

On the Definition of the Excess Permittivity of a Fluid Mixture: Thermodynamic Formalism

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Dielectrics research is a highly interdisciplinary field because the permittivity of materials is a fundamental property. In a survey between 1980 and 2004, Youngs and colleagues¹ found this growing field to be a blend of physics, electrical engineering, materials science and chemistry. The permittivity of binary systems, both homogeneous liquid mixtures and random composite materials, has attracted much research since the 19th century, and the literature in the field is voluminous. In a lively historical account, Brosseau² gives a stimulating well-researched and equation-free overview of the development of this subject. A long-standing yet unsolved question relates to the definition of ideal dielectric behavior of a mixture. It is generally agreed that the relative permittivity or, traditionally, the dielectric constant of the ideal binary mixture should be a linear function of the composition. However, there is general disagreement with respect to the choice of composition scale for this purpose. This controversy began in the 19th century with proposals for using either volume fractions or mass fractions in the ideal mixing law, to which mole fractions were added later. The volume fraction has long been the exclusive composition variable in theoretical and experimental research on composite materials. In the field of liquid mixtures, however, two main positions consolidated, one advocating a mole-fraction mixing law and the other a volume-fraction mixing law. Although scarcely used, mass fractions were still employed in the late 20th century for representing ideal dielectric behavior.^{3,4} This choice is not a lesser matter. As Decroocq⁵ pointed out, for components with greatly different molar volumes, a change happen in the sign of increments or deviations in the relative permittivity, De_r , when it is considered in terms of volume-fraction, f ,

$$De_r(f) = e_r - (f_A e_{r,A} + f_B e_{r,B}) \quad (1)$$

or in terms of mole fractions, x ,

$$De_r(x) = e_r - (x_A e_{r,A} + x_B e_{r,B}) \quad (2)$$

e_r and $e_{r,i}$ are respectively the relative permittivity of the mixture and the component i . This change of sign can be illustrated by four mixtures (comprise both organic/organic and aqueous organic mixtures) selected from literature, at 298.15 K: tetraglyme(A)/dimethyl carbonate(B), in which $e_{r,A}/e_{r,B} = 2.49$ and $V_A^*/V_B^* = 2.61$;⁶ dibutyl ether(A)/benzene(B), in which $e_{r,A}/e_{r,B} = 1.34$ and $V_A^*/V_B^* = 0.52$;⁷ water(A)/2-methoxyethanol(B), in which $e_{r,A}/e_{r,B} = 4.58$ and $V_A^*/V_B^* = 0.23$;⁸ and water(A)/2-butoxyethanol(B), in which $e_{r,A}/e_{r,B} = 8.31$ and $V_A^*/V_B^* = 0.14$.⁸ These examples have different relative permittivity ratios of the pure components, $e_{r,A}/e_{r,B}$, and also of their molar volumes, V_A^*/V_B^* . Obviously, when that change of sign happens, interpretation of the observed increments $De_r(f)$ and $De_r(x)$, in terms of molecular interactions, would lead to contradictory conclusions. Since the permittivity is an electric property of materials, it might be argued that the estimation of its value in thermodynamically ideal liquid mixtures would fall outside the realm of thermodynamics. Nonetheless, for dielectric systems in the presence of an electric field, the change of electric dipole moment is associated with a change of energy, and therefore has to do with thermodynamics. In the present work, we demonstrate using a thermodynamic formalism that the relative permittivity of a thermodynamically ideal liquid mixture is given by the volume-fraction-weighted average of the pure component relative permittivities.

$$e_r^{id} = f_A^{id} e_{r,A}^{id} + f_B^{id} e_{r,B}^{id} \quad (3)$$

f_i^{id} is the volume fraction of component i in the ideal mixture. In a binary mixture, $f_A^{id} + f_B^{id} = 1$. This equation states that the relative permittivity of a thermodynamically ideal liquid mixture at specified temperature, pressure and electric field strength is the volume-fraction-weighted mean of the pure component relative permittivities. Then the excess relative permittivity, e_r^E , is defined by

$$e_r^E = e_r - e_r^{id} = e_r - (f_A^{id} e_{r,A}^{id} + f_B^{id} e_{r,B}^{id}) \quad (4)$$

Also, other excess electric properties of mixtures, from equation (3), are determined: dielectric polarizations, electric susceptibilities and molar electric dipole moments.

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