

Dielectric properties of liquid systems: the ideal complex permittivity in liquid mixtures

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Abstract

A general definition for ideal complex permittivity in a liquid mixture was reached by considering a thermodynamically ideal mixture under the effect of an applied harmonic electric field. The resulting definition is independent of any particular dielectric model, as well as the polarity of the components.

Key Words: Dielectric Properties, Complex Permittivity, Binary Mixtures, Excess Functions.

1. Introduction

In general, at low frequencies, works reported in the literature on dielectric properties of liquid solutions use different definitions for the ideal dielectric constant ε' of a mixture [1–11]. On the other hand, no definition for the ideal frequency-dependent dielectric constant ε' and the ideal frequency-dependent loss factor ε'' of a mixture has been found in the literature.

To overcome the first deficiency, in a previous work [12], a general definition for the static ideal dielectric behavior of a liquid mixture has been reached considering the change in the Gibbs energy when a low frequency electric field ($< 10^{-6} \text{ s}^{-1}$, upper limit of the so called static permittivity) is applied to both the pure compounds and the solution. Recently, using a molecular formalism [13], it was shown that, in the definition of the ideal dielectric permittivity, the pure components should be weighted by their volume fractions. However, in both cases, the treatments used to obtain the ideal behavior of a mixture were developed only for a single low frequency, without studying the influence of changes in the frequency of the applied electric field.

In order to study in detail the structure and dynamics of a mixture in both the static and dynamic regions, it seems necessary to extend the definition of ideal definition to frequencies varying between 10^6 s^{-1} and 10^{16} s^{-1} . Therefore, the main content of this paper is an attempt to find a general definition for the ideal

dielectric behavior of a liquid mixture that can be used for frequencies less than 10^{-16} s^{-1} . This definition was developed in this work, as in the static case, by considering the change in the Gibbs energy, but now by applying a harmonic electrical field to both the pure components and their solution.

2. Discussion

A homogeneous binary liquid mixture can be assumed to contain N_A moles of component A and N_B moles of component B . If this system is taken to be a special case of a thermodynamically ideal solution, the change in Gibbs energy at constant temperature and pressure that result when the components are mixed, is described by the equation

$$\begin{aligned} \Delta G = G_F - G_I &= N_A [\mu_A^* + RT \ln X_A] + N_B [\mu_B^* + RT \ln X_B] - N_A \mu_A^* - N_B \mu_B^* \\ &= NRT [X_A \ln X_A + X_B \ln X_B] \end{aligned} \quad (1)$$

wherein μ_I^* is the chemical potential of the I^{th} component ($I = A, B$) in the pure state, N is the total amount of moles in the liquid ($N = N_A + N_B$), X_I is the mole fraction of the I^{th} component, R is the gas constant and T is the absolute temperature.

If now this same mixture is placed inside a condenser with a harmonic potential difference applied between its plates, there exists a macroscopic electrical field of intensity $E_o \cos(\omega t)$. As a result, there is an amount of electrical work that has to be taken into account in the Gibbs energy of both the pure components and the solution.

If the real and imaginary parts of the permittivity of the pure components and the mixture are $\varepsilon'_A(\omega)$, $\varepsilon'_B(\omega)$, $\varepsilon''_A(\omega)$, $\varepsilon''_B(\omega)$, $\varepsilon'_M(\omega)$ and $\varepsilon''_M(\omega)$, respectively, the initial and final Gibbs energies can be written as

$$G_I = N_A \mu_A^* + W_A + N_B \mu_B^* + W_B \quad (2)$$

$$G_F = N_A [\mu_A^* + RT \ln X_A] + N_B [\mu_B^* + RT \ln X_B] + W_M \quad (3)$$

wherein W_I ($I = A, B, M$) is the electrical work that can be calculated as [14]

$$W_I = \left[\frac{V_I E_0^2}{4\pi} \right] \left[\varepsilon'_I \int \cos(\omega t) d(\cos(\omega t)) + \varepsilon''_I \int \cos(\omega t) d(\sin(\omega t)) \right], \quad (4)$$

and where V_I are the volumes occupied, respectively, by the mixture and components.

The total amount of work done on the dielectric during each quarter of cycle is

$$[W_I]_{1/4} = \left[\frac{V_I E_0^2}{16} \right] \varepsilon''_I \pm \left[\frac{V_I E_0^2}{8\pi} \right] \varepsilon'_I. \quad (5)$$

Here, the (+) is applied during the 2^{nd} and 4^{th} quarters and the (-) is applied during the 1^{st} and 3^{rd} quarters.

Although the first term on the right hand side of the equation (5), that is the dissipated energy, is the only one that is non-zero in a cycle, the second term on the right hand side can acquire relevance if we consider the total work in periods that are different from one cycle. Then, this term could be non-zero per unit of time if this unit is not an integer number of half period $\left(\frac{\pi}{\omega}\right)$.

On the other hand, the second term acquires importance at sufficiently low frequencies so that the electrical work reduces to $\left[\frac{V_I E_0^2}{8\pi}\right] \varepsilon'_I$, that is the work necessary to maintain the dielectric medium polarization.

Now, from equations (2) to (5), the change in Gibbs energy at constant temperature and pressure during each quarter of cycle can be written as

$$\begin{aligned} \Delta G^M = & NRT [X_A \ln X_A + X_B \ln X_B] + [\varepsilon''_M V_M - \varepsilon''_A V_A - \varepsilon''_B V_B] \left[\frac{E_0^2}{16}\right] \\ & \pm [\varepsilon'_M V_M - \varepsilon'_A V_A - \varepsilon'_B V_B] \left[\frac{E_0^2}{8\pi}\right] \end{aligned} \quad (6)$$

wherein the last two terms on the right hand side indicate the difference in electrical work between the mixture and its components. On the other hand, the first term describes the behavior of a thermodynamically ideal mixture in the absence of an applied electrical field.

With equation (6) it is now possible to calculate the changes in entropy ΔS^M , enthalpy ΔH^M and volume ΔV^M that originate when mixing is performed while keeping ω constant. This leads to the following relations:

$$\begin{aligned} \Delta S^M = & - \left. \frac{\partial \Delta G^M}{\partial T} \right|_P = -NR [X_A \ln X_A + X_B \ln X_B] - \left[\frac{E_0^2}{16}\right] \frac{\partial [\varepsilon''_M V_M - \varepsilon''_A V_A - \varepsilon''_B V_B]}{\partial T} \\ & \pm \left[\frac{E_0^2}{8\pi}\right] \frac{\partial [\varepsilon'_M V_M - \varepsilon'_A V_A - \varepsilon'_B V_B]}{\partial T} \end{aligned} \quad (7)$$

$$\begin{aligned} \Delta H^M = & - T^2 \left. \frac{\partial (\Delta G^M / T)}{\partial T} \right|_P = - \left[\frac{T^2 E_0^2}{16}\right] \left\{ \frac{\partial [1/T]}{\partial T} [\varepsilon''_M V_M - \varepsilon''_A V_A - \varepsilon''_B V_B] \right. \\ & \left. + [1/T] \frac{\partial [\varepsilon''_M V_M - \varepsilon''_A V_A - \varepsilon''_B V_B]}{\partial T} \right\} \\ & \pm \left[\frac{T^2 E_0^2}{8\pi}\right] \left\{ \frac{\partial [1/T]}{\partial T} [\varepsilon'_M V_M - \varepsilon'_A V_A - \varepsilon'_B V_B] \right. \\ & \left. + \left[\frac{1}{T}\right] \frac{\partial [\varepsilon'_M V_M - \varepsilon'_A V_A - \varepsilon'_B V_B]}{\partial T} \right\} \end{aligned} \quad (8)$$

$$\Delta V^M = \left. \frac{\partial \Delta G^M}{\partial P} \right|_T = \left[\frac{E_0^2}{16}\right] \frac{\partial [\varepsilon''_M V_M - \varepsilon''_A V_A - \varepsilon''_B V_B]}{\partial P} \pm \left[\frac{E_0^2}{8\pi}\right] \frac{\partial [\varepsilon'_M V_M - \varepsilon'_A V_A - \varepsilon'_B V_B]}{\partial P}. \quad (9)$$

Equations (6) to (9) can now be used as starting points to define the ideal behavior of a mixture under the effect of an applied harmonic electrical field of low intensity.

Therefore, one possibility to define the ideal dielectric behavior of a mixture is to consider that there are no differences between the electrical work done on the solution as a whole and the sum of the electrical work done on its components over the whole range of composition and frequencies. There should also be no changes with temperature and pressure. As a consequence of the above discussion, and considering that there are no differences among each quarter of cycle, the ideal dielectric behavior exists under the following conditions:

$$\varepsilon'_M V_M - \varepsilon'_A V_A - \varepsilon'_B V_B|_{T,P} = 0 \quad (10)$$

$$\varepsilon''_M V_M - \varepsilon''_A V_A - \varepsilon''_B V_B|_{T,P} = 0 \quad (11)$$

$$\left. \frac{\partial [\varepsilon'_M V_M - \varepsilon'_A V_A - \varepsilon'_B V_B]}{\partial T} \right|_P = 0 \quad (12)$$

$$\left. \frac{\partial [\varepsilon_M'' V_M - \varepsilon_A'' V_A - \varepsilon_B'' V_B]}{\partial T} \right|_P = 0 \quad (13)$$

$$\left. \frac{\partial [\varepsilon_M' V_M - \varepsilon_A' V_A - \varepsilon_B' V_B]}{\partial P} \right|_T = 0 \quad (14)$$

$$\left. \frac{\partial [\varepsilon_M'' V_M - \varepsilon_A'' V_A - \varepsilon_B'' V_B]}{\partial P} \right|_T = 0. \quad (15)$$

This means that under these stated conditions, in a mixture defined as dielectrically ideal, there is no volume change, there is no heat of mixing, and the change in entropy is entirely due to the spatial distribution of the species present.

Since the volume occupied by the mixture is equal to the sum of the volumes of each of the components ($V_M = V_A + V_B$), the real and imaginary parts of the permittivity of an ideal solution, at constant temperature and pressure, are linear functions of the ideal volume fraction of any of the components. Thus we can write:

$$\varepsilon'_{M_{IDEAL}} = \varepsilon'_A \left(\frac{V_A}{V_M} \right) + \varepsilon'_B \left(\frac{V_B}{V_M} \right) = \varepsilon'_A \Phi_A^0 + \varepsilon'_B \Phi_B^0 \quad (16)$$

$$\varepsilon''_{M_{IDEAL}} = \varepsilon''_A \left(\frac{V_A}{V_M} \right) + \varepsilon''_B \left(\frac{V_B}{V_M} \right) = \varepsilon''_A \Phi_A^0 + \varepsilon''_B \Phi_B^0, \quad (17)$$

where Φ_A^0 and Φ_B^0 are the ideal volume fractions.

From equations (10) to (15) we see that if $\omega \rightarrow 0$ the equation (16) is that of ideal static permittivity, and if $\omega \rightarrow \infty$ the case of ideal permittivity at high frequencies is obtained [12].

From this discussion it is evident that the relations defining the ideal case result from a general treatment and do not depend on the use of any specific model or on the polarity of the components in the mixture.

The above definitions (Equations (16) and (17)) can now be used to define an excess permittivity for the real and imaginary parts of the complex permittivity. These excesses can be written as

$$\varepsilon'^E = \varepsilon'_{M_{EXP}} - (\varepsilon'_A \Phi_A^0 + \varepsilon'_B \Phi_B^0) \quad (18)$$

$$\varepsilon''^E = \varepsilon''_{M_{EXP}} - (\varepsilon''_A \Phi_A^0 + \varepsilon''_B \Phi_B^0), \quad (19)$$

wherein $\varepsilon'_{M_{EXP}}$ and $\varepsilon''_{M_{EXP}}$ are the experimental data of the mixture.

Finally, we can say that the excess permittivity for the real part of the complex permittivity at low frequencies was studied and successfully explained for several mixtures using models developed to predict the permittivity of mixtures [15, 16].

3. Conclusions

Starting from thermodynamical considerations a definition was reached for ideal dielectrics in a mixture over a wide range of frequencies ($< 10^6 \text{ s}^{-1}$ up to 10^{16} s^{-1}). The resulting ideal permittivity is independent of any particular dielectric model, as well as of the polarity of the components and the real and imaginary parts of the permittivity are linear functions of the ideal volume fraction of any of the components.

The proposed definition of an ‘ideal’ over the whole range of frequencies clarifies which kind of interactions exist in mixtures where a change of sign appear in the excess permittivity when the ideal permittivity is considered as a linear function of the volume fractions or a linear function of the mole fractions [4, 11].

Lastly, the use of this definition of ideal for all frequencies has the advantage of allowing comparison of departures from the ideal and the dynamics of different mixtures.

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