

AN ABSTRACT OF THE THESIS OF

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Modeling the Excess Gibbs Free Energy for

Selected Binary and Ternary Alcohol - Water Mixtures

Abstract approved: Charles Gunter

The excess Gibbs free energy provides a useful means for the analysis of the non-ideality of chemical solutions. Several models [Margules, van Laar, Wilson, and non-random two liquid (NRTL)] are used to predict the behavior of isothermal vapor-liquid equilibrium data for binary mixtures of methanol + water, ethanol + water, methanol + ethanol, and the ternary system methanol + ethanol + water at 323.15 K, 328.15 K, and 333.15 K. Only the Wilson and the NRTL equations have the ability to give good fit for the activity coefficients over the entire composition range. Nonlinear regression techniques are used to fit the Wilson and NRTL models. The experimental data are checked for thermodynamic consistency.

Modeling the Excess Gibbs Free Energy for
Selected Binary and Ternary Alcohol - Water Mixtures

A Thesis

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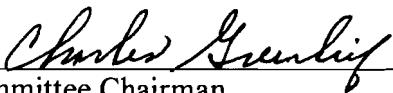
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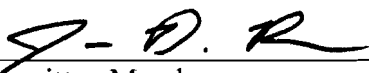
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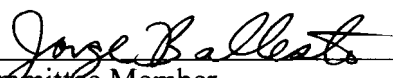
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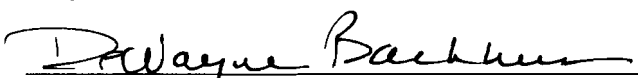
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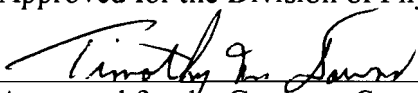
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Solo Dei Gloria

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Chapter 1

INTRODUCTION

1.1 Ideal Solutions

The concept of an ideal solution is useful in the study of real solutions, just as the concept of an ideal gas is useful in the study of real gases. Ideal behavior provides a convenient basis upon which correction factors are introduced to quantitatively express real behavior. Ideal solution behavior is defined by

$$f_i = x_i f_i^\circ \quad (1.1)$$

Equation (1.1) states that the fugacity f_i of component i is proportional to its mole fraction x_i for all values of x_i and the temperature T . The constant of proportionality is f_i° , the fugacity of component i as a pure liquid at the temperature and pressure of the solution.¹

The chemical potential of component i in an ideal solution is given by the relationship

$$\mu_i = G_i^\circ + RT \ln x_i \quad (1.2)$$

The superscript $^\circ$ now denotes a pure liquid at the T and pressure P of the solution. G is the Gibbs free energy. Upon suitable differentiation of Equation (1.2), one obtains the following ideal solution equations.

$$V(\text{solution}) - x_1 V_1^\circ - x_2 V_2^\circ = \Delta V^{\text{mix}} \quad (1.3)$$

$$\Delta V^{\text{mix}} = 0 \quad (1.4)$$

$$\Delta H^{\text{mix}} = 0 \quad (1.5)$$

$$\Delta S^{\text{mix}} = -R[x_1 \ln x_1 + x_2 \ln x_2] \quad (1.6)$$

$$\Delta G^{\text{mix}} = RT[x_1 \ln x_1 + x_2 \ln x_2] \quad (1.7)$$

The properties of an ideal solution are thus simply related to those of the pure components in their standard states and pure liquid at the T and P of the solution.²

The volume of the ideal solution is equal to the sum of its pure component volumes; no change of volume takes place upon mixing the pure components to make the solution. Similarly, the enthalpy of the ideal solution is equal to the sum of the pure component enthalpies; there is no heat effect upon mixing. These relationships are sometimes useful for making rough estimates of the properties of real solutions, just as ideal-gas equations are useful for similar purposes in connection with real gases. However, the most important use of the ideal-solution equations is to provide a basis for the definition and evaluation of correction factors that express the behavior of real solutions.

1.2 Real Solutions

All real solutions deviate from ideal-solution behavior since the components are different in size, shape, mass, and chemical nature. The deviations from ideal-solution behavior are quantitatively expressed in terms of activity coefficients γ_i defined by²

$$\gamma_i = f_i / x_i f_i^\circ \quad (1.8)$$

For a component that follows ideal-solution behavior, $\gamma = 1$. Therefore, in the real solution, the chemical potential will be given by the following equation:

$$\mu_i = G_i^\circ + RT \ln x_i + RT \ln \gamma_i \quad (1.9)$$

By summing the chemical potentials of the components, one obtains, for the solution,

$$G = \sum_i x_i G_i^0 + RT \sum_i x_i \ln x_i + RT \sum_i x_i \ln \gamma_i \quad (1.10)$$

Equation (1.10) shows that the change in G upon mixing the components is³

$$G^{\text{mix}} = RT \sum_i x_i \ln x_i + RT \sum_i x_i \ln \gamma_i \quad (1.11)$$

The last term is defined to be the excess Gibbs free energy of the solution.⁴

$$G^{\text{ex}} = RT \sum_i x_i \ln \gamma_i \quad (1.12)$$

1.3 Binary Systems

The Gibbs free energy of mixing for a binary solution is

$$\Delta G^{\text{mix}} = RT[x_1 \ln x_1 + x_2 \ln x_2] + RT[x_1 \ln \gamma_1 + x_2 \ln \gamma_2] \quad (1.13)$$

The first term describes ideal solution behavior and the second term describes deviations from the ideal.

The representation of excess free energy of a mixture by an empirical function provides one way of efficiently describing its nonideal behavior. A single function representing the dependence of G^{ex} on the mole fraction is sufficient to completely describe the nonideal behavior of a system. The activity coefficients of the components are derived from evaluating the partial molar excess Gibbs free energy. In this research, different models describing the behavior of selected alcohol – water mixtures are compared. Also, given a limited amount of experimental data, one can determine the parameters in the appropriate polynomial expansion, and then predict the excess Gibbs free energy and liquid phase activity coefficients over the entire composition range. Of course, any expression chosen for the excess Gibbs free energy must satisfy the Gibbs-Duhem equation. In this research the Margules, the

van Laar, the Wilson and the non-random two liquid (NRTL) models for the excess Gibbs free energy are compared with the experimental data of selected binary and ternary alcohol systems.⁵

1.4 Margules Model

Margules proposed equations for the activity coefficients that are equivalent to a power series expansion in the composition. For binary solutions, these equations are usually written as follows

$$\ln \gamma_1 = [A_{12} + 2(A_{21} - A_{12})x_1]x_2^2 \quad (1.14)$$

$$\ln \gamma_2 = [A_{21} + 2(A_{12} - A_{21})x_2]x_1^2 \quad (1.15)$$

Further, it is convenient to define excess functions

$$M^{\text{ex}} = M(\text{solution}) - M^{\text{ideal}} \quad (1.16)$$

$$G^{\text{ex}}/(RT) = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 = x_1 x_2 [A_{21}x_1 + A_{12}x_2] \quad (1.17)$$

$$G^{\text{ex}}/(x_1 x_2 RT) = A_{12} + (A_{21} - A_{12}) x_1 \quad (1.18)$$

1.5 van Laar Model

The van Laar equations for the activity coefficients may be written in the following form:

$$\ln \gamma_1 = B_{12} \left(1 + \frac{B_{12}x_1}{B_{21}x_2}\right)^{-2} \quad (1.19)$$

$$\ln \gamma_2 = B_{21} \left(1 + \frac{B_{21}x_2}{B_{12}x_1}\right)^{-2} \quad (1.20)$$

The excess Gibbs free energy may be written in the following linear form:

$$\frac{x_1 x_2 RT}{G^{ex}} = \frac{1}{B_{12}} + \frac{B_{12} - B_{21}}{B_{12} B_{21}} x_1 \quad (1.21)$$

Both the Margules and the van Laar equations assume the ratio of species 1 to species 2 in the vicinity of any molecule is, on the average, the same as the ratio of the mole fractions.⁶ A different class of excess Gibbs free energy models can be formulated by assuming that the ratios of species 1 to species 2 are different. Thus, around each molecule there is a local composition that is different from the bulk composition. From this picture, several binary mixture models have been developed.

The first model of this type developed is the two-parameter (Λ_{12} , Λ_{21}) Wilson equation.⁷ The second model is the three-parameter (α , ν_{12} , ν_{21}) NRTL equation.⁴ In both models the expressions for $\ln \gamma_2$ may be obtained from the equation for $\ln \gamma_1$ by interchanging the subscripts 1 and 2. Also, note that in these models there are different weightings for the mole fractions of the species due to the parameters (Λ_{12} , and ν_{12}), which depend on differences in size and energy of the molecules in the mixture. Wilson obtained an empirical function for representing G^{ex} by considering the preferential orientation of molecules due to energy effects. He postulated that the local concentration in the neighborhood of a central molecule could differ from the bulk concentration because of competition among the various molecular species due to their interactions with the central molecule.

1.6 Wilson Model

The Wilson equations for the activity coefficients are ⁸

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right] \quad (1.22)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right] \quad (1.23)$$

and the excess Gibbs free energy expression is

$$\frac{G^{ex}}{RT} = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(x_2 + \Lambda_{21}x_1) \quad (1.24)$$

and the temperature dependence of the parameters Λ_{12} and Λ_{21} is given by the expressions

$$\Lambda_{12} = \frac{V_2^L}{V_1^L} \exp\left(-\frac{\lambda_{12}}{RT}\right) \quad \Lambda_{21} = \frac{V_1^L}{V_2^L} \exp\left(-\frac{\lambda_{21}}{RT}\right) \quad (1.25)$$

where λ_{ij} is equal to $g_{ij} - g_{ii}$, and g_{ij} and g_{ii} represent the energy of interaction between unlike and like pairs of molecules, respectively. Although g_{ii} is equal to the negative of the heat of vaporization per mole of pure i under identical pressure and temperature as the system, $g_{ij} - g_{ii}$ is treated as a parameter to be determined by fitting the experimental data. V_i^L is the liquid molar volume of component i at the temperature of the mixture.

When a gas, liquid, or solid is added to two partially miscible or completely immiscible solvents, it will, depending on the amount of solute present, either partially or completely dissolve and be distributed unequally between the two liquid

phases. Most chemists and chemical engineers first encounter this phenomenon in the organic chemistry laboratory where diethyl ether, which is virtually immiscible with water, is used to extract reaction products from aqueous solutions. The distribution of a solute between coexisting liquid phases is of industrial importance in purification procedures such as liquid extraction and partition chromatography, and of pharmacological interest in the distribution of drugs between lipids and body fluids. The weakness of the Wilson equation is its limitation to completely miscible systems. Renon and Prauniz ⁴ further developed Wilson's concept of local compositions with the view of obtaining a general equation that would be applicable to partially miscible liquids.

1.7 Non-Random Two Liquid (NRTL) Model

The excess Gibbs free energy for the NRTL model ⁴ is given by

$$\frac{G^{ex}}{RT} = x_1 x_2 \left[\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right] \quad (1.26)$$

where $\tau_{21} = (g_{21} - g_{11}) / RT$, $\tau_{12} = (g_{12} - g_{22}) / RT$, $G_{21} = \exp(-\alpha_{21}\tau_{21})$, $G_{12} = \exp(-\alpha_{12}\tau_{12})$,

and $g_{ij} = g_{ji}$, $\alpha_{ij} = \alpha_{ji}$, and $G_{ii} = G_{jj} = 1$.

The parameter g_{ij} is the interaction energy between the binary pairs of molecules i-j. The parameter α_{ij} characterizes the tendency of the components to mix in a non-random manner. When $\alpha_{ij} = 0$ the local mole fractions are equal to the overall mole fractions and mixing is random. If $\tau_{12} = \tau_{21} = 0$, then $G^{ex}/RT = 0$ and the solution is ideal. The first derivative of the excess Gibbs free energy allows one to calculate the activity coefficients:

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \quad (1.27)$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{21}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \quad (1.28)$$

1.8 Equation of State (EOS)

Several hundred equations of state have been proposed since van der Waals⁹ introduced an equation in 1873 and achieved success in qualitatively describing some important features of the volumetric properties of real fluids. The motivation for the continual effort over the past century stems from several sources. From a practical point of view, the usefulness of a reliable equation exceeds by far the mere description of the P-V-T behavior since it leads directly to departures from ideal-gas values of thermodynamic properties such as enthalpy, entropy, and free energy. As a result, fugacity, vapor pressure, heat of vaporization, activity coefficients, and phase equilibrium in fluid mixtures can all be derived from an EOS.

Even with the potential of large economic rewards, a convenient equation has yet to be found to give accurate results over a wide range of densities and temperatures. This is of course the reason why generalized correlations in the form of tables and graphs are widely used.

The development of equations of state received a fresh stimulus with the advent of electronic computers. New equations are reported at an accelerated rate each year. The equations can vary greatly in complexity and generality. Some very complex equations may be designed to describe only one substance. For instance, one equation containing more than forty constants accurately describes the properties of

steam, and indeed the latest steam tables were generated from it. Other equations may be intended only for a restricted range of conditions. Still others may be very generally applicable, but not highly accurate. However, all existing theoretical equations are practical modifications of either the virial equation, the hard-core equation, or both.

1.9 Thermodynamic Consistency

Several forms of thermodynamics consistency testing exist. They are all based on the Gibbs-Duhem equation. The form of the Gibbs-Duhem equation for the activity coefficients of a binary system may be written as ¹⁰

$$x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,P} + x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_1} \right)_{T,P} = 0 \quad (1.29)$$

If the vapor-liquid data is thermodynamically consistent, then a plot of $\ln(\gamma_1/\gamma_2)$ versus x_1 yields a curve such that the area between the curve and the $\ln(\gamma_1/\gamma_2) = 0$ line are equal and cancel. It may be shown that

$$\frac{1}{RT} \left(\frac{\partial G^{ex}}{\partial x_1} \right)_{T,P} = \ln(\gamma_1 / \gamma_2) \quad (1.30)$$

The right-hand side of this equation is zero since G^{ex} is equal to zero when $x_1 = 0$ and when $x_1 = 1$. Therefore, the integral of $(\partial G^{ex} / \partial x_1)_{T,P}$ over the mole fraction must be zero.

$$\frac{1}{RT} \int_0^1 \left(\frac{\partial G^{ex}}{\partial x_1} \right)_{T,P} dx_1 = \int_0^1 \ln \left(\frac{\gamma_1}{\gamma_2} \right) dx_1 = 0 \quad (1.31)$$

Van Ness has shown that the area test is a necessary, but not a sufficient, condition for consistency.¹¹ Recently he suggested that the residuals $\delta[\ln(\gamma_1/\gamma_2)]$ offer

a better opportunity for consistency testing.¹¹

This thesis is not a comprehensive study of fluid phase thermodynamics, but it does consider a number of activity coefficient models applied to vapor – liquid equilibria at low to moderate pressures. Emphasis has been placed on models that fit the experimental binary and ternary systems of methanol, ethanol, and water.

Chapter 2

THEORY

2.1 Computational Methods

There are two general methods for the computation of vapor-phase compositions from vapor-pressure data. The one¹² which has received the greatest attention, uses the Gibbs-Duhem equation as an auxiliary to produce expressions for the liquid-phase activity coefficients. Vapor-phase compositions are then calculated from the activity coefficients. Usually, an analytic expression is assumed to give the dependence of the excess free energy on liquid composition. The activity coefficient equations are then deduced from it. A trial procedure is employed to determine the coefficients in these equations so the equilibrium and material balance requirements are met. The simplifying assumptions usually required are least restrictive in the case of constant temperature.

The other computational method, which is the subject of this research, allows the direct calculation of vapor compositions from vapor-pressure data. This direct relationship connecting the variables is called the general coexistence equation, because it is an equation that must be satisfied when phases coexist at equilibrium. It is a first-order differential equation, which is suitable for numerical solution, and most conveniently accomplished with the aid of a digital computer. One starts with a general form of the Gibbs-Duhem equation. The common forms of this equation, valid only at constant temperatures and

pressures, are of course inadequate for the treatment of data taken with varying temperature or pressure. A single function representing the dependence of G^{ex} on the mole fractions is sufficient to completely describe the nonideal behavior of a system.

The excess quantities are obtained from empirical correlations or theoretical considerations. These can be expressed in terms of activity coefficients following the appropriate differentiation of following Equation (2.1):

$$G_i^{ex} = RT \ln \gamma_i \quad (2.1)$$

$$V_i^{ex} = RT \left[\frac{\partial(\ln \gamma_i)}{\partial p} \right]_T \quad (2.2)$$

$$S_i^{ex} = -R \left[\frac{\partial(T \ln \gamma_i)}{\partial T} \right]_P \quad (2.3)$$

$$H_i^{ex} = -RT^2 \left[\frac{\partial(\ln \gamma_i)}{\partial T} \right]_P \quad (2.4)$$

If G^{ex} is obtained from theory, the activity coefficients in a binary mixture can be determined according to Equation (2.1) from the intercepts of the tangent to the curve at the composition of the mixture. The activity coefficients of the components are determined after evaluating the partial molar excess Gibbs energy. From Equation (2.1),

$$\gamma_i = \exp(G_i^{ex}/RT) \quad (2.5)$$

The activity coefficients thus derived satisfy the Gibbs-Duhem relation,

$$\left(\sum_i x_i d \ln \gamma_i = 0 \right)_{T,P} \quad (2.6)$$

Equation (2.6) is a special form of the general Gibbs-Duhem equation applied to G^{ex} . Thus, the activity coefficient equations for the various components are

ensured to be thermodynamically consistent.

2.2 Binary Systems

The relationship between activity coefficient and free energy will be derived first and the usefulness of activity coefficients will be briefly discussed. The total Gibbs free energy, G , of a binary homogeneous system can be written as follows:

$$G = n_1 G_1^0 + n_2 G_2^0 + n_1 RT \ln x_1 + n_2 RT \ln x_2 + (n_1 + n_2) \Delta G \quad (2.7)$$

In which n_1 and n_2 are numbers of moles, x_1 and x_2 are mole fractions, G_1^0 and G_2^0 are free energies of one mole of each of the pure substances, and ΔG is the nonideal term. The latter term represents the difference between the free energy of one mole of a real mixture and the free energy of one mole of a mixture of the same composition if it were ideal. For the partial free energies of the components it follows that¹³

$$\frac{\partial G}{\partial n_1} = g_1 = G_1^0 + RT \ln x_1 + \frac{\partial[(n_1 + n_2)\Delta G]}{\partial n_1} = G_1^0 + RT \ln x_1 + RT \ln \gamma_1 \quad (2.8)$$

where γ_1 is the activity coefficient for component 1. Further, it follows that

$$\ln \gamma_1 = \frac{\partial[(n_1 + n_2)\Delta G / RT]}{\partial n_1} \quad (2.9)$$

Correspondingly for the second component

$$\frac{\partial G}{\partial n_2} = g_2 = G_2^0 + RT \ln x_2 + RT \ln \gamma_2 \quad (2.10)$$

$$\ln \gamma_2 = \frac{\partial[(n_1 + n_2)\Delta G / RT]}{\partial n_2} \quad (2.11)$$

Knowledge of the activity coefficients for a substance in mixed phases as a function of the mole fraction permits the establishment of the equilibrium condition for homogeneous and heterogeneous mixtures of this substance in nonideal mixtures of arbitrary composition.

2.3 Margules Equation

For the two-suffix Margules equation (symmetrical systems), the characteristic equation is

$$\frac{\Delta G}{RT} = x_1 x_2 A \quad (2.12)$$

According to Equations (2.9) and (2.11) it follows that

$$\ln \gamma_1 = x_2^2 A \quad \ln \gamma_2 = x_1^2 A \quad (2.13)$$

$$\ln \gamma_2 = x_1^2 A \quad \ln \gamma_1 = x_2^2 A \quad (2.14)$$

The values for infinite dilutions are

$$\lim_{x_1 \rightarrow 0} [\ln \gamma_1] = \lim_{x_2 \rightarrow 0} [\ln \gamma_2] = A \quad (2.15)$$

Theoretically, Equations (2.12) and (2.15) represent the “zeroth approximation” for strictly regular solutions, i.e., roughly speaking they represent for mixtures having molecules of equal size and shape in which no formation of higher chemical complexes or no appreciable change of the complexity of the pure substances occurs.

2.4 van Laar Equation

The equation of van Laar (two-suffix q-equation) may be written ¹³

$$\frac{\Delta G}{RT} = \frac{(q_1 x_1)(q_2 x_2)2a_{12}}{q_1 x_1 + q_2 x_2} \quad (2.16)$$

where q_1 , q_2 and a_{12} are constants. The subscripts of a_{12} indicate that a_{12} appears in a term that contains the product $x_1 x_2$.

This equation may be made plausible by the following analysis. The nonideality term of Equation (2.7) for an arbitrary amount of mixture, $(n_1+n_2)\Delta G$, for the Margules equation has the form

$$(n_1 + n_2)\Delta G = (n_1 + n_2)\left(\frac{n_1}{n_1 + n_2}\right)\left(\frac{n_2}{n_1 + n_2}\right)A \cdot RT \quad (2.17)$$

from which follows Equation (2.12). Equation (2.17) can be made more general by multiplying each n_i on the right side of the equation by an arbitrary factor q_i and each n_2 by q_2 . If $2a_{12}$ is substituted for A , one obtains

$$(n_1 + n_2)\Delta G = (q_1 n_1 + q_2 n_2)\left(\frac{q_1 n_1}{q_1 n_1 + q_2 n_2}\right)\left(\frac{q_2 n_2}{q_1 n_1 + q_2 n_2}\right)2a_{12} \cdot RT \quad (2.18)$$

which is consistent with Equation (2.16).

If the “generalized volume fractions” or “q-fractions”

$$z_1 = \frac{x_1}{x_1 + \frac{q_2}{q_1} x_2} \quad (2.19)$$

and
$$z_2 = \frac{x_2 \frac{q_2}{q_1}}{x_1 + \frac{q_2}{q_1} x_2} \quad (2.20)$$

are introduced, one may write instead

$$\frac{\Delta G}{RT} = (x_1 + \frac{q_2}{q_1} x_2) q_1 \cdot 2a_{12} \cdot z_1 \cdot z_2 \quad (2.21)$$

The abbreviations

$$q_1 2a_{12} = A \quad (2.22)$$

$$q_2 2a_{12} = B \quad (2.23)$$

are used. This leads to the relation

$$\frac{q_1}{q_2} = \frac{A}{B} \quad (2.24)$$

which will be inserted into the Equations (2.19) and (2.20) for the q-fractions z_1

and z_2 . It follows that

$$\frac{\Delta G}{RT} = (x_1 + \frac{B}{A} x_2) A z_1 z_2 = \frac{B x_1 x_2}{x_1 + \frac{B}{A} x_2} \quad (2.25)$$

utilizing the Equations (2.9) and (2.11), one obtains

$$\ln \gamma_1 = A z_2^2 = \frac{A x_2^2}{(\frac{A}{B} x_1 + x_2)^2} ; A = \text{limit } \ln \gamma_{1(x_1 \rightarrow 0)}, \quad (2.26)$$

$$\text{and } \ln \gamma_2 = B z_1^2 = \frac{B x_1^2}{(x_1 + \frac{B}{A} x_2)^2} ; B = \text{limit } \ln \gamma_{2(x_2 \rightarrow 0)} \quad (2.27)$$

where q_1 and q_2 are the van der Waals volumes b_1 and b_2^{10} . It is expected that the

van Laar equation will be valid when neither the pure substances nor the mixtures form higher molecular complexes or when the complexity of the pure phases are not appreciably changed by mixing. This means that van Laar equation can be expected to be valid if the heat of solution does not change much with composition. Large values of A and B appear compatible with van Laar's equation, but a large ratio of B/A or A/B will indicate a situation which is beyond the simple approximation given by the van Laar equation.

2.5 Wilson Equation

Wilson⁷ uses the concept of "local concentration" as a correction to earlier models. His equation has some theoretical background. Based on the Flory-Huggin's theory of athermal solutions, it involves, even for multicomponent systems, only two temperature-independent (over a moderate range) constants for each binary pair.

Wilson suggested the following equation for the local concentrations:

$$\frac{x_{ji}}{x_{ki}} = \frac{x_j \exp(-g_{ji} / RT)}{x_k \exp(-g_{ki} / RT)} \quad (2.28)$$

where x_j is the mole fraction of species j in the bulk solution, and x_{ji} is the local mole fraction of j in the neighborhood of a molecule of species i. The interaction energy between the pair ij is g_{ij} . The local mole fraction of species i at the neighborhood of a central i molecule is based upon normalizing Equation (2.28)¹⁴

$$x_{ii} = \frac{x_i \exp(-g_{ii} / RT)}{\sum_j x_j V_j \exp(-g_{ji} / RT)} \quad (2.29)$$

The local mole fraction is converted into a volume fraction,

$$\phi_{ii} = \frac{x_i V_i \exp(-g_{ii} / RT)}{\sum_j x_j V_j \exp(-g_{ji} / RT)} \quad (2.30)$$

where V_i is the molar volume of component i .

Wilson suggested that local volume fractions determine the mixing quantities of a solution. For the Gibbs free energy of mixing, he chose the following equation, which was suggested by the athermal-solution equation:

$$G^{\text{mix}} = RT \sum_i x_i \ln \phi_{ii} \quad (2.31)$$

Upon substitution of Equation (2.30) into Equation (2.31), one obtains

$$G^{\text{ex}} = -RT \sum_i x_i \ln \sum_j x_j \frac{V_j}{V_i} \exp \frac{-(g_{ji} - g_{ii})}{RT} \quad (2.32)$$

Define

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp \left[\frac{-(g_{ij} - g_{ii})}{RT} \right] \quad (2.33)$$

Then, Equation (2.32) simplifies to

$$G^{\text{ex}} = -RT \sum_i x_i \ln \left(\sum_j x_j \Lambda_{ij} \right) \quad (2.34)$$

Note that, in general, $g_{ij} = g_{ji}$, $\Lambda_{ij} \neq \Lambda_{ji}$, and $\Lambda_{ii} = 1$.

Activity coefficients are obtained from Equation (2.34)

$$\ln \gamma_i = 1 - \ln \left(\sum_j x_j \Lambda_{ij} \right) - \sum_k \left(\frac{x_k \Lambda_{ki}}{\sum_j x_j \Lambda_{kj}} \right) \quad (2.35)$$

For a binary solution, Equation (2.34) reduces to

$$G^{ex} = -RT[x_1 \ln(x_1 + \Lambda_{12}x_2) + x_2 \ln(\Lambda_{21}x_1 + x_2)] \quad (2.36)$$

and the activity coefficients are given by

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right] \quad (2.37)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right] \quad (2.38)$$

Equations (2.37) and (2.38) are usually considered to contain two empirical constants Λ_{12} and Λ_{21} for each binary system. The value of the constants can be determined by fitting the equations to experimental data for the activity coefficients.

2.6 NRTL Equation

Renon and Prausnitz⁴ further developed Wilson's concept of local concentration with objective of obtaining a general equation that would be applicable to partially miscible liquids. By analogy with Equation (2.29), they suggested the following expression for the local mole fractions in a binary solution:

$$x_{21} = \frac{x_2 \exp[-\alpha_{12}(g_{21} - g_{11})/RT]}{x_1 + x_2 \exp[-\alpha_{12}(g_{21} - g_{11})/RT]} \quad (2.39)$$

$$x_{12} = \frac{x_1 \exp[-\alpha_{12}(g_{12} - g_{22})/RT]}{x_2 + x_1 \exp[-\alpha_{12}(g_{12} - g_{22})/RT]} \quad (2.40)$$

The α factor is assumed to be a constant for a given binary system. Thus, $\alpha_{11} =$

$$\alpha_{22} = \alpha_{12}.$$

The partial contribution of component 1 to the excess Gibbs free energy of the solution is assumed to be of the form

$$G^{ex} = g^1 - g^{1^0} \quad (2.41)$$

and similarly for component 2. The quantity g^1 expresses the free energy of molecule 1 located in its own neighborhood in the solution and is given by

$$g^1 = x_{11} g_{11} + x_{21} g_{21} \quad (2.42)$$

For component 1 in its pure liquid state, Equation (2.42) reduces to

$$g^{1^0} = g^{11} \quad (2.43)$$

The working equations for the activity coefficients are obtained by substituting Equations (2.39), (2.40), (2.42) and (2.43) into Equation (2.41):

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \frac{\exp(-2\alpha_{12}\tau_{21})}{[x_1 + x_2 \exp(-\alpha_{12}\tau_{21})]^2} + \tau_{12} \frac{\exp(-\alpha_{12}\tau_{12})}{[x_2 + x_1 \exp(-\alpha_{12}\tau_{12})]^2} \right] \quad (2.44)$$

Similarly, for component 2,

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \frac{\exp(-2\alpha_{12}\tau_{12})}{[x_2 + x_1 \exp(-\alpha_{12}\tau_{12})]^2} + \tau_{21} \frac{\exp(-\alpha_{12}\tau_{21})}{[x_1 + x_2 \exp(-\alpha_{12}\tau_{21})]^2} \right] \quad (2.45)$$

where

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT} \quad (2.46)$$

$$\tau_{21} = \frac{g_{21} - g_{11}}{RT} \quad (2.47)$$

with $g_{12} = g_{21}$.

The general equation for a multi-component solution is

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k G_{kj} x_k} \right) \quad (2.48)$$

where

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (2.49)$$

The NRTL equation contains three constants for each binary system, i.e.,

τ_{12} , τ_{21} , and α_{12} that are determined from the experimental data. The parameters in these models are adjustable parameters that must be determined from an experimental set of activity coefficients as a function of composition. While the local composition models have a basis in molecular theory, they do not have a strong basis in thermodynamics and therefore they can not be expected to apply in all cases. Each of the models discussed in this study includes either two or three adjustable parameters. Accurate correlations require the determination of values of the parameters that best fit the data set. The concept and method of determining the best fit will be introduced in Chapter 3.

Chapter 3

METHOD

3.1 Least-Squares Method

For the calculation and optimization of separation processes in chemical engineering, knowledge of reliable thermodynamic data of multicomponent systems is required. The software program SigmaPlot¹⁵ was used to fit the data to a model equation by varying the parameters (coefficients) of an equation, and especially determining the parameters, which cause the equation to most closely fit the data. Both equation and the value of the initial parameter must be provided. All built-in equations have the curve and initial parameters predefined. The curve fitter accepts up to 25 parameters and ten independent variables. Up to 25 parameter constraints may be specified, which limits the search area of the curve fitter while checking for parameter values. The regression curve fitter can also use weighted least squares for greater accuracy.

3.2 Curve-Fitting Algorithm

The SigmaPlot[®] curve fitter uses the Marquardt-Levenberg algorithm to find the coefficients (parameters) of the independent variable(s) that give the “best fit” between the equation of choice and the data. ¹⁶This algorithm seeks the values of the parameters that minimize the sum of the squared differences between the values of the observed and predicted values of the dependent variable, i. e.,

$$SS = \sum_{i=1}^n W_i (y_i - y')^2 \quad (3.1)$$

where y_i is the observed and y' is the predicted value of the dependent variable.

This process is iterative - the curve fitter begins with a “guess” of the parameters, checks to see how well the equation fits the data, then the curve fitter makes a better guess and the process continues until the differences between the residual sum of squares no longer decreases significantly. This condition is known as convergence.

3.3 Thermodynamics of Vapor-Liquid Equilibrium (VLE)

The usual thermodynamic description of VLE in an N-component mixture consists of equations representing G^{ex} as a function of liquid phase composition (x -mole fraction), temperature T and an adjustable parameter C :

$$G^{ex} = G^{ex}(x, T, C) \quad (3.2)$$

The activity coefficients of each component in the mixture can be derived from Equation (3.2) as a partial molar property. The total pressure can be calculated according to

$$P(x, T, C) = \sum_{i=1}^N P_i(T) \cdot x_i \cdot \gamma_i(x, T, C) \quad (3.3)$$

The composition of the vapor phase is then calculated by means of equations representing the activity coefficients as a function of the liquid phase composition and temperature by means of the following equation:

$$y_i = x_i \cdot \gamma_i(x, T, C) \cdot P_i(T) / P(x, T, C) \quad i=1,2,\dots,N \quad (3.4)$$

The excess Gibbs free energy data were calculated using the following relation:

$$\Delta G^{\text{ex}} = RT[x_1 \ln \gamma_1 + x_2 \ln \gamma_2] \quad (3.5)$$

and thus the experimental VLE-data are correlated with the excess Gibbs free energy data.

3.4 Fitting Procedure

The fitting procedure to obtain numerical values of the model parameters with the use of n experimental data points represents a nonlinear problem solved by minimizing the sum of squares of the differences between the measured and calculated values of the thermodynamic variables. The parameters can be estimated for the equation

$$Y = f(x, C) \quad (3.6)$$

in which

$$Y = (Y_1, \dots, Y_{NY})$$

$$X = (x_1, \dots, x_{NX})$$

$$C = (c_1, \dots, c_N)$$

Minimization of the sum of squares yields:

$$S(c) = \sum_{j=1}^n \sum_{k=1}^{NY} w_{k,j} (Y_{k,j}^{\text{exp}} - Y_{k,j}^{\text{cal}})^2 \quad (3.7)$$

in which

$$W_{k,j} = 1 \quad \text{and}$$

$$Y_{k,j}^{\text{cal}} = f_k(x_{i,j}^{\text{exp}}, \dots, x_{NX,j}^{\text{exp}}, C) \quad \text{for } k = 1, 2, \dots, NY \quad (3.8)$$

For example, consider the fitting procedure for the Wilson model. This method is concerned with minimization of the function F.

$$F = \sum_i^n \gamma_i^2 \quad (3.9)$$

where

$$\gamma_i = (Y_{\text{exp}} - Y_{\text{cal}})_i = Y_{\text{exp}} + x_1 \ln(x_1 + \Lambda_{12}x_2) + x_2 \ln(\Lambda_{21}x_1 + x_2) \quad (3.10)$$

Step 1. Assume initial values of $(\Lambda_{12}^0, \Lambda_{21}^0)$. The initial values were chosen to

be

$$\Lambda_{12}^0 = \Lambda_{21}^0 = 0.5.$$

Step 2. Evaluate corrections $(\Delta\Lambda_{12}, \Delta\Lambda_{21})$ to $(\Lambda_{12}^0, \Lambda_{21}^0)$ by solving the

following simultaneous equations:

$$\sum_{i=1}^n \left(\frac{\partial\gamma_i}{\partial\Lambda_{12}}\right)^2 \cdot \Delta\Lambda_{12} + \sum_{i=1}^n \left(\frac{\partial\gamma_i}{\partial\Lambda_{12}}\right)\left(\frac{\partial\gamma_i}{\partial\Lambda_{21}}\right)\Delta\Lambda_{21} = \sum_{i=1}^n \left(\frac{\partial\gamma_i}{\partial\Lambda_{12}}\right)\gamma_i \quad (3.11)$$

$$\sum_{i=1}^n \left(\frac{\partial\gamma_i}{\partial\Lambda_{21}}\right)^2 \cdot \Delta\Lambda_{21} + \sum_{i=1}^n \left(\frac{\partial\gamma_i}{\partial\Lambda_{21}}\right)\left(\frac{\partial\gamma_i}{\partial\Lambda_{12}}\right)\Delta\Lambda_{12} = \sum_{i=1}^n \left(\frac{\partial\gamma_i}{\partial\Lambda_{21}}\right)\gamma_i \quad (3.12)$$

where

$$\left(\frac{\partial\gamma_i}{\partial\Lambda_{12}}\right) = \frac{x_1 x_2}{x_1 + \Lambda_{12} x_2}, \quad (3.13)$$

$$\left(\frac{\partial\gamma_i}{\partial\Lambda_{21}}\right) = \frac{x_2 x_1}{x_1 + \Lambda_{21} x_2} \quad (3.14)$$

and γ_i and their partial derivatives are evaluated at $(\Lambda_{12}^0, \Lambda_{21}^0)$.

Step 3. New values $(\Lambda_{12}^N, \Lambda_{21}^N)$ are evaluated by subtracting the corrections from

the old constants:

$$\Lambda_{21}^N = \Lambda_{21}^0 - \Delta\Lambda_{21}^N$$

$$\Lambda_{21}^N = \Lambda_{21}^0 - \Delta\Lambda_{21}^N \quad (3.15)$$

Step 4. Return to Step 1 with the $\Lambda_{12}^N, \Lambda_{21}^N$. The procedure is iterated until $\Delta\Lambda_{12}$ and $\Delta\Lambda_{21}$ are such that $|\Delta\Lambda_{12}| + |\Delta\Lambda_{21}| < 10^{-4}$.

SigmaPlot's regression wizard was used to regress the parameters in the vapor – liquid models by minimizing the error in the excess Gibbs free energy. The regression programs were designed to deal only with binary interaction parameters. The results of these calculations are discussed in Chapter 4.

Chapter 4

DATA ANALYSES

4.1 Correlation of Results for Binary Systems

Isothermal P-x-y data and pure component vapor pressures for the binary systems methanol + water¹⁷, ethanol + water^{17, 18}, and methanol + ethanol¹⁹ as well as for the ternary mixture methanol – ethanol – water¹⁷ have recently been measured. These data are shown in Table 1 and 2. The liquid phase mole fraction is labeled as x_1 , vapor phase mole fraction is labeled as y_1 , and activity coefficients are labeled γ_1 and γ_2 . The P-x₁-y₁ plots for ethanol (1) - water (2) system are graphically represented in Figure 1 for the ethanol (1) - water (2) system at 323.15 K. Figure 2 shows the experimental data for the excess Gibbs free energy for ethanol (1) - water (2) system at 323.15 K.

In this research, four different models were used to model the excess Gibbs free energy. The models studied include the Margules, van Laar, Wilson, and NRTL. Figures 3 and 4 show the results of trying to graph the relationship between excess Gibbs free energy and the liquid phase composition using the Margules and van Laar models. According to Equations (1.18) and (1.20) the data plotted in these coordinates should produce a straight line. Hence, it is obvious that these two models do not fit this experimental system.

Hence the data were analyzed using the two local composition models. The results of calculations for the Wilson and NRTL models are compared with the ethanol (1) - water (2) experimental data in Figures 5 - 7. Figure 8 shows the

methanol (1) - water (2) experimental data compared with the calculated NRTL results. These figures show that both the Wilson model and the NRTL model predict values close to the experimental data.

Frequently there are other useful ways of presenting the data. One such useful way is to plot the activity coefficient versus the liquid mole fraction as given in Figure 9. Similar results are presented in Figures 10 -15 for ethanol (1) – water (2) and methanol (1) – water (2) at the three temperatures, and the data are shown in Tables 3 - 8.

Figures 16 and 17 display the residuals for ethanol (1) - water (2) and methanol (1) - water (2) system at 323.15 K. Both the Wilson model and the NRTL model provide excellent correlations for the experimental data of the methanol (1) - water (2) and ethanol (1) - water (2) systems. However, a residual analysis of the data shows that the NRTL model fits the experimental data slightly better than Wilson model. This conclusion is supported by Figure 16 which shows the residuals as a function of mole fraction for the ethanol (1) - water (2) system at 323.15 K. The NRTL model results in a smaller scatter from the zero reference line and does not show any “structure.” In Figure 17 both the Wilson and NRTL models give similar residual results.

4.2 Temperature Dependence

Figure 18 shows the temperature dependence of the Wilson parameter Λ_{ij} for the ethanol (1) - water (2) system. Within the accuracy of the data, Equation (1.25) predicts the correct temperature dependence shown. The $\ln \Lambda_{ij}$ versus $1/T$ plot is a straight line. The temperature dependence of the methanol (1) - water (2)

system is shown in Figure 19.

The Wilson parameters as a function of temperature for methanol (1) - water (2) and ethanol (1) - water (2) are shown in Table 9. Not only the temperature dependence of the Wilson parameters has been analyzed, but the temperature dependence of the NRTL energy parameters $g_{ij} - g_{ii}$ are presented in Figures 20 and 21 for the cases of ethanol (1) - water (2) and methanol (1) - water (2). Even though there are only three data points, the points appear to show a linear relationship as required by the theory. The NRTL parameters as a function of temperature for methanol (1) - water (2) and ethanol (1) - water (2) are shown in Table 10. The methanol (1) - ethanol (2) system behaves almost ideally. Thus Figure 22 shows the methanol (1) - ethanol (2) system at 313.15 K plotted as an ideal solution.

4.3 Thermodynamic Consistency

Thermodynamics and specifically the Gibbs-Duhem equation set requirements on the relationship between $\ln \gamma_1$ and $\ln \gamma_2$. The “so called” equal area test for methanol (1) - water (2) and ethanol (1) - water (2) at 323.15 K are shown in Figures 23 and 24 and the integrated results for methanol (1) - water (2) and ethanol (2) – water (2) are shown for the three temperatures in Table 11. The area test is a gross test and there is the possibility of cancellation of errors.

Van Ness¹¹ suggested a better test in 1995. The test Van Ness suggested is termed a direct test. In the direct test one plots $\delta[\ln(\gamma_1/\gamma_2)]$ versus x_1 . Figures 25 and 26 show the direct test for methanol (1) - water (2) and ethanol (1) - water (2) at 323.15 K. Based on using the root-mean square, RMS, of the residuals as a

statistical test of the data one obtains the values shown in Table 12. Van Ness¹¹ assigned a consistency index of 1 (excellent data) to data that has a RMS residual value between 0.000 and 0.025 and a consistency index of 2 for a RMS residual value between 0.025 and 0.050. These data have a consistency index of either 1 or 2 depending on the binary system and/or the temperature. Again, one reaches the conclusion that the NRTL model provides a slightly better correlation of the data than does the Wilson model.

4.4 Ternary Systems^{17,20}

From the definition of the Wilson parameters,

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp\left[\frac{-(g_{ij} - g_{ii})}{RT}\right] \quad (2.33)$$

Therefore, taking the ln of both sides of the equation

$$\ln \Lambda_{12} = \ln\left(\frac{V_2}{V_1}\right) - (g_{12} - g_{11})/RT \quad (4.1)$$

$$\ln \Lambda_{21} = \ln\left(\frac{V_1}{V_2}\right) - (g_{12} - g_{22})/RT \quad (4.2)$$

For, in a ternary system:

$$\ln\left(\frac{\Lambda_{12}}{\Lambda_{21}}\right) = 2 \ln\left(\frac{V_2}{V_1}\right) + (g_{11} - g_{22})/RT \quad (4.3)$$

$$\ln\left(\frac{\Lambda_{13}}{\Lambda_{31}}\right) = 2 \ln\left(\frac{V_3}{V_1}\right) + (g_{11} - g_{33})/RT \quad (4.4)$$

$$\ln\left(\frac{\Lambda_{23}}{\Lambda_{32}}\right) = 2 \ln\left(\frac{V_3}{V_2}\right) + (g_{22} - g_{33})/RT \quad (4.5)$$

Subtracting Equation (4.5) and (4.3) from Equation (4.4) yields,

$$\begin{aligned}
 & -\ln\left(\frac{\Lambda_{12}}{\Lambda_{21}}\right) + \ln\left(\frac{\Lambda_{13}}{\Lambda_{31}}\right) - \ln\left(\frac{\Lambda_{23}}{\Lambda_{32}}\right) \\
 & = -2\ln\left(\frac{V_2}{V}\right) + 2\ln\left(\frac{V_3}{V_1}\right) - 2\left(\ln\left(\frac{V_3}{V_2}\right) + [(g_{11} - g_{11} + g_{22} - g_{22} + g_{33} - g_{33})/RT]\right) \\
 & = \left(\frac{V_3}{V_1}\right)^2 \left(\frac{V_2}{V_3}\right)^2 \left(\frac{V_1}{V_2}\right)^2 = 1
 \end{aligned} \tag{4.6}$$

Hence,

$$(\Lambda_{21}/\Lambda_{12}) (\Lambda_{13}/\Lambda_{31}) (\Lambda_{32}/\Lambda_{23}) = 1 \tag{4.7}$$

In a ternary system, Equation (2.47) may be written for a binary phase

$$RT (\tau_{21} - \tau_{12}) = (g_{22} - g_{11}) \tag{4.8}$$

$$RT (\tau_{31} - \tau_{13}) = (g_{33} - g_{11}) \tag{4.9}$$

$$RT (\tau_{32} - \tau_{23}) = (g_{33} - g_{22}) \tag{4.10}$$

$$RT[(\iota_{31} - \iota_{13}) - (\iota_{21} - \iota_{12}) - (\iota_{32} - \iota_{23})] = (g_{33} - g_{11}) - (g_{33} - g_{22}) - (g_{22} - g_{11}) = 0 \tag{4.11}$$

$$(\iota_{31} - \iota_{13}) - (\iota_{21} - \iota_{12}) - (\iota_{32} - \iota_{23}) = 0 \tag{4.12}$$

Since the activity coefficients of the methanol (1) – ethanol (2) system are 1.00 within experimental error, the Wilson parameters were set equal to 1.00 (ideal solution behavior). The normalization conditions for the Wilson model²¹ is given as Equation (4.7) and the normalization condition for the NRTL model is given as Equation (4.12). In contrast, the NRTL parameters for methanol – ethanol were set equal to the ideal solution values of zero. The results of applying

these normalization conditions to the three binary systems are shown in Table 13. The results do not agree well with theory. The product of the lambdas (Λ) for the Wilson model does not yield a value of one, and the difference of the taus (τ) for the NRTL model does not yield a value of zero. This non-agreement may be due to several causes. Possible causes include weaknesses in the models, experimental error, or an error in the parameter determination due to the parameters being correlated. It appears that our models yield good correlations, but they do not correspond with reality. The accurate prediction of model parameters requires experimental errors to be small, random errors, and a Gaussian distribution of those errors. Systematic errors may be introduced into experimental measurements. The local composition models are able to correlate a wider range of mixtures and thus they are discussed in Chapter 5.

Chapter 5

DISCUSSION

5.1 Local Composition

Wilson⁷ provided a superior method for the correlation of vapor-liquid equilibrium in totally miscible systems. The derivation of the Wilson equation in terms of local composition differs from that of most of the other commonly used expressions in that it is based primarily on entropic arguments, whereas the van Laar and Margules equations represent primarily energetic or enthalpic effects. For this reason the Wilson equation has been especially successful to represent the activity coefficients for associating solutions. The central idea of this concept is that when viewed microscopically, a liquid mixture is not homogeneous; the composition at one point in the mixture is not necessarily the same as that at another point.²² It is obvious that the probability of finding molecule *i* in the neighborhood of central molecule *j* is affected not only by their mutual interaction g_{ij} , but also by the interaction of molecule *i* with all of its neighbors. The potential energy of every molecule changes with the composition of the mixture and weighting factor w_{ij} in Equation (5.1)²³

$$\frac{x_{ij}}{x_{ji}} = \frac{x_i}{x_j} w_{ji} \quad (5.1)$$

where x_{ij} is the mole fraction of component *i* in the first coordination sphere of a molecule of component *j*. The weighting function w_{ij} is assumed to be proportional to a Boltzmann-type factor $\exp[(-g_{ii}-g_{ji})/RT]$ where $(g_{ii}-g_{ji})$ is an

adjustable parameter (g_{ij} denotes the energy of interaction between i - j pairs of molecules). In the Wilson model, Λ_{12} and Λ_{21} are as follows:

$$\Lambda_{12} = \frac{V_2^L}{V_1^L} \exp\left(-\frac{\lambda_{12}}{RT}\right), \quad \Lambda_{21} = \frac{V_1^L}{V_2^L} \exp\left(-\frac{\lambda_{21}}{RT}\right) \quad (5.2)$$

and the parameter λ_{ij} is equal to $g_{ij} - g_{ii}$.

In the NRTL model, $\tau_{21} = [(g_{21} - g_{11})/RT]$ and $\tau_{12} = [(g_{12} - g_{22})/RT]$. Therefore, both the Wilson and NRTL models utilize the concept of local composition.

Figure 27 shows the consequence of considering local composition effects. Within the mixture the proportion of species 1 and species 2 are not randomly mixed, and the proportion will change based on the nature of the components. In case A of the figure, the black box has 4 green balls and 2.5 red balls; while in case B, the same size box has about 4 red balls and 2.5 green balls. Both cases have the same background with the boxes. This shows that the local composition concept has a strong influence upon the calculation.

5.2 Limits of Applicability of the Wilson Equation

The Wilson equation cannot be used for a solution forming two liquid phases.⁴ Wilson's equation appears to provide a good representation of excess Gibbs energies for a variety of miscible mixtures. When Wilson's equation is substituted into the equations of thermodynamic stability for a binary system, no parameter values of the Λ_{12} and Λ_{21} can be found that indicate the existence of two stable liquid phases.^{1, 7} The Wilson equation, therefore, should be used only for liquid systems which are completely miscible or else for those limited regions

of partially miscible systems where only one liquid phase is present. However, for the cases considered here this is not a problem since methanol, ethanol, and water are miscible in all proportions. In those systems where two immiscible phases are present, the NRTL equation is capable of modeling the situation.

The goal of theoretical work such as this is to use a limited number of data points to interpolate or extrapolate to other conditions. The key is to obtain the maximum information out of a small data set. Chapter 6 discussed the results of our analysis.

Chapter 6

CONCLUSIONS

6.1 Discussion of Findings

Neither the Margules nor the van Laar models can adequately describe the methanol + water, the ethanol + water, or the methanol + ethanol binary systems.

This conclusion is based on plotting the experimental data according to Equation (1.18) for the Margules model and according to Equation (1.21) for the van Laar model. If the experimental systems followed these models one would obtain a linear relationship between the left-hand side of the respective equation and x_1 . The plots show strong curvature and deviate from linearity.

Both the Wilson and NRTL models provide excellent fits to the experimental data; however, the NRTL model is to be slightly preferred. The temperature dependence of the Wilson and NRTL models shows consistency with the experimental data. The Wilson equation gives not only an expression for the activity coefficients as a function of composition, but also an estimate of the variation of the activity coefficients with temperature. This may prove to be an advantage for isobaric calculations where the temperature varies as the composition changes. The temperature dependence of the Wilson and NRTL models is shown to be consistent with the experimental data. For the Wilson model, $\ln \Lambda$ has a linear relationship with $(1/T)$; for the NRTL model, the parameters $(g_{12} - g_{22})$ and $(g_{21} - g_{11})$ appear to be linear functions of temperature. The normalization conditions generated by the Wilson and NRTL are not

satisfied by these systems.

6.2 Suggestions for Future Work

The local composition models allow one to predict heats of mixing. The enthalpy of mixing for the mixture is given by the following equations:

$$\Delta G^{ex} / RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \quad (6.1)$$

$$-T^2 d(\Delta G^{ex} / T) / dT = \Delta H^{ex} = -RT^2 [x_1 (d \ln \gamma_1 / dT) + x_2 (d \ln \gamma_2 / dT)] \quad (6.2)$$

$$-\Delta H^{ex} / RT^2 = [x_1 (d \ln \gamma_1 / dT) + x_2 (d \ln \gamma_2 / dT)] \quad (6.3)$$

For the Wilson Model

$$\ln \gamma_1 = -\ln (x_1 + \Lambda_{12} x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21} x_1} \right] \quad (6.4)$$

Define $B = \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21} x_1} \right]$, then

$$\frac{d \ln \gamma_1}{dT} = \frac{-x_2}{(x_1 + x_2 \Lambda_{12})} \frac{d\Lambda_{12}}{dT} + x_2 \frac{dB}{dT} \quad (6.5)$$

$$\frac{d \ln \gamma_2}{dT} = \frac{-x_1}{(x_1 + x_2 \Lambda_{12})} \frac{d\Lambda_{21}}{dT} - x_1 \frac{dB}{dT} \quad (6.6)$$

and

$$\frac{d\Lambda_{ij}}{dT} = \frac{\lambda_{ij} \Lambda_{ij}}{RT^2} \quad (6.7)$$

Thus,

$$H^{ex} = x_1 x_2 \left[\frac{\lambda_{12} \Lambda_{12}}{x_1 + x_2 \Lambda_{12}} + \frac{\lambda_{21} \Lambda_{21}}{x_2 + x_1 \Lambda_{21}} \right] \quad (6.8)$$

For the Wilson model, the relationship for the excess enthalpy of mixing is given

by Equation (6.8). Using the same mathematical relationships, the enthalpy of mixing for the NRTL model can be shown to be given by Equation (6.9):

$$\frac{H^{ex}}{RT} = x_1 x_2 \left[\frac{t_{12} G_{21}}{x_1 + x_2 G_{21}} + \frac{t_{21} G_{12}}{x_2 + x_1 G_{12}} \right] \quad (6.9)$$

Therefore, from theory, the enthalpy of mixing can be calculated. This has the potential of being very valuable to thermodynamists.

Future calculations will include both the Poytning pressure correction factor and gas phase non-ideality. These corrections will require a modification of the methods used to evaluate parameters for the various models.

This research tests the Margules, van Laar, Wilson, and NRTL models by fitting the experimental data to the excess Gibbs free energy. Research reported in the current literature usually determines the parameters in these models by fitting them to the pressure measurements. Determining the model parameters by fitting the G^{ex} provides a more sensitive test of the model.

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Table 2 Isothermal Vapor-Liquid Equilibrium Data for Methanol (1) - Water (2)

323.15 K					328.15 K					333.15 K				
P/kPa	x(1)	y(1)	$\gamma(1)$	$\gamma(2)$	P/kPa	x(1)	y(1)	$\gamma(1)$	$\gamma(2)$	P/kPa	x(1)	y(1)	$\gamma(1)$	$\gamma(2)$
30.6200	0.2842	0.7029	1.3799	1.0259	40.8350	0.3339	0.7280	1.3104	1.0543	39.2230	0.1686	0.5714	1.6014	1.0105
31.1350	0.2940	0.7109	1.3714	1.0291	42.1430	0.3610	0.7432	1.2762	1.0708	40.3440	0.1814	0.5867	1.5712	1.0178
32.7900	0.3338	0.7373	1.3182	1.0436	42.7600	0.3733	0.7504	1.2640	1.0767	40.6460	0.1910	0.5914	1.5152	1.0258
35.3210	0.4028	0.7772	1.2388	1.0636	44.2370	0.4137	0.7693	1.2089	1.1005	42.9840	0.2167	0.6268	1.4953	1.0232
36.2760	0.4316	0.7873	1.2022	1.0956	45.1840	0.4346	0.7799	1.1911	1.1120	47.0230	0.2773	0.6751	1.3745	1.0559
38.0850	0.4872	0.8100	1.1494	1.1389	46.7430	0.4753	0.7947	1.1472	1.1562	48.8520	0.3039	0.6943	1.3390	1.0714
39.3410	0.5314	0.8254	1.1085	1.1831	48.1810	0.5078	0.8079	1.1245	1.1888	50.4280	0.3303	0.7101	1.2998	1.0901
40.1600	0.5513	0.8326	1.0998	1.2092	50.5000	0.5669	0.8315	1.0855	1.2421	52.7840	0.3681	0.7345	1.2616	1.1074
40.6120	0.5688	0.8410	1.0886	1.2087	51.1000	0.5897	0.8401	1.0665	1.2590	56.6520	0.4461	0.7742	1.1757	1.1532
42.0490	0.6145	0.8569	1.0623	1.2599	51.9740	0.6030	0.8495	1.0723	1.2457	58.4270	0.4775	0.7877	1.1518	1.1853
44.9160	0.6989	0.8890	1.0336	1.3367	52.2270	0.6091	0.8502	1.0675	1.2654	60.6140	0.5282	0.8085	1.1077	1.2284
45.9430	0.7290	0.8991	1.0246	1.3810	52.6640	0.6217	0.8557	1.0612	1.2701	62.2600	0.5572	0.8216	1.0953	1.2525
47.3340	0.7730	0.9160	1.0135	1.4143	52.2450	0.6600	0.8709	1.0472	1.3024	63.9980	0.6044	0.8383	1.0583	1.3062
					54.9560	0.6781	0.8770	1.0395	1.3278	67.9240	0.6804	0.8733	1.0378	1.3449
					55.9800	0.7032	0.8866	1.0318	1.3525	68.1410	0.6835	0.8751	1.0384	1.3430
					59.2080	0.7808	0.9183	1.0165	1.3958	70.2290	0.7255	0.8922	1.0271	1.3776
										71.5970	0.7530	0.9039	1.0251	1.3916
										72.8320	0.7776	0.9141	1.0171	1.4055

Table 3. Vapor-Liquid Equilibrium Data for Ethanol (1) - Water (2) at 323.15 K

P/kPa	x1	y1	lnγ1	lnγ2	lnγ1(Wilson)	lnγ2(Wilson)	lnγ1(NRTL)	lnγ2(NRTL)
12.921	0.0043	0.0478	1.5830	0.0000	1.9213	0.0001	1.7141	0.0001
14.249	0.0152	0.1450	1.5360	0.0005	1.8167	0.0011	1.6556	0.0006
15.555	0.0272	0.2259	1.4860	0.0016	1.7110	0.0034	1.5928	0.0020
17.379	0.0463	0.3182	1.4070	0.0046	1.5610	0.0091	1.4968	0.0056
19.088	0.0678	0.3893	1.3200	0.0099	1.4135	0.0180	1.3938	0.0119
20.333	0.0874	0.4341	1.2388	0.0185	1.2947	0.0279	1.3044	0.0194
20.904	0.0967	0.4549	1.2117	0.0190	1.2431	0.0332	1.2635	0.0235
21.522	0.1098	0.4738	1.1520	0.0263	1.1747	0.0411	1.2076	0.0300
22.796	0.1411	0.5120	1.0372	0.0453	1.0295	0.0618	1.0816	0.0480
23.585	0.1710	0.5355	0.9218	0.0706	0.9102	0.0838	0.9705	0.0686
23.663	0.1756	0.5372	0.9032	0.0949	0.8934	0.0874	0.9543	0.0719
24.336	0.2065	0.5562	0.8034	0.1116	0.7884	0.1121	0.8499	0.0966
24.570	0.2253	0.5636	0.7388	0.1265	0.7310	0.1279	0.7907	0.1129
24.961	0.2468	0.5753	0.6829	0.1402	0.6705	0.1466	0.7267	0.1327
25.024	0.2552	0.5761	0.6541	0.1674	0.6483	0.1540	0.7028	0.1407
25.436	0.2856	0.5890	0.5798	0.1926	0.5737	0.1817	0.6209	0.1710
25.815	0.3133	0.6008	0.5215	0.2001	0.5128	0.2077	0.5526	0.2002
25.933	0.3238	0.6044	0.4976	0.2382	0.4913	0.2177	0.5282	0.2116
26.259	0.3535	0.6133	0.4381	0.2598	0.4347	0.2467	0.4633	0.2448
26.481	0.3773	0.6226	0.3962	0.2667	0.3934	0.2704	0.4156	0.2722
26.572	0.3884	0.6270	0.3769	0.2820	0.3753	0.2817	0.3946	0.2853
26.694	0.3999	0.6311	0.3594	0.2980	0.3573	0.2934	0.3737	0.2989
26.836	0.4175	0.6370	0.3304	0.3102	0.3310	0.3115	0.3432	0.3199
26.898	0.4258	0.6397	0.3176	0.3558	0.3192	0.3202	0.3294	0.3300
27.284	0.4691	0.6563	0.2603	0.3937	0.2626	0.3660	0.2640	0.3829
27.535	0.4987	0.6660	0.2227	0.3971	0.2284	0.3980	0.2249	0.4196
27.564	0.5049	0.6681	0.2142	0.4225	0.2218	0.4047	0.2173	0.4272
27.701	0.5218	0.6741	0.1954	0.4415	0.2041	0.4233	0.1973	0.4482
27.881	0.5421	0.6840	0.1781	0.4682	0.1843	0.4459	0.1752	0.4734
28.101	0.5692	0.6971	0.1560	0.4864	0.1599	0.4764	0.1483	0.5070
28.131	0.5808	0.6989	0.1388	0.4971	0.1501	0.4896	0.1378	0.5213
28.216	0.5907	0.7050	0.1342	0.5368	0.1421	0.5009	0.1292	0.5334
28.448	0.6242	0.7205	0.1087	0.5486	0.1171	0.5395	0.1028	0.5742
28.489	0.6343	0.7239	0.0985	0.5898	0.1102	0.5513	0.0957	0.5863
28.711	0.6697	0.7434	0.0785	0.6119	0.0879	0.5931	0.0732	0.6283
28.828	0.6868	0.7523	0.0692	0.6379	0.0782	0.6135	0.0638	0.6482
29.006	0.7245	0.7735	0.0495	0.6519	0.0592	0.6590	0.0460	0.6909
29.154	0.7586	0.7940	0.0359	0.6970	0.0446	0.7009	0.0330	0.7281
29.176	0.7638	0.7981	0.0340	0.7011	0.0426	0.7073	0.0312	0.7336
29.195	0.7811	0.8081	0.0263	0.7302	0.0362	0.7289	0.0259	0.7518
29.253	0.8084	0.8286	0.0201	0.7479	0.0274	0.7631	0.0187	0.7795
29.346	0.8299	0.8429	0.0128	0.7880	0.0213	0.7905	0.0141	0.8006
29.406	0.8454	0.8555	0.0118	0.8009	0.0175	0.8103	0.0112	0.8153
29.470	0.8559	0.8639	0.0096	0.8029	0.0151	0.8238	0.0095	0.8250
29.478	0.8579	0.8664	0.0094	0.8132	0.0147	0.8263	0.0092	0.8268
29.480	0.8638	0.8699	0.0090	0.8245	0.0135	0.8340	0.0083	0.8322
29.487	0.8454	0.8769	0.0067	0.8266	0.0120	0.8437	0.0073	0.8389
29.498	0.8801	0.8849	0.0067	0.8310	0.0104	0.8552	0.0062	0.8466
29.510	0.8906	0.8942	0.0063	0.8315	0.0086	0.8689	0.0050	0.8557
29.511	0.8911	0.8948	0.0057	0.8370	0.0085	0.8695	0.0050	0.8561
29.517	0.8993	0.9019	0.0051	0.8382	0.0072	0.8803	0.0042	0.8631
29.527	0.9031	0.9065	0.0050	0.8388	0.0067	0.8853	0.0038	0.8662
29.529	0.9136	0.9151	0.0041	0.8563	0.0053	0.8991	0.0030	0.8748
29.529	0.9245	0.9250	0.0039	0.8580	0.0040	0.9135	0.0022	0.8834
29.531	0.9263	0.9273	0.0038	0.8605	0.0038	0.9159	0.0021	0.8849
29.538	0.9344	0.9337	0.0035	0.8784	0.0030	0.9267	0.0016	0.8911
29.548	0.9480	0.9470	0.0023	0.8846	0.0019	0.9448	0.0010	0.9014
29.558	0.9528	0.9512	0.0020	0.8933	0.0016	0.9513	0.0008	0.9049
29.558	0.9537	0.9531	0.0014	0.8937	0.0015	0.9525	0.0008	0.9055
29.560	0.9732	0.9724	0.0011	0.9016	0.0005	0.9787	0.0002	0.9192
29.566	0.9815	0.9808	0.0001	0.9073	0.0002	0.9901	0.0001	0.9249

Table 4. Vapor-Liquid Equilibrium Data for Ethanol (1) - Water (2) at 328.15 K

P/kPa	x_1	y_1	$\ln\gamma_1$	$\ln\gamma_2$	$\ln\gamma_1$ (Wilson)	$\ln\gamma_2$ (Wilson)	$\ln\gamma_1$ (NRTL)	$\ln\gamma_2$ (NRTL)
27.7740	0.1161	0.4841	1.1392	0.0258	1.1048	0.0417	1.1172	0.0307
29.0170	0.1445	0.5123	1.0200	0.0459	0.9833	0.0599	1.0128	0.0463
31.3910	0.2338	0.5712	0.7245	0.1061	0.6881	0.1279	0.7317	0.1115
31.7670	0.2506	0.5760	0.6752	0.1288	0.6437	0.1420	0.6861	0.1261
32.4750	0.2938	0.5923	0.5656	0.1711	0.5418	0.1801	0.5784	0.1663
33.0480	0.3306	0.6058	0.4872	0.2085	0.4669	0.2141	0.4969	0.2033
33.3500	0.3551	0.6106	0.4325	0.2426	0.4222	0.2374	0.4474	0.2291
33.6110	0.3777	0.6191	0.3922	0.2641	0.3842	0.2594	0.4050	0.2536
34.0120	0.4123	0.6294	0.3326	0.3057	0.3314	0.2938	0.3458	0.2922
34.3430	0.4470	0.6465	0.2880	0.3292	0.2843	0.3292	0.2929	0.3320
34.5190	0.4598	0.6557	0.2788	0.3314	0.2683	0.3425	0.2749	0.3470
35.0170	0.5127	0.6682	0.2029	0.4118	0.2091	0.3985	0.2087	0.4095
35.2150	0.5273	0.6801	0.1979	0.4115	0.1945	0.4142	0.1926	0.4270
35.5070	0.5541	0.6845	0.1628	0.4642	0.1696	0.4435	0.1653	0.4591
35.5160	0.5626	0.6874	0.1520	0.4746	0.1622	0.4529	0.1573	0.4693
36.0550	0.6194	0.7138	0.1081	0.5408	0.1181	0.5166	0.1101	0.5373
36.5300	0.6841	0.7480	0.0682	0.6133	0.0781	0.5914	0.0691	0.6137
36.7790	0.7174	0.7667	0.0519	0.6546	0.0613	0.6307	0.0527	0.6522
36.8120	0.7276	0.7714	0.0448	0.6720	0.0566	0.6429	0.0482	0.6639
36.9730	0.7558	0.7937	0.0394	0.6833	0.0448	0.6768	0.0371	0.6957
37.1720	0.7979	0.8211	0.0243	0.7358	0.0300	0.7283	0.0238	0.7419
37.2230	0.8165	0.8340	0.0182	0.7591	0.0245	0.7513	0.0191	0.7618
37.3070	0.8334	0.8470	0.0153	0.7766	0.0200	0.7724	0.0153	0.7796
37.3250	0.8436	0.8554	0.0135	0.7839	0.0175	0.7851	0.0133	0.7901
37.3520	0.8502	0.8595	0.0111	0.7991	0.0160	0.7934	0.0120	0.7969
37.3780	0.8616	0.8688	0.0093	0.8106	0.0136	0.8078	0.0101	0.8085
37.3930	0.8714	0.8775	0.0083	0.8160	0.0117	0.8203	0.0086	0.8184
37.3950	0.8798	0.8848	0.0070	0.8223	0.0102	0.8310	0.0074	0.8267
37.4160	0.8854	0.8891	0.0061	0.8326	0.0092	0.8381	0.0066	0.8322
37.4150	0.8925	0.8946	0.0042	0.8457	0.0081	0.8472	0.0058	0.8392
37.4210	0.9002	0.9019	0.0039	0.8486	0.0070	0.8571	0.0049	0.8466
37.4250	0.9131	0.9130	0.0020	0.8672	0.0052	0.8737	0.0036	0.8589
37.4370	0.9342	0.9331	0.0012	0.8833	0.0030	0.9011	0.0020	0.8786
37.4120	0.9566	0.9550	0.0000	0.9027	0.0013	0.9304	0.0008	0.8988

Table 5. Vapor-Liquid Equilibrium Data for Ethanol (1) - Water (2) at 333.15 K

P/kPa	x_1	y_1	$\ln\gamma_1$	$\ln\gamma_2$	$\ln\gamma_1$ (Wilson)	$\ln\gamma_2$ (Wilson)	$\ln\gamma_1$ (NRTL)	$\ln\gamma_2$ (NRTL)
31.6470	0.0742	0.4130	1.3339	0.0037	1.2707	0.0172	1.2553	0.0131
34.5400	0.1071	0.4742	1.1907	0.0171	1.1132	0.0328	1.1222	0.0264
36.8400	0.1511	0.5196	1.0009	0.0416	0.9368	0.0589	0.9622	0.0500
37.6110	0.1705	0.5326	0.9251	0.0580	0.8691	0.0718	0.8977	0.0624
38.3870	0.1899	0.5473	0.8645	0.0701	0.8066	0.0856	0.8367	0.0758
38.9990	0.2133	0.5587	0.7843	0.0897	0.7372	0.1031	0.7675	0.0932
40.1750	0.2606	0.5814	0.6528	0.1287	0.6144	0.1411	0.6412	0.1324
41.2300	0.3168	0.6006	0.5153	0.1866	0.4932	0.1902	0.5126	0.1845
42.1570	0.3813	0.6209	0.3848	0.2560	0.3800	0.2507	0.3900	0.2500
42.6350	0.4036	0.6316	0.3560	0.2754	0.3462	0.2726	0.3532	0.2738
43.3680	0.4548	0.6502	0.2822	0.3305	0.2772	0.3244	0.2782	0.3301
43.7300	0.4794	0.6688	0.2657	0.3305	0.2479	0.3500	0.2466	0.3578
43.7560	0.4808	0.6682	0.2624	0.3356	0.2463	0.3515	0.2449	0.3594
44.3360	0.5298	0.6788	0.1939	0.4155	0.1949	0.4039	0.1899	0.4155
44.4470	0.5390	0.6887	0.1936	0.4066	0.1862	0.4140	0.1806	0.4261
44.9350	0.5800	0.7070	0.1570	0.4502	0.1503	0.4595	0.1431	0.4738
45.2820	0.6141	0.7175	0.1221	0.5062	0.1242	0.4982	0.1162	0.5136
45.5570	0.6417	0.7333	0.1057	0.5292	0.1053	0.5300	0.0971	0.5459
45.8810	0.6764	0.7468	0.0782	0.5863	0.0842	0.5708	0.0761	0.5864
46.2180	0.7156	0.7674	0.0561	0.6382	0.0637	0.6178	0.0562	0.6318
46.3380	0.7347	0.7834	0.0528	0.6393	0.0549	0.6411	0.0479	0.6539
46.5470	0.7656	0.7968	0.0330	0.7040	0.0422	0.6792	0.0361	0.6892
46.8680	0.8246	0.8395	0.0174	0.7657	0.0230	0.7536	0.0189	0.7558
46.9150	0.8353	0.8477	0.0152	0.7773	0.0201	0.7673	0.0165	0.7676
46.9980	0.8538	0.8616	0.0112	0.8028	0.0157	0.7912	0.0127	0.7881
46.9870	0.8646	0.8715	0.0099	0.8052	0.0134	0.8053	0.0108	0.7999
47.0200	0.8823	0.8860	0.0067	0.8266	0.0101	0.8284	0.0080	0.8192
47.0450	0.8873	0.8908	0.0070	0.8276	0.0092	0.8350	0.0073	0.8246
47.0480	0.8966	0.8987	0.0054	0.8388	0.0077	0.8473	0.0061	0.8346
47.0600	0.9091	0.9095	0.0037	0.8554	0.0059	0.8639	0.0046	0.8480
47.0550	0.9154	0.9151	0.0029	0.8634	0.0051	0.8723	0.0040	0.8547
47.0550	0.9206	0.9195	0.0020	0.8737	0.0045	0.8793	0.0035	0.8602
47.0440	0.9255	0.9242	0.0015	0.8771	0.0040	0.8859	0.0030	0.8654
47.0260	0.9458	0.9444	0.0010	0.8853	0.0021	0.9133	0.0016	0.8867
47.0390	0.9479	0.9467	0.0015	0.8829	0.0019	0.9161	0.0014	0.8889
46.9940	0.9583	0.9562	-0.0003	0.9085	0.0012	0.9302	0.0009	0.8997

Table 6. Vapor-Liquid Equilibrium Data for Methanol (1) - Water (2) at 323.15 K

P/kPa	x₁	y₁	lnγ₁	lnγ₂	lnγ₁ (Wilson)	lnγ₂ (Wilson)	lnγ₁ (NRTL)	lnγ₂ (NRTL)
30.6200	0.2842	0.7029	0.3220	0.0256	0.2716	0.0474	0.2680	0.0295
31.1350	0.2940	0.7109	0.3158	0.0287	0.2637	0.0507	0.2624	0.0318
32.7900	0.3338	0.7373	0.2763	0.0427	0.2331	0.0647	0.2400	0.0421
35.3210	0.4028	0.7772	0.2141	0.0617	0.1850	0.0927	0.2020	0.0642
36.2760	0.4316	0.7873	0.1842	0.0913	0.1668	0.1057	0.1867	0.0752
38.0850	0.4872	0.8100	0.1392	0.1301	0.1346	0.1331	0.1580	0.0997
39.3410	0.5314	0.8254	0.1030	0.1681	0.1116	0.1569	0.1361	0.1224
40.1600	0.5513	0.8326	0.0951	0.1900	0.1020	0.1682	0.1266	0.1336
40.6120	0.5688	0.8410	0.0849	0.1895	0.0940	0.1785	0.1184	0.1440
42.0490	0.6145	0.8569	0.0604	0.2310	0.0747	0.2065	0.0979	0.1738
44.9160	0.6989	0.8890	0.0330	0.2902	0.0451	0.2631	0.0636	0.2396
45.9430	0.7290	0.8991	0.0243	0.3228	0.0364	0.2847	0.0527	0.2667
47.3340	0.7730	0.9160	0.0134	0.3466	0.0254	0.3178	0.0383	0.3103

Table 7. Vapor-Liquid Equilibrium Data for Methanol (1) - Water (2) at 328.15 K

P/kPa	x₁	y₁	lnγ₁	lnγ₂	lnγ₁ (Wilson)	lnγ₂ (Wilson)	lnγ₁ (NRTL)	lnγ₂ (NRTL)
30.7100	0.1587	0.5660	0.4823	0.0022	0.4083	0.0180	0.4089	0.0177
33.3680	0.1980	0.6154	0.4264	0.0120	0.3646	0.0275	0.3656	0.0271
39.0380	0.2961	0.7019	0.3098	0.0443	0.2695	0.0586	0.2705	0.0582
40.2150	0.3171	0.7182	0.2934	0.0480	0.2516	0.0666	0.2525	0.0662
40.8350	0.3339	0.7280	0.2703	0.0529	0.2378	0.0732	0.2386	0.0729
42.1430	0.3610	0.7432	0.2439	0.0684	0.2165	0.0845	0.2172	0.0842
42.7600	0.3733	0.7504	0.2343	0.0739	0.2073	0.0899	0.2079	0.0896
44.2370	0.4137	0.7693	0.1897	0.0958	0.1787	0.1084	0.1791	0.1083
45.1840	0.4346	0.7799	0.1749	0.1062	0.1649	0.1186	0.1652	0.1186
46.7430	0.4753	0.7947	0.1373	0.1451	0.1399	0.1394	0.1400	0.1396
48.1810	0.5078	0.8079	0.1173	0.1729	0.1217	0.1570	0.1216	0.1573
50.5000	0.5669	0.8315	0.0820	0.2168	0.0924	0.1911	0.0921	0.1917
51.1000	0.5897	0.8401	0.0644	0.2303	0.0823	0.2049	0.0819	0.2056
51.9740	0.6030	0.8495	0.0698	0.2197	0.0767	0.2132	0.0763	0.2139
52.2270	0.6091	0.8502	0.0653	0.2354	0.0742	0.2170	0.0738	0.2177
52.6640	0.6217	0.8557	0.0594	0.2391	0.0692	0.2250	0.0688	0.2257
52.2450	0.6600	0.8709	0.0461	0.2642	0.0552	0.2499	0.0548	0.2508
54.9560	0.6781	0.8770	0.0387	0.2835	0.0492	0.2621	0.0488	0.2629
55.9800	0.7032	0.8866	0.0313	0.3020	0.0415	0.2792	0.0411	0.2801
59.2080	0.7808	0.9183	0.0164	0.3335	0.0221	0.3350	0.0218	0.3355

Table 8. Vapor-Liquid Equilibrium Data for Methanol (1) - Water (2) at 333.15 K

P/kPa	x_1	y_1	$\ln\gamma_1$	$\ln\gamma_2$	$\ln\gamma_1$ (Wilson)	$\ln\gamma_2$ (Wilson)	$\ln\gamma_1$ (NRTL)	$\ln\gamma_2$ (NRTL)
39.2230	0.1686	0.5714	0.4709	0.0104	0.4332	0.0252	0.4346	0.0246
40.3440	0.1814	0.5867	0.4518	0.0176	0.4160	0.0288	0.4175	0.0282
40.6460	0.1910	0.5914	0.4155	0.0255	0.4034	0.0317	0.4050	0.0311
42.9840	0.2167	0.6268	0.4023	0.0229	0.3712	0.0399	0.3729	0.0393
47.0230	0.2773	0.6751	0.3181	0.0544	0.3029	0.0623	0.3044	0.0618
48.8520	0.3039	0.6943	0.2919	0.0690	0.2760	0.0733	0.2774	0.0728
50.4280	0.3303	0.7101	0.2622	0.0863	0.2510	0.0849	0.2522	0.0845
52.7840	0.3681	0.7345	0.2324	0.1020	0.2181	0.1025	0.2189	0.1024
56.6520	0.4461	0.7742	0.1619	0.1425	0.1597	0.1426	0.1598	0.1429
58.4270	0.4775	0.7877	0.1413	0.1700	0.1395	0.1599	0.1394	0.1604
60.6140	0.5282	0.8085	0.1023	0.2057	0.1105	0.1892	0.1100	0.1900
62.2600	0.5572	0.8216	0.0910	0.2251	0.0957	0.2067	0.0952	0.2077
63.9980	0.6044	0.8383	0.0567	0.2671	0.0745	0.2362	0.0738	0.2373
67.9240	0.6804	0.8733	0.0371	0.2963	0.0467	0.2860	0.0460	0.2872
68.1410	0.6835	0.8751	0.0377	0.2949	0.0457	0.2881	0.0450	0.2892
70.2290	0.7255	0.8922	0.0267	0.3203	0.0337	0.3168	0.0330	0.3178
71.5970	0.7530	0.9039	0.0248	0.3305	0.0269	0.3360	0.0263	0.3368
72.8320	0.7776	0.9141	0.0170	0.3404	0.0215	0.3534	0.0210	0.3541

Table 9. Wilson Model Parameters for Vapor-Liquid Equilibrium Systems

T/K	<i>Methanol(1)-Water(2)</i>		<i>Ethanol(1)-Water(2)</i>	
	Λ_{12}	Λ_{21}	Λ_{12}	Λ_{21}
323.15	0.6771	0.8253	0.1839	0.8373
328.15	0.5924	0.9010	0.1823	0.8434
333.15	0.4955	0.9838	0.2086	0.8218

Table 10. NRTL Model Parameters for Vapor-Liquid Equilibrium Systems

T/K	Methanol(1) -Water(2)			Ethanol(1) -Water(2)		
	τ_{12}	τ_{21}	α	τ_{12}	τ_{21}	α
323.15	0.0313	0.5174	0.1063	-1.9502	3.9413	0.0790
328.15	-0.2659	0.8945	0.1624	-6.0903	8.7131	0.0247
333.15	-1.3879	2.2493	0.0752	-0.7236	2.4118	0.1543

Table 11. The Equal Area Test for Thermodynamic Consistency of the Methanol (1) – Water (2) and Ethanol (1) – Water (2) Vapor- Liquid Equilibrium Systems.

T/K	Methanol (1) – Water (2)	Ethanol (1) – Water (2)
323.15	0.0191	-0.0154
328.15	0.0413	0.0004
333.15	0.0263	0.0194

Table 12. The Direct Test for Thermodynamic Consistency of the Methanol (1) – Water (2) and Ethanol (1) – Water (2) Vapor- Liquid Equilibrium Systems.

T/K	Methanol (1) – Water (2)		Ethanol (1) – Water (2)	
323.15	0.230	0.0234	0.0446	0.0536
328.15	0.0201	0.0199	0.0010	0.0047
333.15	0.0125	0.0121	0.0132	0.0148
Correlating Equation	Wilson	NRTL	Wilson	NRTL

Table 13. Text of the Normalization Conditions for Wilson and NRTL Models for the Methanol – Ethanol –Water Ternary Vapor –Liquid Equilibrium Systems.

T/K	Wilson	NRTL
323.15	5.55	6.38
328.15	6.98	3.25
333.15	7.82	4.00

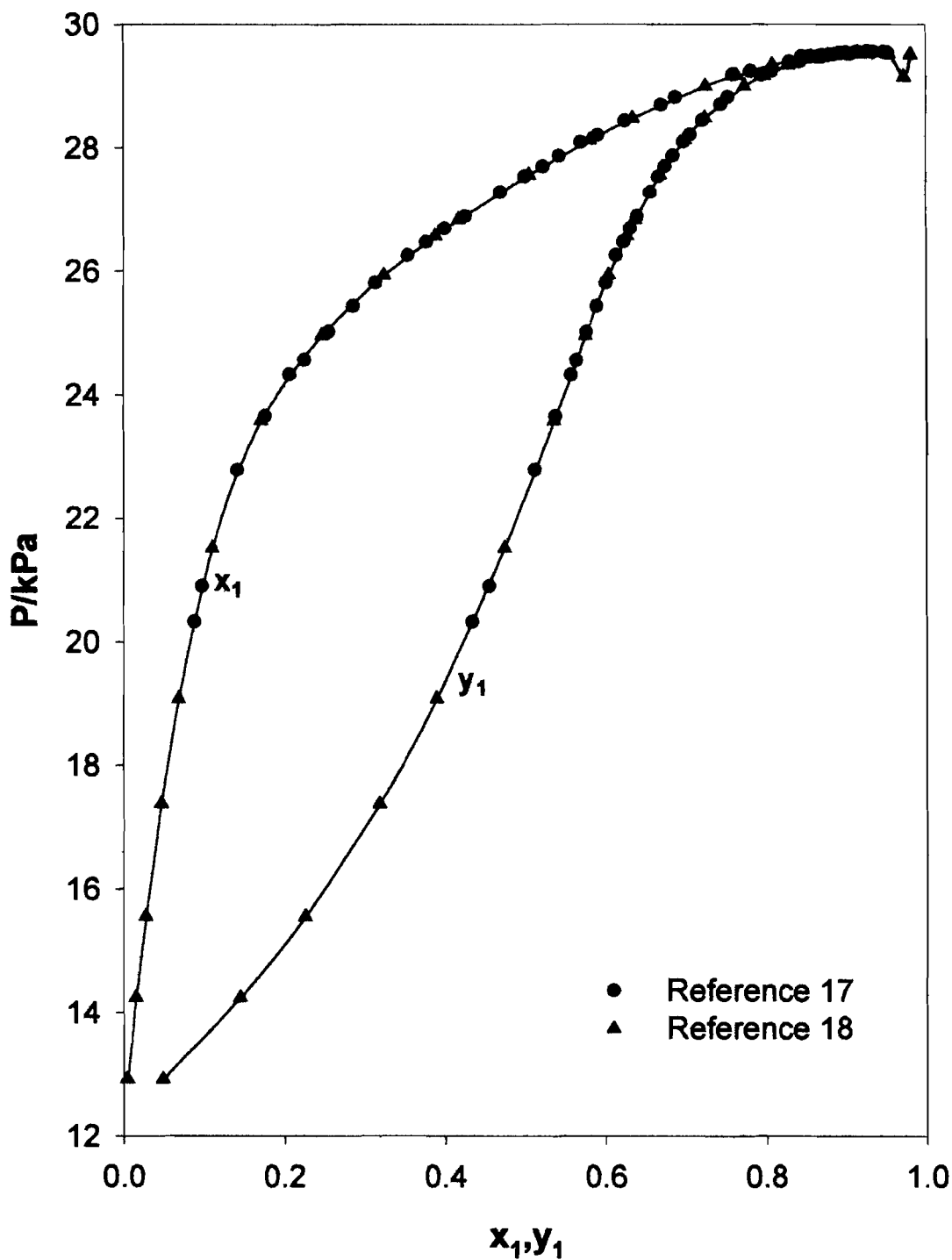


Figure 1. Pressure - Composition Diagram for Ethanol (1) - Water (2) at 323.15 K

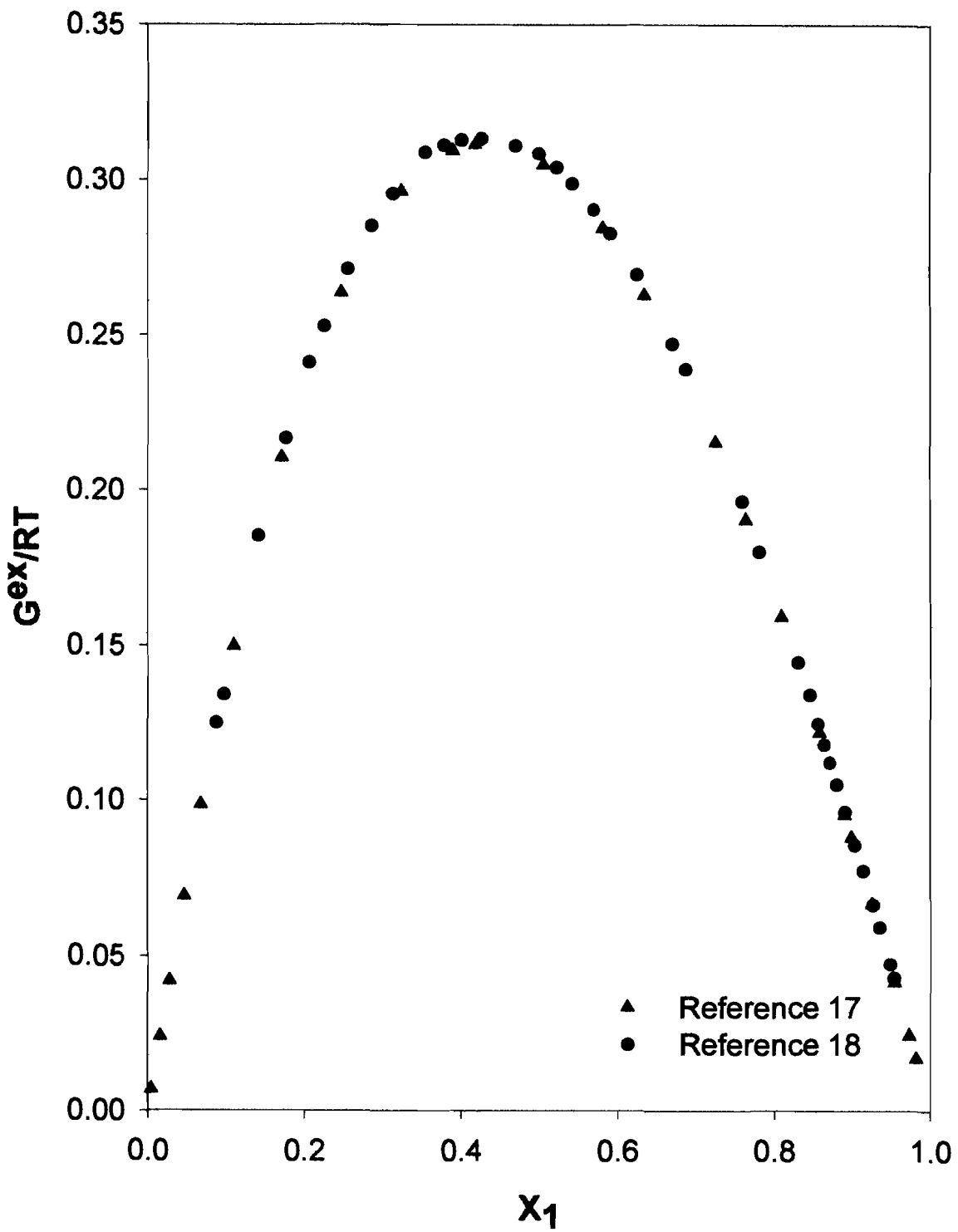
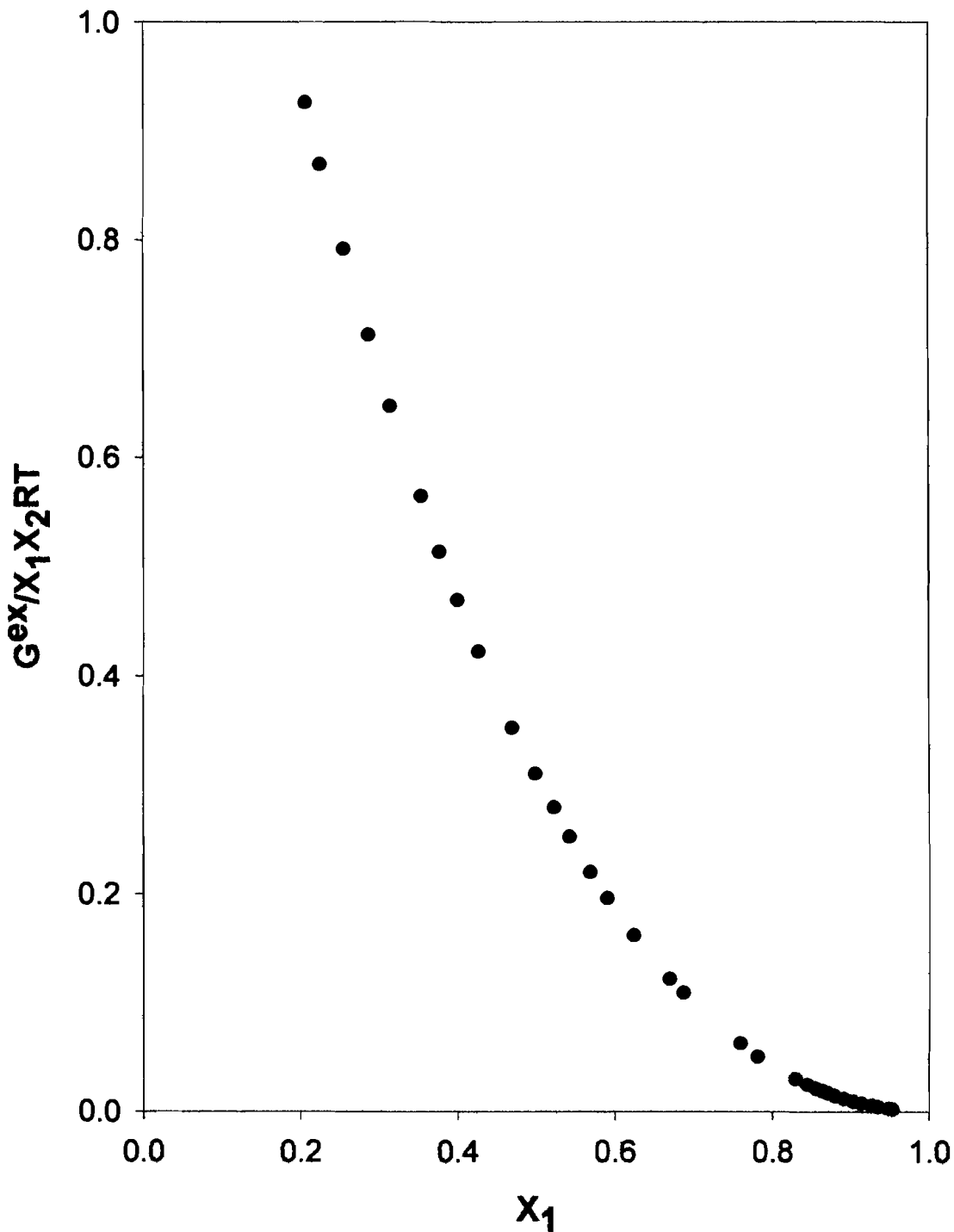
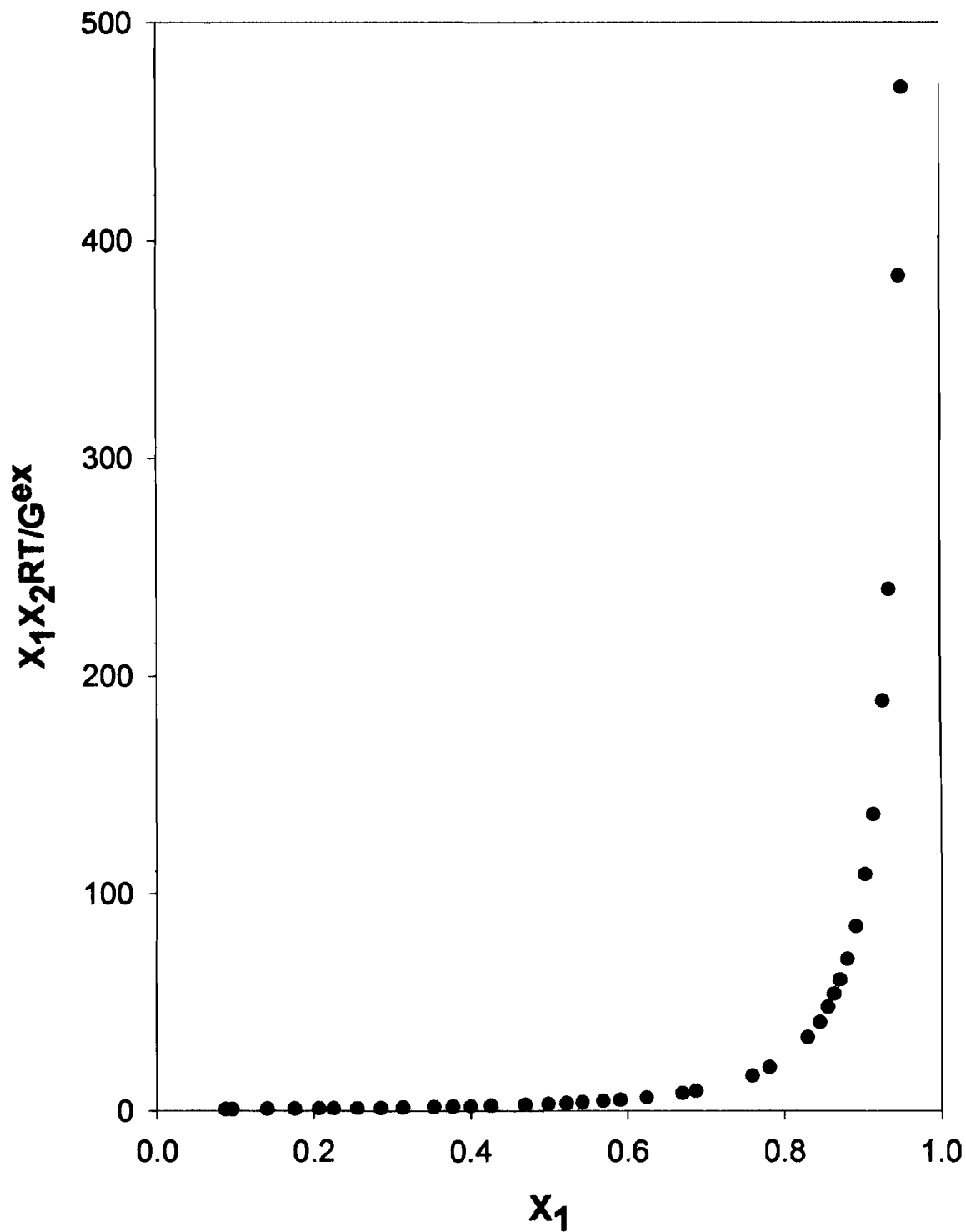


Figure 2. Ethanol (1) - Water (2) at 323.15 K



**Figure 3. Ethnaol (1) - Water (2) at 323.15 K
Margules Equation**



**Figure 4. Ethanol (1) - Water (2) at 323.15 K
van Laar Equation**

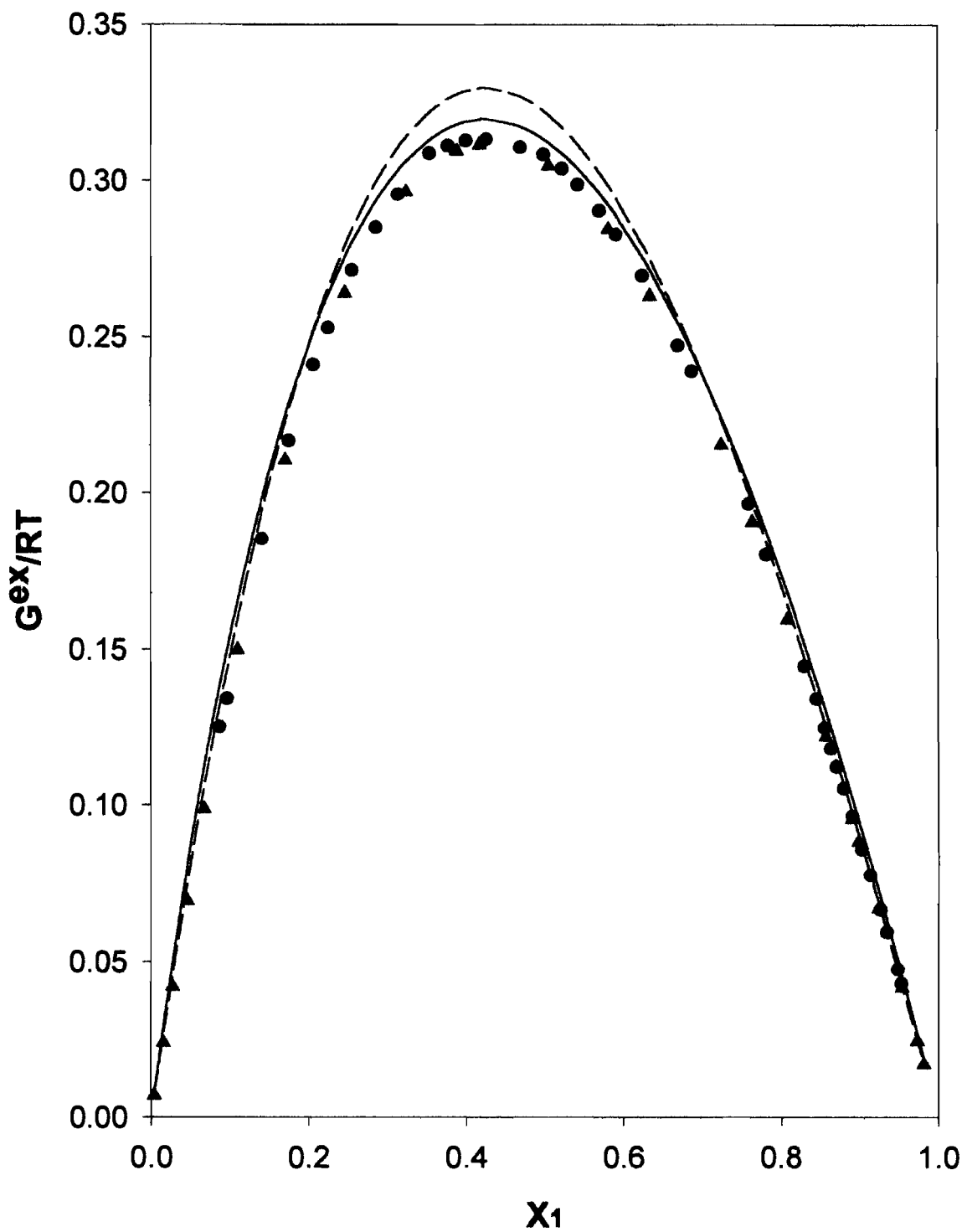


Figure 5. Ethanol(1) - Water(2) System at 323.15 K
(—)Wilson;(- - -)NRTL

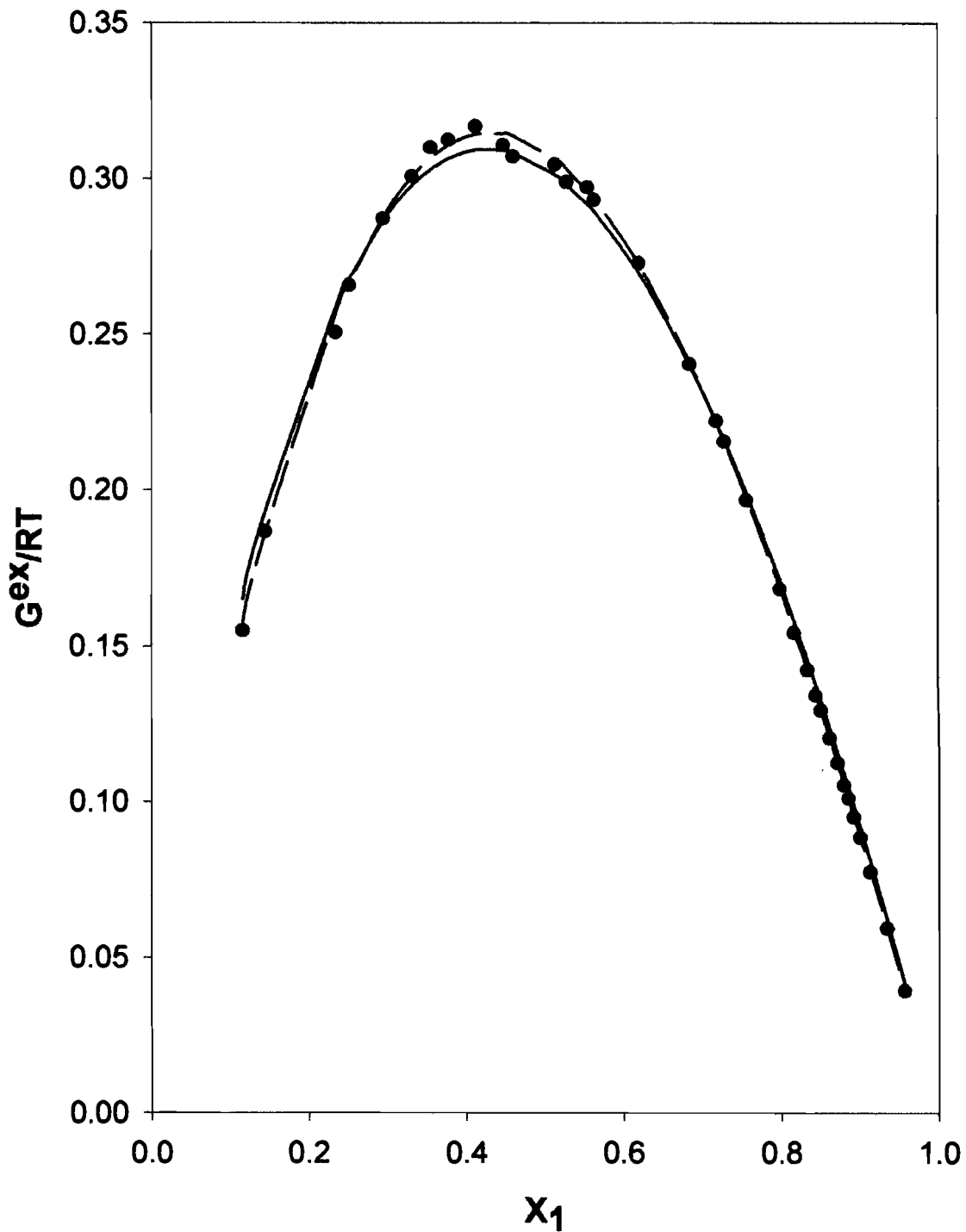


Figure 6. Ethanol(1) - Water(2) System at 328.15 K

(—)Wilson;(----)NRTL

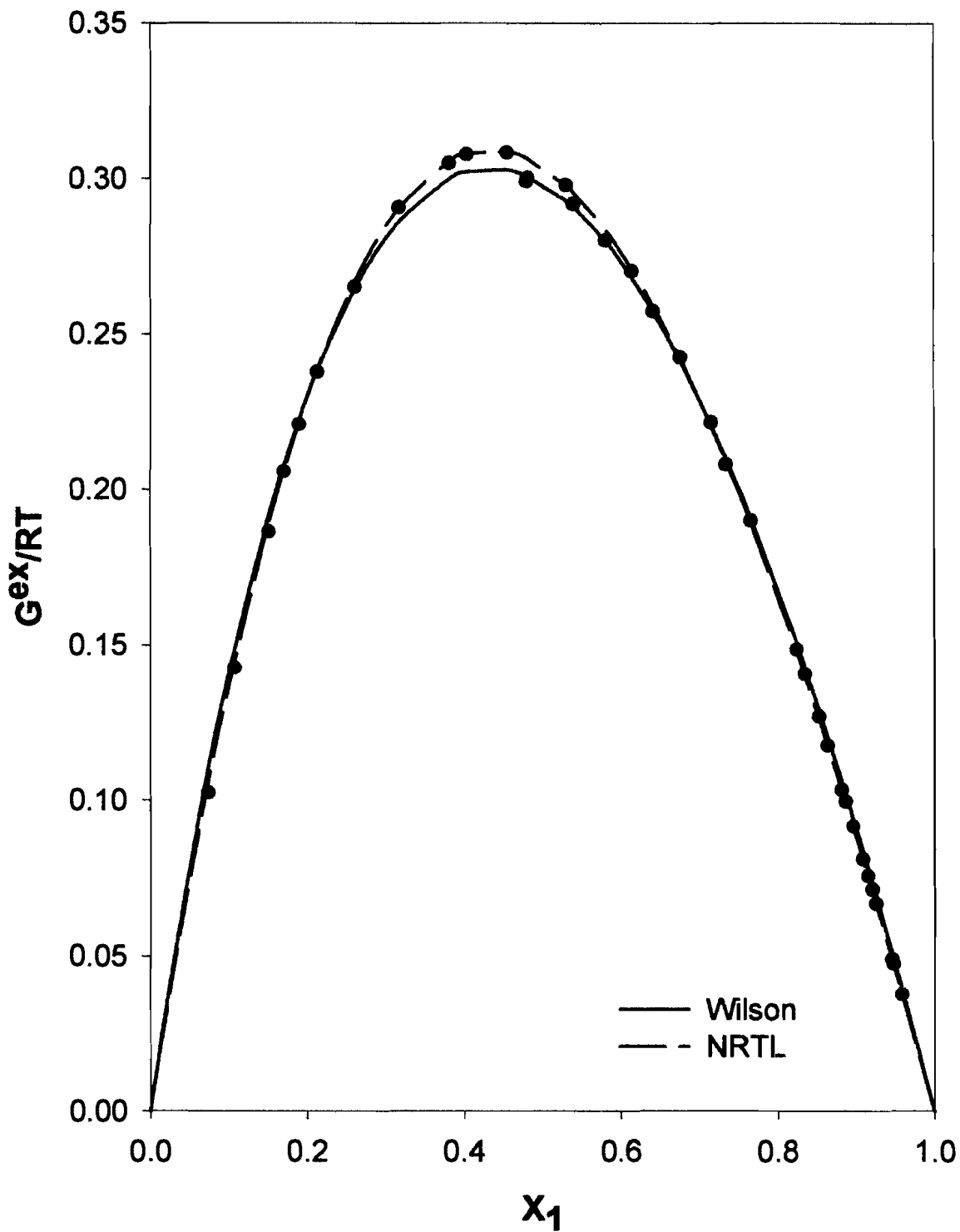
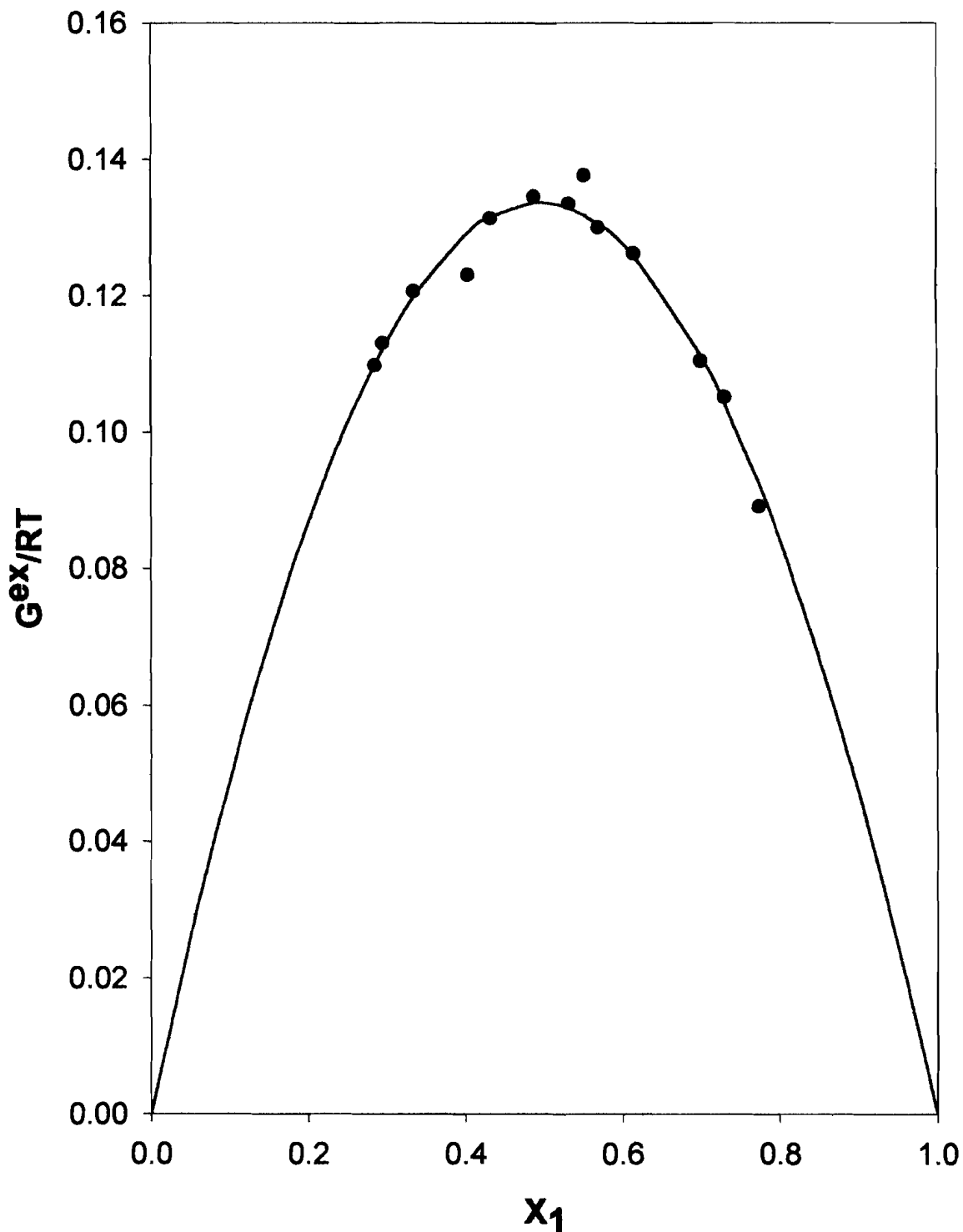


Figure 7. Ethnaol (1) - Water (2) System at 333.15 K



**Figure 8. Methanol (1) - Water (2) at 323.15 K
NRTL Equation**

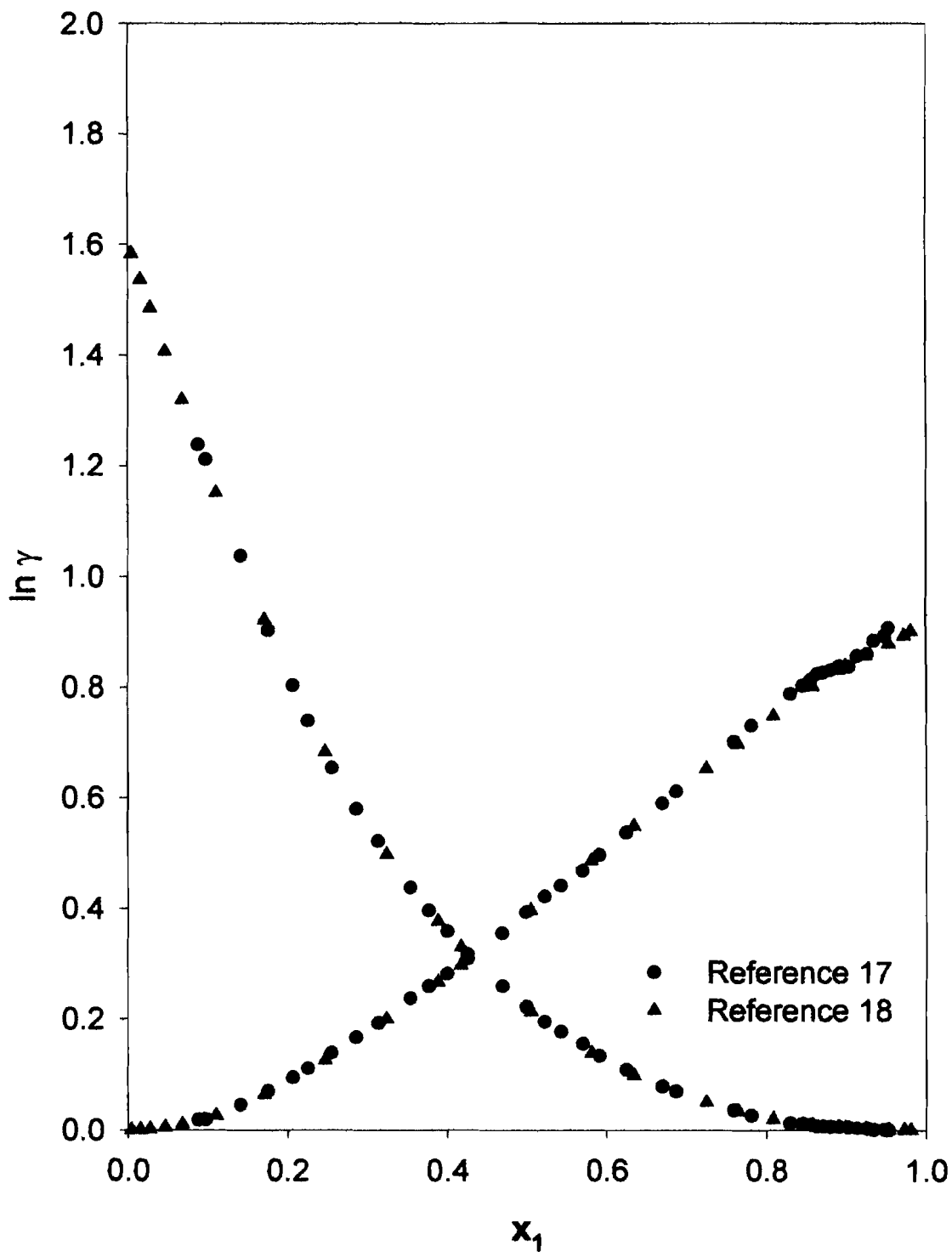


Figure 9. Ethanol (1) - Water (2) at 323.15 K

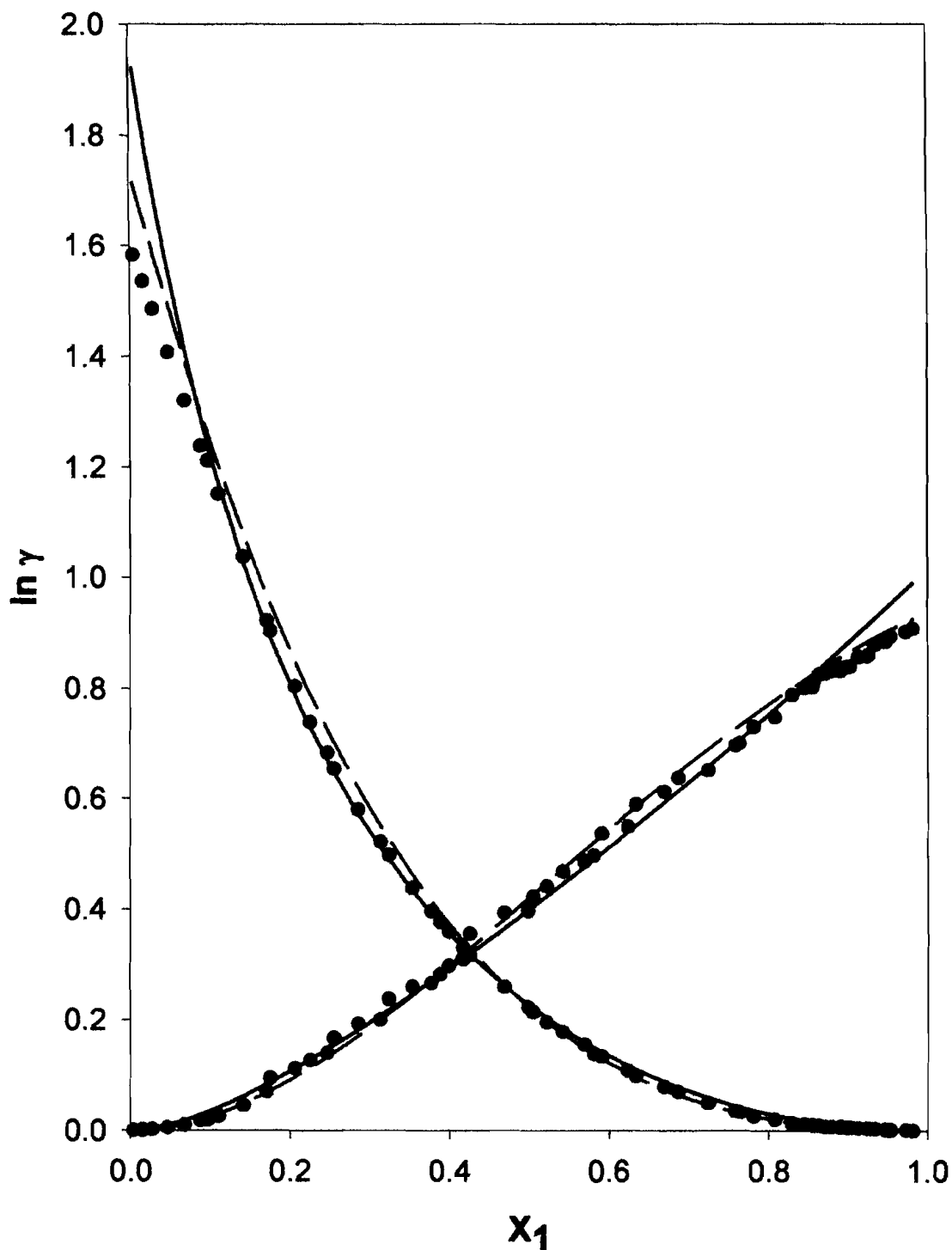


Figure 10. Ethanol (1) - Water (2) System at 323.15 K
 (—)Wilson; (----)NRTL

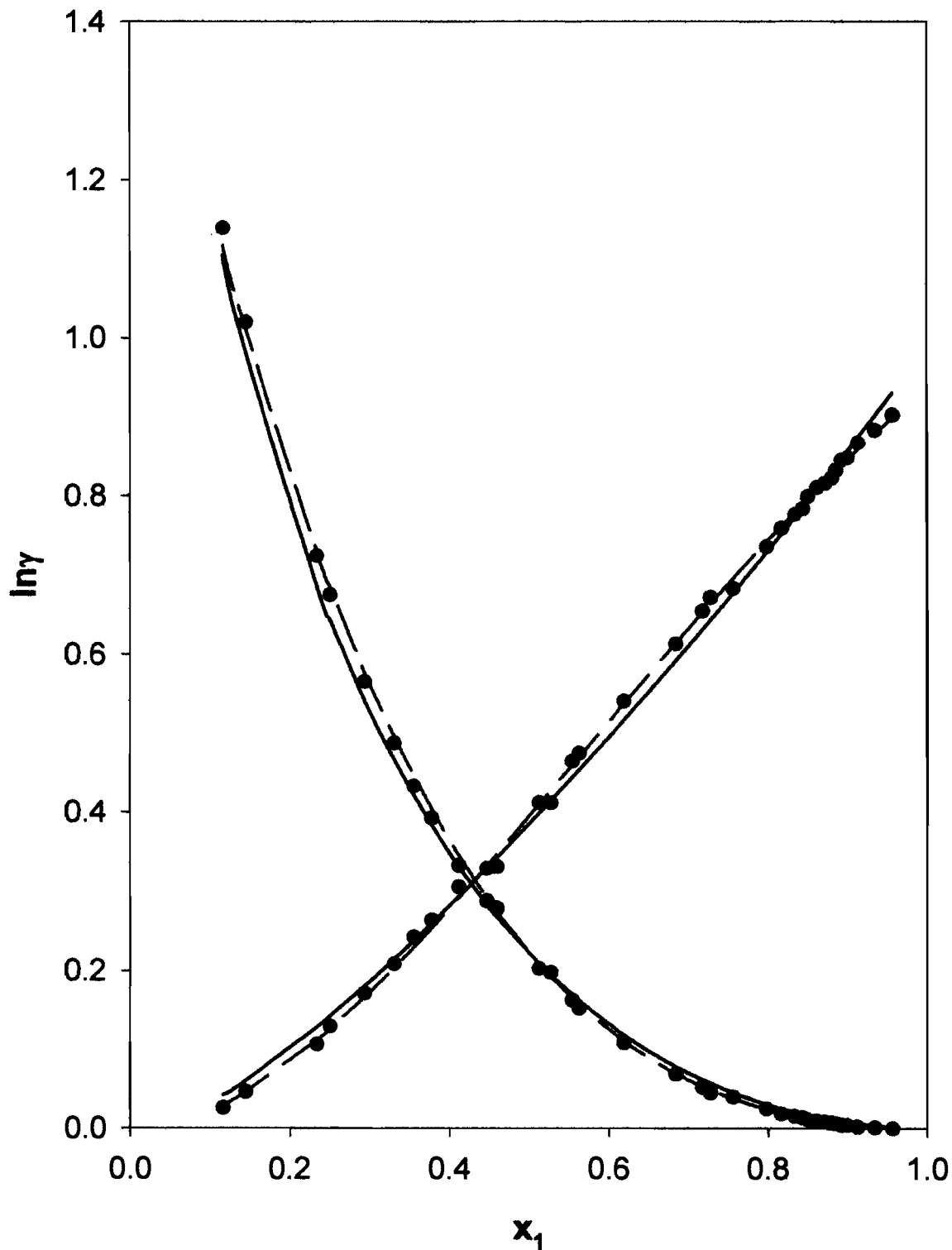


Figure 11. Ethnaol(1) - Water(2) System at 328.15 K

(—)Wilson, (----)NRTL

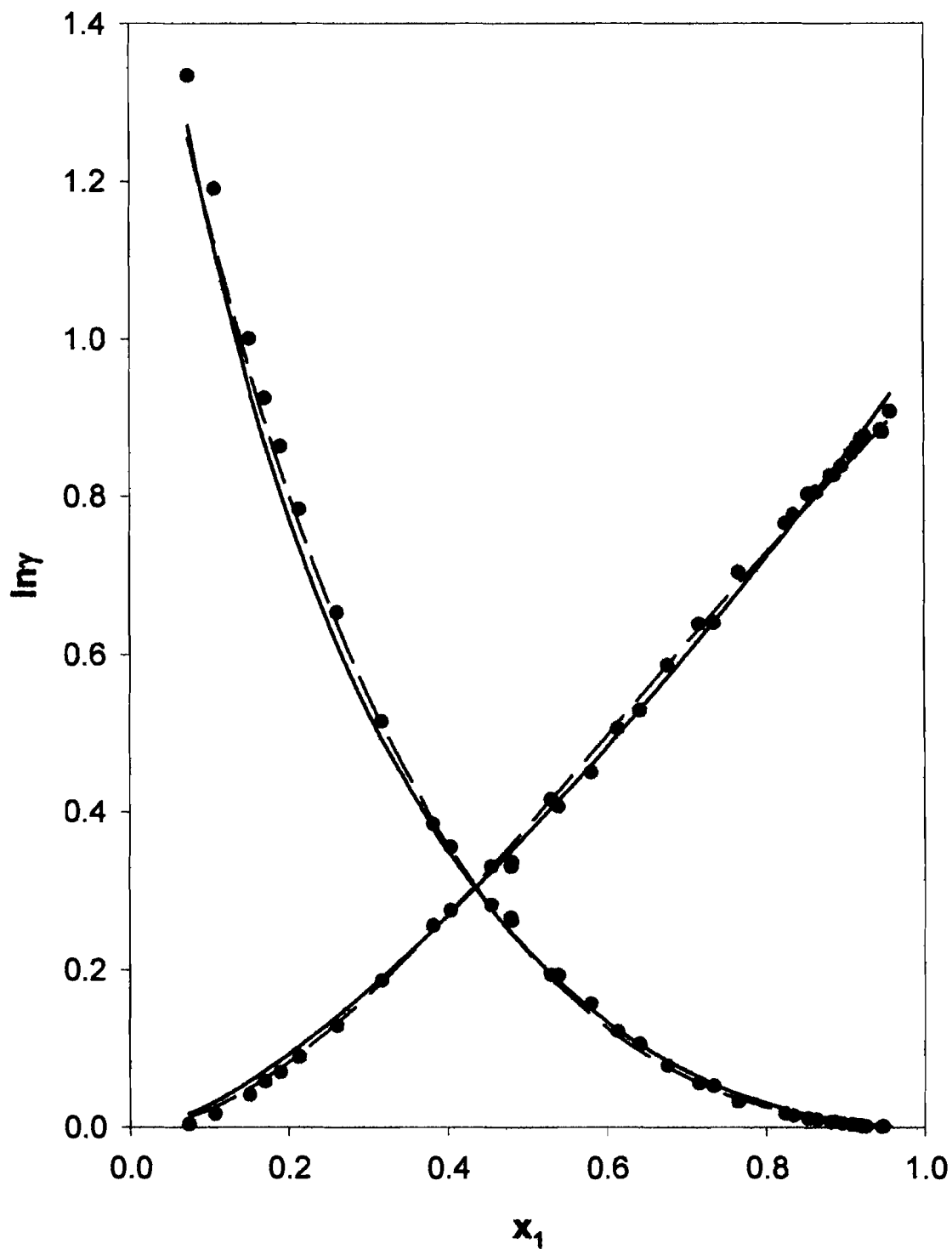


Figure 12. Ethanol(1) - Water(2) System at 333.15 K

(—)Wilson; (---)NRTL

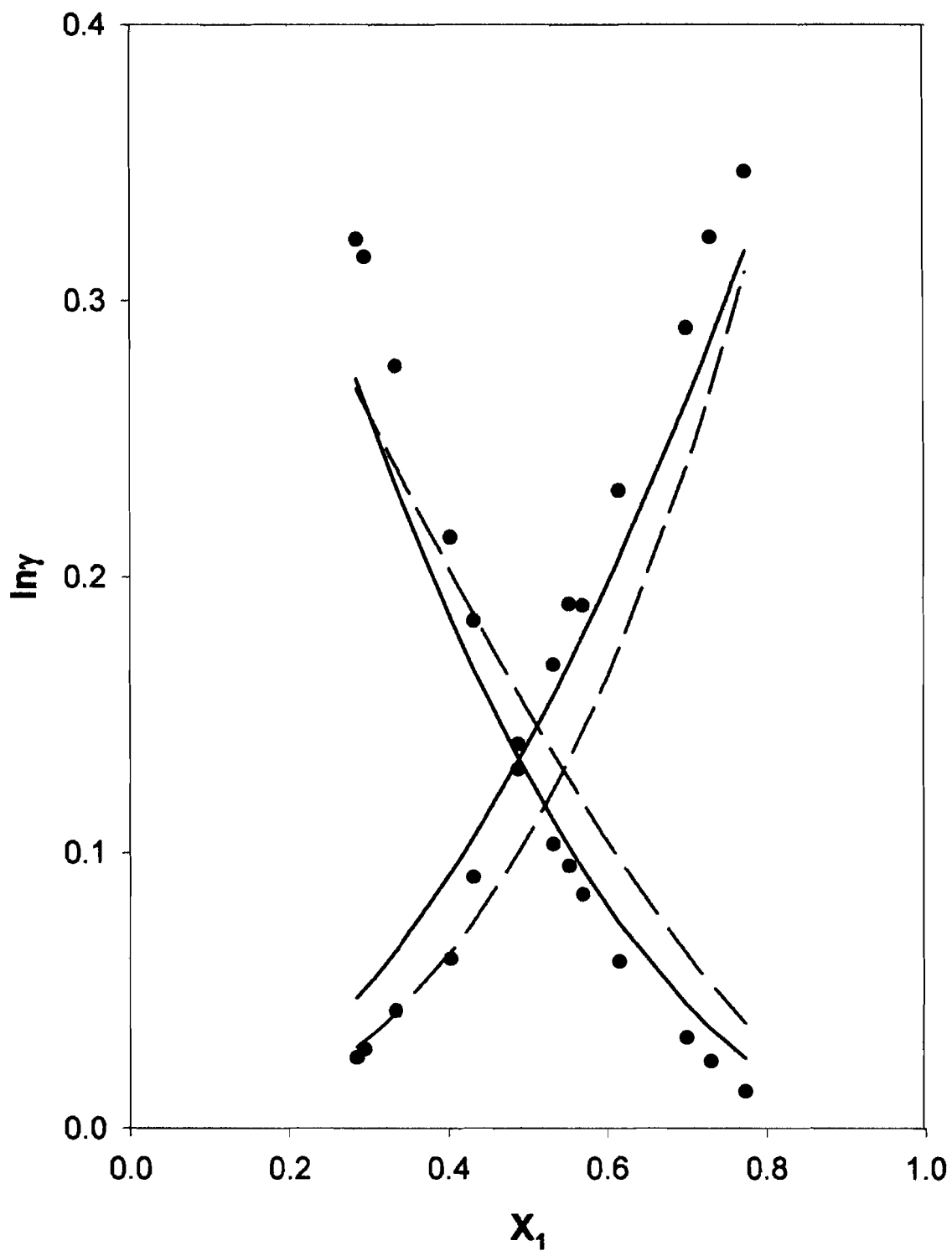


Figure 13. Methanol(1) - Water(2) System at 323.15 K
 (—)Wilson;(- - -)NRTL

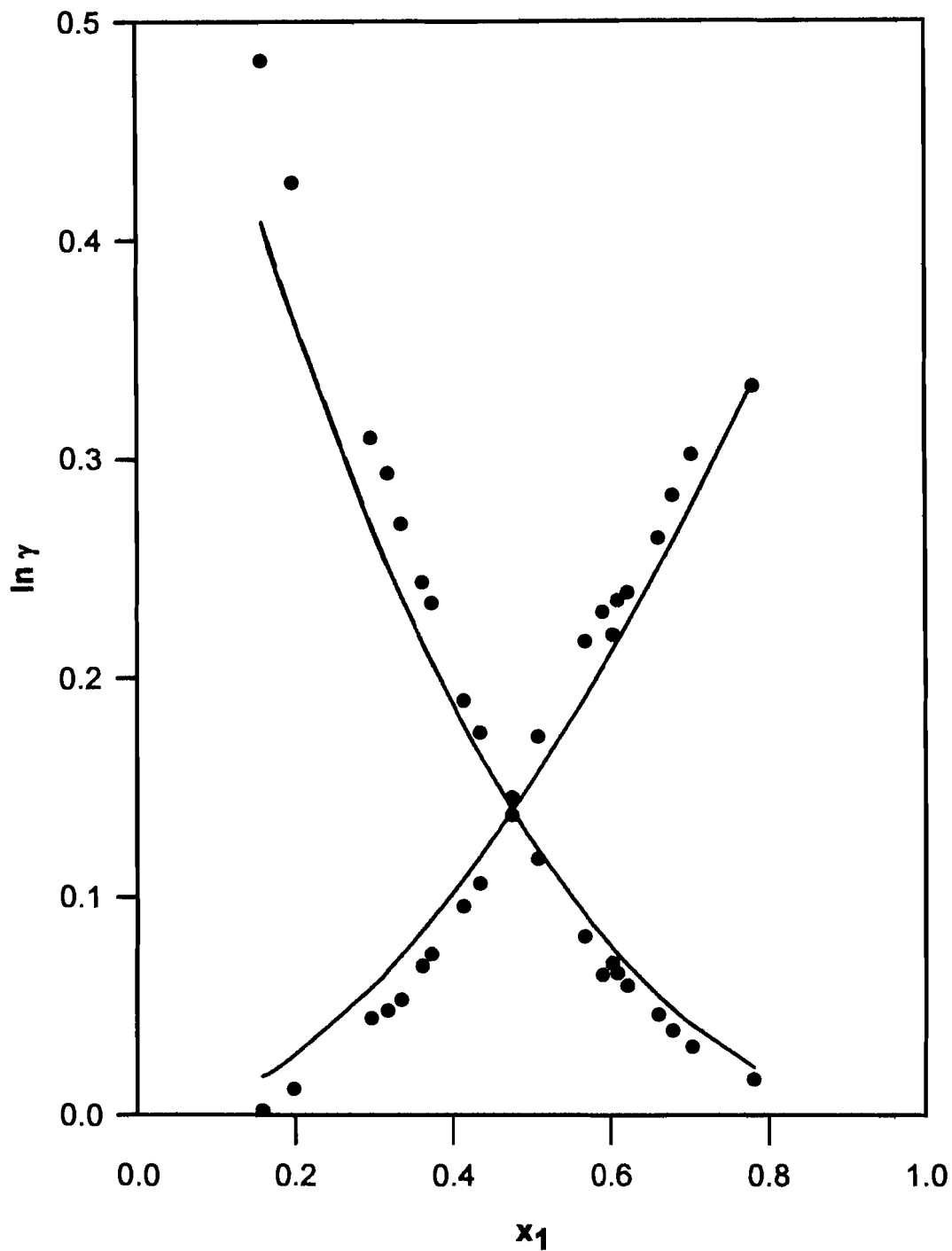


Figure 14. Methanol(1) - Water(2) at 328.15 K
 (—)Wilson; (----)NRTL

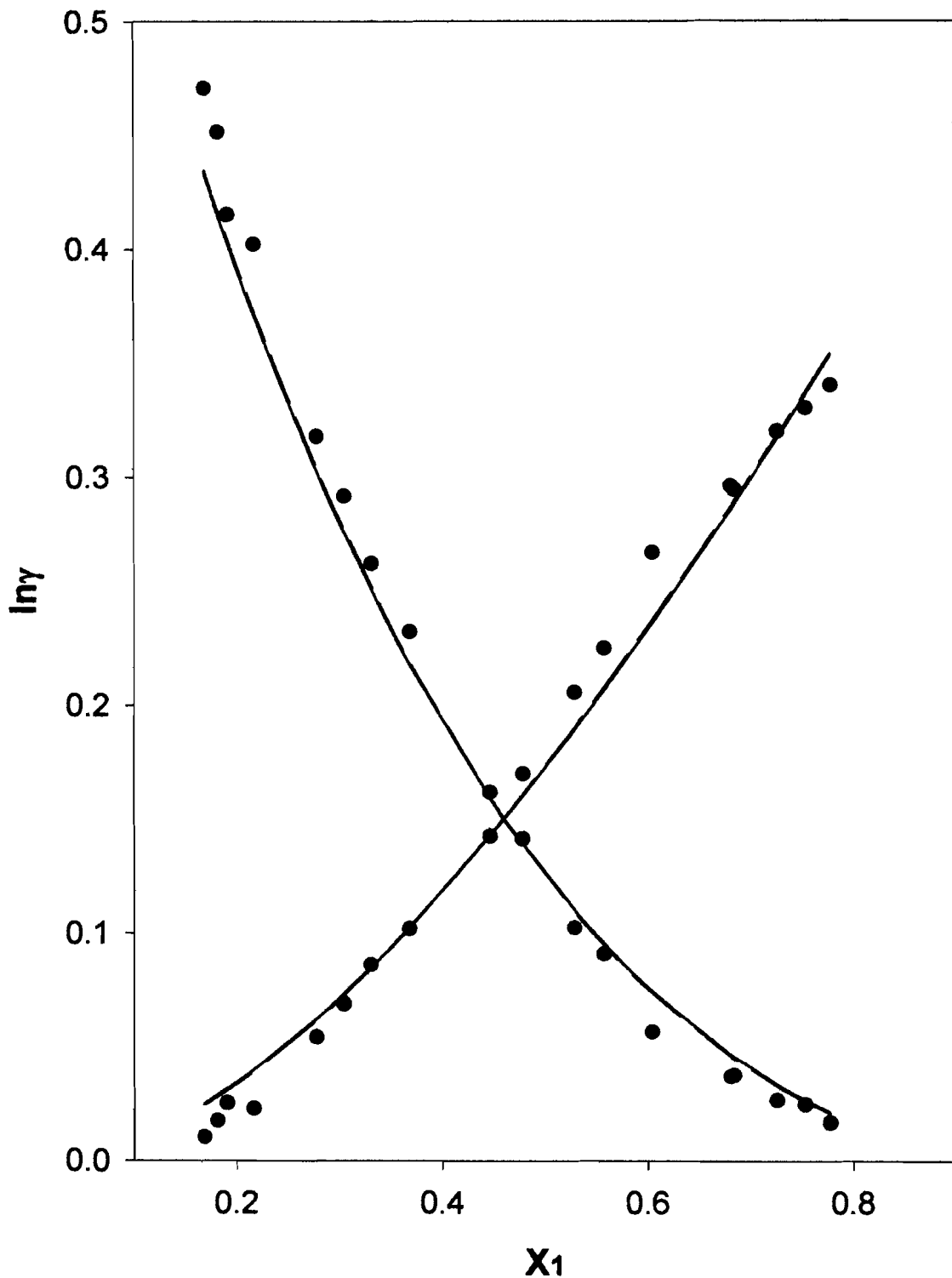


Figure 15. Methanol(1) - Water(2) System at 333.15 K
 (—)Wilson;(- - -)NRTL

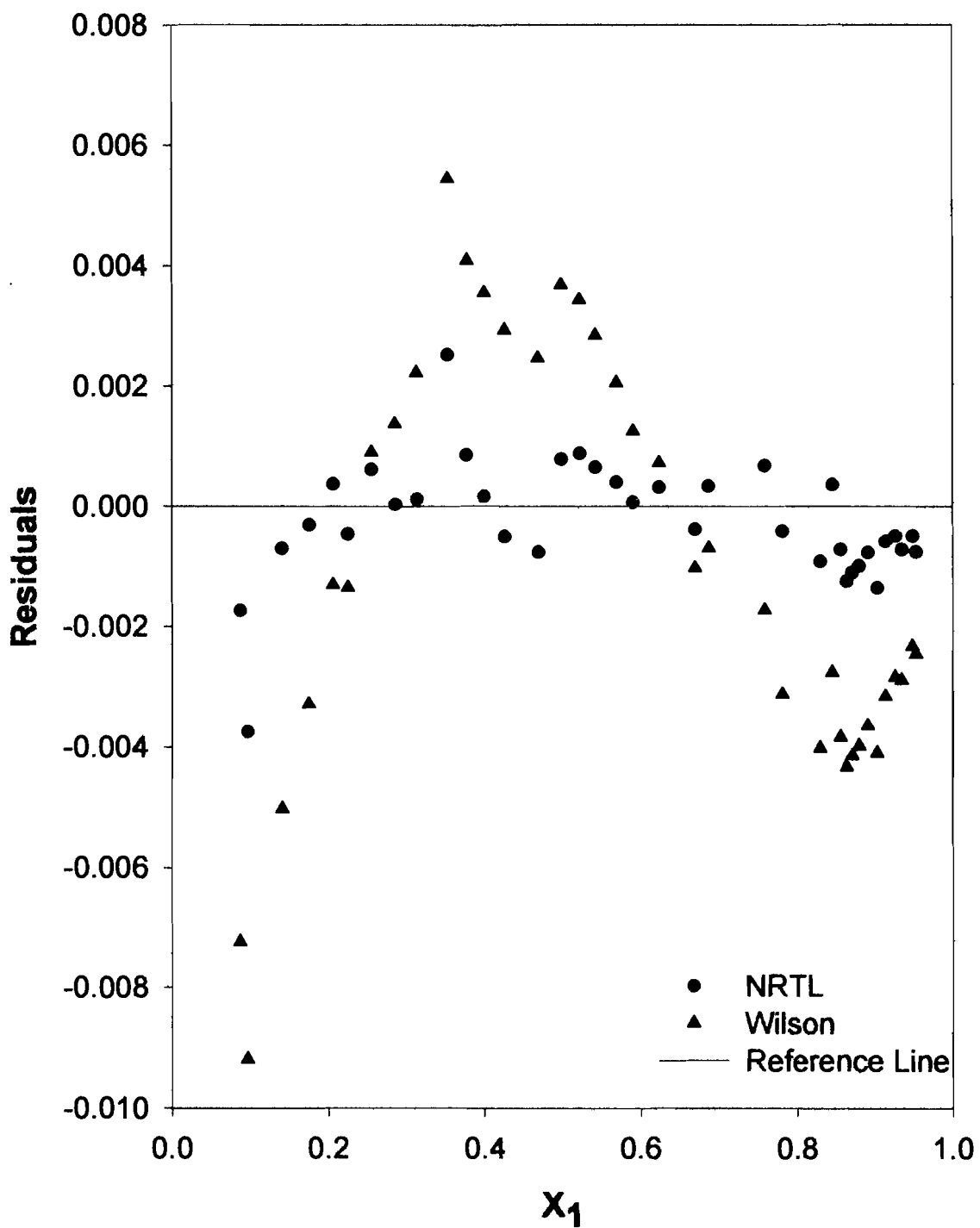


Figure 16. Ethanol(1) - Water(2) at 323.15 K

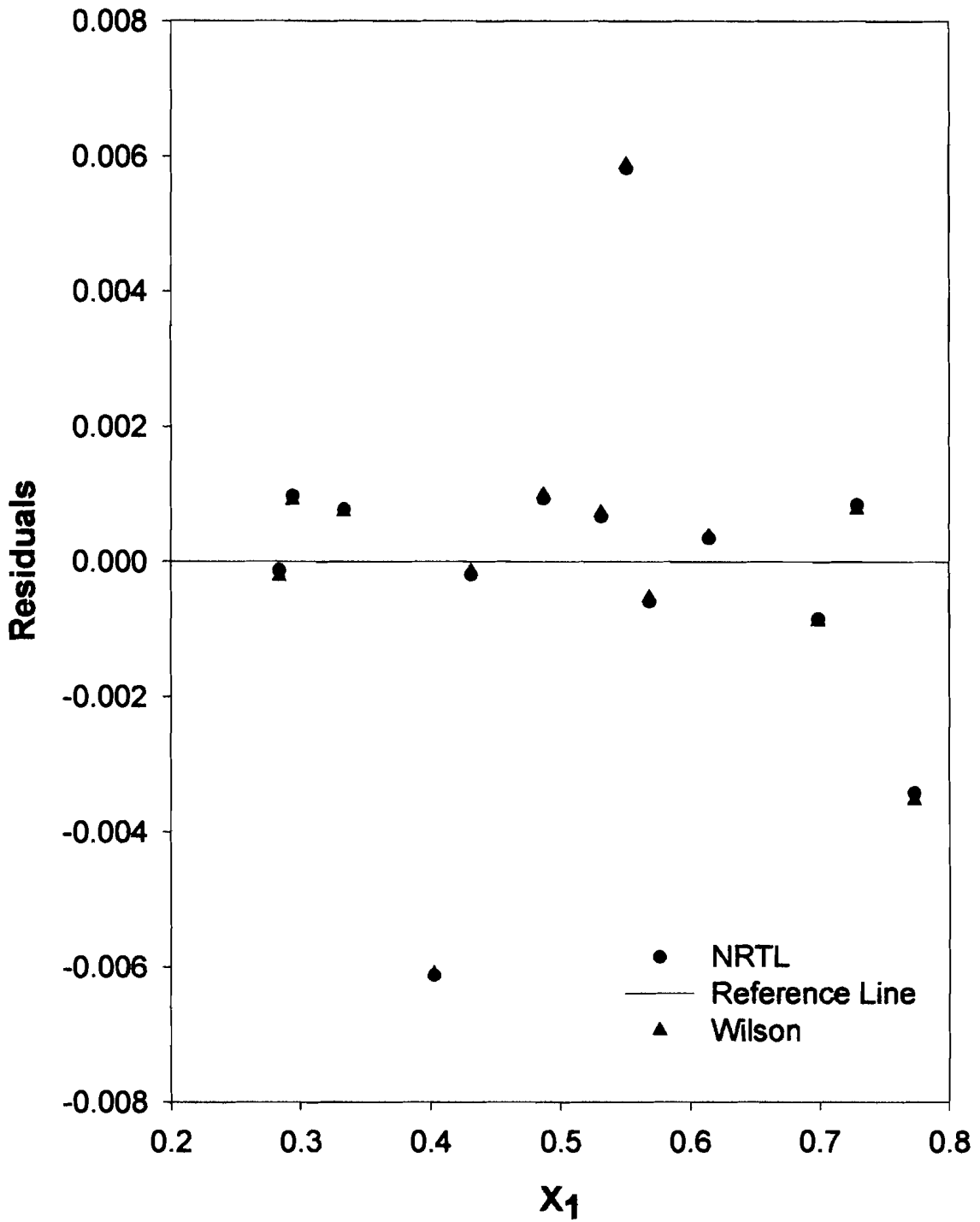


Figure 17. Methanol (1) - Water (2) at 323.15 K

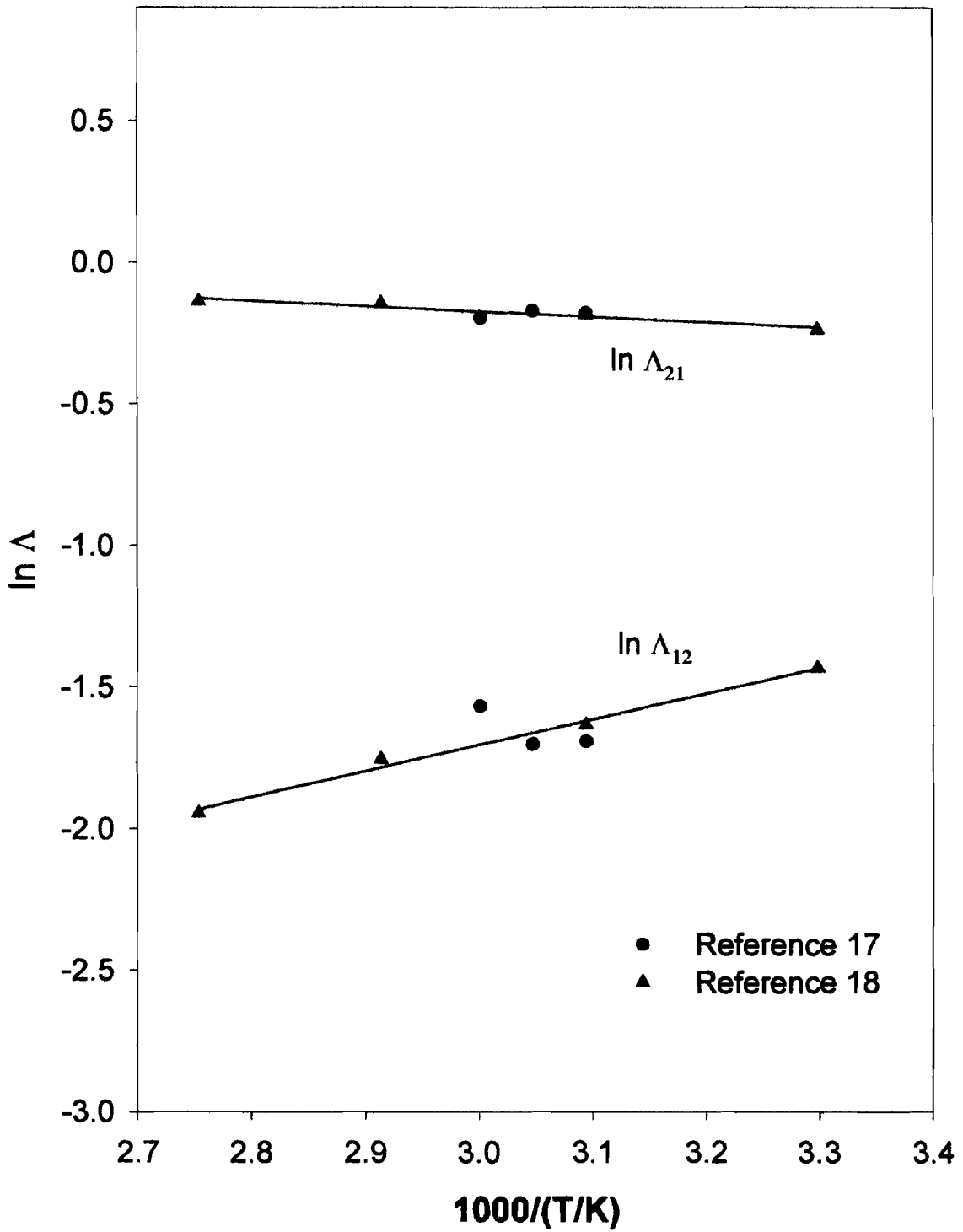


Figure 18. Ethanol(1) - Water(2) Temperature Dependence of Wilson Parameters

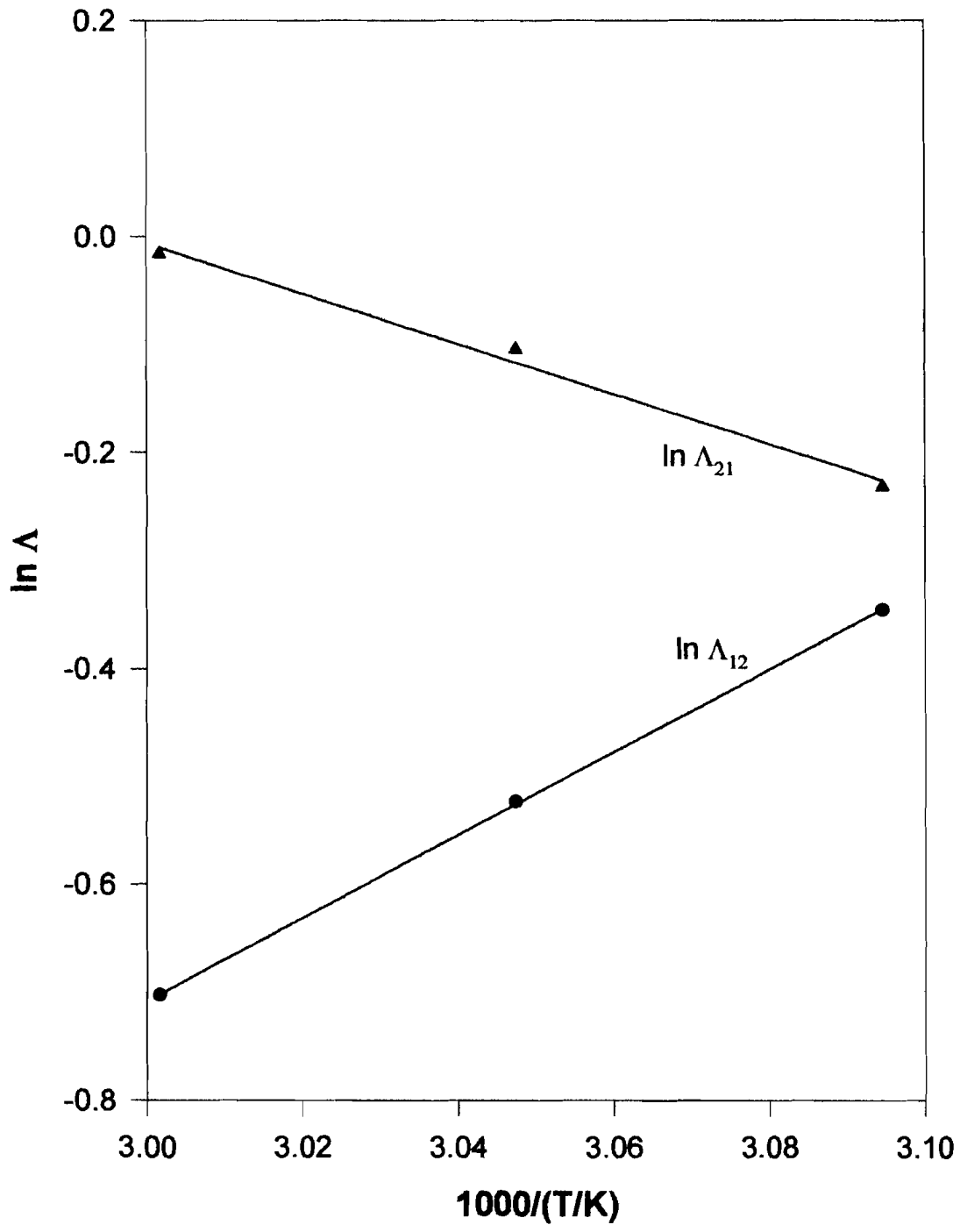


Figure 19. Methanol(1) - Water(2) Temperature Dependence of Wilson Parameters

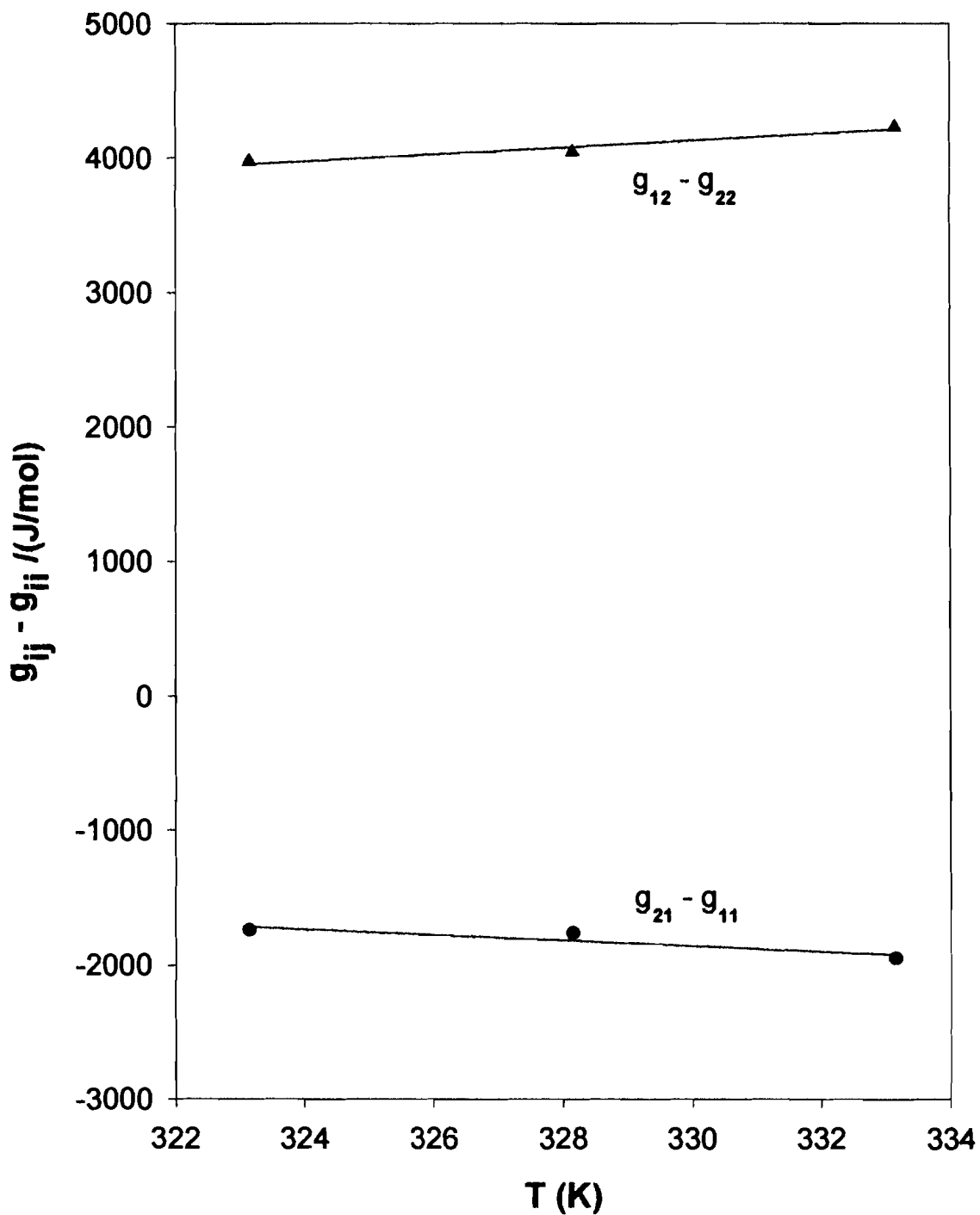


Figure 20. Ethanol(1) - Water(2) Temperature Dependence of NRTL Parameters

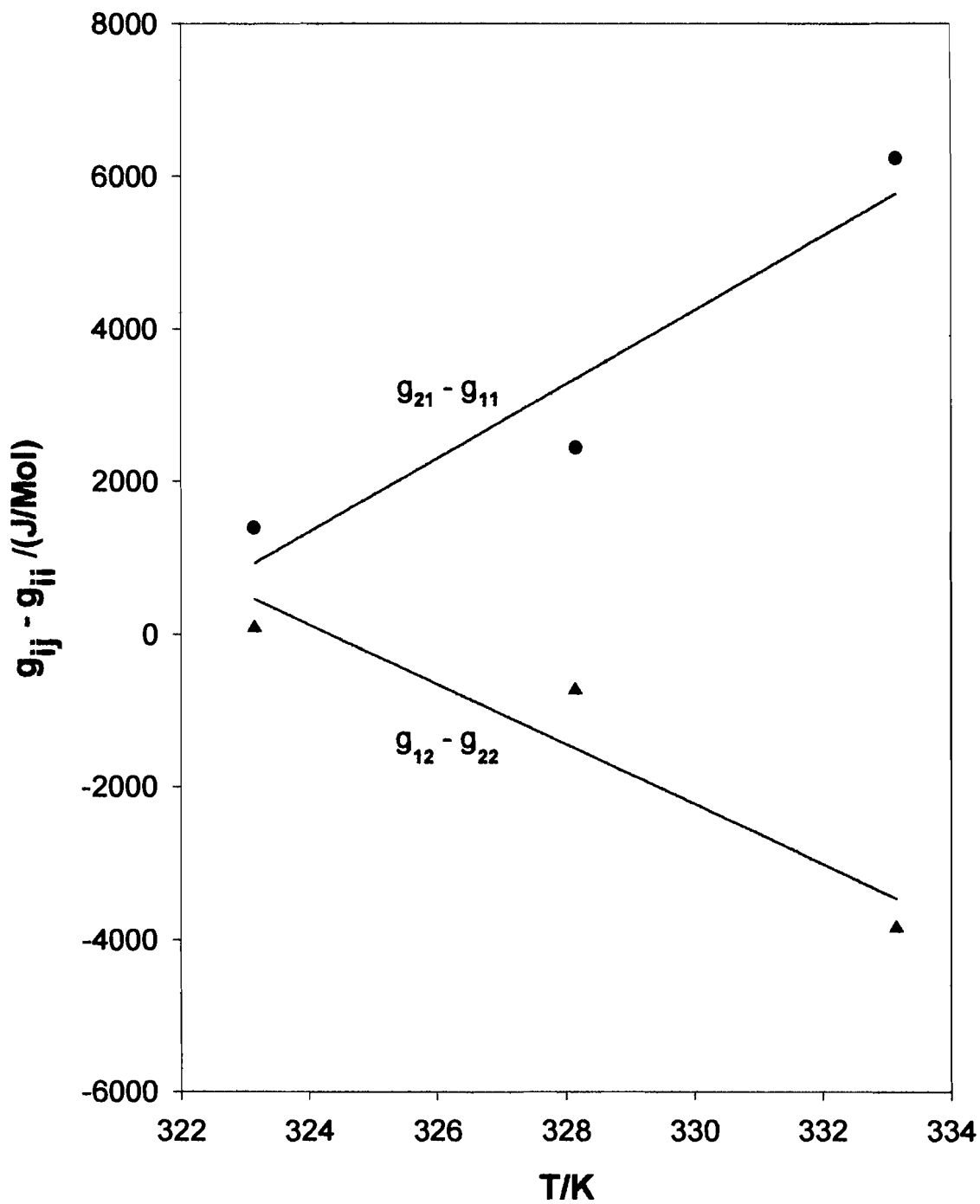


Figure 21. Methanol(1) - Water(2) Temperature Dependence of NRTL Parameters

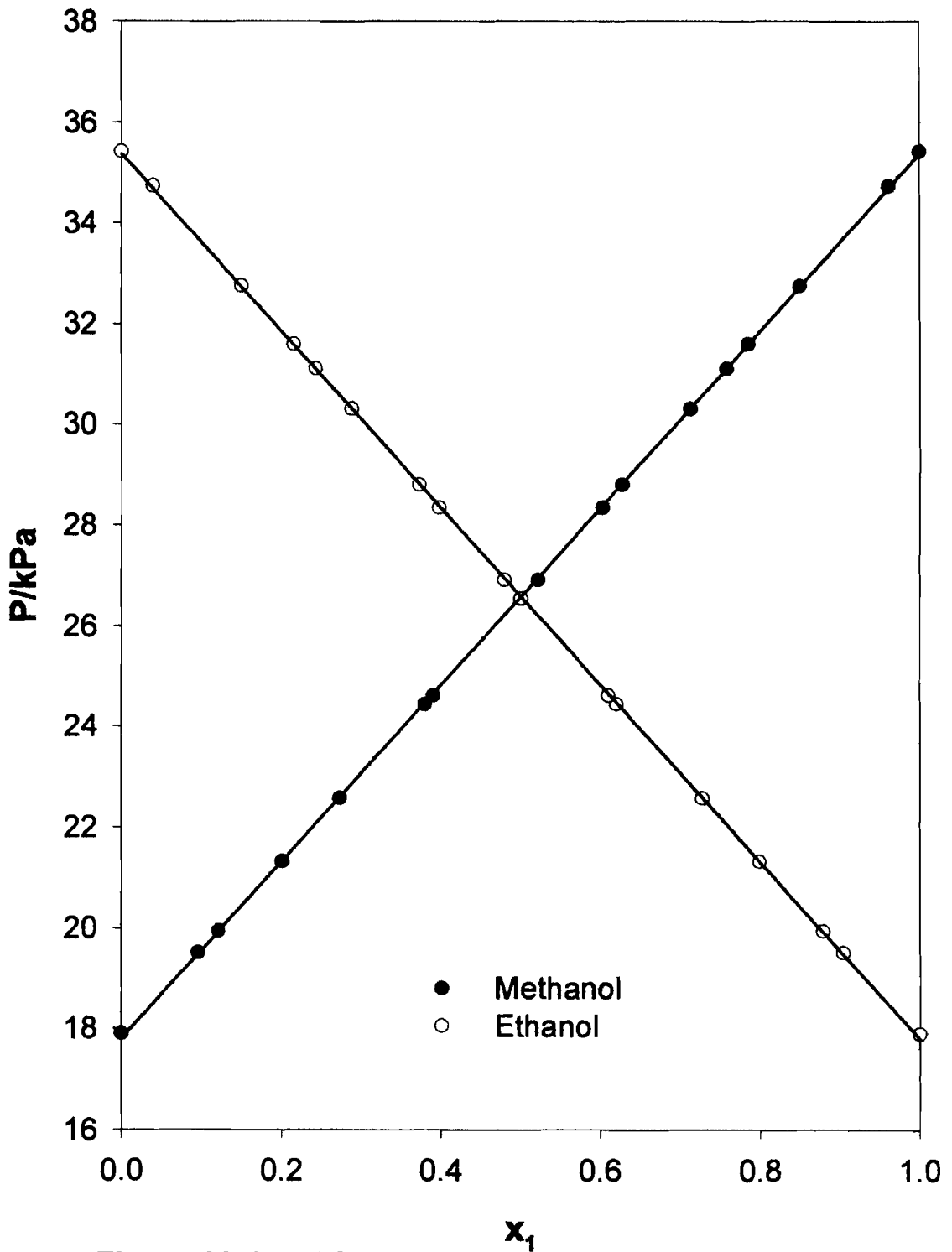
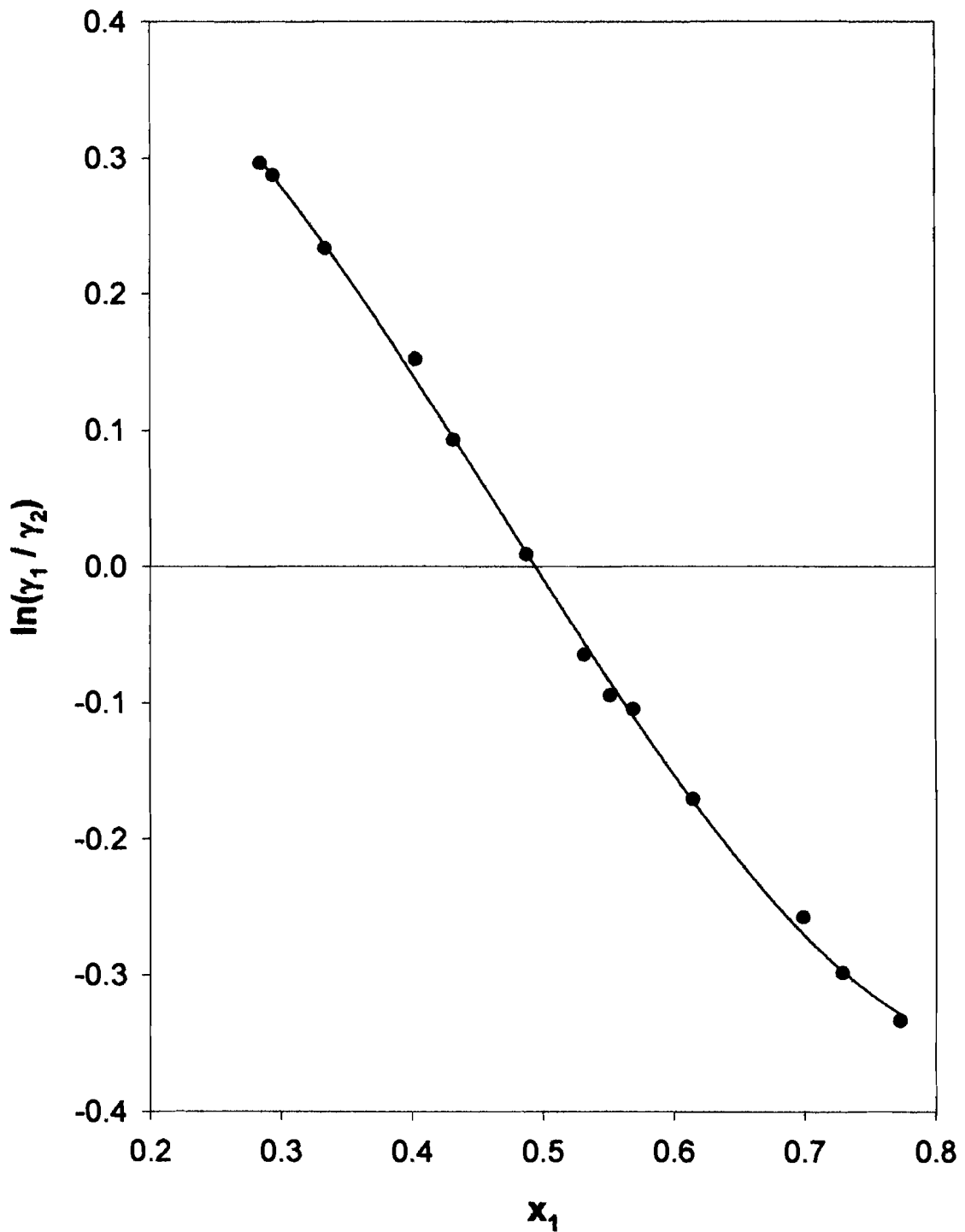


Figure 22. Ideal Solution Plot for Methanol(1) - Ethanol(2) at 313.15 K



**Figure 23. Area Test for Methanol(1) - Water(2)
at 323.15 K**

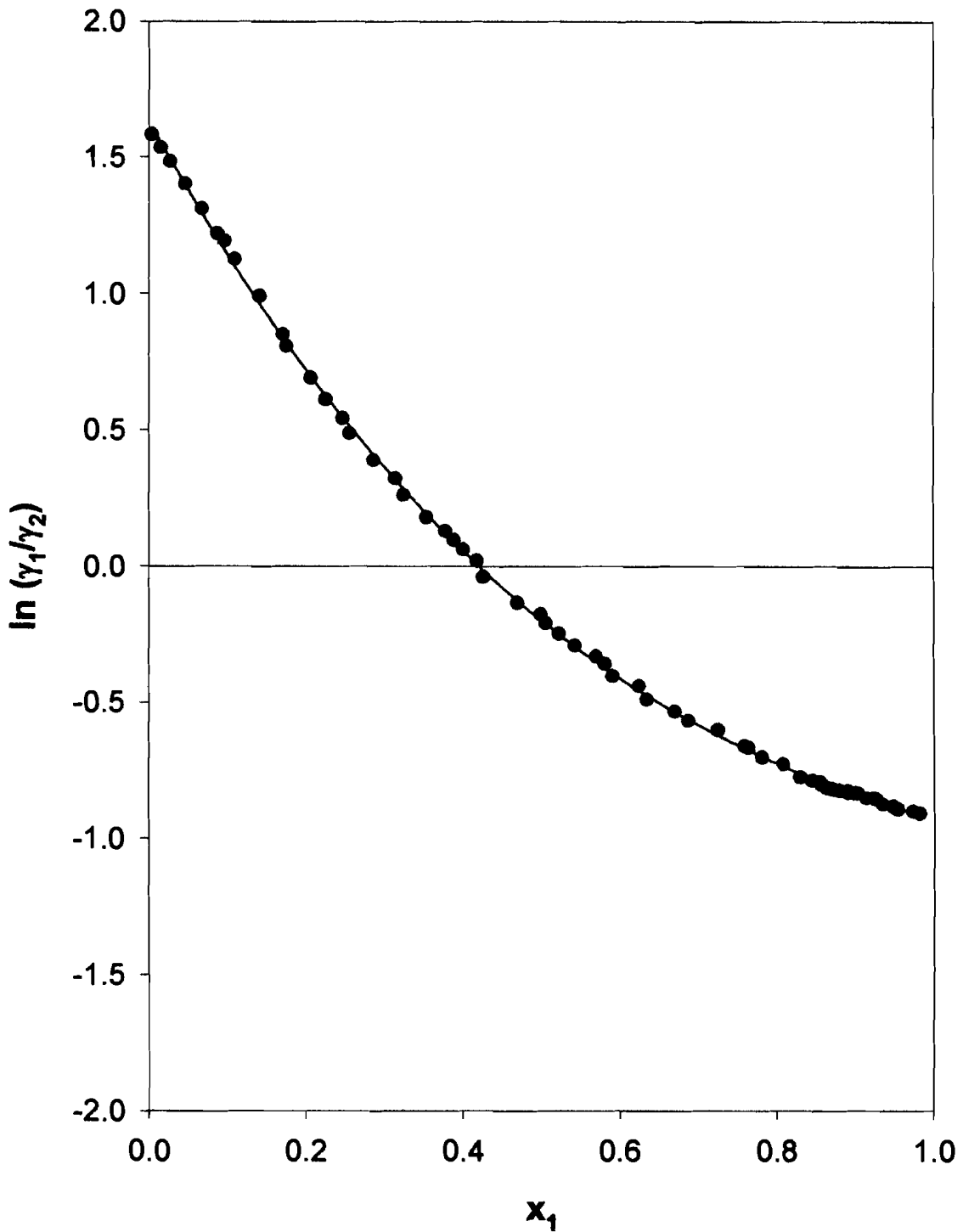


Figure 24. Area Test for Ethanol(1) - Water(2) at 323.15 K

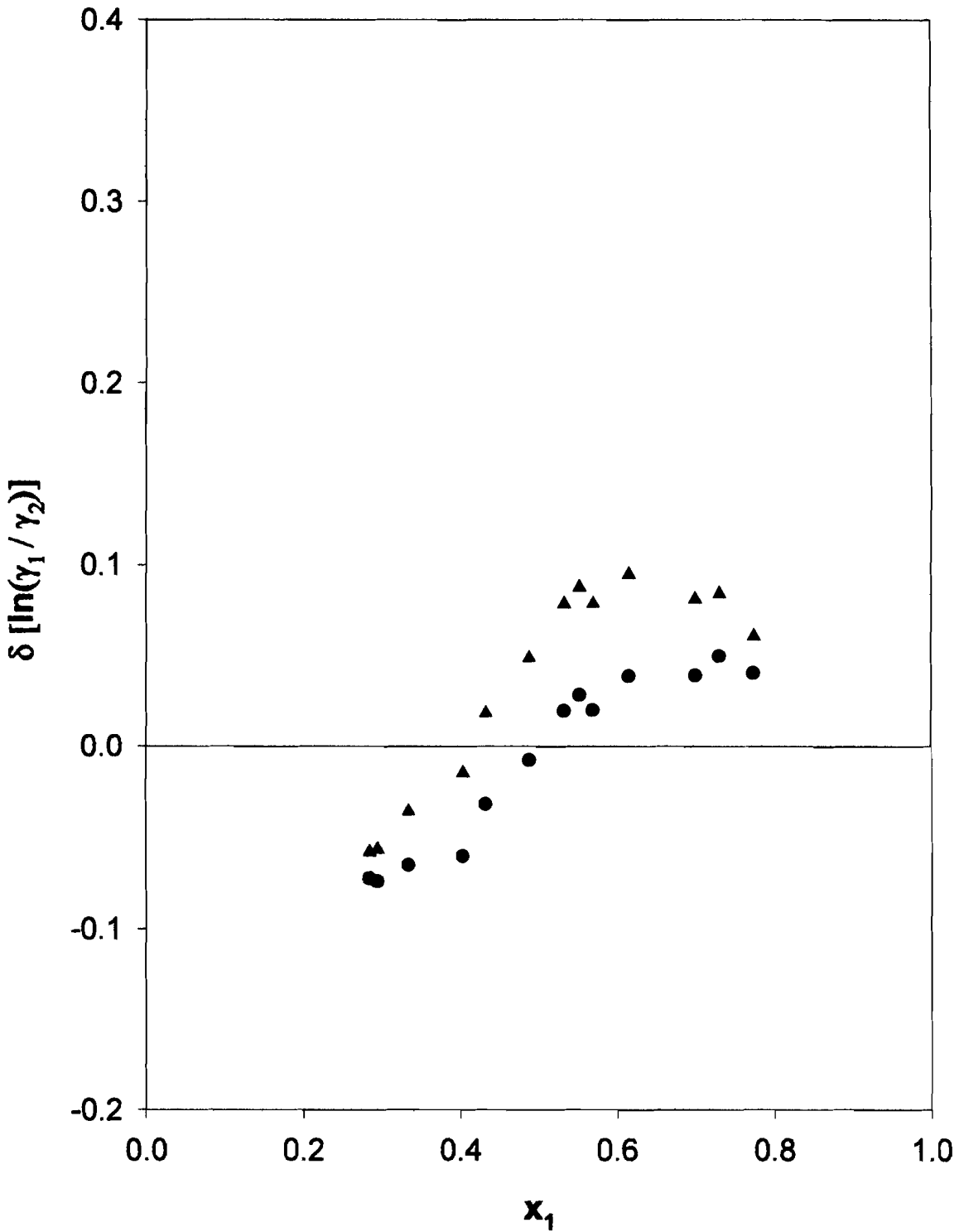


Figure 25. Direct Test of Methanol(1) - Water(2) System at 323.15 K

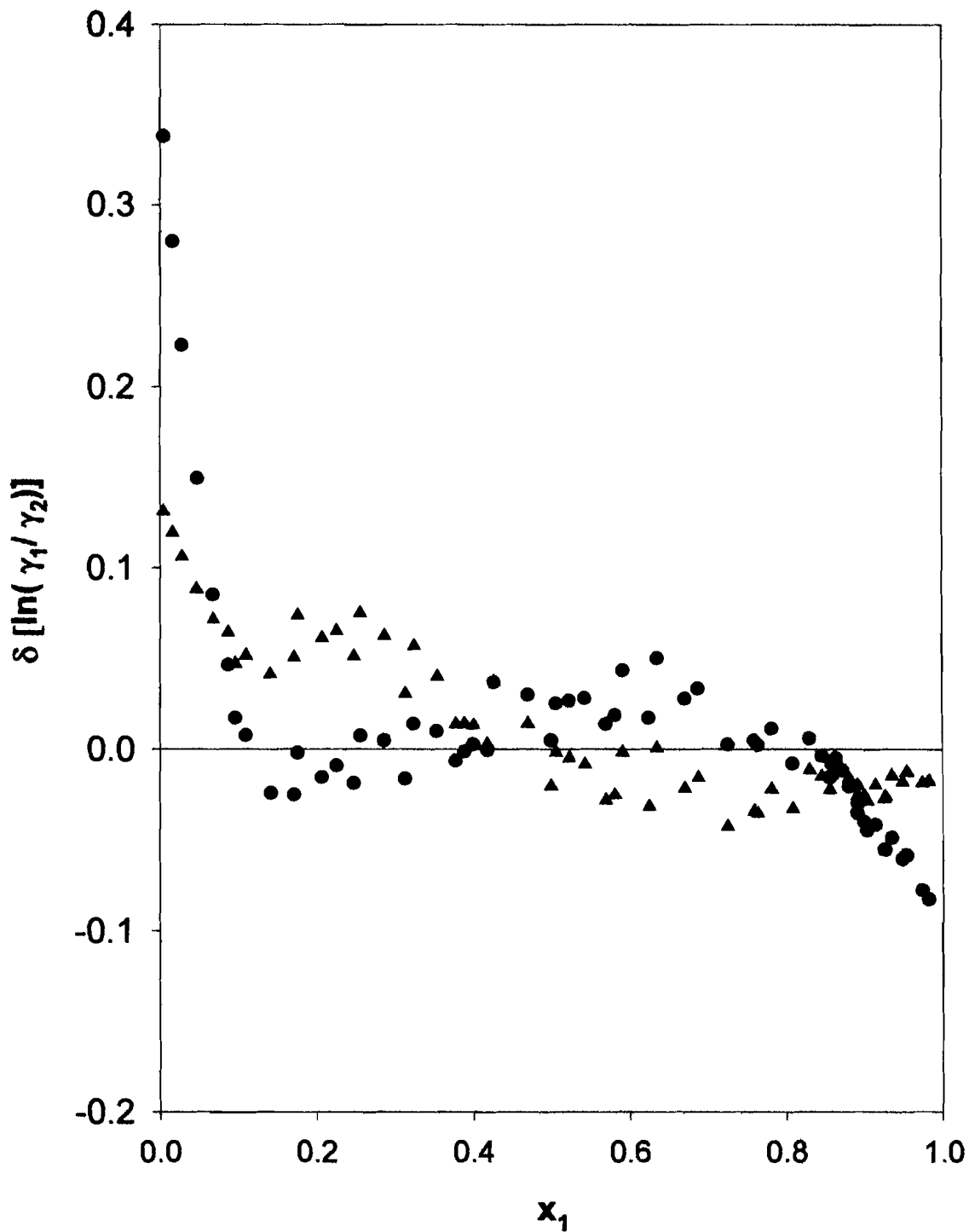


Figure 26. Direct Test for Ethanol(1) - Water(2) at 323.15 K
(●)Wilson;(▲)NRTL

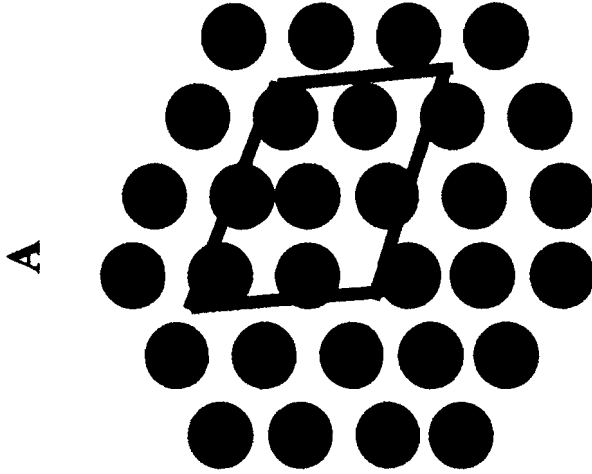
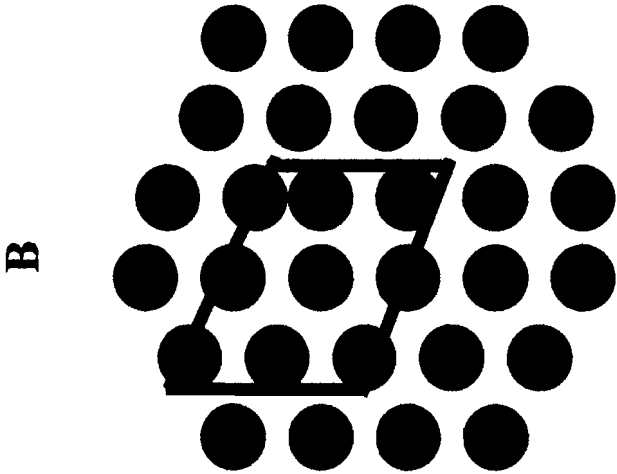


Figure 27. Local Composition

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Shuchen Hsieh

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5-10-99

Date

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Title of Thesis

Don Cooper

Signature of Graduate Office Staff

May 10, 1999

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