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November 1986

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Dielectric Constants of Fluid Mixtures over a Wide Range of Temperature and Density

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ABSTRACT

A new expression is derived for estimating the dielectric constant of a fluid mixture as a function of temperature, density, and composition. The estimated dielectric constants (and their derivatives) are required for phase-equilibrium calculations, based on an equation of state, for systems containing electrolytes and nonelectrolytes. The new expression holds for the entire range of fluid densities, from zero to liquid-like densities. Mixing of components is performed on a volume-fraction basis at constant temperature and constant reduced density. For polar components where data are not available at the temperature and/or reduced density of interest, the well-characterized behavior of water is used to extrapolate the available pure-component data. The importance of using the correct density of the mixture is shown, and a further improvement is suggested using one adjustable parameter for each nonideal binary subsystem.

November 1986

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

1. INTRODUCTION

The static dielectric constant is of central importance in the thermodynamics of electrolyte solutions. In particular, the dielectric constant and its derivatives with respect to density and composition play important roles in an equation of state now under development for vapor-liquid equilibria in fluid mixtures containing electrolytes.⁽¹⁾ For calculating fugacity coefficients from an equation of state, it is necessary to compute the dielectric constant and its derivatives over the entire composition range, at densities ranging from zero to liquid-like densities, and at all temperatures of interest. We present here an expression for the dielectric constant which is suitable for use over this broad spectrum of conditions, utilizing the dielectric theory of Kirkwood⁽²⁾ and the equation of Uematsu and Franck⁽³⁾ which describes the dielectric constant of water over a wide range of temperature and density.

2. CONVENTIONAL METHOD

The most successful theory for the dielectric constant of a pure fluid is that due to Kirkwood⁽²⁾ where the polarization is expressed as a function of polarizability α , dipole moment μ , and the g-factor, which represents the amount of correlation between neighboring dipoles:

$$p = \rho \frac{4\pi N_{Av}}{3} \left(\alpha + \frac{\mu^2 g}{3kT} \right) \quad (1)$$

Here ρ is the molar density, N_{Av} is Avogadro's number, and p is the polarization per unit volume, related to the static dielectric constant D by

$$p = \frac{(D-1)(2D+1)}{9D} \quad (2)$$

Other theories are often successful for limited situations, but only Kirkwood's correctly describes the behavior of associated liquids such as water.

A rigorous extension of Kirkwood's theory to mixtures would require a complicated description of orientational correlations among various polar

species in the mixture; this is clearly not practical. Oster⁽⁴⁾ assumed that the polarization (and hence the g-factor) for each pure component was unchanged upon mixing at constant temperature T and pressure P¹, producing the following expression for the polarization of a mixture of n components

$$p_m = \rho_m \sum_{i=1}^n x_i v_i p_i \quad (3)$$

where x_i is the mole fraction of species i, v_i and p_i are the molar volume and polarization per volume for pure component i at T and P, and subscript m refers to the mixture.

Equation (3) is often simplified by assuming zero volume change upon mixing; in that event

$$p_m = \sum_{i=1}^n \phi_i p_i \quad (4)$$

where ϕ_i is the volume fraction based on pure-component molar volumes:

$$\phi_i = \frac{x_i v_i}{\sum_{j=1}^n x_j v_j} \quad (5)$$

As shown later, this approximation can lead to significant errors in systems with large excess volumes such as alcohol/water mixtures.

Despite the neglect of mixing effects on intermolecular correlations, Equation (3) is often fairly successful in predicting the dielectric constants of liquid mixtures from the dielectric constants of the pure components. The density of the mixture is required, but that can often be estimated using the relatively large amount of available excess-volume data.⁽⁵⁾

Oster's rule is limited, however, by its use of pure-component molar volumes v_i at T and P. There are many cases where, for some species i, v_i at T and P either does not exist (this will be the case if i is an ion) or does not

¹ P in this work always signifies the pressure and should not be confused with the total polarization which is sometimes given this symbol in the literature.

describe the state of component i in the mixture. The latter occurs, for example, when component i , at a temperature above its boiling point at pressure P , is a component in a liquid phase. In such a case, the vapor-like volume v_i is inappropriate for species i in the liquid mixture. A hypothetical liquid density might be extrapolated from temperatures below the boiling point, but such extrapolation becomes impractical for components above their critical temperatures.

An even more severe limitation is the requirement for pure-component dielectric-constant data at T and P , as required to compute p_i from Equation (2). These data generally exist only for liquids at temperatures up to the normal boiling point, or often only at 25 °C. Therefore, Oster's rule cannot be readily applied at temperatures where some component of the mixture is outside the range of available pure-component data, or at densities below normal liquid densities. This limitation is particularly serious for equation-of-state calculations which must be performed over the entire density range from zero to liquid-like densities.

3. NEW METHOD

We replace Oster's mixing rule by a more general formulation in which we bring each component to a density corresponding to the reduced density of the mixture, thus insuring that all molar volumes in the mixing rule are physically appropriate. We then mix the components at constant temperature and constant reduced density. To estimate pure-component polarizations at conditions where no dielectric-constant data exist, we use water as a model substance for polar and associating fluids and Equation (1) (with $\mu = 0$) for nonpolar components. We replace Equation (3) by

$$p_m = \sum_{i=1}^n \Phi_i^\dagger p_i^\dagger \quad (6)$$

where superscript \dagger signifies a property evaluated at a density corresponding to

ρ_{rm} , the reduced density of the mixture, defined by

$$\rho_{rm} = \rho_m \sum_{i=1}^n x_i v_i^* \quad (7)$$

where ρ is the molar density and v_i^* is some characteristic molar reducing volume for component i . The density corresponding to ρ_{rm} for a pure component i is

$$\rho_i^\dagger = \frac{\rho_{rm}}{v_i^*} \quad (8)$$

It is this density at which p_i^\dagger is evaluated.

In equation-of-state work, it is often convenient to use σ^3 as the reducing volume, where σ is a hard-core molecular diameter. Another reasonable choice is the molar volume at the critical point; that is what we use here. The volume fractions Φ_i^\dagger are also defined using these reducing volumes:

$$\Phi_i^\dagger = \frac{x_i v_i^*}{\sum_{j=1}^n x_j v_j^*} \quad (9)$$

Computation of the mixture dielectric constant D_m then reduces to calculation of all p_i^\dagger , the polarization per unit volume for each component i at temperature T and density ρ_i^\dagger given by Equation (8). Then p_m is computed from Equation (6), and Equation (2) is used to solve for the mixture dielectric constant D_m .

When component i is water, the equation of Uematsu and Franck⁽³⁾ (which gives the dielectric constant for water as a function of temperature and density) can be used directly to calculate a dielectric constant and thus p_i^\dagger from Equation (2) at T and ρ_i^\dagger .

For nonpolar components, if there are no dielectric-constant data, we compute p_i^\dagger at ρ_i^\dagger from Equation (1) (with $\mu = 0$), which is sufficiently accurate at all fluid densities. This computation requires polarizability α , which is tabulated.⁽⁶⁾ For many nonpolar organic compounds a single dielectric-constant

datum is known; in this case, the functional form of Equation (1) (where p is linear in density) is used to adjust the polarization from the density at that data point to ρ_i^\dagger .

For polar or associating components, it is likely that dielectric-constant data are not available at T and ρ_i^\dagger . Often there exists a value for the saturated liquid at or near T , or perhaps only at 25°C. If there are data points at temperatures both above and below T , we interpolate D and ρ between these points to get reference values D_i^o and ρ_i^o at $T_i^o = T$. Otherwise we choose D_i^o and ρ_i^o at the T_i^o closest to T . To extrapolate from the reference point to T and ρ_i^\dagger , we assume that the dependence of the polarization per volume p_i on temperature and density is the same as that for water when the substances are at the same reduced density and reduced temperature. This gives

$$p_i^\dagger = p_i(T_i^o, \rho_i^o) \left[\frac{p_{H_2O}(T / \tau_i, \rho_i^\dagger \nu_i)}{p_{H_2O}(T_i^o / \tau_i, \rho_i^o \nu_i)} \right] \quad (10)$$

$$\tau_i = \frac{T_{c,i}}{T_{c,H_2O}} \quad (10a)$$

$$\nu_i = \frac{v_i^*}{v_{H_2O}^*} \quad (10b)$$

where T_c is the critical temperature. Polarizations p_{H_2O} in Equation (10) can be computed from the equation of Uematsu and Franck and Equation (2).

Finally, we consider the possibility that component i might be an ion. In our application we only wish to consider the contribution of the electronic and atomic polarizabilities of the ion; hence we do not attempt to predict the full dielectric decrement observed in electrolyte solutions. We consider the ions as uncharged nonpolar molecules and use equation (1) to calculate p_i^\dagger . In an equation of state, σ_i^3 can be used for the characteristic volume v_i^* . If critical volumes are used, a reasonable estimate is given by:

$$v_i^* = 1.8 \sigma_i^3 \quad (11)$$

where v_i^* is in cm^3 per mole and σ_i is in Angstroms. The constant 1.8 was obtained by comparing critical volumes and hard-sphere diameters for the noble gases from neon to xenon.

Regardless of the composition of the mixture, the analytic form of the equation of Uematsu and Franck or of Equation (1) makes it possible to differentiate p_m in Equation (6) with respect to density or composition for equation-of-state calculations.

4. RESULTS

For liquid mixtures of components which exist as pure liquids at the temperature of interest, there is very little difference between our method [Equation (6)] and the original equation of Oster [Equation (3)]. However, for alcohol/water systems, the approximate Equation (4) produced larger errors due to the neglect of the excess volume. Figure 1 shows results for the water/methanol system at 25 °C. Density data are taken from Eastel and Woolf⁽⁷⁾ and dielectric-constant data are from Albright and Gosting⁽⁸⁾. The dashed line represents the approximation given by Equation (4); the solid line represents both our method and results from Oster's rule (These two lines are almost indistinguishable on the scale shown.)

The important advantage of our method is its flexibility; upon using water as a model compound for polar and associating fluids within Kirkwood's theory, we can estimate the dielectric constant from zero density to liquid-like densities and over a wide range of temperatures. The equation for water covers the range from 0-550°C; therefore our method is useful for the corresponding range of reduced temperatures for each polar component:

$$0.42 < \frac{T}{T_{c,i}} < 1.27 \quad (12)$$

To illustrate the broad range of application of our method, we consider

first calculations for the water/ethanol system at 80 °C; dielectric constants were measured by Åkerlöf.⁽⁹⁾ Since this temperature is above the boiling point of ethanol, no dielectric-constant data for liquid ethanol at T exist to use in Oster's rule. However, we are able to compute the curve in Figure 2 using only the dielectric constant and density of pure ethanol at 60°C and the binary density estimates of Westmeier.⁽¹⁰⁾

In Figures 3 and 4 we present results for the entire composition range and for densities from zero to liquid densities. Figure 3 is for the water/methanol system at 80 °C, a temperature above the normal boiling point of methanol. Since methanol is an associated fluid, the density and temperature dependences of its polarization are determined by Equation (10). Figure 4 shows results for water/methane at 25 °C, where methane is a supercritical fluid. Since methane is nonpolar, Equation (1) is used to compute its polarization. For each system, we are able to compute the dielectric constant at all compositions and at all densities of interest (The curves shown are truncated at a reduced density approximately 5% above that for pure water at atmospheric pressure.)

In Figures 3 and 4, some of the combinations of density and composition are not physically realizable for a single fluid phase (e.g., at 25°C, single-phase water does not exist at densities intermediate between the vapor and liquid regions). However, for phase equilibria in mixtures, iterative equation-of-state calculations often require computations in hypothetical (physically unattainable) regions of composition/density space; it is therefore necessary to compute a dielectric constant (and its derivatives) for such hypothetical conditions.

5. A SIMPLE EXTENSION

The behavior shown in Figure 1 is typical of that for many binary systems such as alcohol/water mixtures. Even when the correct density data are used,

the linear volume-fraction mixing rules of Equations (3) or (6) do not quite reproduce the data. The disagreement reflects an increased or decreased degree of correlation between neighboring molecules in the mixture.

The regular nature of the deviations in these systems suggests that a quadratic mixing rule should provide an improvement over the linear rule. We therefore propose the following extension of Equation (6):

$$p_m = \sum_{i=1}^n \sum_{j=1}^n \phi_i^\dagger \phi_j^\dagger p_{ij}^\dagger \quad (13)$$

We define p_{ij}^\dagger by

$$p_{ij}^\dagger = \frac{1}{2}(p_i^\dagger + p_j^\dagger) (1 + \delta_{ij}) \quad (14)$$

where δ_{ij} is a binary parameter, close to zero, fit to dielectric-constant data for the i-j binary system. Equation (13) reduces to Equation (6) if all $\delta_{ij} = 0$. Binary parameter δ_{ij} gives some indication of the mixing effects on the g-factor, but it is perhaps best regarded as an empirical adjustment to the linear mixing rule.

Figure 5 shows results from Equation (13) for the water/methanol system at six different temperatures. The fit was obtained with $\delta_{ij} = 0.046$. The results could be improved slightly by giving δ_{ij} a small temperature dependence, but that small improvement does not justify the use of an additional adjustable parameter.

Our procedure does not in general correlate the deviant dielectric behavior caused by specific interactions in the dilute regions of some binaries, as for example by the apparent structure-breaking effect of small concentrations of water in long-chain alcohols.⁽¹¹⁾

6. CONCLUSIONS

We have developed a systematic method for predicting the dielectric constant of a multicomponent mixture using only pure-component data. Equation

(6) can be used in situations where the pure-component properties required in the conventional method are not available. Equation (6) is based on the concept of isothermal mixing at constant reduced density and upon using the well-studied properties of water to extrapolate dielectric-constant data for other polar substances over wide ranges of temperature and density.

Equation (13) provides a simple improvement over the linear mixing rule. Each parameter δ_{ij} can be fitted to available binary dielectric-constant data or set equal to zero if data are insufficient. We are currently fitting values of δ_{ij} to several binary systems to test Equation (13) for predicting dielectric constants of ternary mixtures.

ACKNOWLEDGEMENTS

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Part of this work was performed while A. H. held a National Science Foundation Graduate Fellowship.

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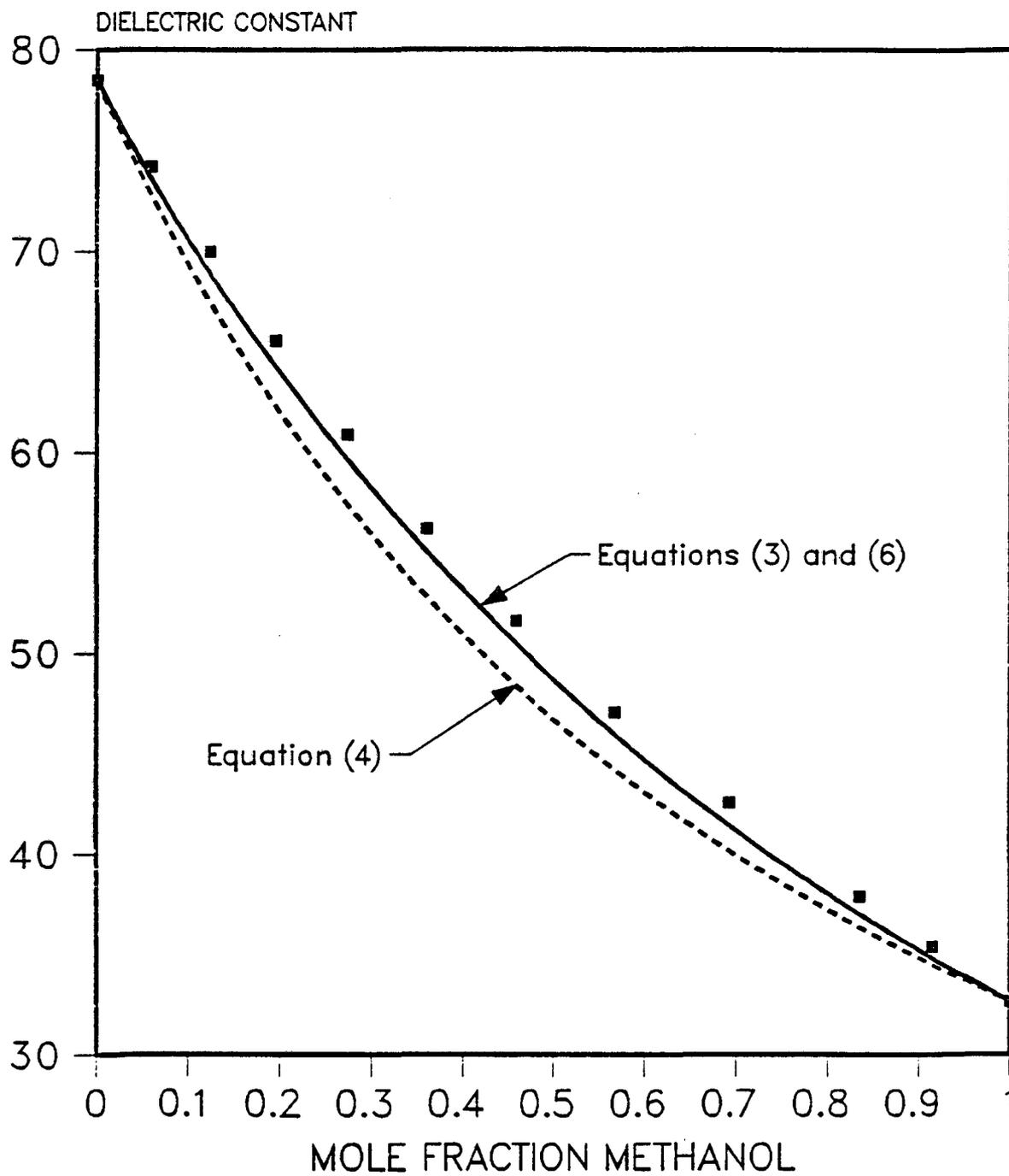


Figure 1. Static dielectric constant for the water/methanol system at 25°C.

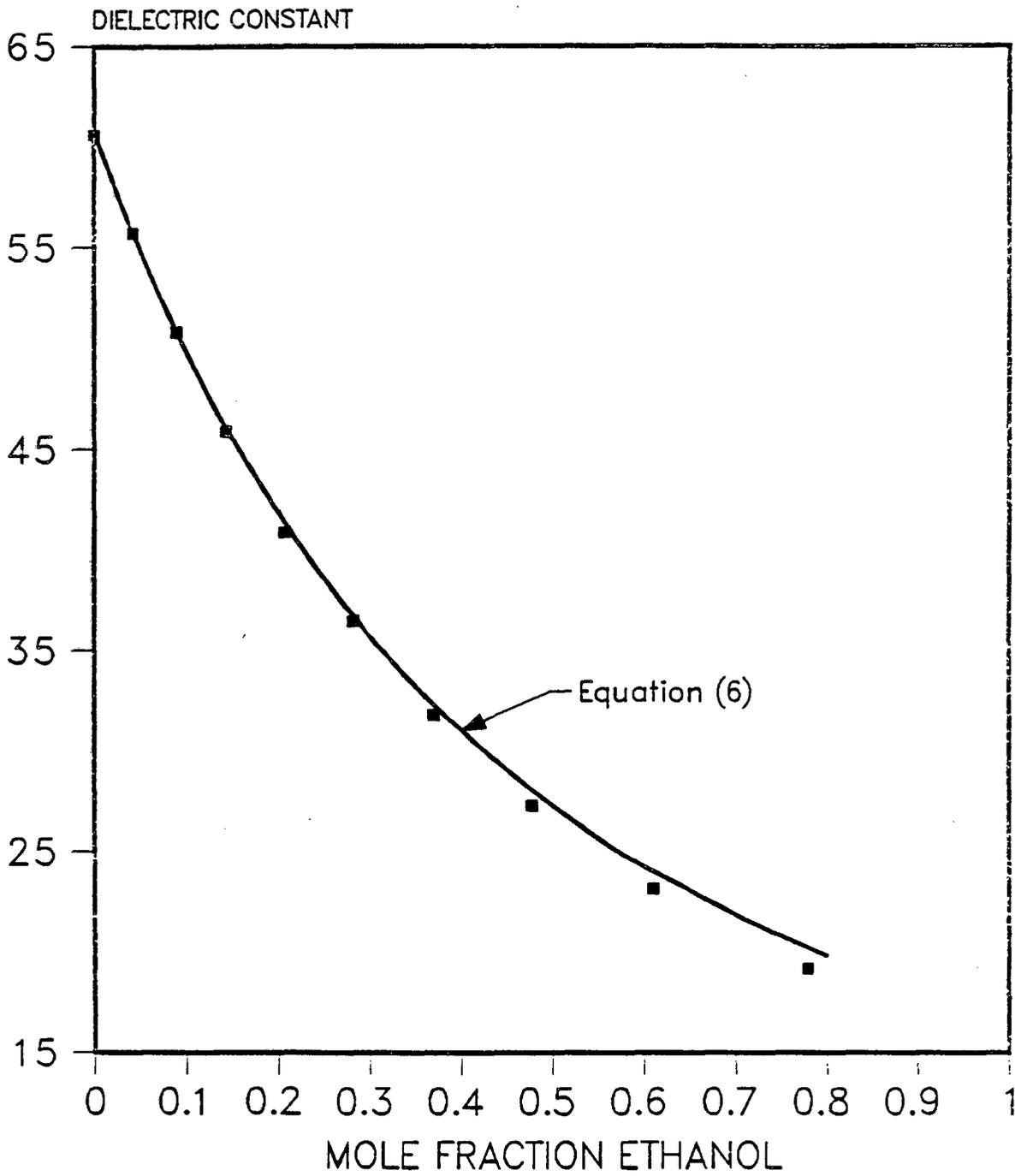


Figure 2. Static dielectric constant for the water/ethanol system at 80°C.

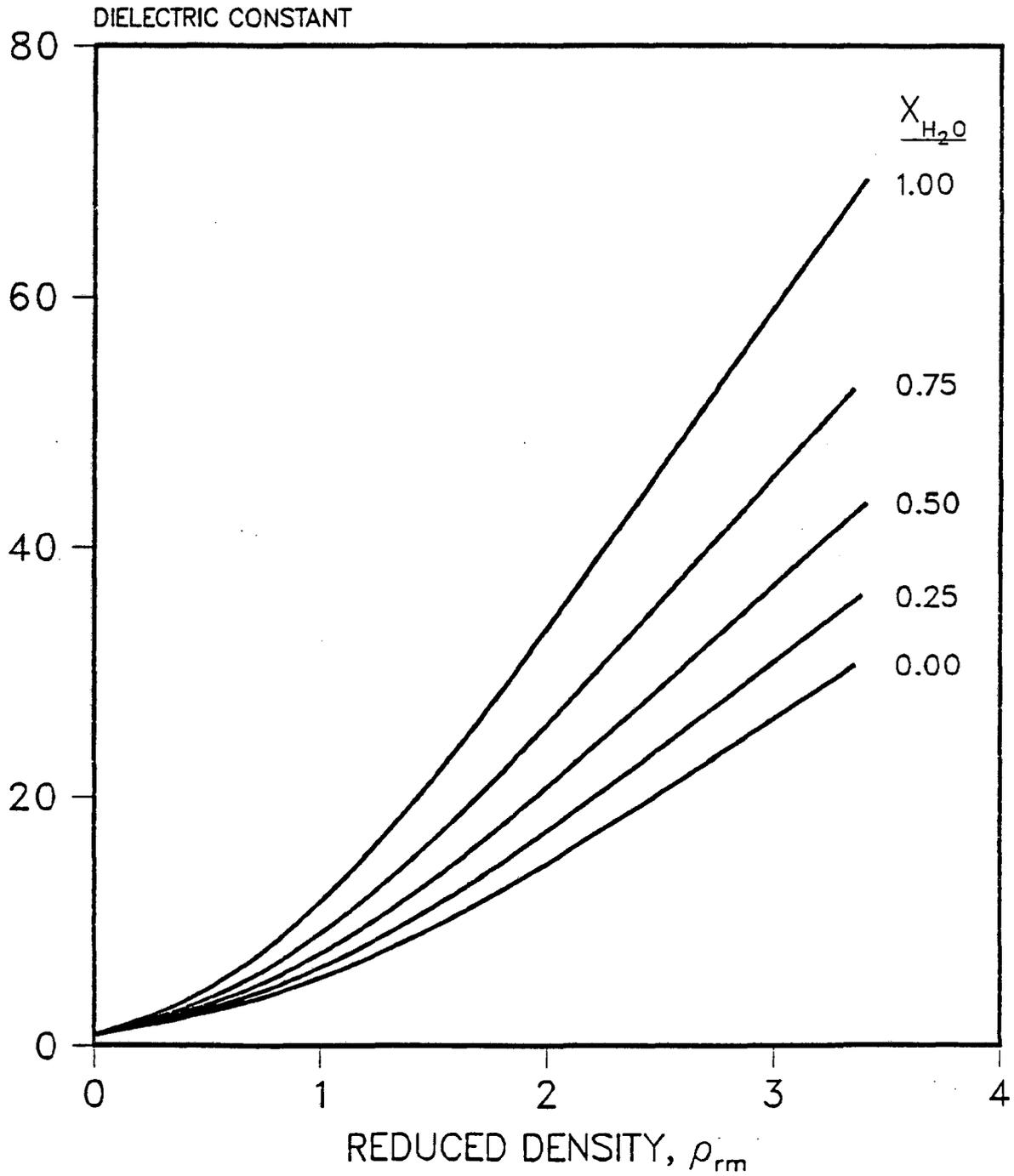


Figure 3. Dielectric constant over the entire density range for water/methanol mixtures at 80°C.

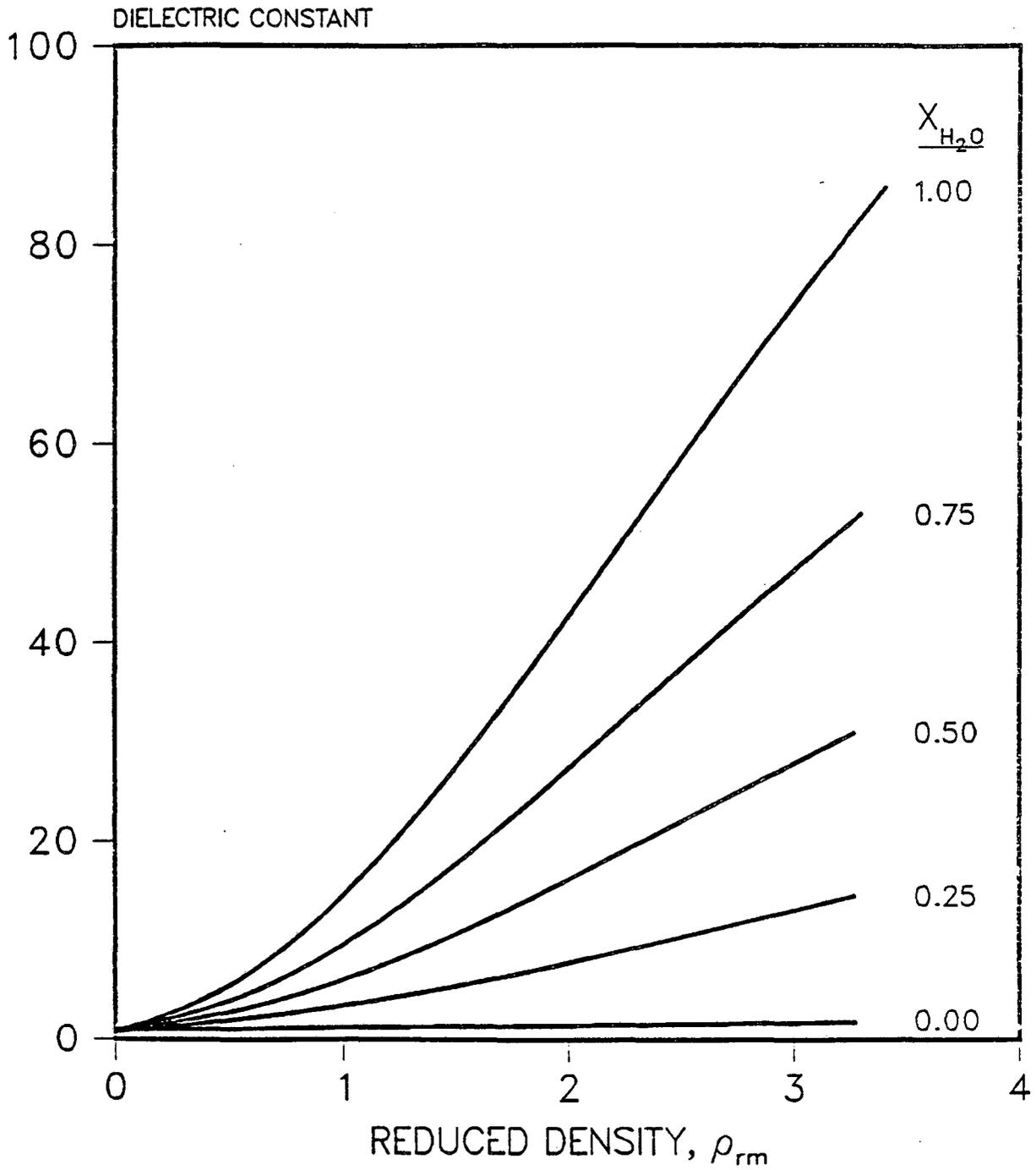


Figure 4. Dielectric constant over the entire density range for water/methane mixtures at 25°C.

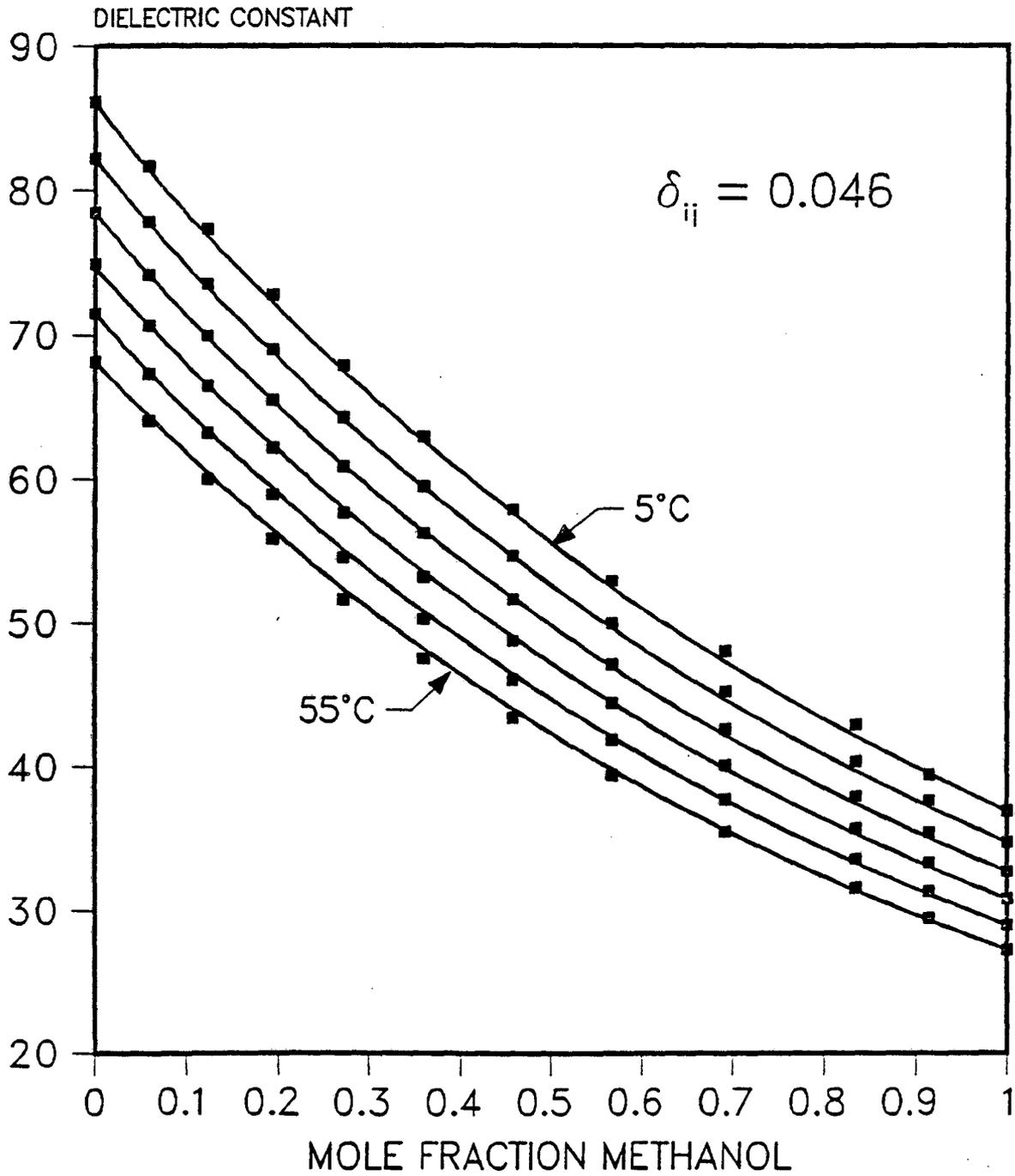


Figure 5. Dielectric constant for the water/methanol system at ten-degree temperature intervals. Fit with one binary parameter.

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