed in Eq. (9). This self-amplifying effect of the background reaction field leads to the observed nonlinear dependence of the dielectric constant of the water–oil mixture on the water volume fraction. It should be noted that the degree of this nonlinearity is fully determined by the dielectric parameters of pure water, without any adjustable parameter. The comparison of the solid and the dashed curves shows that for the studied mixtures, the term $c_w(\epsilon)$ can, indeed, be well approximated by $\frac{3}{2}(n_w^2 - 1)$.

In Fig. 2(b), we show the calculated and measured[30,31] dielectric response of water–alcohol mixtures. These mixtures contain two polar components that contribute to the dipolar background reaction field. The dependence of the dielectric response is governed by the relative strengths of the background reaction fields of these components. Methanol has a stronger background reaction field than water, leading to a convex form of the dependence of ϵ on the water volume fraction. The stronger background reaction field of methanol can be explained from the fact that for alcohols, the molecular dipole moments are more aligned with the hydrogen bonds than for water, leading to a stronger local correlation of the orientation of the dipole moments. For isopropanol and tertiary butanol, the background reaction field is weaker than for water probably because these alcohols have larger apolar groups, leading to larger distances between the dipoles. The weaker background field of isopropanol and butanol leads to a concave form of the dependence of ϵ on the water volume fraction, similar to what is observed for mixtures of water and an apolar liquid [Fig. 2(a)]. For ethanol, the background reaction field is similar to that for water probably because the two effects (better alignment of the dipoles with the hydrogen bonds for ethanol and larger distances between the dipoles because of the hydrophobic part of ethanol) compensate each other. The similarity of the background reaction fields of pure water and pure ethanol leads to a nearly linear dependence of the dielectric response of water–ethanol mixtures on the water volume fraction. In Fig. 3, we compare the dependence of the dielectric response of water–methanol and water–ethanol mixtures on the water volume fractions at different temperatures. For all compositions, the dielectric response decreases with an increase in temperature.
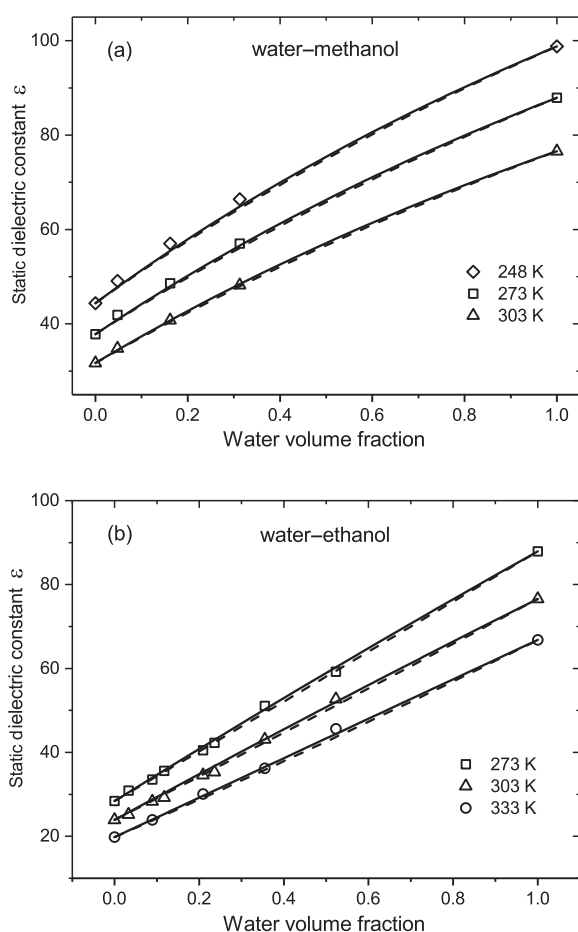
FIG. 3. Static dielectric constant as a function of water volume fraction f_w for different temperatures: (a) for mixtures of water and methanol[32] and (b) for mixtures of water and ethanol.[31,32] The solid curves are calculated with Eq. (19), and the dashed curves with Eq. (27).

In Table I, we present the static dielectric constants of pure water, methanol, and ethanol at different temperatures and the corresponding values of b_k and h_k, calculated with Eqs. (18) and (11), respectively. The dielectric response of pure liquid water at 248 K is obtained by extrapolating the measured dielectric constant of supercooled water.[35] For all three liquids, the parameter h_k ($=\mathbf{E_B}/\mathbf{E}$), which represents the relative strength of the background reaction field, increases with a decrease in temperature.

The parameter n_k^2 of each component k of the mixture represents the low-frequency response of the polarizability α of the molecules. This parameter affects the static dielectric response in several ways, the most important being that the reaction field induced by the polarizability α enhances the torque electric field $\mathbf{E_T}$ felt by the dipoles. In the reaction-field model, the parameter n_k^2 is defined as the low-frequency limit of all the vibrational and electronic responses that does not include a reorientation of the dipole moment. This means that for polar liquids, n_k^2 includes the

high-frequency intramolecular vibrations and electronic transitions and does not include relaxation (Debye) modes and other intermolecular modes such as librations. We estimated the value of n_k^2 to be somewhat higher than the square of the refractive index at optical frequencies because n_k^2 contains the low-frequency limit of the response of the high-frequency molecular vibrations, whereas the refractive index at higher frequencies contains the (smaller) high-frequency range of this response. The values of n_k^2 of the pure components that we used in the calculations are presented in Table I.

The reaction-field model can also be used to determine the frequency-dependence of the dielectric response of the mixture, by expressing the dielectric response $\epsilon(\omega)$ of the mixture at each frequency ω in terms of the dielectric responses $\epsilon_k(\omega)$ of the components contained in the mixture. The reaction-field parameter b_k is also a frequency-dependent function that can be evaluated for each pure component k from $\epsilon_k(\omega)$ and the relaxation time constant(s) of that component. An interesting question is how these relaxation time constants change when the molecules of component k become part of a mixture. The frequency dependence of the dielectric response of mixtures will be the subject of future study.

The background reaction field is expected to possess a certain characteristic length. An indication of this length can be obtained from the dependence of the dielectric constant of water molecules in the center of a water droplet on the size of the droplet. Molecular dynamics simulations show that the droplet size has to be quite large, typically tens of nanometers, for the water molecules in the center to acquire the static dielectric constant of water.[36] This finding indicates that the extension of the background reaction field is on the order of tens of nanometers. In the derivation of Eqs. (19) and (27), we assumed that the background reaction field scales with the volume fractions of the different components contained in the mixture (effective medium description). In case the length scale of the structure/inhomogeneity of the medium becomes larger than the length scale of the background reaction field, this effective medium approach will break down, and the dielectric response of the mixtures is expected to show a more linear dependence on the volume fractions. The deviation of the calculated curves from the experimental points for large water volume fractions observed for mixtures of water and iso-propanol/butanol [Fig. 2(b)] may be caused by this effect. For large water volume fractions, the volumes of the water clusters in the mixture may become very large due to aggregation of the iso-propanol and butanol molecules and may, thus, well exceed the characteristic length of the background dipolar reaction field of water, thus leading to a breakdown of the effective medium approach.

CONCLUSIONS

We present a new effective-medium model for the dielectric response of mixtures with components possessing molecular polarizability and a permanent dipole moment. This model differs from the previous models for the dielectric response of polar molecules of Frohlich and Kirkwood in the description of the correlated motion of the dipoles in the applied electric field. In the present model, this motion follows from the interaction of each local dipole moment

with the dipolar reaction fields of neighboring dipolar molecules. The strength of the dipolar reaction field of the mixture follows from the volume fractions of the different components contained in the mixture and the reaction fields of the pure components. The reaction field of each pure component is defined by a new parameter b_k that follows unambiguously from like the density, the molecular dipole moment, and the static dielectric constant of the pure component [Eq. (18)]. The values b_k of different polar liquids can be tabulated and subsequently used to calculate the dielectric response of any mixture containing these components, irrespective of the volume fractions.

The reaction-field model leads to Eq. (19) that expresses the dielectric response ϵ of the mixture in terms of the volume fractions and the dielectric parameters of the pure components (including the new parameters b_k). Equation (23), in general, has to be evaluated numerically, but in good approximation can be simplified to Eq. (27). For a mixture of a single polar and an apolar liquid, Eq. (27) reduces to expression (28).

We compare the reaction-field model with previous effective medium theories and with experimental data for water–oil mixtures and water–alcohol mixtures. For water–oil mixtures, the dielectric response shows a strong nonlinear dependence on the water volume fraction, which is well accounted for by the reaction-field model. For water–alcohol mixtures, the dependence of the dielectric response on the water volume fraction depends on the nature of the alcohol, changing from a convex shape for methanol to a concave shape for isopropanol and butanol. The convex form of the dielectric response of water–methanol mixtures can be explained by the stronger reaction field of pure methanol compared to pure water. For water–methanol and water–ethanol mixtures, the model provides an accurate description of the observed dielectric response for all volume fractions and at different temperatures. For mixtures of water and larger alcohols, the reaction-field model does not provide a good description of the experimental observations at large water volume fractions probably because the alcohol molecules aggregate, leading to a microscopic phase separation and a breakdown of the effective medium approach.

SUPPLEMENREY MATERIAL

See the supplementary material for the derivation of Eqs. (2) and (3) and the prefactor of the torque electric field of Eq. (6).

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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