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A dielectric binary mixture formula with an interaction term

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A new dielectric binary mixture formula that generalizes Beer's equation is derived by imposing an effective medium theory on the simple rule of mixtures modified by the addition of an interaction term. Dielectric constants of the binary system carbon tetrachloride/1,2-dichloroethane measured at different frequencies and of carbon tetrachloride/butan-2-ol at different temperatures are used to test the applicability of the new mixture formula. Goodness of fit to the experimental data is found. © *1998 Kluwer Academic Publishers*

1. Introduction

For binary systems in which the constituents are miscible, a simple and useful formula for predicting the overall properties is the simple mixture rule. We are here concerned specifically with the dielectric permittivity of such systems. For systems with no or little interaction between the two constituents, the simple mixture rule is appropriate. Examples abound in the literature: a typical case is shown in Fig. 1 for the 1,1,2,2-tetrachloroethane/1,2-dichloroethane system [1], where the dielectric constant ε is plotted against the volume fraction V of 1,2-dichloroethane. However, for many other systems, the simple mixture rule can be totally unsatisfactory, as in the cases where there is a tendency for constituents to form strong complexes [2–4]. In between are systems with weakly interacting constituents [5] which may be appropriately studied by the incorporation of additional terms into the simple linear relationship to take care of the interaction.

A natural and usual way to modify the simple mixture rule to code for these systems is to include a single interaction term [6] so that the modified rule becomes

$$\varepsilon = x(1-V) + \alpha V + \lambda V(1-V) \qquad (1)$$

Here x and α are the dielectric constants of the constituents, V is the volume concentration of the α-constituent, ε the overall or effective dielectric constant and $\lambda V(1-V)$ the interaction term. When the interaction is negligible, i.e. $\lambda = 0$, then the simple rule of mixtures is recovered from Equation 1. λ is assumed to be a constant for a given binary system, and is aptly called an interaction parameter since it is associated with the product of the concentration of the two constituents in Equation 1. The notion of the constancy of λ has to be evaluated by measurements of ε, x, α at different temperatures and frequencies. The presence of λ gives a curvature to the otherwise linear relationship between ε and V. This curvature can be either positive or negative, depending on λ, because $\varepsilon_{VV} = -2\lambda$ (subscripts denote partial derivatives), and is a primary feature which provides versatility to Equation 1 for the description of binary systems with weakly interacting constituents.

When the constituents are interchanged together with their respective concentrations, i.e. $x \leftrightarrow \alpha$ and $V \leftrightarrow (1-V)$, then ε in Equation 1 maintains the same form if λ is regarded as a genuine constant. This symmetry is of course expected of a binary system consisting of miscible components.

In this paper we first argue that λ cannot in general be a true constant, i.e. λ cannot be independent of x and α. Having established that, we then ask how λ, now regarded as a function of x and α, may be determined. We employ as the basis for the present discussion the concepts and results developed in our previous work on symmetric dielectric binary mixtures [7].

2. Theoretical considerations

2.1. λ cannot be an arbitrary constant

The conclusion that λ cannot be a constant follows from the illustration below. Consider a mixture M_1 of x and α in which the volume ratio is $(1-V_1):V_1$, and another mixture M_2 with the ratio $(1-V_2):V_2$. According to Equation 1, their dielectric constant ε_1 and ε_2 respectively are given by

$$\varepsilon_1 = x(1-V_1) + \alpha V_1 + \lambda V_1(1-V_1) \qquad (2)$$

and

$$\varepsilon_2 = x(1-V_2) + \alpha V_2 + \lambda V_2(1-V_2) \qquad (3)$$

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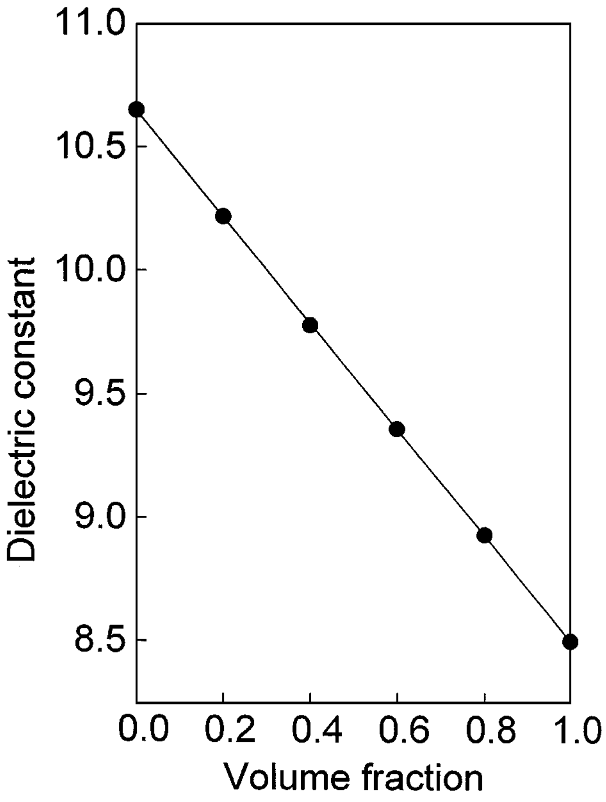

Figure 1 ε versus V for the 1,1,2,2-tetrachloroethane ($C_2H_2Cl_4$)/1,2-dichloroethane ($C_2H_4Cl_2$) system, measured at 1.8 MHz and 20 °C; data from [1]. The values at $V = 0$ and $V = 1$ are the dielectric constant of pure 1,1,2,2-tetrachloroethane and 1,2-dichloroethane, respectively.

We now consider a third mixture, M_3, this time of M_1 and M_2 in the ratio $(1 - V_3) : V_3$. The same equation will give

$$\varepsilon_3 = \varepsilon_1(1 - V_3) + \varepsilon_2 V_3 + \lambda V_3(1 - V_3) \qquad (4)$$

where ε_3 is the dielectric constant of M_3. Of course M_3 is just a mixture of x and α, and careful accounting will show that they occur in the ratio $(1 - V) : V$ where

$$V = V_1(1 - V_3) + V_2 V_3 \qquad (5)$$

This will mean that according to Equation 1

$$\varepsilon_3 = x(1 - V) + \alpha V + \lambda V(1 - V) \qquad (6)$$

In writing down Equation 4, we assume λ is a constant as long as the mixture is still basically one of x and α.

Now when Equations 2 and 3 are put into Equation 4, we get

$$\begin{aligned}\varepsilon_3 = x(1 - V) + \alpha V + \lambda[&V_1(1 - V_1)(1 - V_3)\\ &+ V_2(1 - V_2)V_3 + V_3(1 - V_3)] \qquad (7)\end{aligned}$$

which is generally not consistent with Equation 6. This inconsistency implies that λ cannot strictly be interpreted as independent of the dielectric constants of the mixture constituents. If this is so, then $\lambda = \lambda(x, \alpha)$ in Equation 1. The inconsistency is removed because λ in Equation 4 will now be $\lambda(\varepsilon_1, \varepsilon_2)$ and we will not obtain Equation 7, but a more complicated one in its stead:

$$\begin{aligned}\varepsilon_3 = x(1 - V) + \alpha V + \{&\lambda(x, \alpha)[V_1(1 - V_1)(1 - V_3)\\ &+ V_2(1 - V_2)V_3] + \lambda(\varepsilon_1, \varepsilon_2)V_3(1 - V_3)\} \qquad (8)\end{aligned}$$

Here ε_1 and ε_2 are given by Equations 2 and 3.

The foregoing is practically an application of the effective medium concept of [8] to a specific symmetric dielectric formula. We have in this case established that λ in Equation 1 must be regarded as a function of x and α if the effective medium concept is to hold, and that $\lambda(x, \alpha)$ is constrained by the consistency requirement between Equations 6 and 8, which implies

$$\lambda(\varepsilon_1, \varepsilon_2) = (V_1 - V_2)^2 \lambda(x, \alpha) \qquad (9)$$

2.2. The functional form of $\lambda(x, \alpha)$

We next come to ask how may $\lambda(x, \alpha)$ be determined. One way is to proceed from Equation 9 and attempt to solve for $\lambda(x, \alpha)$. An alternative approach is to make use of results already derived in [7] from a general consideration of consistency required by the effective medium concept. We shall take the latter approach below.

Let $\varepsilon_V(0)$ and $\varepsilon_V(1)$ denote $(\frac{\partial\varepsilon}{\partial V})_{V=0}$ and $(\frac{\partial\varepsilon}{\partial V})_{V=1}$ and likewise subscripts denote partial derivatives, then it has been shown in [7] that

$$\varepsilon_V(0)\varepsilon_x = (1 - V)\varepsilon_V \qquad (10)$$

and

$$\varepsilon_V(1)\varepsilon_\alpha = V\varepsilon_V \qquad (11)$$

for a symmetric dielectric mixture formula $\varepsilon = \varepsilon(x, \alpha, V)$. In our case

$$\varepsilon(x, \alpha, V) = x(1 - V) + \alpha V + \lambda(x, \alpha)V(1 - V) \qquad (12)$$

from which the relevant derivatives are to be evaluated, thus

$$\varepsilon_V = \alpha - x + \lambda(x, \alpha)(1 - 2V) \qquad (13)$$

$$\varepsilon_V(0) = \alpha - x + \lambda(x, \alpha) \qquad (14)$$

$$\varepsilon_V(1) = \alpha - x - \lambda(x, \alpha) \qquad (15)$$

$$\varepsilon_x = (1 - V)[1 + \lambda_x(x, \alpha)V] \qquad (16)$$

$$\varepsilon_\alpha = V[1 + \lambda_\alpha(x, \alpha)(1 - V)] \qquad (17)$$

Substituting these into Equations 10 and 11, we get

$$(\alpha - x + \lambda(x, \alpha))\lambda_x(x, \alpha) + 2\lambda(x, \alpha) = 0 \qquad (18)$$

and

$$(\alpha - x - \lambda(x, \alpha))\lambda_\alpha(x, \alpha) - 2\lambda(x, \alpha) = 0 \qquad (19)$$

These imply that if $\lambda(x, \alpha)$ is independent of either x or α, then $\lambda(x, \alpha) = 0$, i.e. there will be no interaction. Equation 18 may be integrated w.r.t. x by standard methods to yield

$$(\alpha - x - \lambda(x, \alpha))^2 = 4\beta(\alpha)\lambda(x, \alpha) \qquad (20)$$

where the function $4\beta(\alpha)$ arises as an integration constant. Likewise integrating Equation 19 gives

$$(\alpha - x + \lambda(x, \alpha))^2 = 4\gamma(x)\lambda(x, \alpha) \qquad (21)$$

with $4\gamma(x)$ being the constant of integration. Subtracting Equation 20 from Equation 21, we get

$$\beta(\alpha) + \alpha = \gamma(x) + x \qquad (22)$$

from which it follows that

$$\beta(\alpha) = c - \alpha \qquad (23)$$

$$\gamma(x) = c - x \qquad (24)$$

where c is a separation constant independent of x and α. Using either Equation 23 in Equation 20 or Equation 24 in Equation 21, we obtain

$$\lambda(x, \alpha) = 2c - x - \alpha \pm 2\sqrt{(c - x)(c - \alpha)} \qquad (25)$$

In order to satisfy the physical requirement that $\lambda(x, x) = 0$, i.e. if $\alpha = x$ then $\varepsilon = x$ (cf. Equation 12), we have in this case two possible solutions,

$$\varepsilon = x(1 - V) + \alpha V + \left\{2c - x - \alpha - 2\sqrt{(c - x)(c - \alpha)}\right\} V(1 - V) \quad \text{for } c > \alpha, x \qquad (26)$$

$$\varepsilon = x(1 - V) + \alpha V + \left\{2c - x - \alpha + 2\sqrt{(x - c)(\alpha - c)}\right\} V(1 - V) \quad \text{for } \alpha, x > c \qquad (27)$$

Now $\lambda(x, \alpha)$ in Equation 25 may be rewritten as

$$\begin{aligned} \lambda(x, \alpha) &= \left[\sqrt{c - \alpha} - \sqrt{c - x}\,\right]^2 \quad \text{for } c > \alpha, x \\ &= -\left[\sqrt{\alpha - c} - \sqrt{x - c}\,\right]^2 \quad \text{for } \alpha, x > c \end{aligned} \qquad (28)$$

which may be positive or negative and it can be verified that either one satisfies Equation 9. When put back into Equation 12, we have the possibilities

$$\varepsilon = x(1 - V) + \alpha V + \left[\sqrt{c - \alpha} - \sqrt{c - x}\,\right]^2 V(1 - V) \quad \text{for } c > \alpha, x \qquad (29)$$

and

$$\varepsilon = x(1 - V) + \alpha V - \left[\sqrt{\alpha - c} - \sqrt{x - c}\,\right]^2 V(1 - V) \quad \text{for } \alpha, x > c \qquad (30)$$

for "positive" (Equation 29) as well as "negative" (Equation 30) interactions. A positive interaction enhances ε to values higher than those given by the simple mixture rule; the reverse is true for the negative interaction.

Finally, we note that Equation 29 may be obtained from

$$(c - \varepsilon)^{1/2} = (1 - V)(c - x)^{1/2} + V(c - \alpha)^{1/2} \qquad (31)$$

and Equation 30 from

$$(\varepsilon - c)^{1/2} = (1 - V)(x - c)^{1/2} + V(\alpha - c)^{1/2} \qquad (32)$$

by squaring both sides. These now conform to the general expression expected of symmetric formulae [7], and may be regarded as generalizations to Beer's formula [9]:

$$\varepsilon^{1/2} = (1 - V)x^{1/2} + V\alpha^{1/2} \qquad (33)$$

Equations 31 and 32 are "exact" expressions arising from this theory for the dielectric constant of binary systems whose constituents interact weakly in a way that Equation 1 holds or, more realistically, the interaction is such that the first order interaction is already a sufficiently good approximation. The significance of the constant c is that it should characterize such a binary system, and its value should remain constant for different measurement frequencies and temperatures. To see how well this theoretical expectation is borne out in actuality, we shall study some experimental systems that may be nearly described by Equation 1. For a given binary system consisting of constituents x and α, measurements of dielectric constant for various compositions of x and α in the range $V = 0$ to $V = 1$ can be made. The set of data may be fitted by Equation 1 to obtain λ and by Equation 31 or 32 to obtain c. Similar measurements can be made at different frequencies and/or different temperatures, and λ and c similarly determined. We shall then examine the "constancy", or not, of c in comparison to λ, as a function of frequency and/or temperature.

3. Experimental

In order to test the applicability of the Equations 31 and 32 for a binary system measured at different frequencies, measurements of dielectric constant in the frequency range 5 kHz to 1 MHz were made at room temperature (20 °C) with an HP4194A high frequency gain/phase analyser for various compositions of the two constituents of carbon tetrachloride/1,2-dichloroethane system. Analytical grade chemicals were used. The stainless steel liquid sample cell was guarded and the electrode area was 3.0×10^3 mm^2.

4. Results and discussion

The results for carbon tetrachloride/1,2-dichloroethane system are shown in Fig. 2, in which curves fitted by Equation 29 are also drawn. The frequency variation of λ and c obtained by the least-squares fit with Equation 1

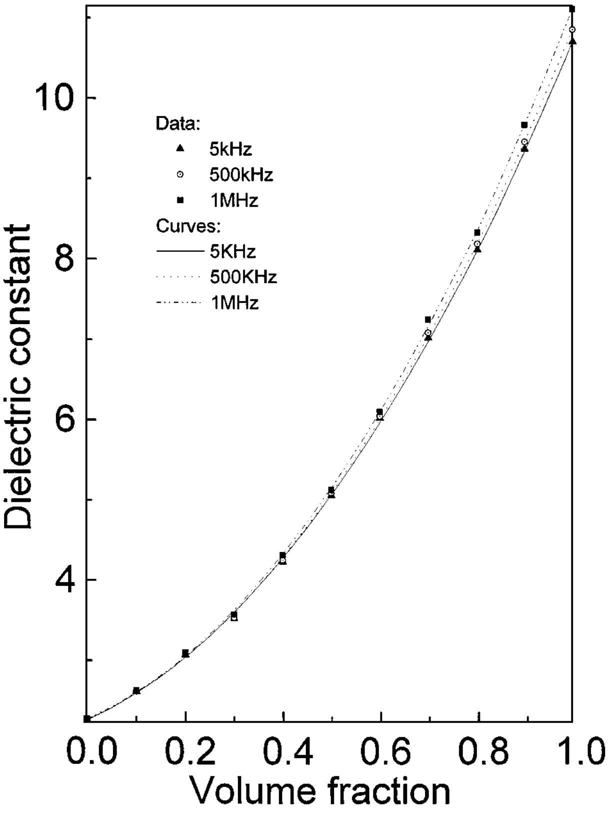

Figure 2 ε versus V for the carbon tetrachloride (CCl_4)/1,2-dichloroethane ($C_2H_4Cl_2$) measured at 20 °C and different frequencies. Curves are fitted by Equation 29. The values at $V = 0$ and $V = 1$ are the dielectric constant of pure carbon tetrachloride and 1,2-dichloroethane, respectively.

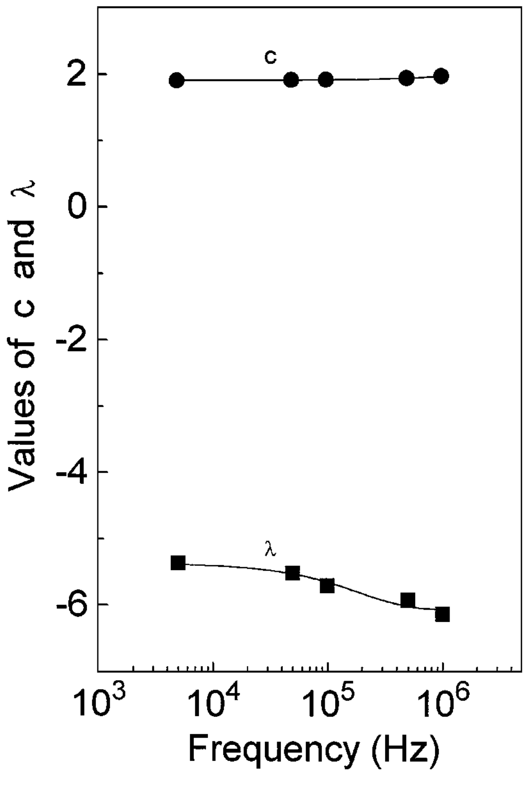

Figure 3 The frequency variation of c and λ for the carbon tetrachloride (CCl_4)/1,2-dichloroethane ($C_2H_4Cl_2$) system.

and Equation 29, respectively, of the experimental data are plotted in Fig. 3. It is noted that c stays fairly constant when compared with λ.

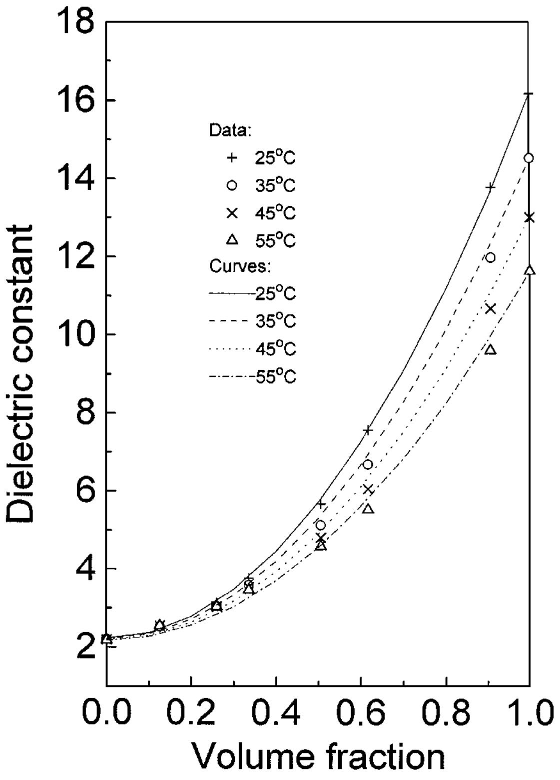

Figure 4 ε versus V for the carbon tetrachloride (CCl_4)/butan-2-ol ($C_4H_{10}O$) system at various temperatures; data from [1]. Curves are fitted by Equation 29. The values at $V = 0$ and $V = 1$ are the dielectric constant of pure carbon tetrachloride and butan-2-ol, respectively.

For temperature variation, dielectric constant data are found from [1] for the carbon tetrachloride/butan-2-ol system measured at 25 °C, 35 °C, 45 °C and 55 °C. Data and curves fitted by Equation 29 are shown in Fig. 4. The temperature variation of λ and c obtained by the least-squares fit with Equation 1 and Equation 29, respectively, are plotted in Fig. 5, where by comparison c is also fairly constant.

The constant c is actually a coefficient characterizing the interaction between the two constituents of a binary system but independent of the contribution of the dielectric constant of each constituent (i.e. independent of the values of x and α). It shows a more constant behavior w.r.t. change in frequency and temperature than λ. One may legitimately interpret this phenomenon by use of Equation 28 and say that c emerges from λ by getting rid of the effects of temperature and frequency dependencies implicitly associated with x and α.

The significance of the derived Equation 31 or 32 as compared with the original formula Equation 1 is that the new equations always satisfy the effective medium concept which is a plausible requirement for miscible binary systems. Since many well-known dielectric binary mixture formulae, although derived from different routes, are found to satisfy the effective medium theory [8], we believe the latter is a useful and reasonable theory from which this work follows. Equation 1 should therefore only be regarded as a convenient mathematical way to describe the experimental data of a binary system because of its simplicity in expression; Equations 31 and 32 are the improved expressions.

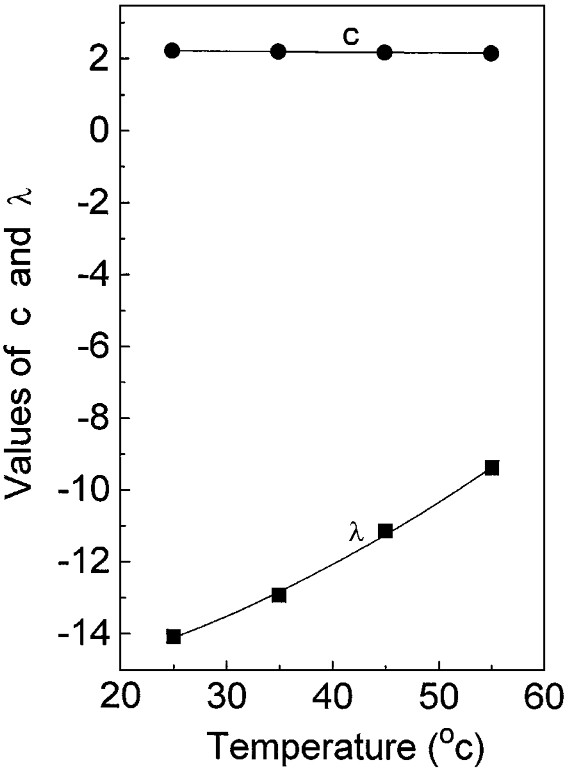

Figure 5 The temperature variation of *c* and λ for the carbon tetrachloride (CCl_4)/butan-2-nol ($C_4H_{10}O$) system.

In fact Equations 31 and 32 also give a very good fit to the dielectric constant of the systems in [5] which form 1 : 1 weak molecular complexes. The Redlich-Kister equation used in [5]

$$Q^E = V(1 - V) \sum_{i=0}^{3} A_i (2V - 1)^i \qquad (34)$$

where Q^E is the excess value, is a generalized case of Equation 1. Nevertheless, this equation should also be tested with the effective medium theory. For those systems with strong complexes [2–4], higher order terms may be needed to give a satisfactory explanation.

5. Conclusion

We conclude from the foregoing paragraphs that indeed c behaves roughly like a constant, i.e. it varies with temperature and frequency to a much lesser extent than λ, thus conforming to our expectation. Equations 31 and 32, the main result of this paper, thus appear to describe binary mixtures of weakly interacting constituents. These equations emerge as a result of imposing the effective medium theory on Equation 1, an equation that modifies the simple rule of mixtures by the addition of an interaction term.

Acknowledgements

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