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ABSTRACT

Title of Thesis: Prediction and Correlation of Liquid-Liquid Equilibria

Jose Simonetty Jr., Master of Science, 1981

Thesis directed by: Dimitrios Tassios, Professor of Chemical Engineering

The NRTL, LEMF, and UNIQUAC models are used in the prediction and correlation of liquid-liquid equilibrium data for ten type I systems. The results indicate that best predictions are obtained with the LEMF equation, with an overall average absolute percentage error in distribution coefficients of 19.5 as compared to 23.0 and 24.7 with the NRTL and UNIQUAC equations, respectively. Good correlation of liquid-liquid equilibrium data alone is obtained with all three models; the LEMF equation is slightly better with an overall average absolute percentage error in distribution coefficients of 5.5 as compared to 6.7 and 5.9 for the NRTL and UNIQUAC equations, respectively. The same applies for the simultaneous correlation of liquid-liquid and binary vapor-liquid equilibrium data, where the combined errors for the distribution and activity coefficients are: LEMF, 6.5; NRTL, 8.8; and UNIQUAC, 8.2. In all cases best results are obtained for systems having large mutual solubilities, and become progressively worse as the mutual solubility decreases.

PREDICTION AND CORRELATION OF LIQUID-LIQUID EQUILIBRIA

by
Jose Simonetty Jr.

Thesis submitted to the faculty of the Graduate School of
the New Jersey Institute of Technology in partial fulfillment of
the requirements for the degree of
Master of Science in Chemical Engineering
1981

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CHAPTER I

PREDICTION OF LIQUID-LIQUID EQUILIBRIA

1. Introduction

Prediction of multicomponent liquid-liquid equilibrium (LLE) is of importance in chemical engineering applications such as extraction when no experimental LLE data is available in the literature. Several authors, using different models for the excess Gibbs free energy, have dealt with this problem with varying degrees of success (Renon and Prausnitz, 1968; Joy and Kyle, 1969; Marina and Tassios, 1973; Hiranuma, 1974; Van Zandijcke and Verhoeye, 1974; Abrams and Prausnitz, 1975; Nagata and Ogura, 1975; Tsuboka and Katayama, 1975; Nagata and Nagashima, 1976; Sugi et al., 1976; DeFre and Verhoeye, 1977; Sugi and Katayama, 1977; Sugi and Katayama, 1978; Anderson and Prausnitz, 1978; Soerensen et al., 1979; and Tochigi et al., 1980).

Ternary LLE systems are classified according to the number of partially miscible binary systems (PMBS) into three types: type I (one PMBS), type II (two PMBS), and type III (three PMBS). Type III systems are rarely found in chemical engineering applications, and type II systems can be successfully handled in terms of prediction with the models used by the above authors; therefore this work is focused on type I systems only. An evaluation of the prediction performance of the most successful models (NRTL, Renon and Prausnitz, 1968; LEMF, Marina and Tassios, 1973; and UNIQUAC, Anderson and Prausnitz, 1978) suggests that it would be convenient to classify type I systems into three categories (IA, IB, and IC) according to the breadth of the two-phase region as shown in

Figure 1 given in Appendix A. To complete this classification it is proposed that the mutual solubility ranges presented in Table I given in Appendix B, and chosen somewhat arbitrarily, be used.

A survey of the related literature reveals an uncertainty in the degree of success of the three models (NRTL, LEMF, and UNIQUAC) in predicting LLE for the type IA, IB, and IC systems. For example, the work of Renon and Prausnitz (1968) indicates that good predictions with the NRTL equation can be obtained when mutual solubilities are not too small (greater than 0.05 mole fraction), and the work of Marina and Tassios (1973) with the LEMF equation suggests the same conclusion. However, Joy and Kyle (1969), and Anderson and Prausnitz (1978) conclude that best predictions with the NRTL and UNIQUAC equations, respectively, are obtained for systems having very small mutual solubilities. To eliminate this uncertainty, the performance of the three models in predicting LLE for types IA, IB, and IC systems is investigated here. In addition, the work of Soerensen et al. (1979) evaluates the performance of the NRTL and UNIQUAC equations in predicting LLE for seven systems. Since only seven systems were investigated they do not make any conclusions with regard to which equation is best. The work of these authors did not include the LEMF equation. Thus it is the first objective of this thesis to evaluate the performance of the three models in predicting LLE as a function of the type (IA, IB, and IC) of the system. Ten systems are examined for this purpose (Table II), four of which are of the type IA, three of the type IB, and three of the type IC.

2. The Models

The multicomponent expressions for the activity coefficient (γ_i) for the NRTL and LEMF equations are given by:

$$\ln(\gamma_i) = \frac{\sum_{j=1}^{n} T_{ji} G_{ji} X_j}{\sum_{k=1}^{n} G_{ki} X_k} + \sum_{j=1}^{n} \frac{X_j G_{ij}}{\sum_{k=1}^{n} G_{kj} X_k} \left[T_{ij} - \frac{\sum_{l=1}^{n} X_l T_{lj} G_{lj}}{\sum_{k=1}^{n} G_{kj} X_k} \right] \quad \text{..... (1-1)}$$

where n = number of components

$T_{ji} = (g_{ji} - g_{ii})/RT$

$G_{ji} = \exp(-\alpha_{ji} T_{ji})$

$\alpha_{ji} = \alpha_{ij}$

$g_{ji} = g_{ij}$

$\Delta g_{ji} = (g_{ji} - g_{ii})$, binary parameter

X_i = mole fraction of component i

NRTL: $\alpha_{ij} = 0.2, 0.3, 0.4, 0.47$ (1-2)

LEMF: $\alpha_{ij} = -1.0$ (1-2a)

The choice of α_{ij} in the NRTL equation is accomplished according to the rules of Renon and Prausnitz (1968).

For the UNIQUAC equation:

$$\ln(\gamma_i) = \ln(\Phi_i/X_i) + (z/2)q_i\ln(\theta_i/\Phi_i) + l_i - (\Phi_i/X_i)\sum_j X_j l_j -$$

$$q_i'\ln\left(\sum_j \theta_j'\tau_{ji}\right) + q_i' - q_i'\sum_j \frac{\theta_j'\tau_{ij}}{\sum_k \theta_k'\tau_{kj}} \qquad (1\text{-}3)$$

where $l_j = (z/2)(r_j - q_j) - (r_j - 1)$

$z = 10$

$\Delta u_{ij} = (u_{ij} - u_{jj})$, binary parameter

$\tau_{ij} = \exp(-\Delta u_{ij}/RT)$

$$\Phi_i = \frac{r_i X_i}{\sum_j r_j X_j}$$

$$\theta_i = \frac{q_i X_i}{\sum_j q_j X_j}$$

$$\theta_i' = \frac{q_i' X_i}{\sum_j q_j' X_j}$$

and r, q, and q' are pure component constants.

Table III gives the values of r, q, and q' for the components under investigation. Notice that for components other than water and alcohols, q = q'. The original UNIQUAC model as developed by Abrams and Prausnitz (1975) did not perform as well for systems containing water or alcohols, as compared to systems containing only hydrocarbons or where the OH group is not present. To improve the performance of the UNIQUAC model for systems containing water or alcohols, Anderson and Prausnitz (1978) decided to empirically determine the value of q, which is now q', in the residual part of the model.

In all these models, only binary parameters are included which can be evaluated from the appropriate binary data and then be used for prediction purposes.

3. Procedure

Prediction of ternary LLE is accomplished by determining the binary parameters in the models from the appropriate binary data. These parameters and models are then used to calculate the compositions at equilibrium. The predicted results are evaluated in terms of the average absolute percentage error in distribution coefficients, Q:

$$Q = \frac{\sum_{i=1}^{3} \bar{Q}_i}{3} \qquad (1\text{-}4)$$

where

$$\bar{Q}_i = \frac{\sum_{j=1}^{N} \left| \frac{K_i^{exp} - K_i^{cal}}{K_i^{exp}} \right|_j \times 100}{N} \qquad (1\text{-}5)$$

$(i = 1, 2, 3)$

and

$K_i = X_i^{II}/X_i^{I}$, the distribution coefficient of component i

X_i^{II}, X_i^{I} = mole fraction of component i in phase II and I, respectively.

N = number of tie-lines

exp, cal = experimental and calculated values, respectively

This approach yields a better picture of the quality of the predicted results as compared to a triangular plot, for while small differences in compositions are not visible if plotted on triangular coordinates they may lead to large errors in K in the lower sections of the binodal curve. For example, assume that the predicted results are: $X_2^I = 0.01$ and $X_2^{II} = 0.95$, as compared to the experimental values of 0.015 and 0.95, respectively. While the error in X_2^I is only 0.005, and it would hardly be noticible in a triangular plot, the error in K_2 is 50%.

The following procedure was used in the prediction of ternary LLE.

From thermodynamics it is known that when two phases are in equilibrium, then:

$$\hat{f}_i^I = \hat{f}_i^{II} \tag{1-6}$$

where $\hat{f}_i^I$ and $\hat{f}_i^{II}$ are the fugacities of component i in the liquid phases I and II, respectively. The liquid phase fugacity is given by:

$$\hat{f}_i = X_i \gamma_i f_i^o \tag{1-7}$$

where

X_i = mole fraction of component i

γ_i = activity coefficient of component i

f_i^o = standard state fugacity of pure component i evaluated at the temperature of the system and at some specified pressure

When equation (1-7) is substituted into equation (1-6) one obtains equation (1-8).

$$(X_i \gamma_i)^I = (X_i \gamma_i)^{II} \tag{1-8}$$

For the case of ternary LLE equation (1-8) becomes:

$$(X_1 \gamma_1)^I = (X_1 \gamma_1)^{II} \tag{1-9}$$

$$(X_2 \gamma_2)^I = (X_2 \gamma_2)^{II} \tag{1-10}$$

$$(X_3 \gamma_3)^I = (X_3 \gamma_3)^{II} \tag{1-11}$$

Two additional relationships exist,

$$X_3^I = 1 - X_2^I - X_1^I \tag{1-12}$$

$$X_3^{II} = 1 - X_2^{II} - X_1^{II} \tag{1-13}$$

According to the Gibbs phase rule

$$F = n + 2 - \phi \tag{1-14}$$

where

F = degrees of freedom

n = number of components

ϕ = number of phases

In ternary LLE n = 3 and $\phi = 2$, therefore F = 3. Thus we can specify the temperature, pressure, and one of the compositions. As a result it is possible to solve equations (1-9) through (1-13) for the remaining five compositions. For this purpose the activity coefficients in equations (1-9) through (1-11) are expressed with the NRTL, LEMF, and UNIQUAC equations, using the binary parameters obtained from the corresponding binary data.

The LLE predictions were realized using the nonlinear regression subroutine LSQ2 (Gardner, 1967) by minimizing the function:

$$E = \sum_{i=1}^{3} \left| \frac{(X_i \gamma_i)^I - (X_i \gamma_i)^{II}}{X_i^I - X_i^{II}} \right| \tag{1-15}$$

Equation (1-15) contains the term $(X_i^I - X_i^{II})$ to avoid convergence to the trivial solution $X_i^I = X_i^{II}$. The computer program TLLE given in Appendix C was used to perform these calculations.

Evaluation of the binary parameters was carried out using the following minimization functions. For the two miscible binaries, equation (1-16) was used:

$$H = \left\{ \frac{\sum_{i=1}^{M} \left\{ \left[\frac{\gamma_1^{exp} - \gamma_1^{cal}}{\gamma_1^{exp}} \right]_i^2 + \left[\frac{\gamma_2^{exp} - \gamma_2^{cal}}{\gamma_2^{exp}} \right]_i^2 \right\}}{2M - 1} \right\}^{1/2} \qquad (1\text{-}16)$$

where M is the number of data points. The experimental activity coefficients were calculated by the method outlined by Prausnitz et al. (1967), but the second Virial coefficients were calculated by the correlation of Tsonopoulos (1974). The computer program that performs these calculations can be found in the Master Thesis of Ordaz (1981). The binary parameters in the NRTL and LEMF equations were determined with the computer program found in the Master Thesis of Ordaz. For the UNIQUAC equation the binary parameters were obtained with the program REGRESS-UNIQUAC given in Appendix C. The binary parameters for the PMBS were determined from the mutual solubility data by minimizing equation (1-17).

$$S = \left\{ \frac{\left[(X_1 \gamma_1)^{I} - (X_1 \gamma_1)^{II} \right]^2 + \left[(X_2 \gamma_2)^{I} - (X_2 \gamma_2)^{II} \right]^2}{2} \right\}^{1/2}$$

..... (1-17)

For the NRTL and LEMF equations these parameters were evaluated with the program found in the PhD Thesis of Marina (1973). For the UNIQUAC equation the parameters were determined with the computer program OTILIA-UNIQUAC given in Appendix C. The binary systems under investigation are given in Table IV.

The quality of the binary VLE data was checked with the "area test", in terms of the consistency index (C.I.) defined by equation (1-18).

$$C.I. = \left| \frac{|A_p| - |A_n|}{|A_p| + |A_n|} \right| \qquad (1\text{-}18)$$

where A_p and A_n are the positive and negative areas, respectively, when a plot of $\ln(\gamma_1/\gamma_2)$ versus X_1 is made. Table V gives the consistency index for each of the binary systems used in the investigation. Notice that for the binary system acetone-TCE at 755 mm Hg and acetone-n-propyl acetate at 760 mm Hg, the consistency index is very high. These set of data were used nevertheless since no other data at these conditions could be found.

Here a set of binary VLE data has been arbitrarily assumed to be

thermodynamically consistent if:

For isothermal data C.I. ≤ 0.04

For isobaric data C.I. ≤ 0.06

The reason for the above choice is now discussed. For isothermal data the Gibbs-Duhem equation takes the form of:

$$\int_0^1 \ln(\gamma_1/\gamma_2)dX_1 = -\int_{X_1=0}^{X_1=1} \frac{v^e}{RT} dP \qquad (1\text{-}19)$$

Since at low pressures, well removed from the critical point, the right-hand side of equation (1-19) is close to zero, one would expect then that $|A_p| = |A_n|$. However, since there are experimental uncertainties inherent in the data, one must arbitrarily choose some criterion by which to judge the quality of the data. Prausnitz (1969) recommends that if C.I. ≤ 0.02, then it is very likely that the data is good. In addition, he states that for some systems the value of 0.02 is probably too small. For this reason the value of 0.04 has been chosen here.

For isobaric data the Gibbs-Duhem equation takes the form of:

$$\int_0^1 \ln(\gamma_1/\gamma_2)dX_1 = \int_{X_1=0}^{X_1=1} \frac{h^e}{RT^2} dT \qquad (1\text{-}20)$$

In general, one cannot assume that the right-hand side of equation (1-20) is zero. Thus $|A_p|$ is not equal to $|A_n|$. As a result one is forced to make an arbitrary choice by which to evaluate the quality of a given set of data. For this reason, any set of data where C.I. ≤ 0.06 is assumed to be thermodynamically consistent. For isobaric data the limit of the consistency index is greater than that for isothermal data due to the fact that, in general, the absolute value of the right-hand side of equation (1-20) is greater than the absolute value of the right-hand side of equation (1-19). Notice, however, that the "area test" is a necessary but not sufficient condition by which to evaluate the quality of a given set of binary VLE data. To check the quality of a set of binary isobaric VLE data we could also have used the test of Herington (Herington, 1951). But since Herington's test is empirical and was tested only with mixtures of typical organic liquids, it is probably not applicable to mixtures which are very different than those included in his work. As a result we felt that for our investigation the use of this test was not justified.

The quality of the ternary LLE data was checked with the test of Hand (Hand, 1930), and by the smoothness of a plot of K_3 versus X_2^I. The test of Hand is based on equation (1-21).

$$\log_{10}(X_3^{II}/X_2^{II}) = k_H \log_{10}(X_3^I/X_1^I) + c_H \qquad (1\text{-}21)$$

where k_H and c_H are constants. Therefore the above equation indicates that when a plot of $\log_{10}(X_3^{II}/X_2^{II})$ versus $\log_{10}(X_3^I/X_1^I)$ is made, one

should get a straight line. Figures 2 through 11 show the results of the Hand test for the ten systems. For all the systems it was not necessary to eliminate any LLE data points since in every case the points seem to lie near a straight line.

4. Results and Discussion

The binary parameters for the three models as determined from the binary data are given in Tables VI through VIII. As previously mentioned, prediction of ternary LLE starts with the specification of the concentration of one of the components in one of the phases. Table IX indicates that the specification of the concentration of different components and phases leads to results of different accuracy. It appears that best results are obtained by specifying the composition of the component with the smallest mutual solubility in the phase where it occurs (X_2^I), and it was used here. This should be expected since, usually, the lower the concentration of component i, the larger the error in the predicted K_i. In addition, Table IX indicates that specification of component 3 may lead to extremely poor results. The predicted results for the ten systems with the three models are presented in Table X. It is evident that type IC systems are predicted very poorly, which is in agreement with the observation of Renon and Prausnitz (1968) with the NRTL equation, but not with that of Joy and Kyle (1969) with the NRTL equation, or Anderson and Prausnitz (1978) with the UNIQUAC equation. Reasonably good predictions are obtained for type IA and IB systems with all three models. The LEMF equation, however, gives somewhat better results with an overall average absolute

percentage error in distribution coefficients (Q), for the four type IA systems and three type IB systems, of 14.8 as compared to 17.9 and 19.0 with the NRTL and UNIQUAC equations, respectively. Figures 12 through 21 present the predicted results for the ten systems with the three models. For systems in which the Hand test gave scattering of the LLE data, poor predictions were obtained as compared to systems in which the Hand test showed no scattering of the data. For example, the Hand test for systems 3, 4, and 8, all of which are of the type IB, show that the quality of the LLE data for system 3 is better than that for systems 4 and 8, and the quality of the data for system 4 is better than that for system 8, and note that the values of Q with the LEMF equation for systems 3, 4, and 8 are 9.1, 27.7, and 32.1, respectively. The same conclusion could have been made if the results from the NRTL or UNIQUAC equations had been used.

The work of Soerensen et al.(1979) investigates the predicting performance of the NRTL and UNIQUAC equations only. The LEMF equation was not included in their work. In addition, these authors report the results for seven systems with the UNIQUAC equation, and five systems with the NRTL equation. Since they obtained results for only a small number of systems, no conclusion is made with regard to the performance of the two models. In this work three models are investigated with ten ternary systems. Therefore we provide the process engineer more information than Soerensen et al..

As previously mentioned, our results show that best LLE predictions are obtained with the LEMF equation. However, as noted by Soerensen et

al., it is possible that by choosing a different set of ten systems the NRTL or UNIQUAC equation may perform better than the LEMF equation.

A comparison of the plots of experimental K_3 versus X_2^I (Figures 12 through 21) for the ten systems show that only for systems 1 and 8 the curve exhibits a maximum. For the other eight systems a smooth curve is obtained. It is important to note that for these two systems all three equations did not predict the maximum (see Figures 12 and 19).

When the parameters obtained from the binary data were used to predict the binodal curves for the ten systems with each model, it was observed that the NRTL equation gave good prediction for system 5, reasonable predictions for systems 1, 3, 4, 6, 7, 8, 9, and 10, and poor prediction for system 2. The LEMF equation gave good predictions for systems 2, 3, 6, 7, and 10, and reasonable predictions for systems 1, 4, 5, 8, and 9. The UNIQUAC equation gave good predictions for systems 6 and 8, and reasonable predictions for the remaining systems. In most cases the predicted binodal curves deviated mostly from the experimental curves near the plait point region.

5. Conclusions

In conclusion, it appears that reasonably good predictions for type IA and IB systems can be achieved with all three models, with the LEMF equation yielding the better results. For type IC systems, however, the results are, in general, poor. Specification of X_2^I, the concentration of the least soluble component in the phase where it occurs, gives the best predictions. The quality of the results seem to improve

as we move from type IC to IB and then to IA systems. None of the three models can predict a maximum in a plot of K_3 versus X_2^I.

CHAPTER II

CORRELATION OF LIQUID-LIQUID EQUILIBRIA

1. Introduction

Several investigators have used the NRTL, LEMF, and UNIQUAC equations to correlate LLE data alone, or correlate binary VLE and ternary LLE data simultaneously (Joy and Kyle, 1970; Cohen and Renon, 1970; Bender and Block, 1975; DeFre and Verhoeye, 1976; Newsham and Vahdat, 1977; Anderson and Prausnitz, 1978; and Soerensen et al., 1979). Their results indicate that all three models may be used for this purpose. However, the work of Soerensen et al. (1979) indicates that best LLE correlation is obtained with the UNIQUAC equation rather than with the NRTL or LEMF equations. However, they acknowledge that it is possible to obtain best correlation with the NRTL or the LEMF equation if a different set of systems is used in the investigation. In addition, several procedures have been proposed for correlating the LLE data. For example, Cohen and Renon (1970) used tie-line data and binary VLE data to determine three parameters per binary with the NRTL equation. Bender and Block (1975) used binary VLE data, mutual solubility data, and K_3^{∞} (the distribution coefficient of the solute at infinite dilution) to correlate LLE data with the NRTL equation. DeFre and Verhoeye (1976) used tie-line data alone to obtain two parameters per binary with the NRTL equation. Finally, Anderson and Prausnitz (1978) used binary VLE data together with ternary LLE data to determine the six binary parameters

in the UNIQUAC equation using the maximum likelihood principle. Therefore, the second objective of this thesis is to evaluate the performance of the three models and five methods for correlating LLE data for type IA, IB, and IC systems.

2. Procedure

In this work, five methods for correlating LLE or LLE plus binary VLE data with all three models are investigated. Methods I, II, and V use LLE and binary VLE data, while Methods III and IV use LLE data only.

Method I: In this method the binary parameters for the PMBS (1-2 binary) are determined from the mutual solubility data. The binary parameters for the 1-3 and 2-3 binaries are determined by simultaneously fitting the binary VLE data of the two miscible binaries with K_3^{∞}. A somewhat similar method was used by Bender and Block (1975). The value of K_3^{∞} was obtained by extrapolating to $X_3 = 0$ a plot of K_3 versus X_3^I and X_3^{II}. If the number of tie-lines for a given system is small, the extrapolation is generally poor and thus producing a large uncertainty in the value of K_3^{∞}. This uncertainty is then reflected on the parameters for the 1-3 and 2-3 binaries.

Method II: Same as Method I but the actual tie-line data is used in place of K_3^{∞}.

Method III: Same as Method II but no binary VLE data is used.

Method IV: Here all six binary parameters are determined by regressing the tie-line data, not including the mutual solubility data. This method, used by DeFre and Verhoeye (1976), is important because in the typical case the binary VLE data may not be available. DeFre and Verhoeye used the NRTL equation to regress the LLE data for six and nine parameters and found that the results for six and nine parameters were about the same. For this reason we decided to regress for six parameters only.

Method V: Binary VLE data and ternary LLE data are regressed simultaneously to determine six binary parameters. This method was used by Anderson and Prausnitz (1978).

A summary of the five methods is given in Table XI.

Binary parameters were determined by regression with LSQ2 (Gardner, 1967) using the following minimization function:

$$F = \frac{\sum_{i=1}^{M}\left\{\left[\frac{\gamma_1^{exp}-\gamma_1^{cal}}{\gamma_1^{exp}}\right]_i^2 + \left[\frac{\gamma_3^{exp}-\gamma_3^{cal}}{\gamma_3^{exp}}\right]_i^2\right\}}{M} + \frac{\sum_{i=1}^{L}\left\{\left[\frac{\gamma_2^{exp}-\gamma_2^{cal}}{\gamma_2^{exp}}\right]_i^2 + \left[\frac{\gamma_3^{exp}-\gamma_3^{cal}}{\gamma_3^{exp}}\right]_i^2\right\}}{L} +$$

$$\frac{\sum_{i=1}^{N}\left\{\left[\frac{K_1^{exp}-K_1^{cal}}{K_1^{exp}}\right]_i^2+\left[\frac{K_2^{exp}-K_2^{cal}}{K_2^{exp}}\right]_i^2+\left[\frac{K_3^{exp}-K_3^{cal}}{K_3^{exp}}\right]_i^2\right\}}{N} \quad \ldots\ldots\ldots\ldots (2\text{-}1)$$

where

M, L = number of VLE data points for the 1-3 and 2-3 binary systems, respectively

N = number of ternary tie-lines

Equation (2-1) minimizes the relative errors in distribution coefficients. Other authors minimize absolute errors in mole fractions. Since in extraction calculations one is interested in the distribution coefficients, we feel that our minimization function is more appropriate. The work of Joy and Kyle (1970) also supports the use of equation (2-1). They observed that whenever the solvent selectivity (the selectivity is the ratio of two distribution coefficients) was accurately reproduced, the binodal curve was also accurately calculated, but the inverse was never observed.

The computer program TREG given in Appendix C was used to perform the data correlation. Note that for Methods III and IV the first and second terms in equation (2-1) are not present, and that in Method I the last term is replaced by K_3^{∞}. Once the binary parameters were cal-

culated, the binodal curve was generated using the procedure outlined in Chapter I, and Q values were calculated using equations (1-4) and (1-5). Errors in binary activity coefficients (G) are defined by:

$$G = (\bar{G}_1 + \bar{G}_2)/2 \qquad (2\text{-}2)$$

where

$$\bar{G}_1 = \frac{\sum_{i=1}^{M} \left\{ \left| \frac{\gamma_1^{exp} - \gamma_1^{cal}}{\gamma_1^{exp}} \right|_i + \left| \frac{\gamma_3^{exp} - \gamma_3^{cal}}{\gamma_3^{exp}} \right|_i \right\}}{2M} \times 100 \qquad \ldots\ldots\ldots\ldots \qquad (2\text{-}3)$$

and

$$\bar{G}_2 = \frac{\sum_{i=1}^{L} \left\{ \left| \frac{\gamma_2^{exp} - \gamma_2^{cal}}{\gamma_2^{exp}} \right|_i + \left| \frac{\gamma_3^{exp} - \gamma_3^{cal}}{\gamma_3^{exp}} \right|_i \right\}}{2L} \times 100 \qquad \ldots\ldots\ldots\ldots \qquad (2\text{-}4)$$

3. Results and Discussion

The binary parameters for the three models with the five methods are given in Tables XII through XXVI. Notice that for all three models the binary parameters for the 1-2 binary system with Methods III and IV are, in general, the same. This shows that the binary parameters for the 1-2 binary calculated from the mutual solubility data alone are essentially the same as those calculated from all the ternary LLE data. Results for the performance of each model with each method are presented in Tables XXVII through XXXI, in terms of the average absolute percentage error in distribution coefficients (Q) and binary activity coefficients (G). Figures 22 through 32 present plots of K_3 versus X_2^I for the ten systems with Method IV for each model. The following observations can be made about the five methods and each model.

Method I (Table XXVII) gives, in general, unreliable results probably because of the uncertainty in determining K_3^∞, even though the combined values of Q and G for the ten systems are: NRTL, 13.8; LEMF, 14.7; and UNIQUAC, 14.2.

Method IV (Table XXX) appears to provide the best correlation of the LLE data. The values of Q for the NRTL, LEMF, and UNIQUAC equations are: 6.7, 5.5, and 5.9, respectively, suggesting a slightly better performance by the LEMF equation. And as in the case of prediction, improved performance is realized for all models as we move from type IC to IB and then to IA systems. This method is much simpler than the method used by Bender and Block (1975) since they also adjusted the value of α_{12} to fit the LLE data. A comparison, however, of the results for the system water-TCE-acetone at 25 C, Figure 27, with those presented

by Bender and Block for the same system, indicates that Method IV, while much simpler, yields results that are at least of equal quality.

The results obtained here show that best LLE correlation is obtained with the LEMF equation, while the work of Soerensen et al. (1979) indicates that best LLE correlation is obtained with the UNIQUAC equation. Two reasons may be responsible for the above difference. First, as mentioned by the above authors, the conclusion one makes with regard to the performance of a given activity coefficient equation depends on the particular set of systems investigated. Second, these authors used a different minimization function than the one used here. They minimized absolute errors in mole fraction, while here we minimized relative errors in distribution coefficients.

The results for Q with Method III (Table XXIX) are: NRTL, 10.6; LEMF, 13.1; and UNIQUAC, 10.5. The results are, as expected, inferior to those obtained by regressing for six parameters. Notice that whenever the Hand test (Hand, 1930) showed little scattering of the LLE data, better correlation of the LLE data with Methods III and IV was obtained when compared to systems in which the Hand test showed considerable scattering of the LLE data. For example, the Hand test for systems 3, 4, and 8, all of which are of the type IB, indicates that the quality of the LLE data for system 3 is better than that for systems 4 and 8, and the quality of the data for system 4 is better than that for system 8, and note that the values of Q with the UNIQUAC equation, with Method IV, for systems 3, 4, and 8 are: 2.2, 9.4, and 12.2, respectively. A similar conclusion could have been made if the NRTL equation had been used, but not with the LEMF equation. We do not know why the LEMF equation does not follow this trend. If Method III and any of the three

models had been used to make this comparison, the same conclusion could be made.

Method V (Table XXXI) provides a much better correlation of the LLE and binary VLE data than Method I and Method II (Table XXVIII). On the basis of the combined values of Q and G with Method V for the ten systems of 8.8, 6.5, and 8.2, for the NRTL, LEMF, and UNIQUAC equations, respectively, it is evident that all three models perform well, with an advantage for the LEMF equation. Finally, the quality of the results in fitting the tie-line and binary VLE data suggests that these parameters may be used in the prediction of multicomponent VLE, which is important in three-phase distillation. Notice, however, that the quality of fitting the tie-line data is not as good as that of Method IV. Use of four parameters (Method II), again, gave inferior results with combined values of Q and G of 11.9, 9.1, and 10.9 with the NRTL, LEMF, and UNIQUAC equations, respectively. Notice that Figures 22 and 30 show that all three models can reproduce the K_3 versus X_2^I data for systems exhibiting a maximum.

In the regression subroutine that determines the binary parameters by minimizing equation (2-1), it is necessary to provide a starting value for each parameter. For the PMBS the starting value used is the set of parameters obtained from the mutual solubility data. For Methods I, II, and V the starting value used is the set of parameters obtained by fitting the corresponding binary data. However, in Methods III and IV it was assumed that the binary VLE data is not available. Our preliminary results indicated that while 0.0 as starting value for the parameters led to a good fit of the K data, the same parameters gave, on occasions, poor prediction of binary activity coefficients for the 1-3

and 2-3 systems. In attempting to improve these predictions, starting values corresponding to $\gamma_i = 1.3$ at $X_i = 0.5$ were used since this is what one may expect for a typical binary system. This approach indeed led, in general, to better binary activity coefficients prediction, while not affecting the fit of the K data, and was used for Methods III and IV with the exception of systems 2 and 8. For these two systems, with Method IV, for the NRTL and LEMF equations, it was necessary to use a different starting value (Table XXX). And as in the case of prediction, X_2^I was specified with the exception of systems 2 and 9 (Tables XXVIII through XXXI).

The binary parameters obtained with Methods IV and V were used to calculate the binodal curves for all ten systems with each model. The binodal curves calculated with Method IV with all three models for the ten systems compared well with the experimental curves, including the plait point region. For Method V with the NRTL equation, good fit of the curves for systems 5, 6, 7, and 8 was obtained, and reasonable agreement for the remaining systems. The LEMF equation gave good fit of the curves for systems 2, 3, 5, 6, 7, 8, and 9, and reasonable agreement for the remaining systems. The UNIQUAC equation gave good fit of the curves for systems 4, 5, 6, 7, 8, and 10, and reasonable agreement for the remaining systems. As expected, the results from Method V are not as good as those from Method IV since in Method V the minimization function (equation 2-1) minimizes errors in distribution coefficients and binary activity coefficients simultaneously, and in Method IV only the former errors are minimized.

4. Conclusions

Best correlation of LLE data alone is obtained by regressing for the six binary parameters in the models (Method IV), with the LEMF yielding somewhat better results. Simultaneous correlation of ternary LLE and binary VLE data is best accomplished by regressing the data for six parameters (Method V), with the LEMF equation giving the best results. In all cases the quality of the results seems to improve as we move from type IC to IB and then to IA systems. All models can reproduce a maximum in a plot of K_3 versus X_2^I.

APPENDIX A

THE FIGURES

This appendix contains Figures 1 through 32.

Figure 1: The three categories of systems within the type I classification.

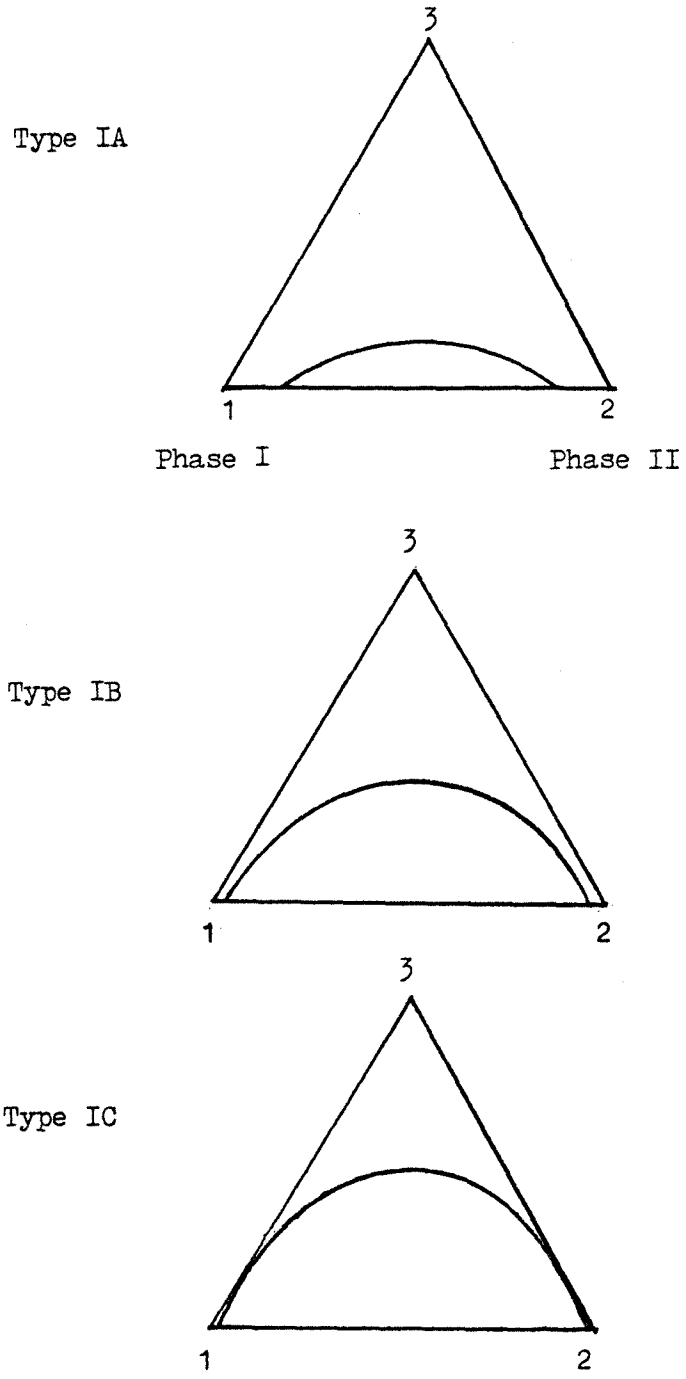


Figure 2: Hand's test for system 1.

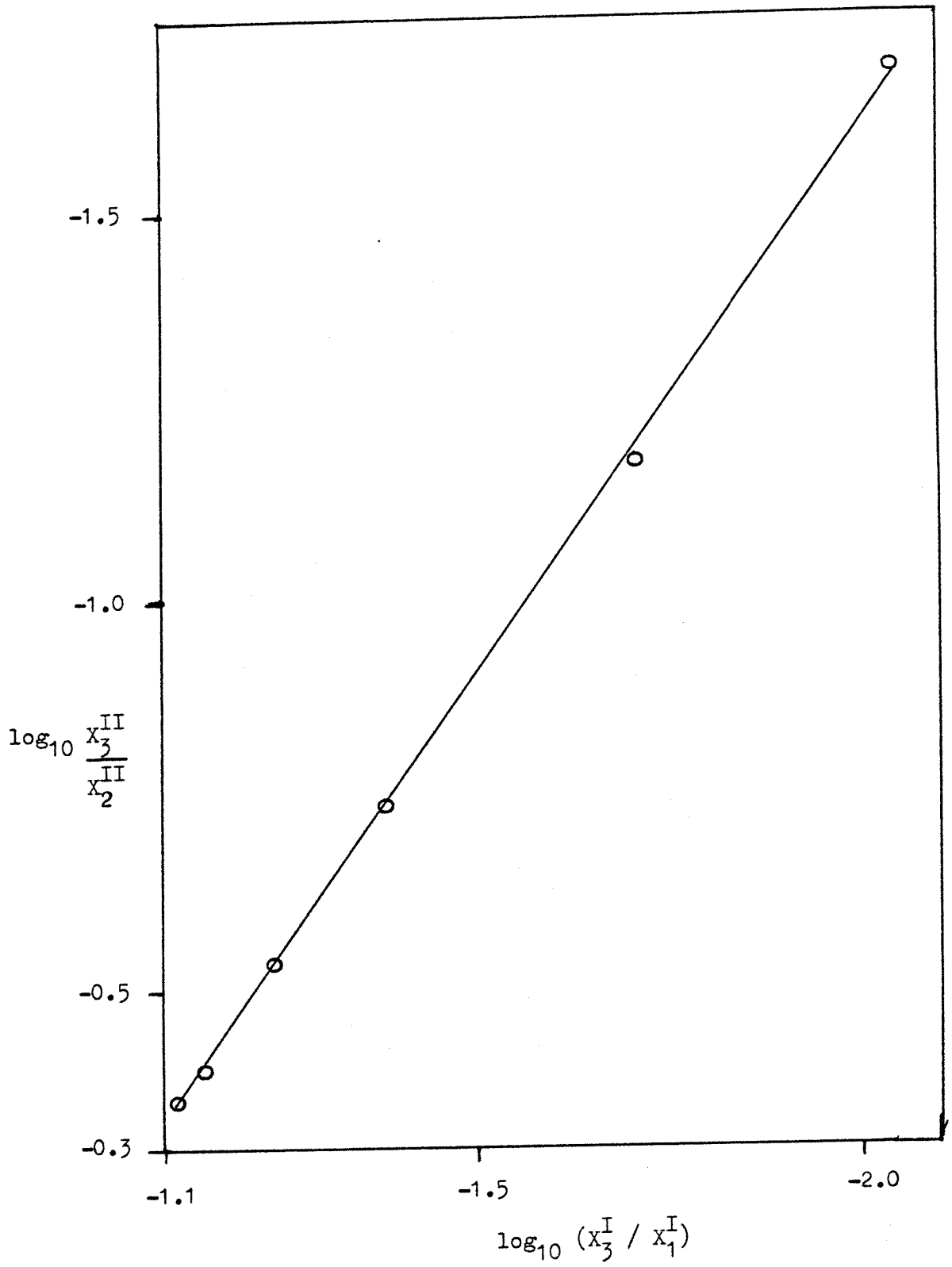


Figure 3: Hand's test for system 2.

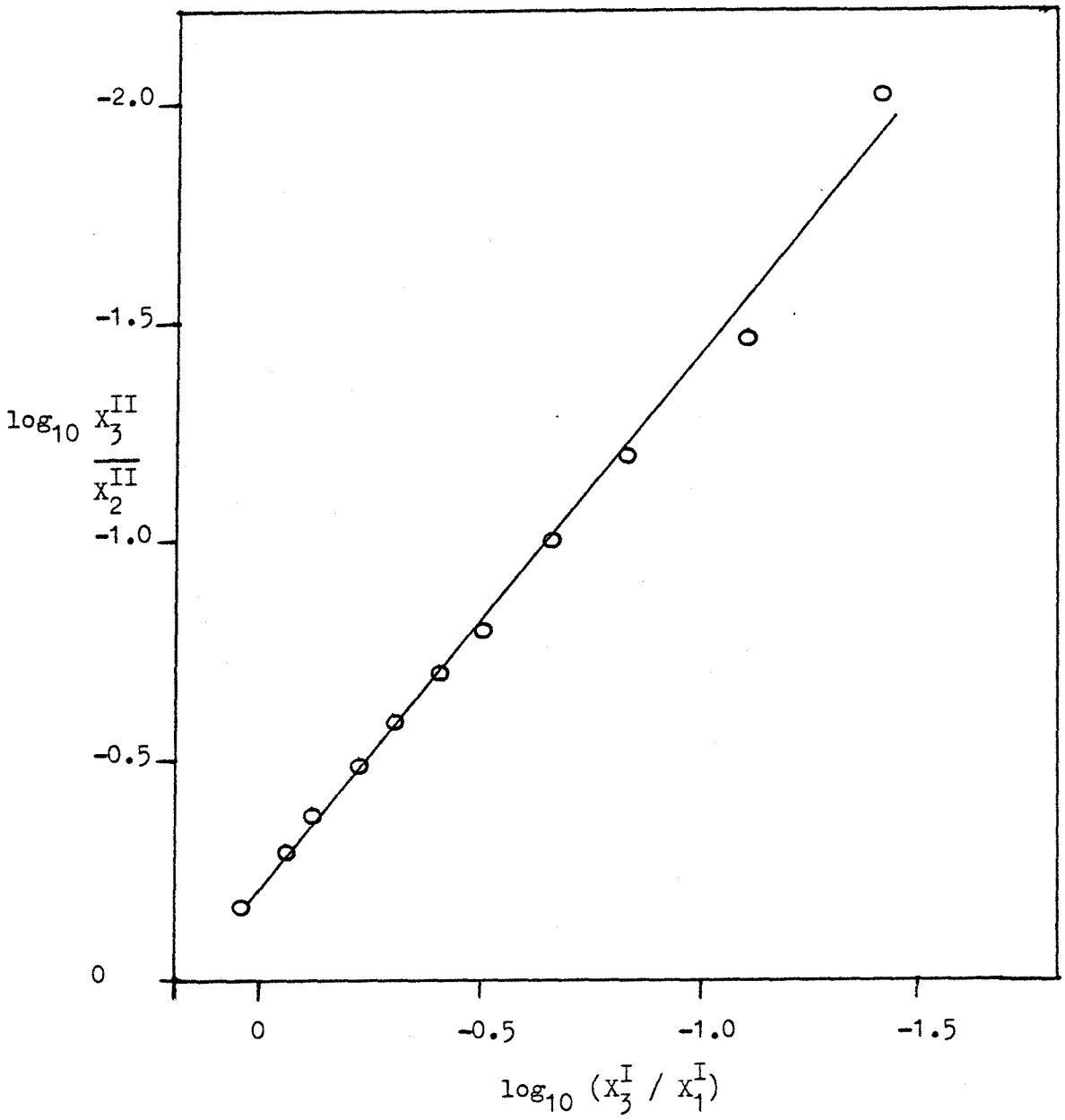


Figure 4: Hand's test for system 3.

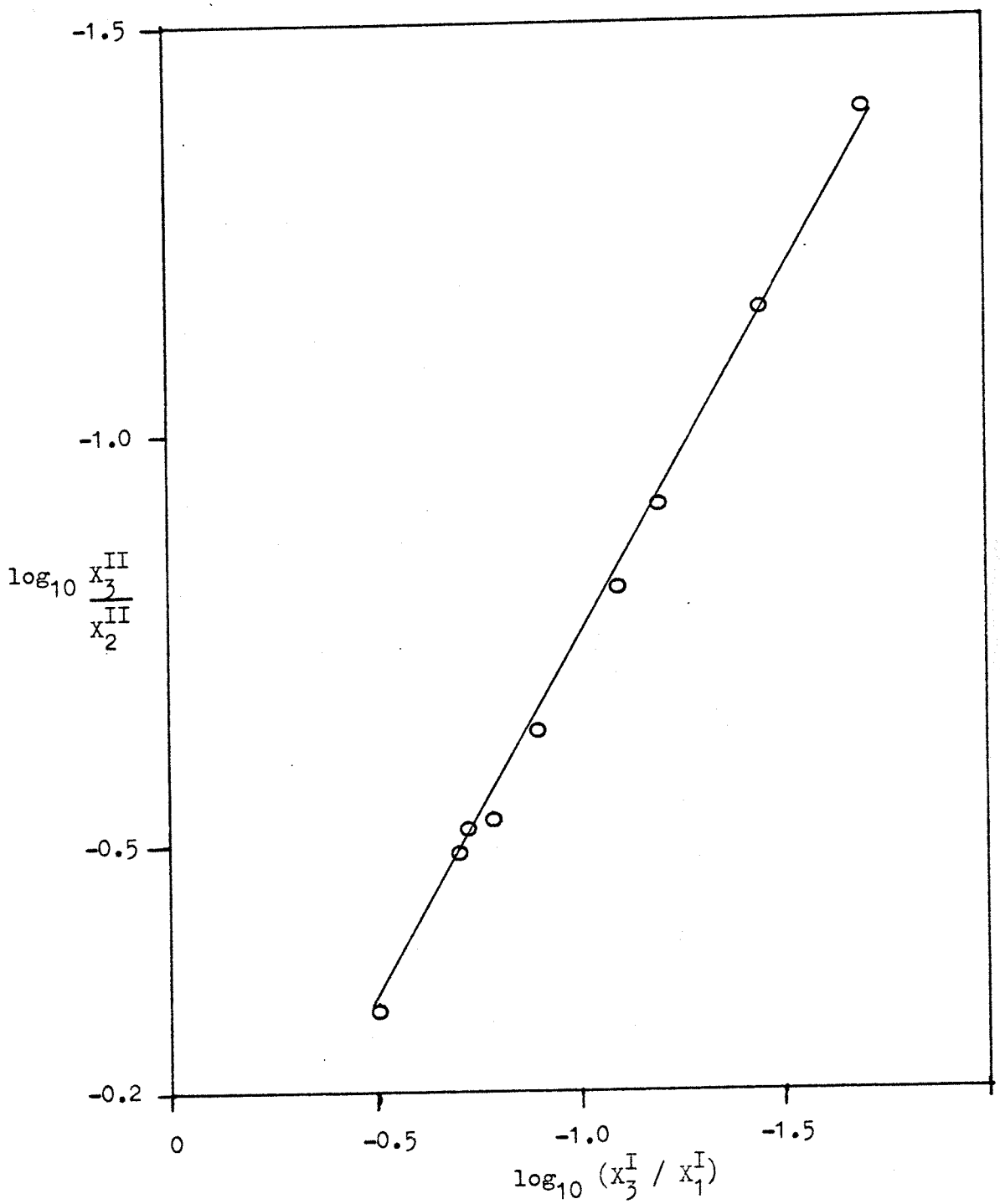


Figure 5: Hand's test for system 4.

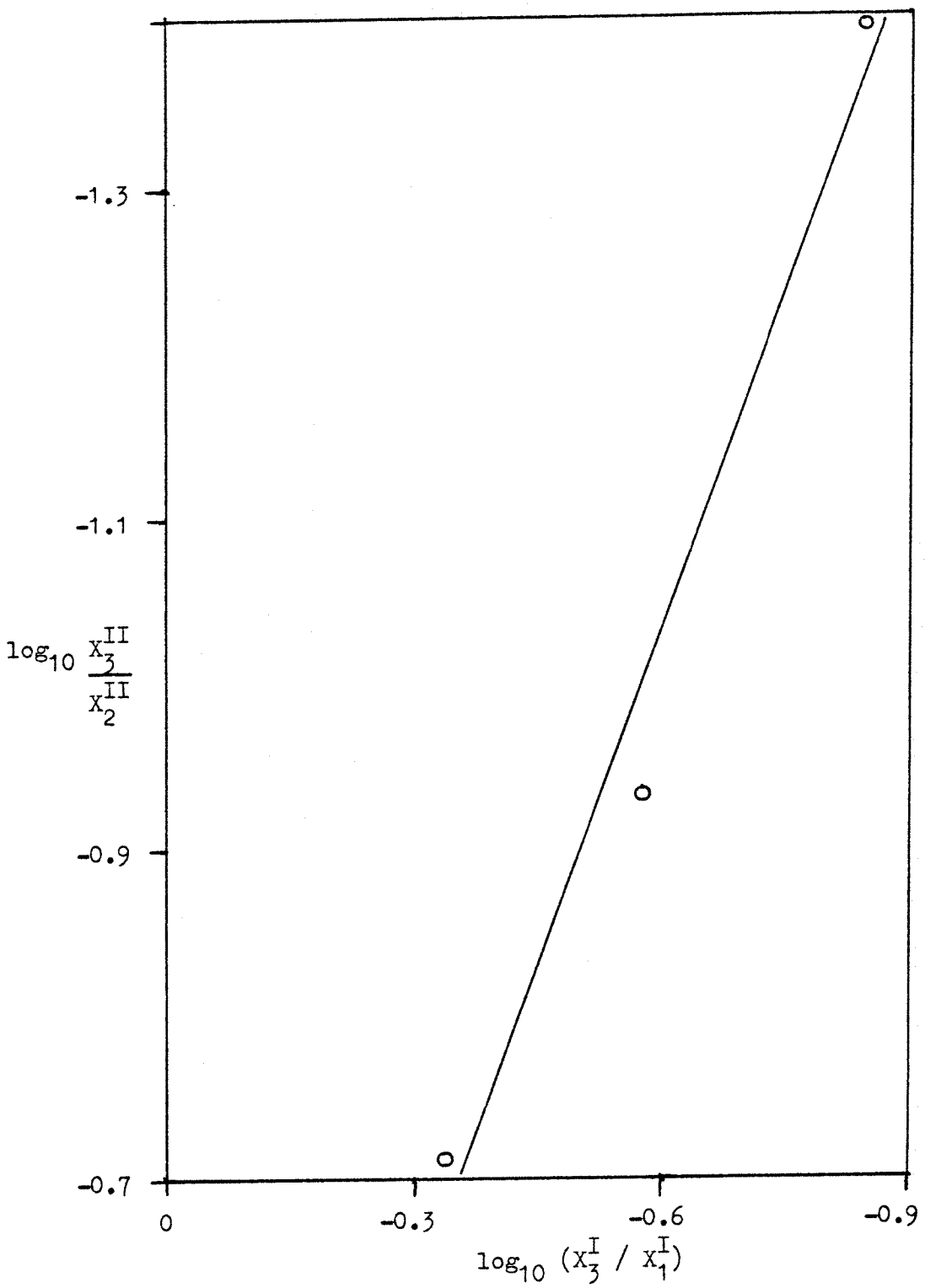


Figure 6: Hand's test for system 5.

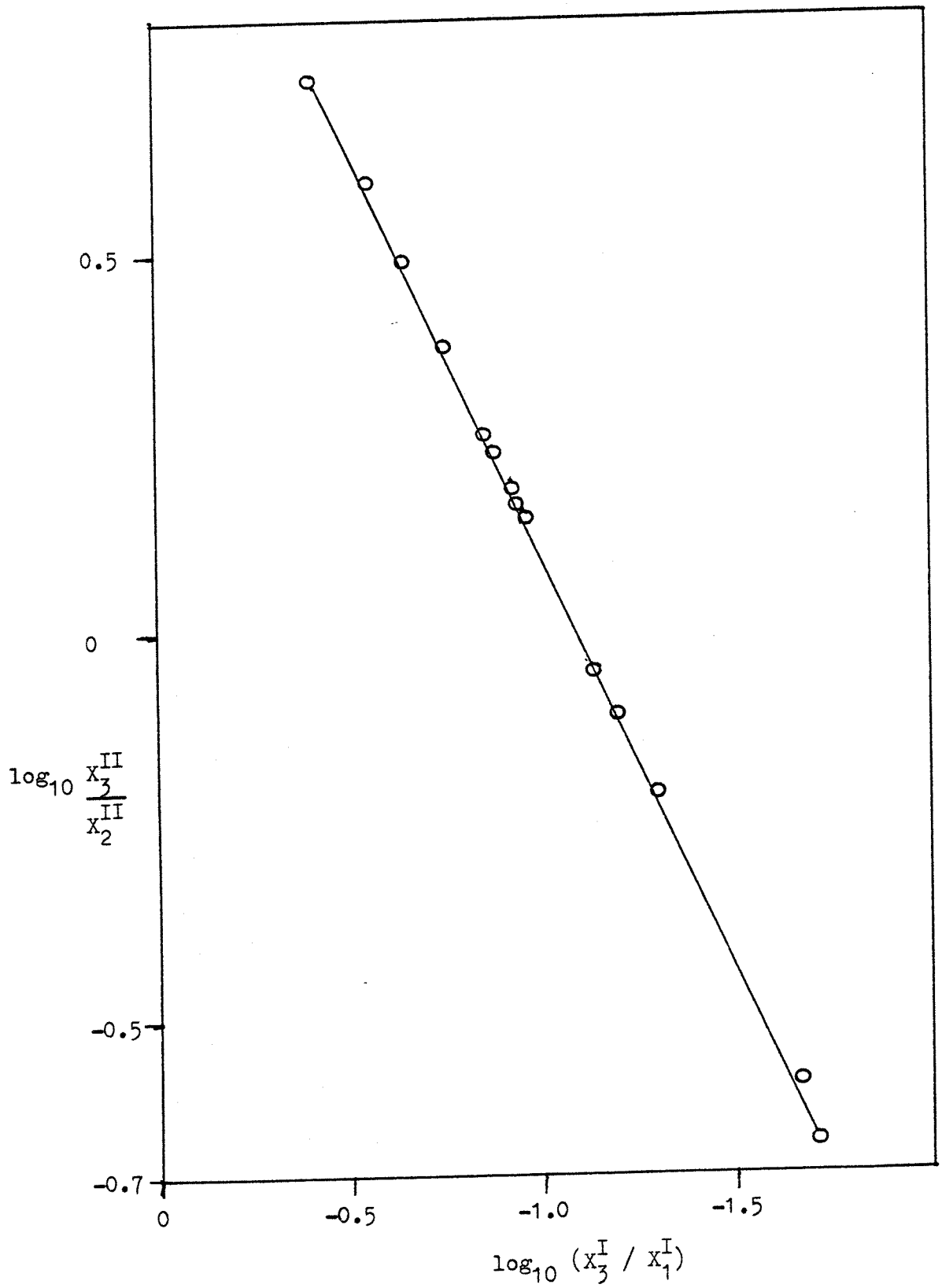


Figure 7: Hand's test for system 6.

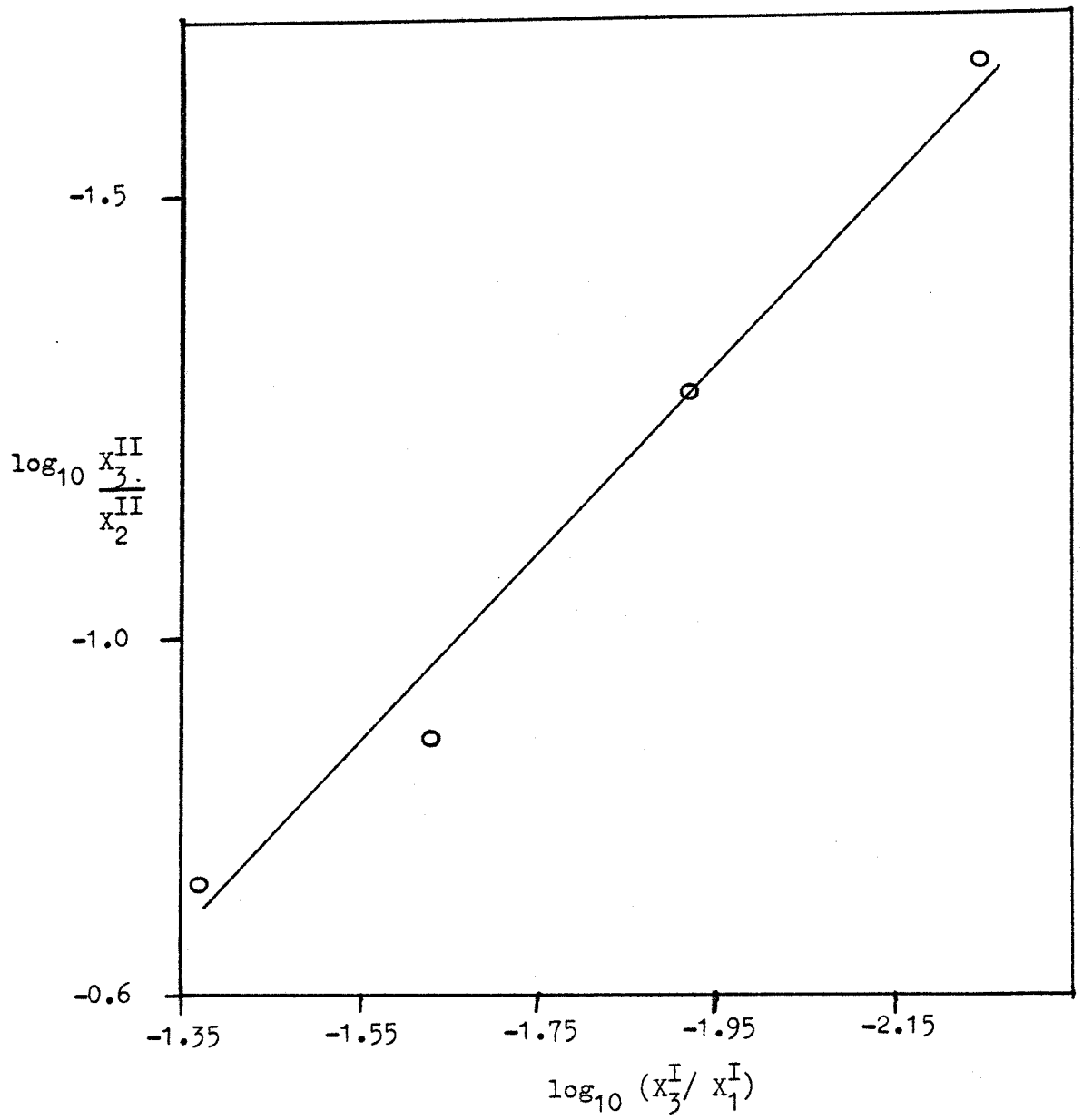


Figure 8: Hand's test for system 7.

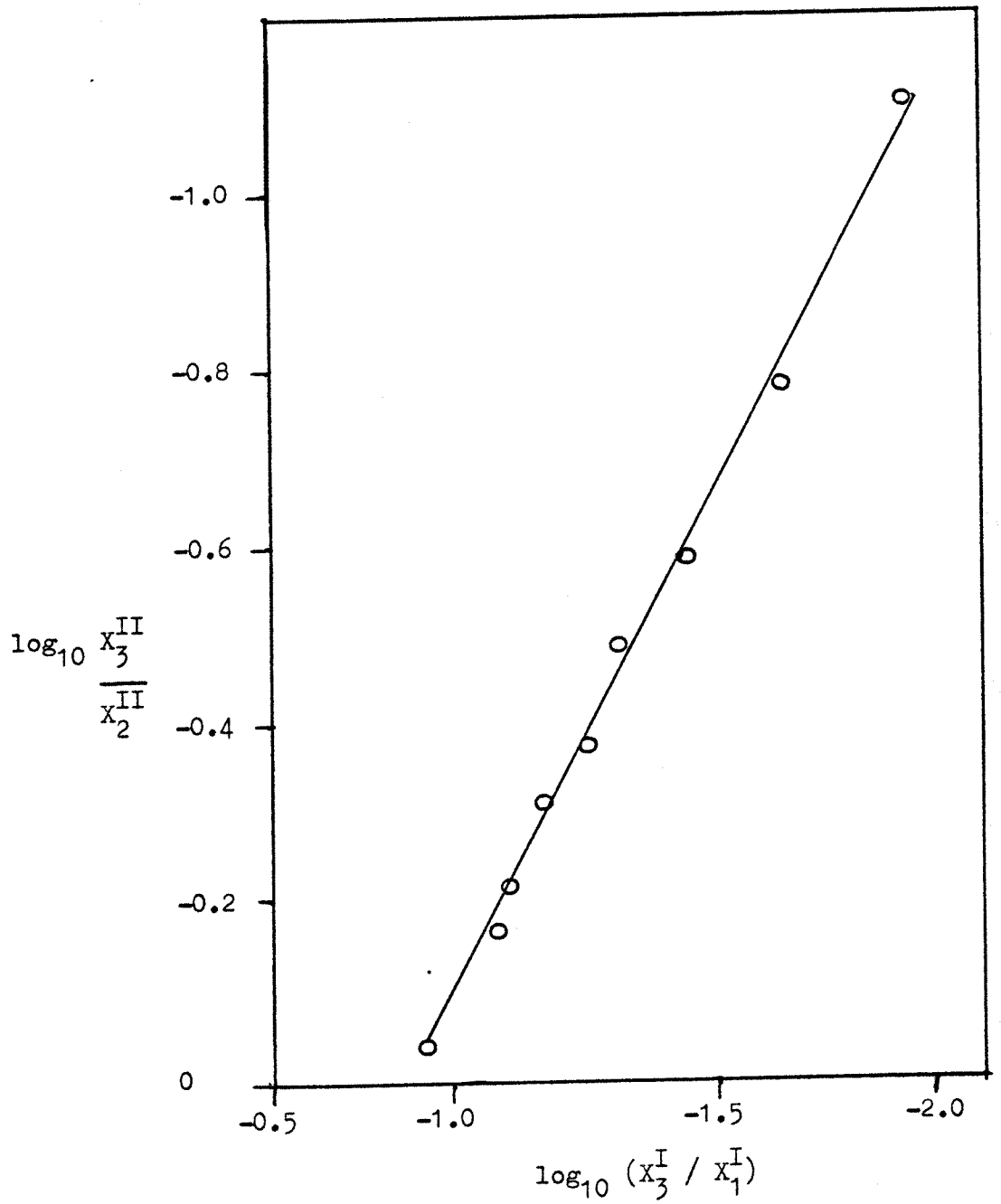


Figure 9: Hand's test for system 8.

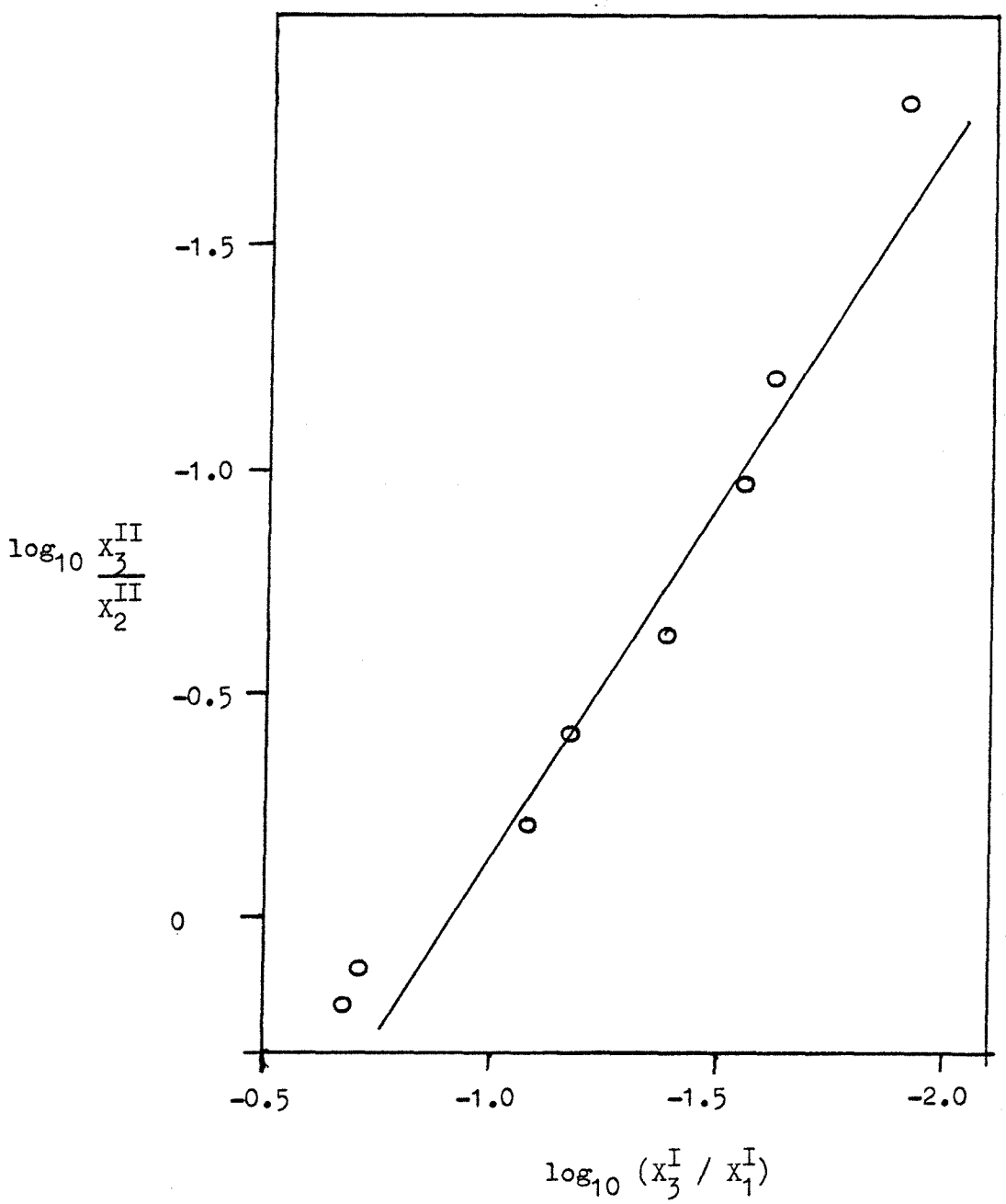


Figure 10: Hand's test for system 9.

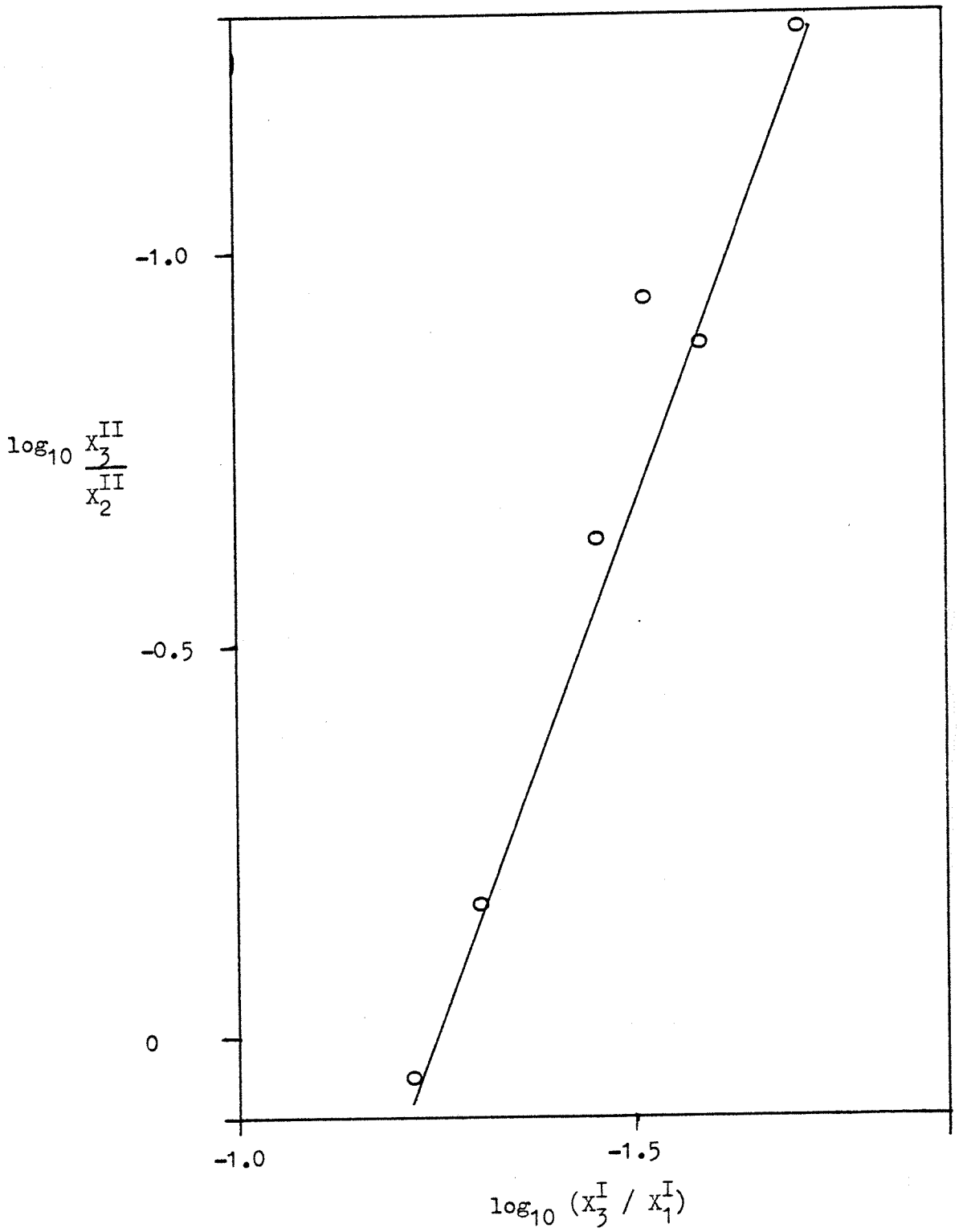


Figure 11: Hand's test for system 10.

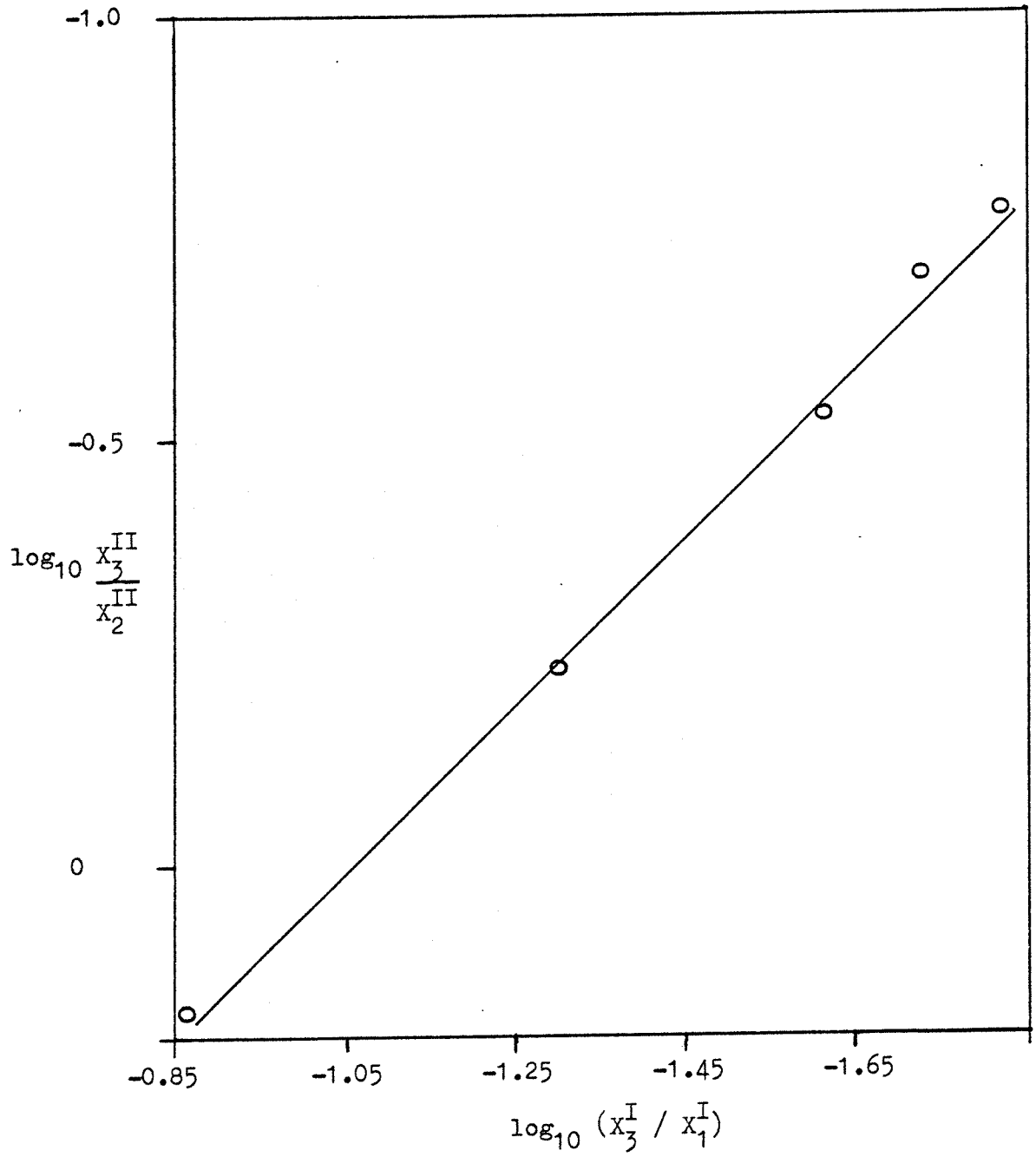


Figure 12: Plot of K_3 versus X_2^I for system 1 (prediction).

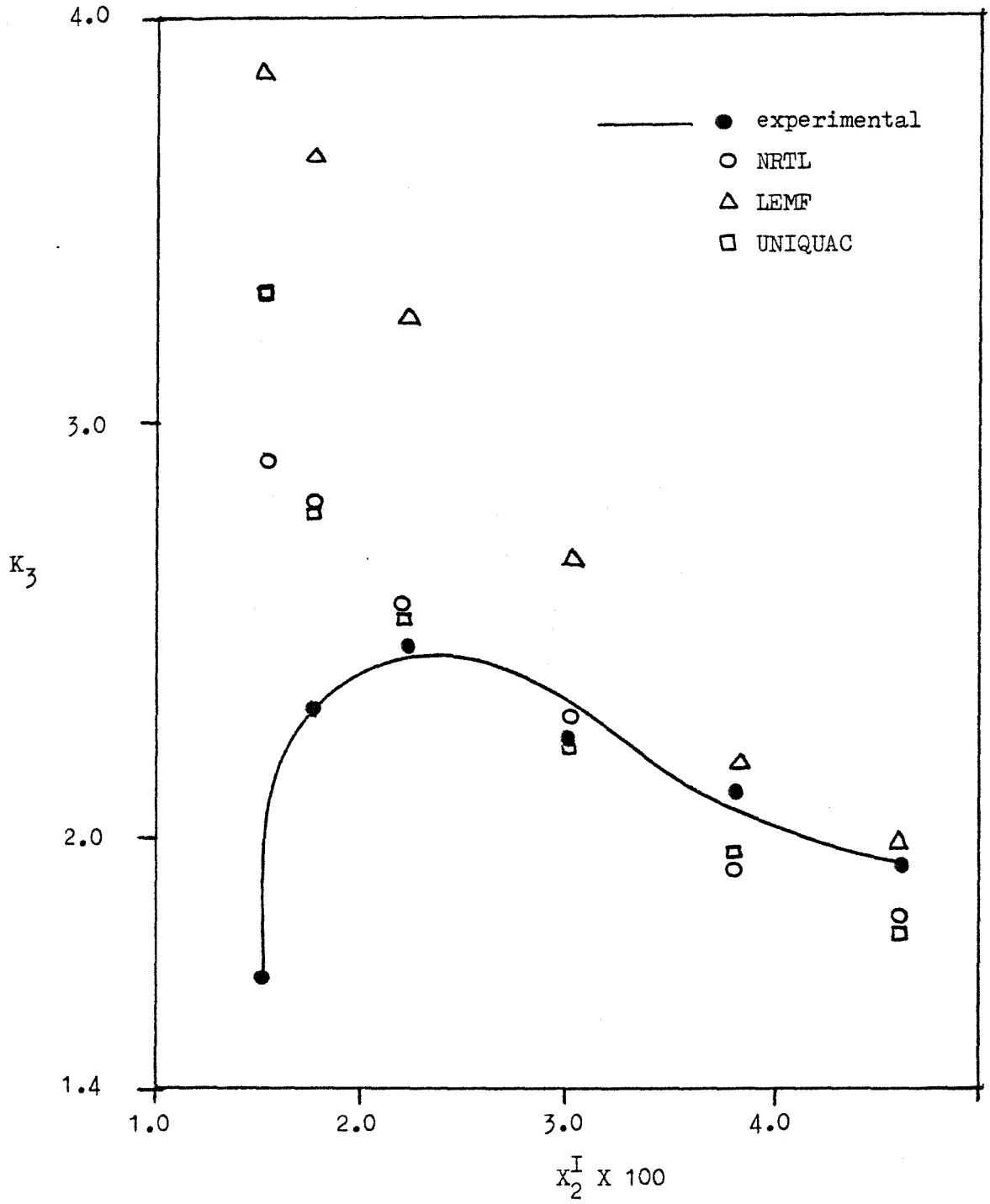


Figure 13: Plot of K_3 versus X_2^I for system 2 (prediction).

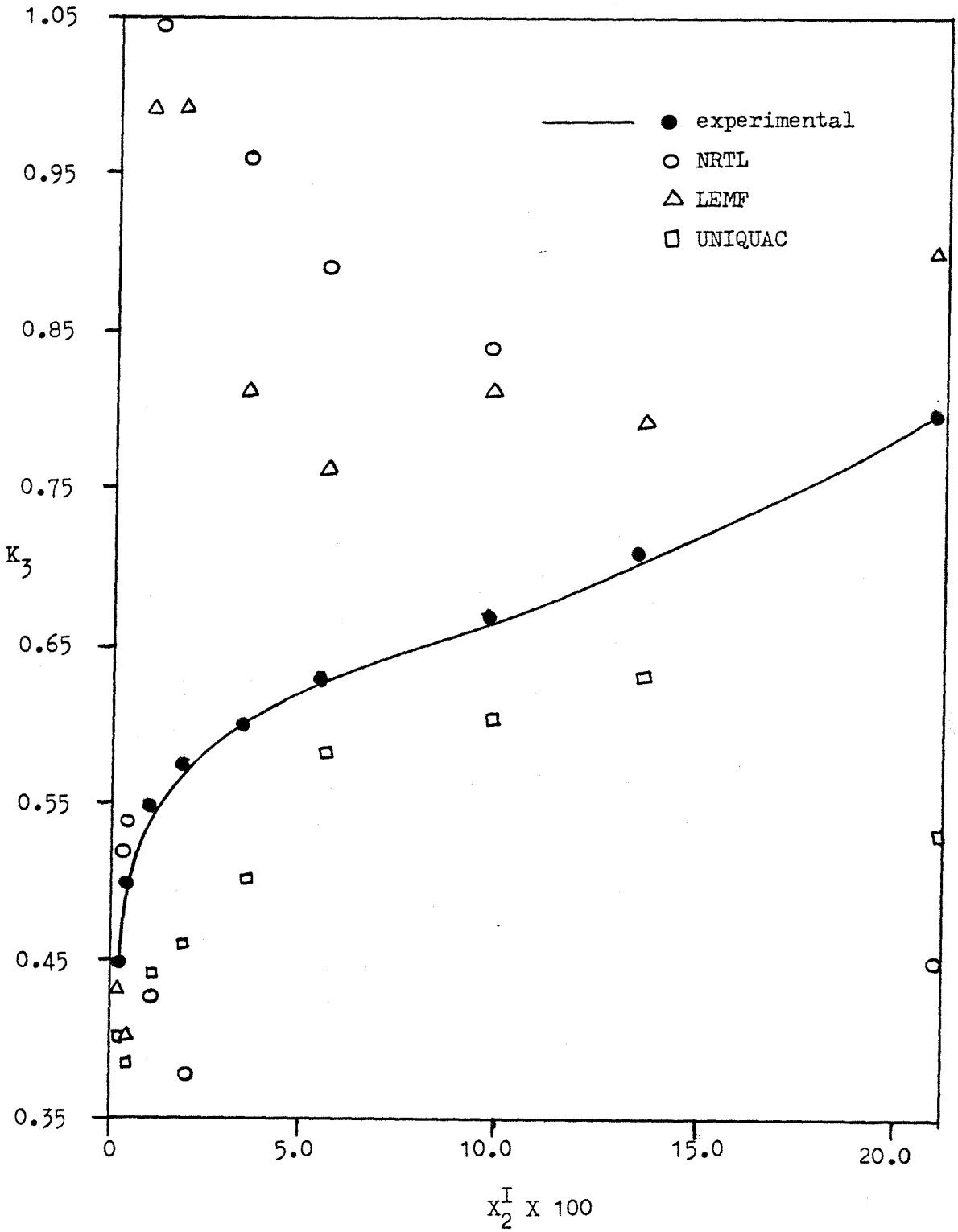


Figure 14: Plot of K_3 versus X_2^I for system 3 (prediction).

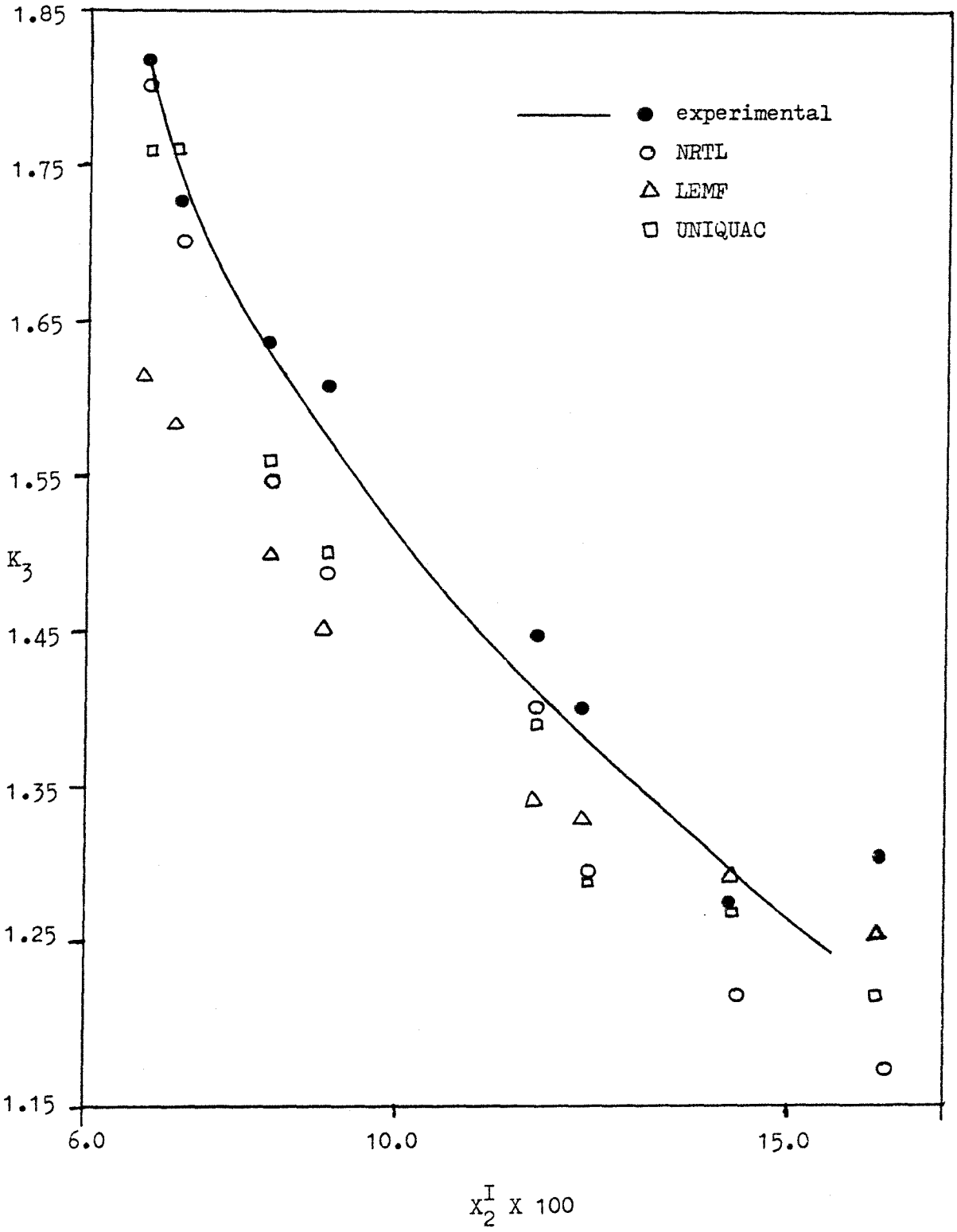


Figure 15: Plot of K_3 versus X_2^I for system 4 (prediction).

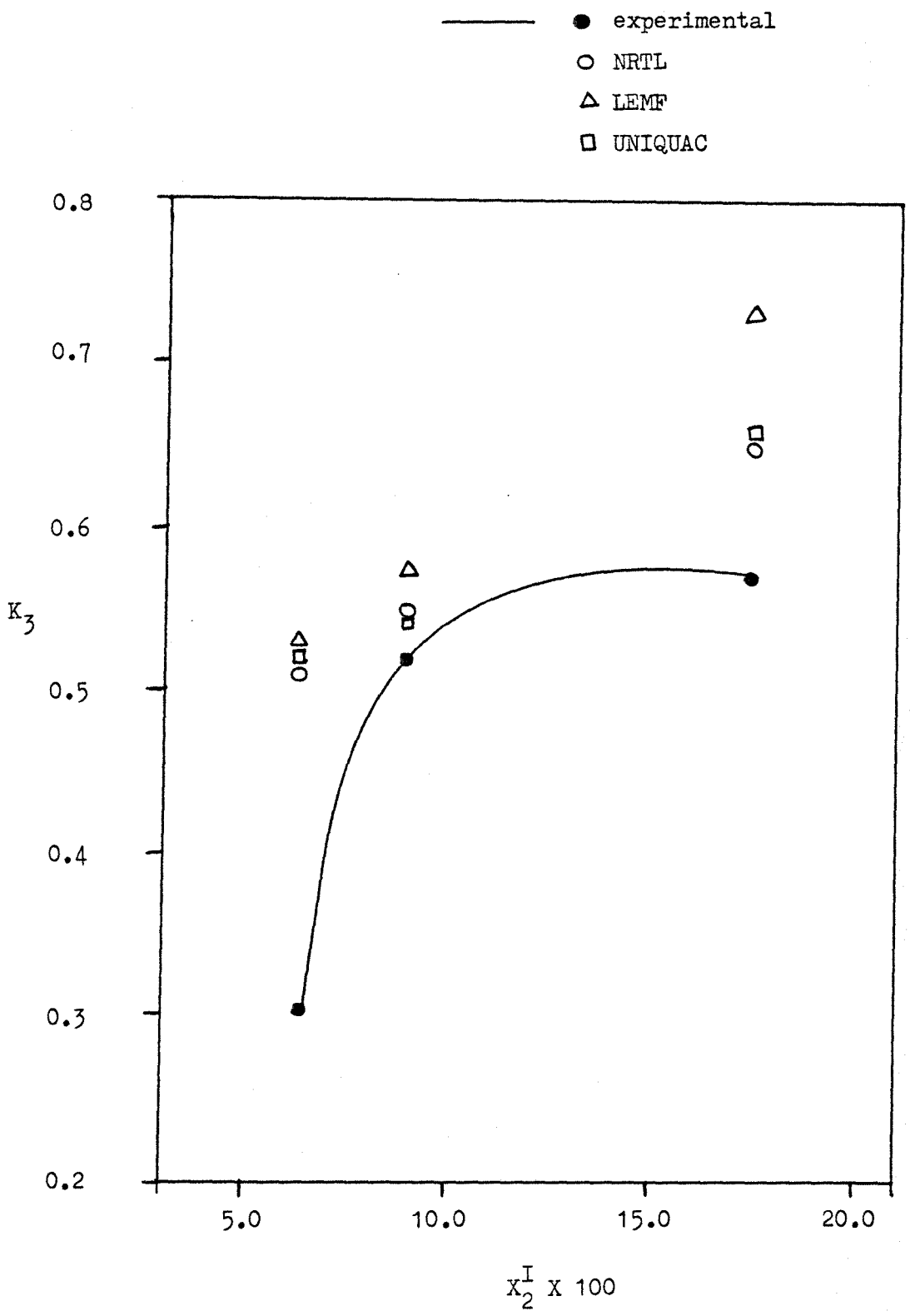


Figure 16: Plot of K_3 versus X_2^I for system 5 (prediction).

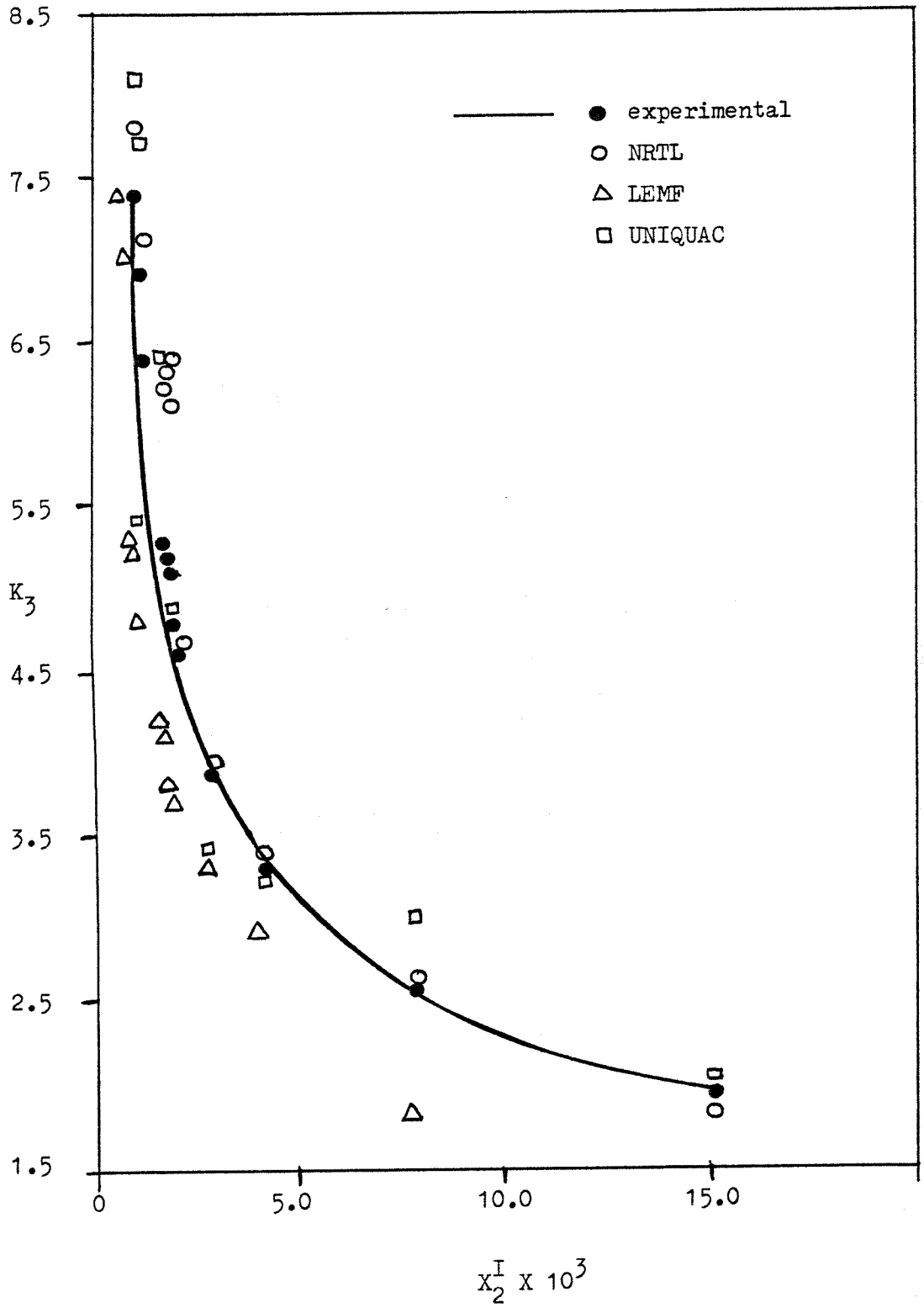


Figure 17: Plot of K_3 versus X_2^I for system 6 (prediction).

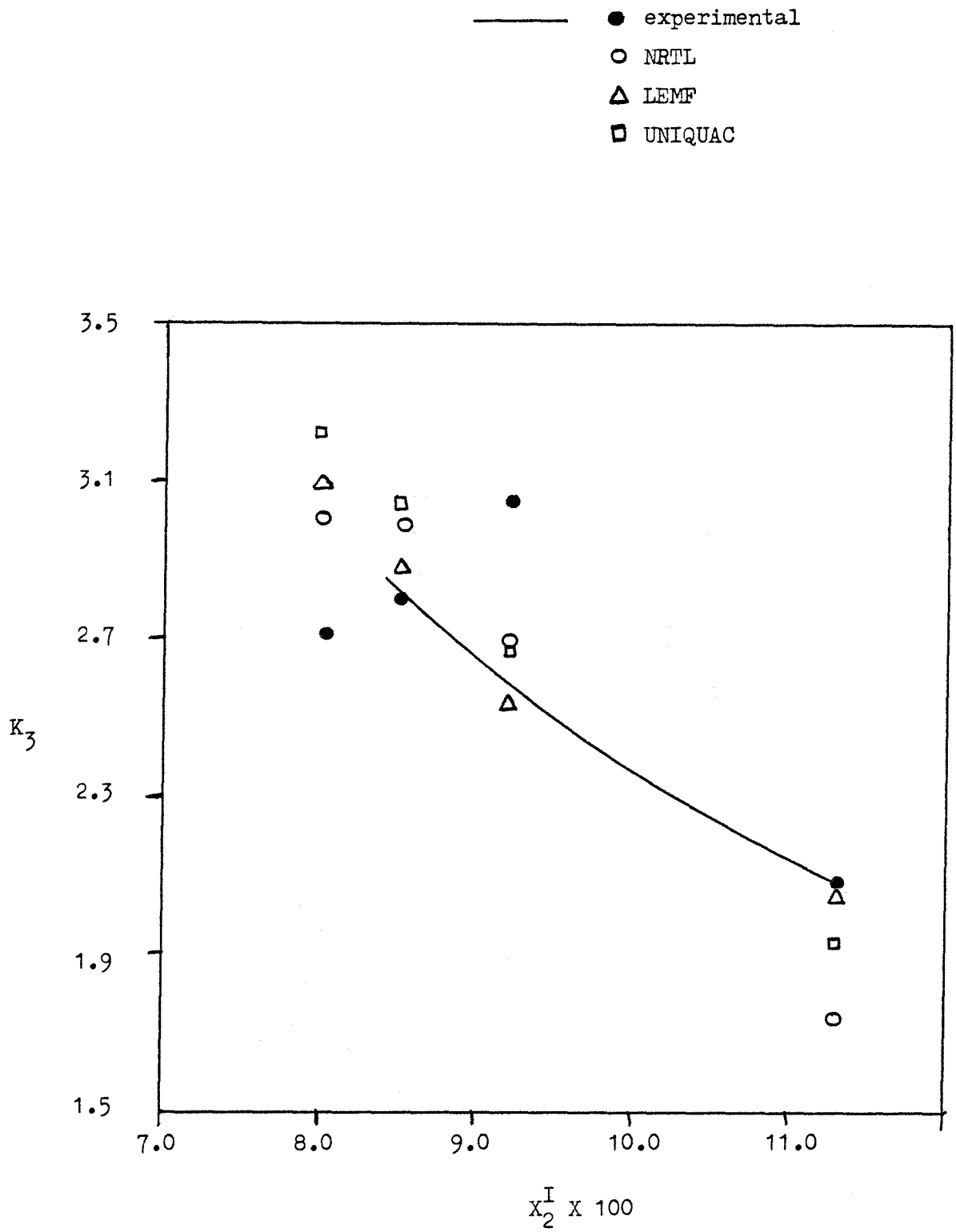


Figure 18: Plot of K_3 versus X_2^I for system 7 (prediction).

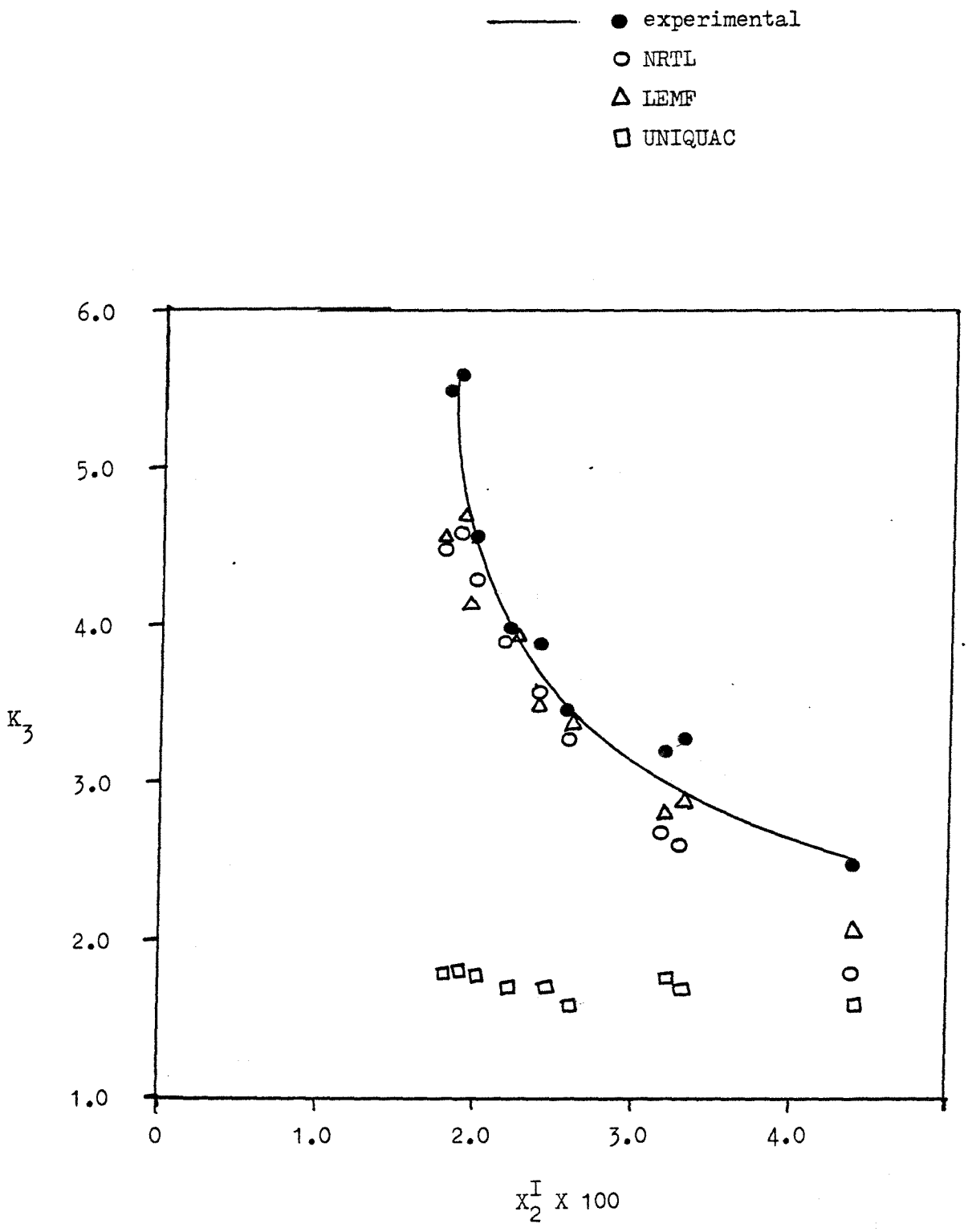


Figure 19: Plot of K_3 versus X_2^I for system 8 (prediction).

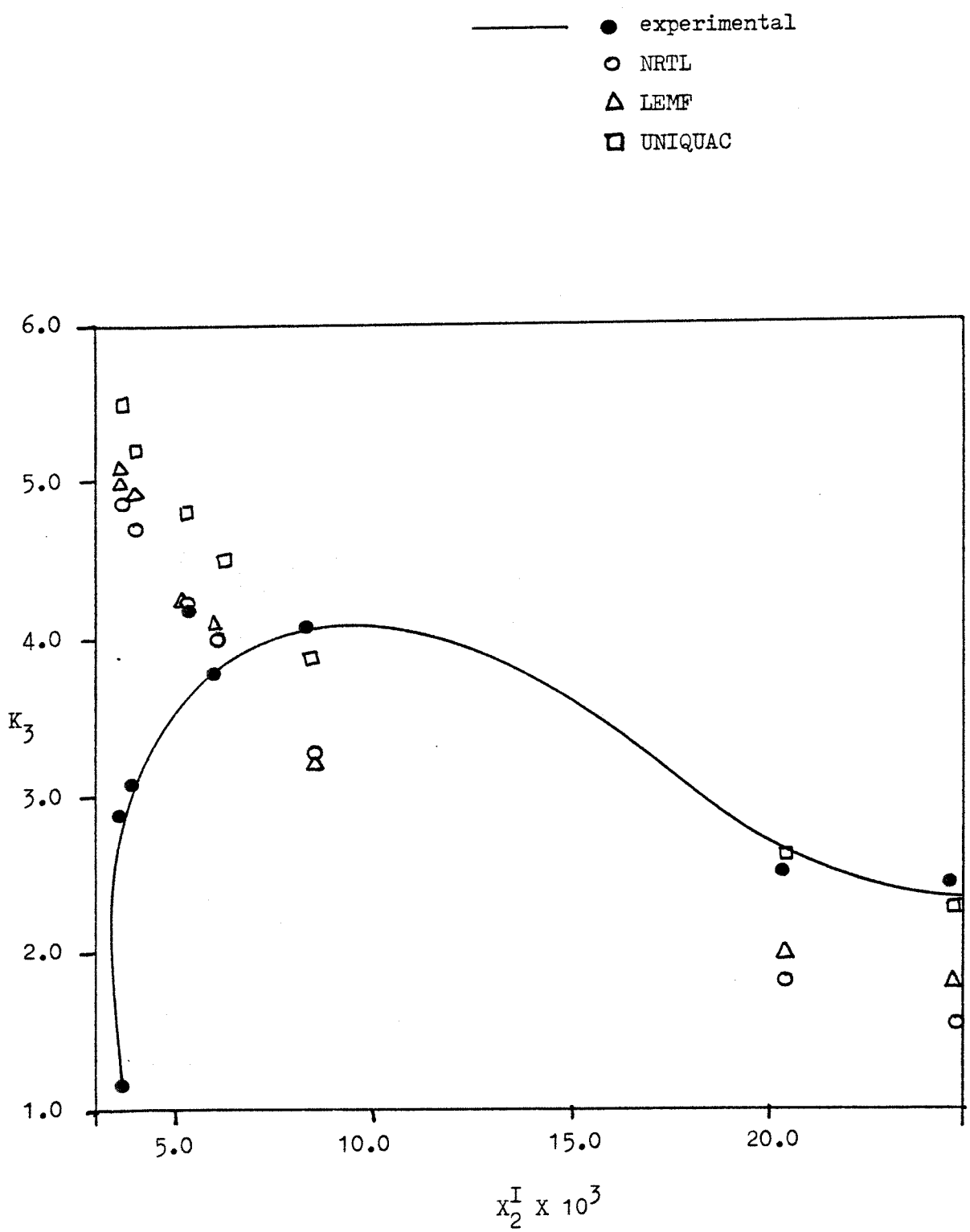


Figure 20: Plot of K_3 versus X_2^I for system 9 (prediction).

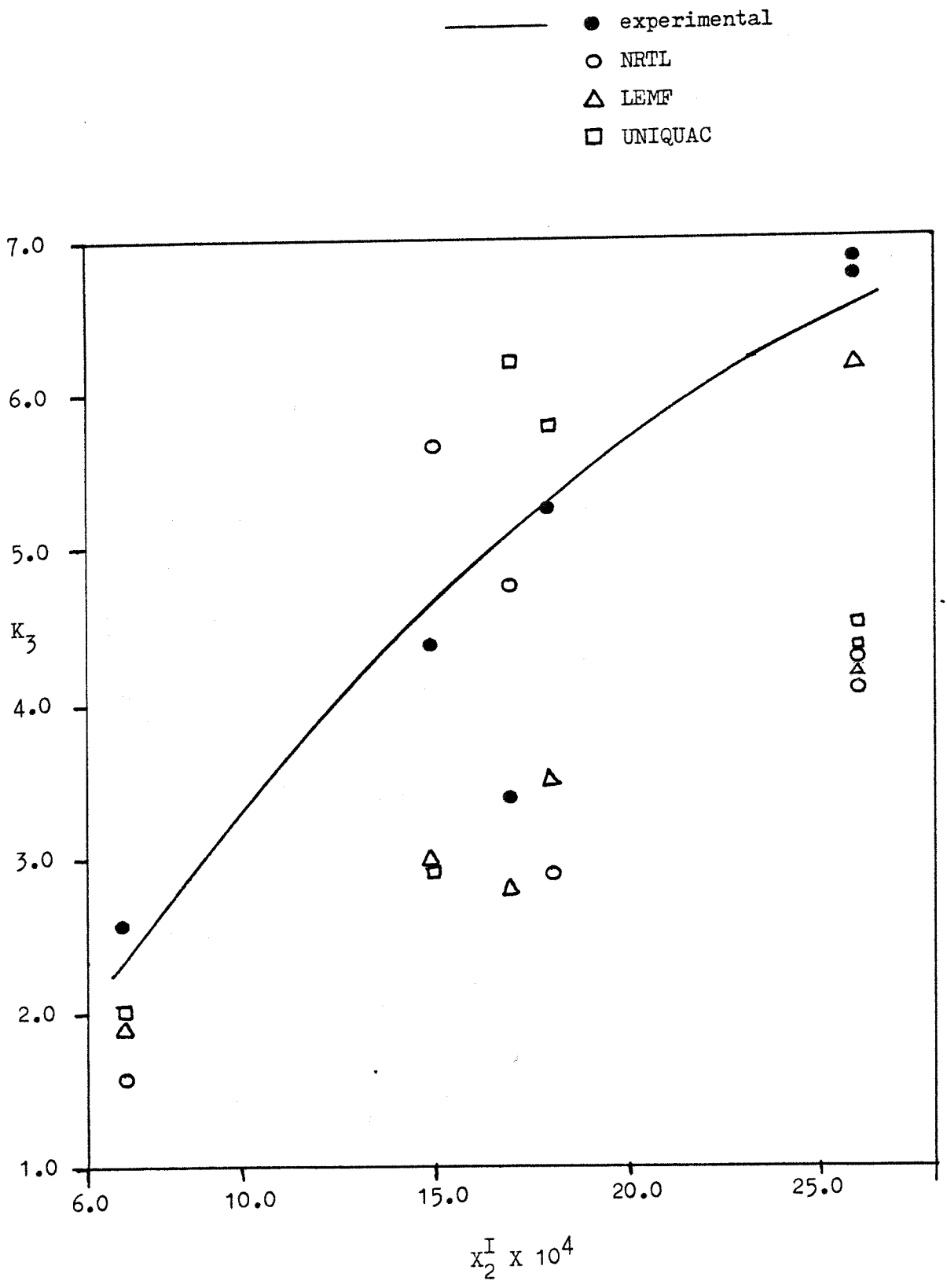


Figure 21: Plot of K_3 versus X_2^I for system 10 (prediction).

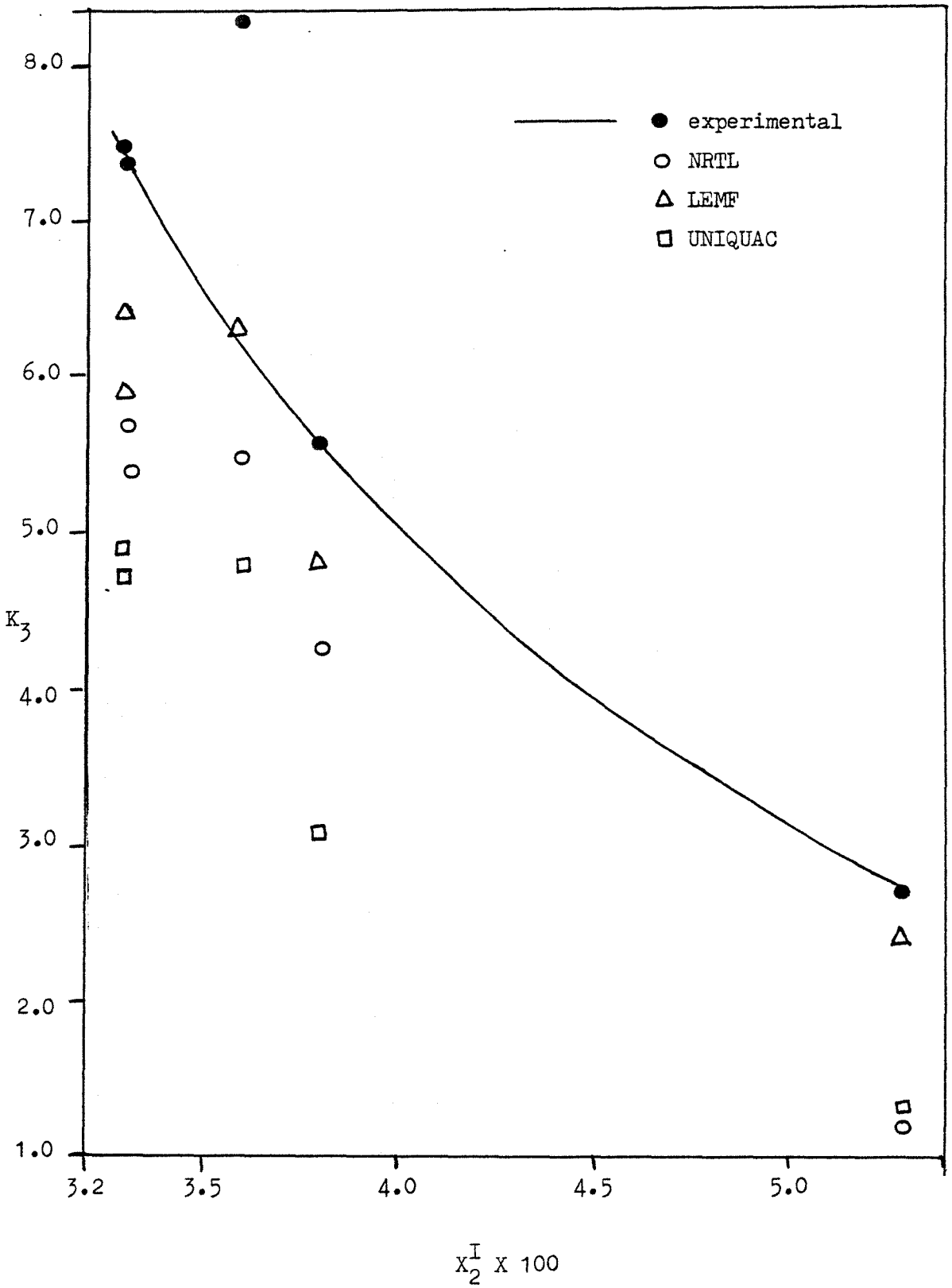


Figure 22: Plot of K_3 versus X_2^I for system 1 (Method IV).

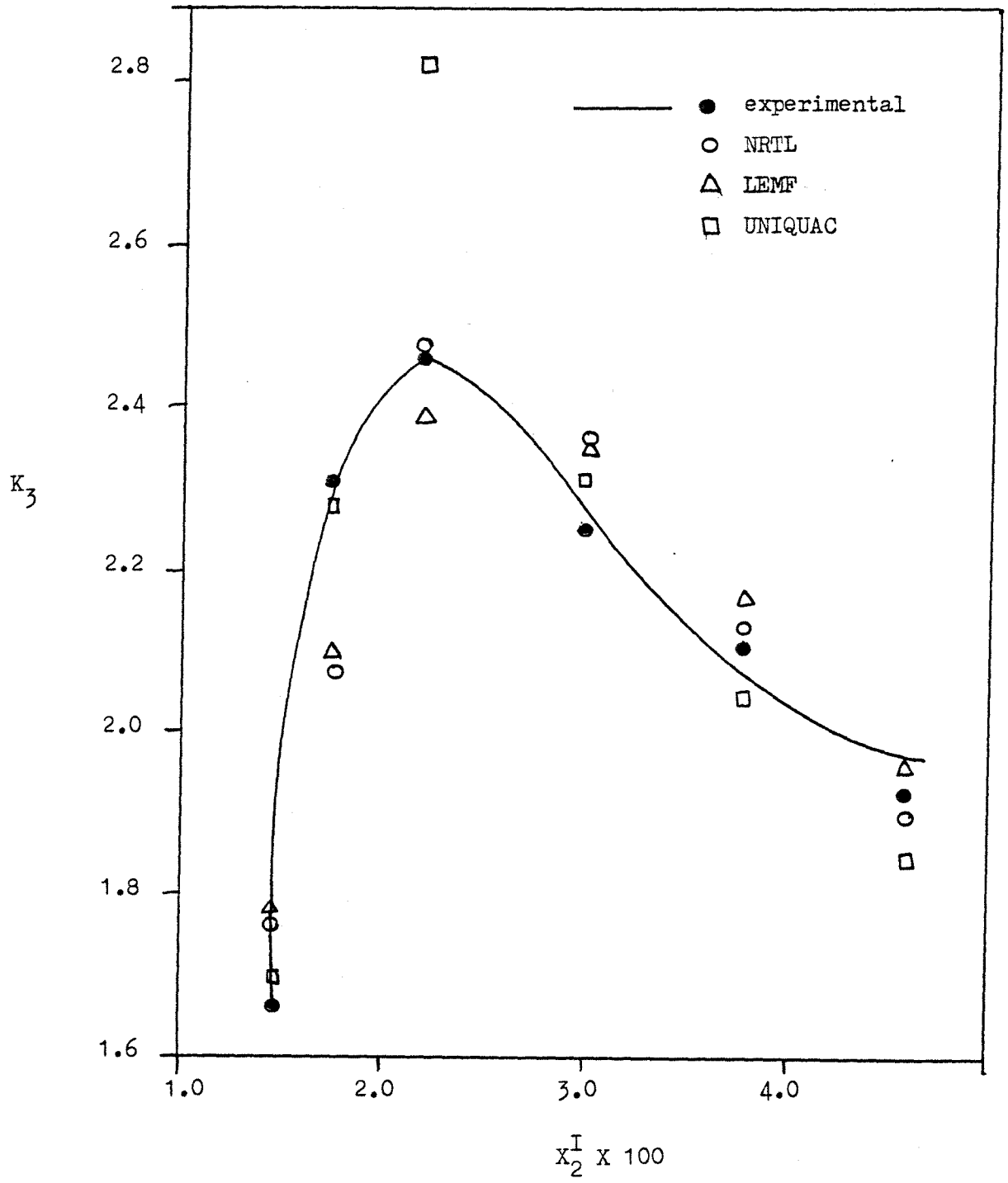


Figure 23: Plot of K_3 versus X_2^I for system 2 (Method IV).

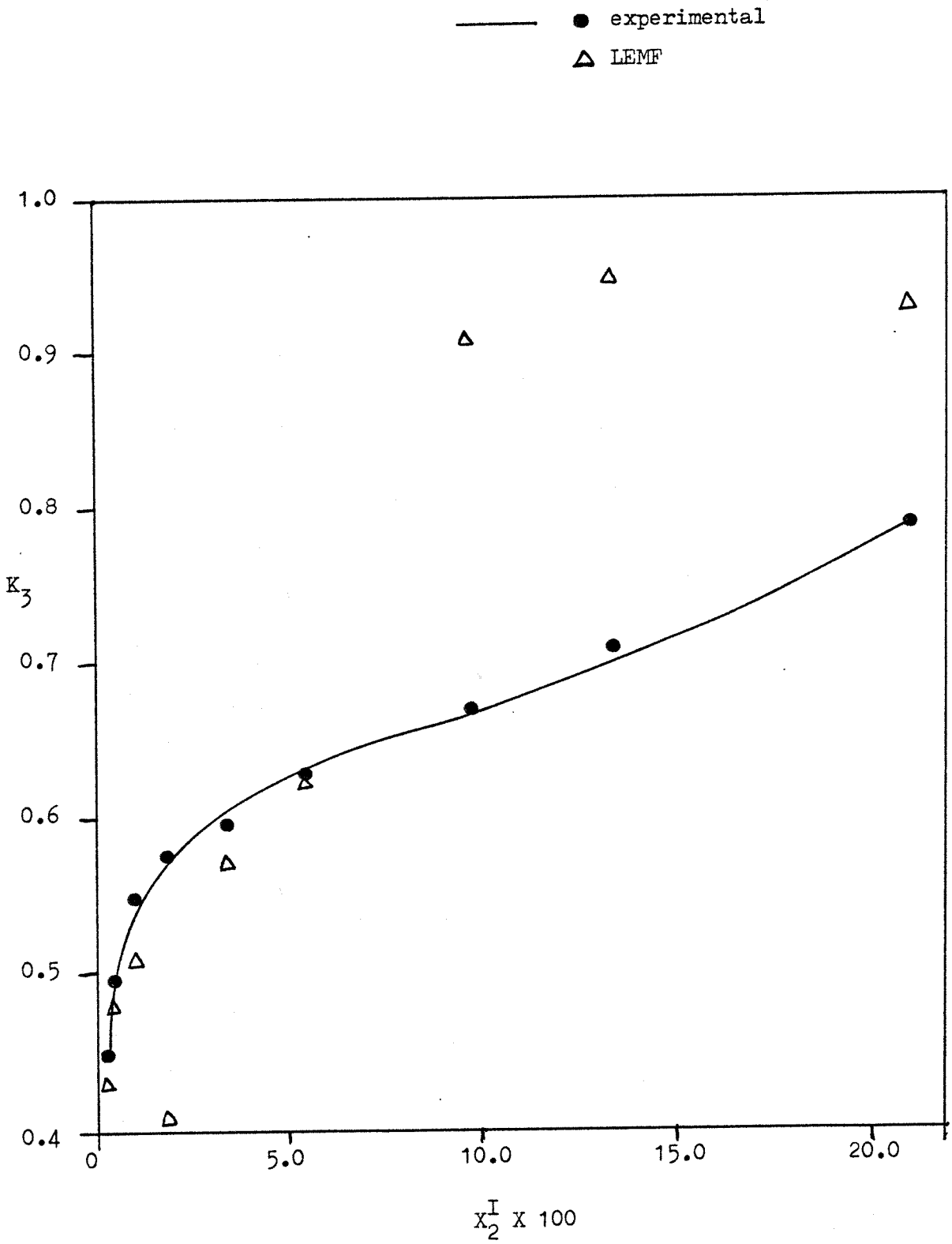


Figure 24: Plot of K_3 versus X_1^{II} for system 2 (Method IV).

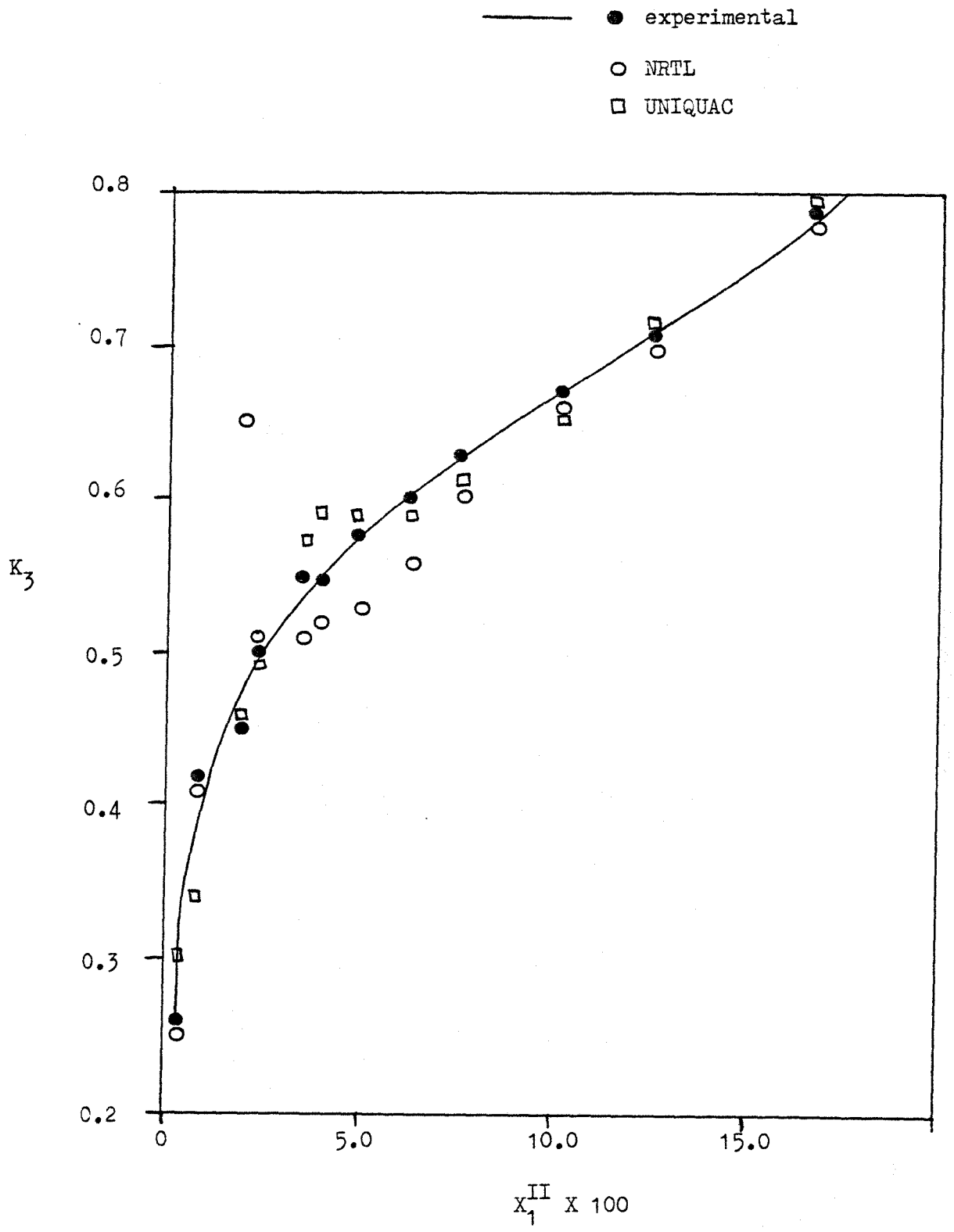


Figure 25: Plot of K_3 versus X_2^I for system 3 (Method IV).

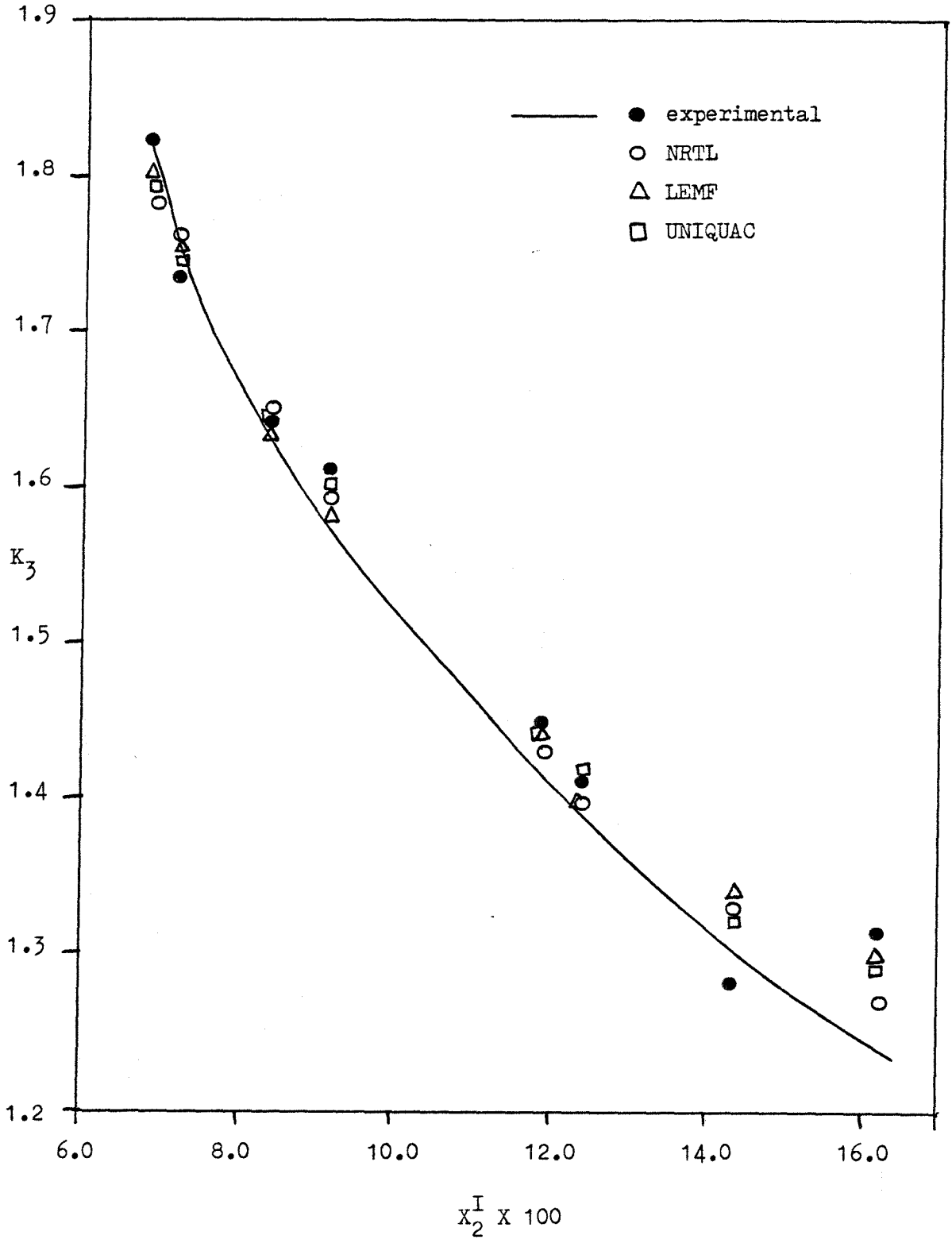


Figure 26: Plot of K_3 versus X_2^I for system 4 (Method IV).

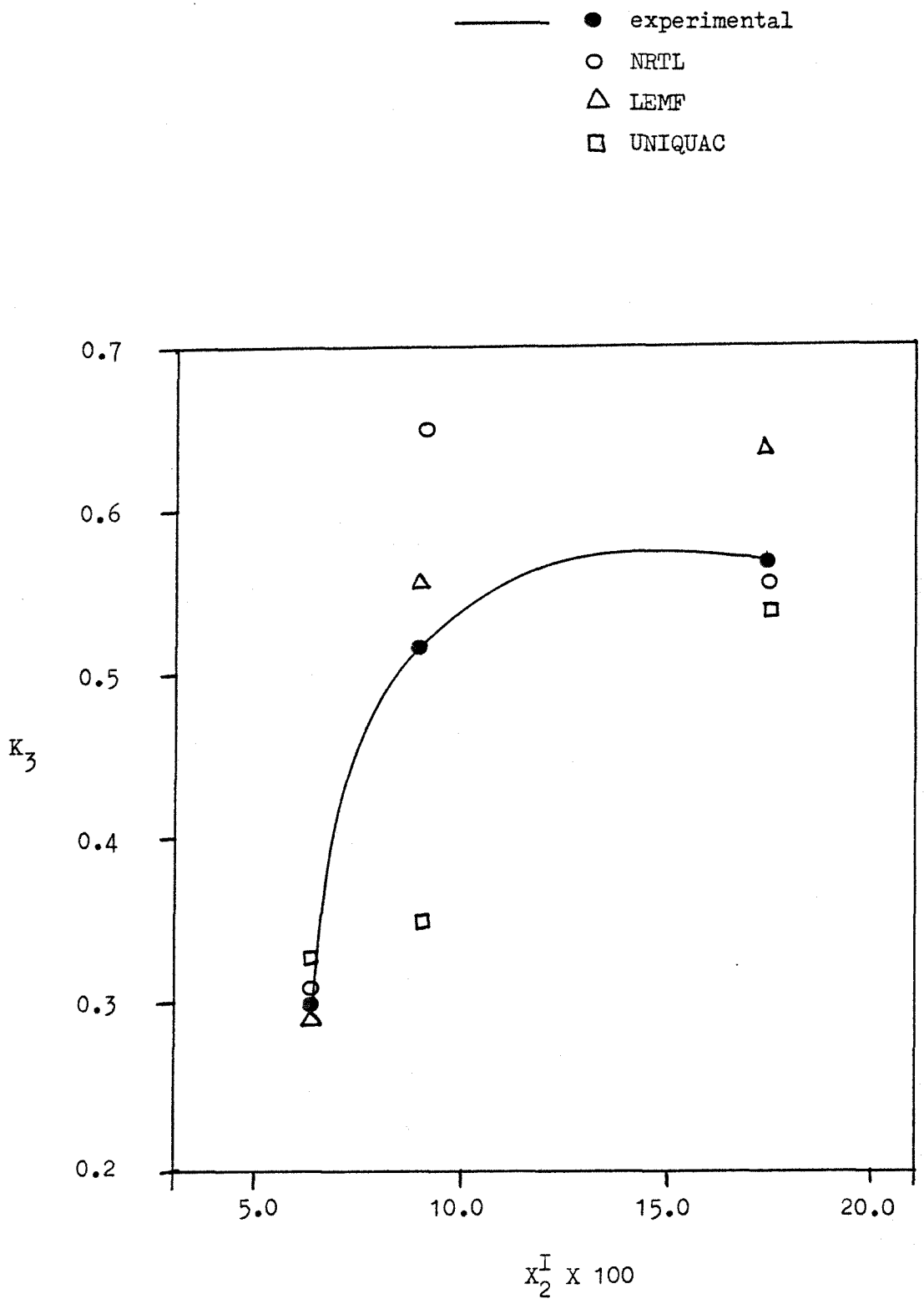


Figure 27: Plot of K_3 versus X_2^I for system 5 (Method IV).

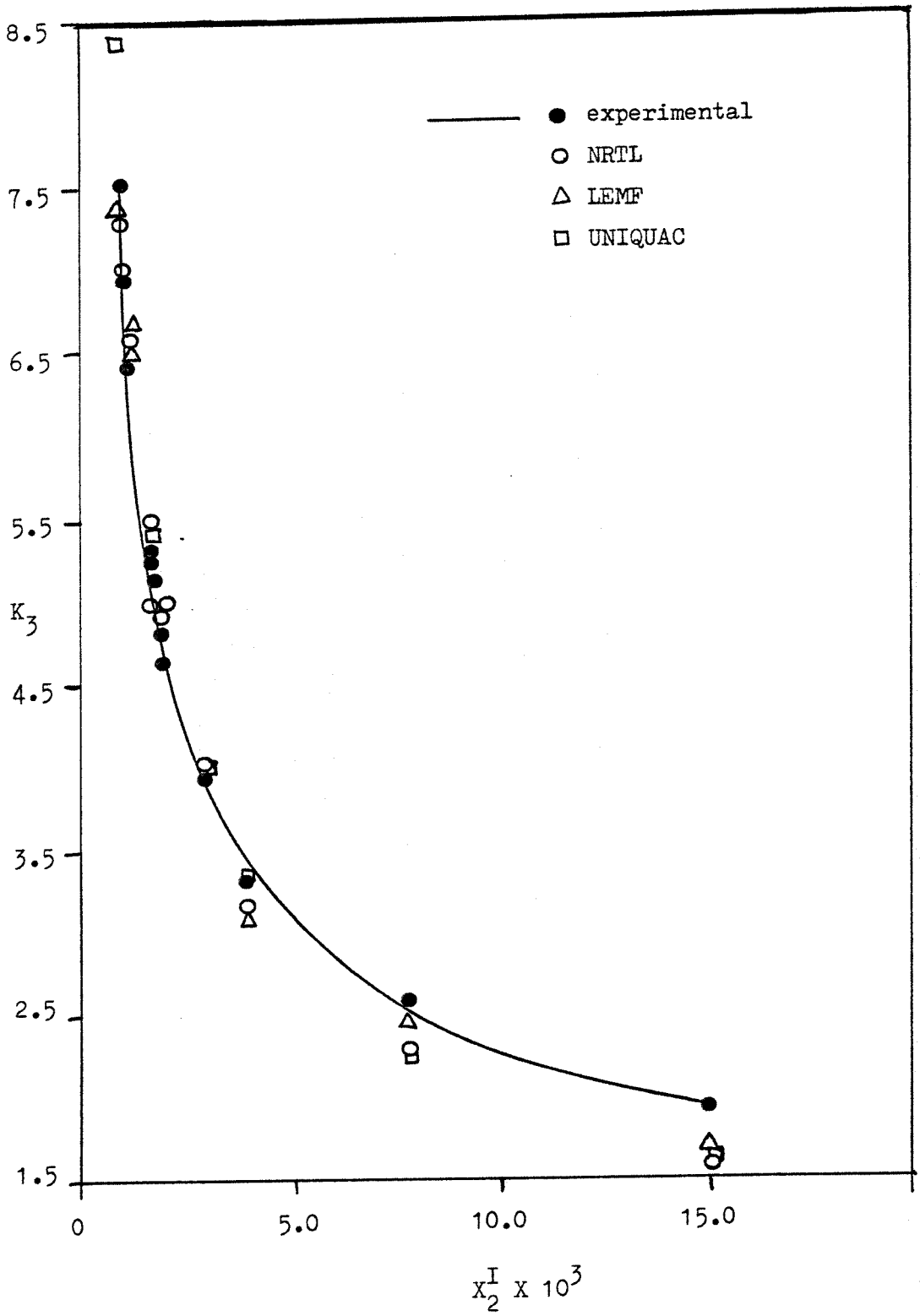


Figure 28: Plot of K_3 versus X_2^I for system 6 (Method IV).

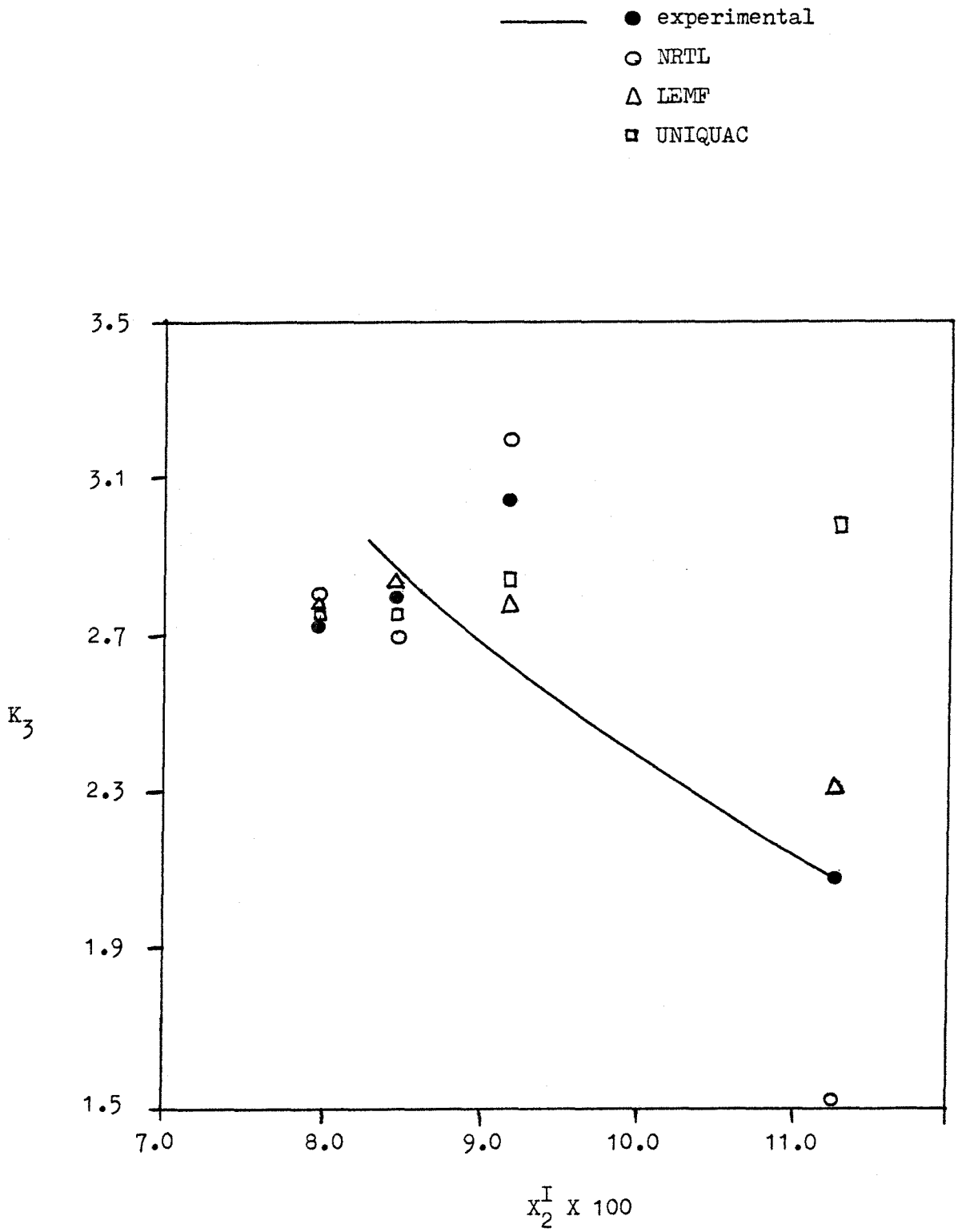


Figure 29: Plot of K_3 versus X_2^I for system 7 (Method IV).

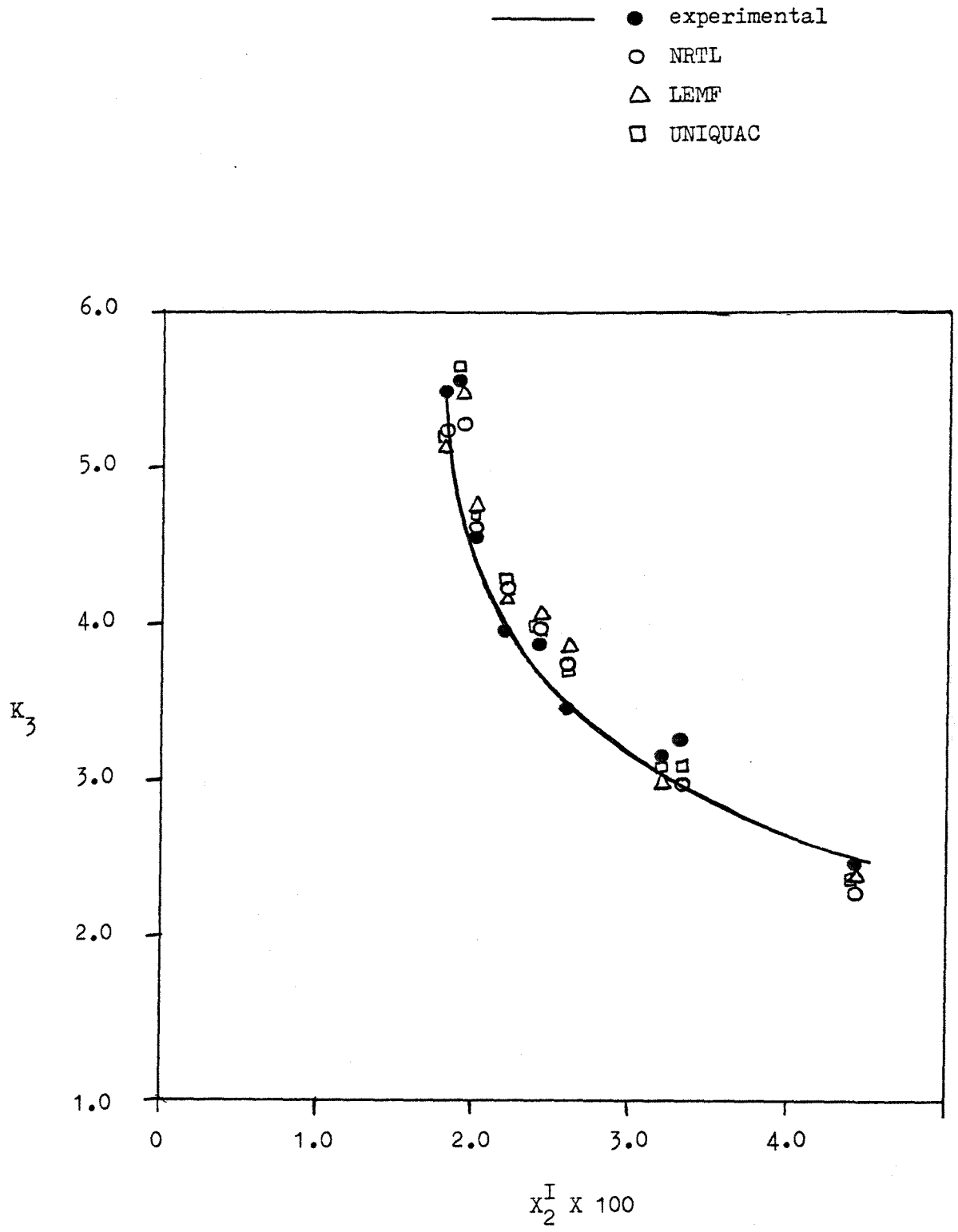


Figure 30: Plot of K_3 versus X_2^I for system 8 (Method IV).

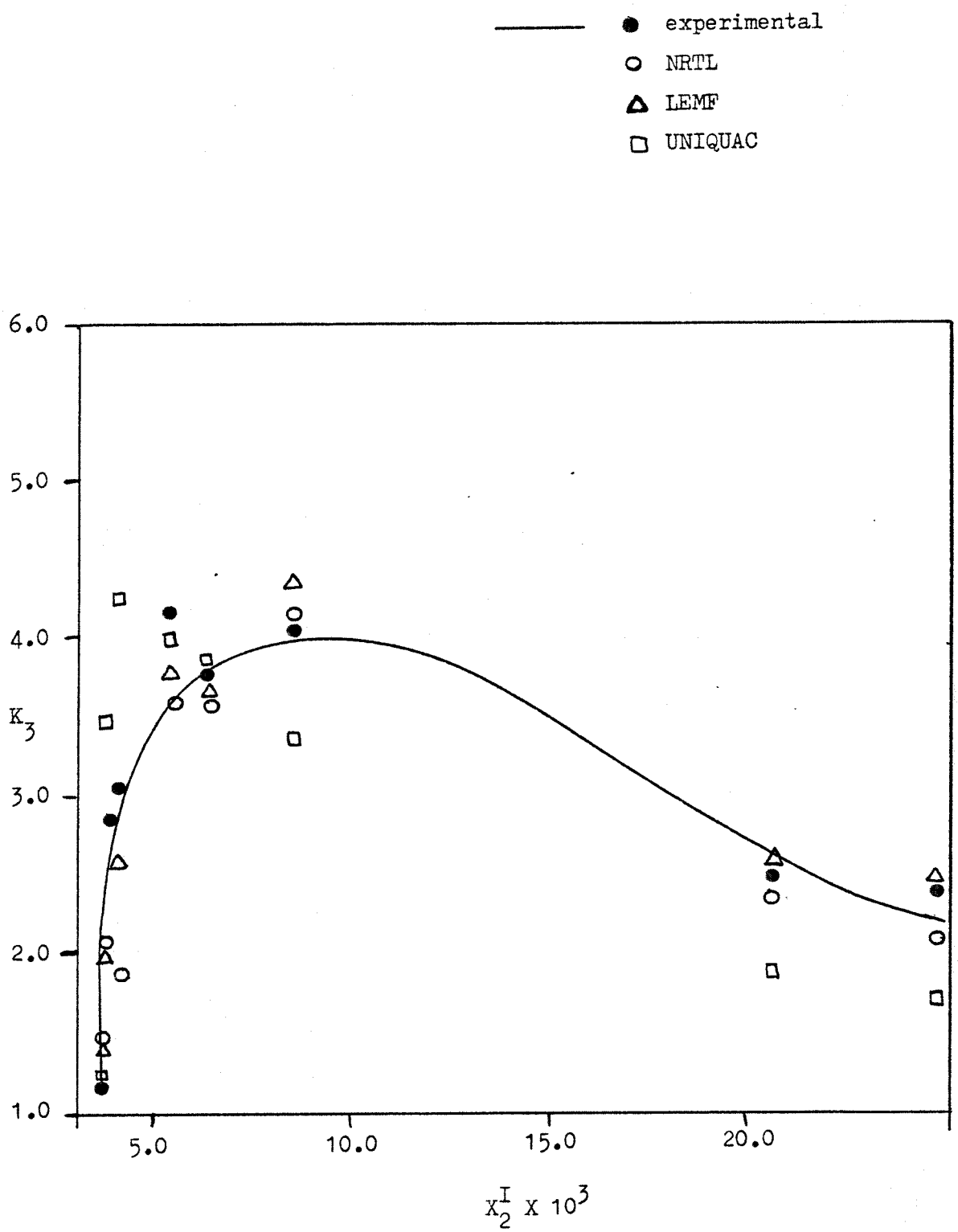


Figure 31: Plot of K_3 versus X_2^I for system 9 (Method IV).

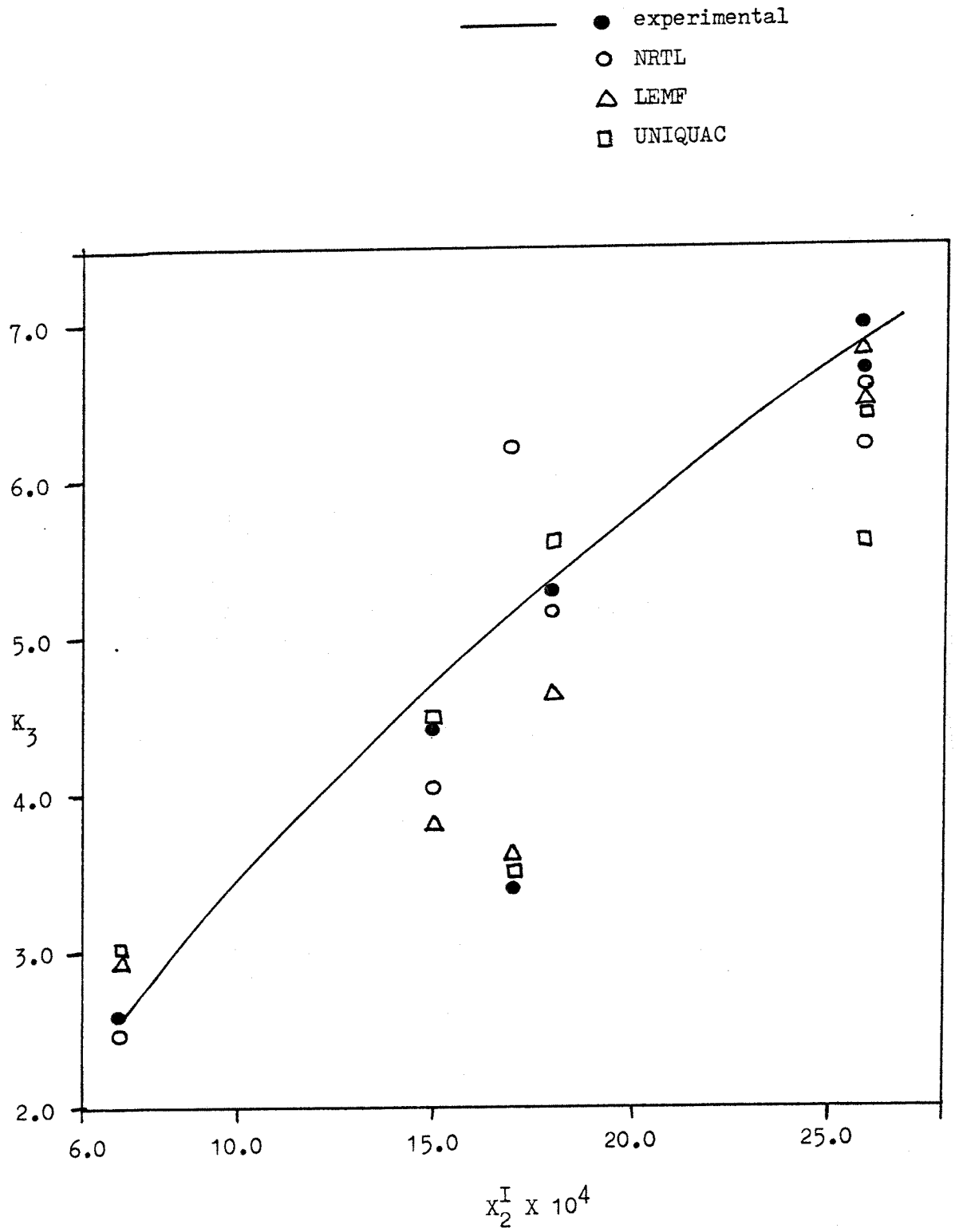
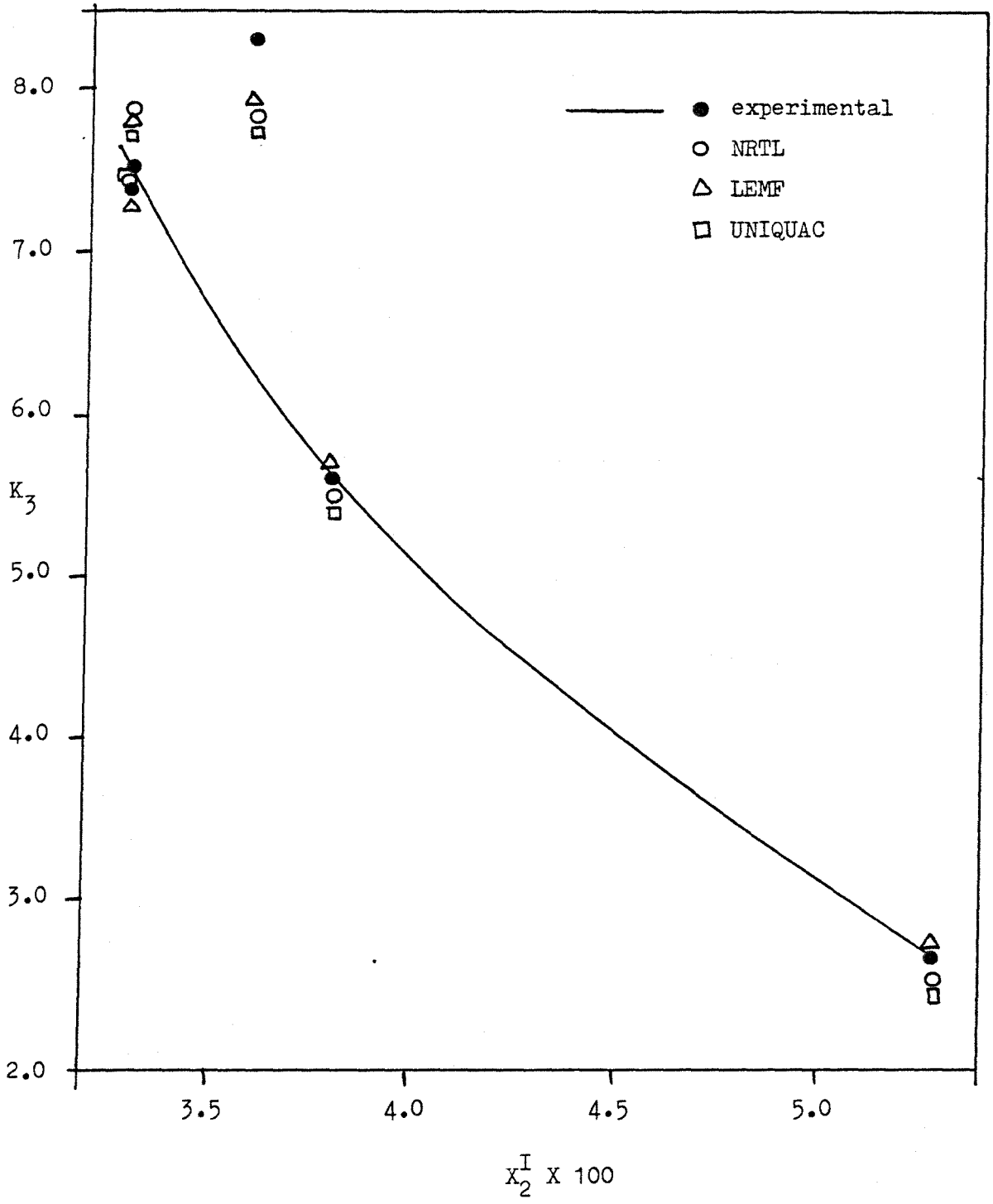


Figure 32: Plot of K_3 versus X_2^I for system 10 (Method IV).



APPENDIX B

THE TABLES

This appendix contains Tables I through XXXI.

Table I: Mutual Solubility Ranges Used to Classify Systems as Type IA, IB, and IC.

System Type	X_2^I	X_2^{II}
IA	> 0.01	< 0.86
IB	> 0.01	> 0.86
IC	< 0.01	> 0.99

Table II: Ternary Systems.

System	System #	Type	Reference
water(1)-ethyl acetate(2)-ethanol(3) at 70 C	1	IA	Griswold (1949)
water(1)-benzene(2)-ethanol(3) at 25 C	2	IC	Bancroft (1942)
acetonitrile(1)-n-heptane (2)-benzene(3) at 45 C	3	IB	Palmer (1972)
cyclohexane(1)-nitromethane (2)-benzene(3) at 25 C	4	IB	Weck (1954)
water(1)-TCE(2)[a]-acetone(3) at 25 C	5	IC	Treybal (1946)
water(1)-methyl acetate(2) -acetone(3) at 30 C	6	IA	Venkataratnam (1957)
water(1)-ethyl acetate(2)-acetone(3) at 30 C	7	IA	Venkataratnam (1957)
water(1)-n-propyl acetate (2)-acetone(3) at 30 C	8	IB	Venkataratnam (1957)
water(1)-benzene(2)-1-propanol(3) at 37.7 C	9	IC	McCants (1953)
water(1)-acrylonitrile(2) -acetonitrile(3) at 60 C	10	IA	Volpicelli (1968)

[a] 1,1,2 trichloroethane

Table III: Pure Component Constants[a] for the UNIQUAC Model.

Component	r	q	q'
water	0.92	1.4	1.0
ethanol	2.11	1.97	0.92
ethyl acetate	3.48	3.12	-
benzene	3.19	2.4	-
acetonitrile	1.87	1.72	-
n-heptane	5.17	4.4	-
cyclohexane	4.05	3.24	-
nitromethane	2.01	1.87	-
TCE	3.53	2.95	-
acetone	2.57	2.34	-
methyl acetate	2.80	2.58	-
n-propyl acetate	3.15	3.66	-
1-propanol	2.78	2.51	0.89
acrylonitrile	2.09	1.64	-

[a] Obtained from Anderson and Prausnitz (1978), and Fredenslund et al. (1975).

Table IV: Binary Systems.

System	Reference
water-ethanol at 760 mm Hg	Hala (1968)
ethanol-ethyl acetate at 760 mm Hg	Griswold (1949)
water-ethyl acetate at 70 C	Griswold (1949)
water-ethanol at 50 mm Hg	Hala (1968)
benzene-ethanol at 25 C	Gmehling (1977)
water-benzene at 25 C	Stephen (1963)
acetonitrile-n-heptane at 45 C	Palmer (1972)
benzene-n-heptane at 45 C	Palmer (1972)
benzene-acetonitrile at 45 C	Palmer (1972)
nitromethane-benzene at 45 C	Hala (1968)
benzene-cyclohexane at 39.99 C	Hala (1968)
cyclohexane-nitromethane at 25 C	Weck (1954)
water-acetone at 25 C	Gmehling (1977)
TCE-acetone at 755 mm Hg	Treybal (1946)
water-TCE at 25 C	Treybal (1946)
acetone-water at 30 C	Gmehling (1977)
acetone-methyl acetate at 50 C	Severns (1955)
water-methyl acetate at 30 C	Venkataratnam (1957)
ethyl acetate-acetone at 760 mm Hg	Subrahmanyam (1964)
water-ethyl acetate at 30 C	Venkataratnam (1957)
n-propyl acetate-acetone at 760 mm Hg	Subrahmanyam (1964)
water-n-propyl acetate at 30 C	Venkataratnam (1957)
water-1-propanol at 40 C	Hala (1968)
benzene-1-propanol at 40 C	Hala (1968)
water-benzene at 37.7 C	Stephen (1963)
water-acetonitrile at 760 mm Hg	Blackford (1965)
acrylonitrile-acetonitrile at 760 mm Hg	Blackford (1965)
water-acrylonitrile at 60 C	Volpicelli (1968)

Table V: Consistency Index(C.I.) for the Miscible Binary Systems.

Binary System	C.I.
ethanol-water at 760 mm Hg	0.07
ethanol-ethyl acetate at 760 mm Hg	0.06
ethanol-water at 50 mm Hg	0.04
benzene-ethanol at 25 C	0.01
acetonitrile-benzene at 45 C	0.04
benzene-n-heptane at 45 C	0.04
benzene-cyclohexane at 39.99 C	0.03
nitromethane-benzene at 45 C	0.04
acetone-TCE at 755 mm Hg	0.59
acetone-water at 30 C	0.02
acetone-methyl acetate at 50 C	0.03
acetone-ethyl acetate at 760 mm Hg	0.11
acetone-n-propyl acetate at 760 mm Hg	0.27
benzene-1-propanol at 40 C	0.04
water-1-propanol at 40 C	0.01
acetonitrile-water at 760 mm Hg	0.01
acetonitrile-acrylonitrile at 760 mm Hg	0.10
acetone-water at 25 C	0.02

Table VI: NRTL Parameters Obtained by Regression of the Binary Data.

System #	α_{12}	α_{13}	α_{23}	Δg_{12}	Δg_{21}	Δg_{13}	Δg_{31}	Δg_{23}	Δg_{32}
1	0.2	0.3	0.3	2938	20	1388	-174	217	359
2	0.2	0.3	0.47	3975	2971	990	-22	1159	233
3	0.2	0.3	0.3	1344	860	387	317	-363	910
4	0.2	0.3	0.3	1390	1245	50	242	461	371
5	0.2	0.3	0.3	3426	1836	710	479	662	-690
6	0.2	0.3	0.3	1799	34	710	479	296	-183
7	0.2	0.3	0.3	2288	313	710	479	150	-48
8	0.2	0.3	0.3	3002	556	710	479	-156	329
9	0.2	0.3	0.47	3650	2236	1608	53	1316	273
10	0.2	0.3	0.3	2103	366	891	747	-445	688

Table VII: LEMF Parameters Obtained by Regression of the Binary Data.

System #	Δg_{12}	Δg_{21}	Δg_{13}	Δg_{31}	Δg_{23}	Δg_{32}
1	413	805	67	544	240	222
2	742	879	135	426	272	507
3	568	615	256	274	390	-230
4	598	614	153	98	290	310
5	672	867	390	384	-368	53
6	425	591	390	384	-52	123
7	455	693	390	384	21	71
8	476	799	390	384	153	-27
9	743	912	173	599	138	562
10	517	704	469	531	230	-192

Table VIII: UNIQUAC Parameters Obtained by Regression of the Binary Data.

System #	Δu_{12}	Δu_{21}	Δu_{13}	Δu_{31}	Δu_{23}	Δu_{32}
1	169	1050	829	-191	1105	-347
2	711	2616	472	-2	2037	-232
3	34	1135	-80	457	-8	117
4	1078	181	202	-84	5	357
5	558	2402	-327	1420	355	-348
6	28	933	-327	1420	215	-153
7	79	1299	-327	1420	216	144
8	468	1681	-327	1420	95	-132
9	687	2492	1153	63	2184	-332
10	382	546	-168	1304	-373	544

Table IX: Effect of Specified Composition[a] on the Average Absolute Percentage Error in Distribution Coefficients, Q.

composition and phase / System #	Q[b]					
	X_1^I	X_1^{II}	X_2^I	X_2^{II}	X_3^I	X_3^{II}
1	24.0	20.0	16.2	14.5	32.2	36.6
2	58.5	60.6	29.4	117.9	71.5	153.6
3	12.8	11.3	9.1	13.9	22.5	23.8
4	24.7	17.3	21.9	22.3	49.6	32.0
5	24.5	62.8	25.8	61.1	21.3	232.6
6	4.7	6.5	5.3	4.8	10.8	11.1
7	21.6	41.1	17.2	37.0	21.0	42.5
8	26.9	15.0	32.3	17.8	34.0	20.5
9	113.4	15.9	48.1	45.1	69.9	52.6
10	15.0	14.7	18.4	17.8	18.8	19.0
Overall	32.6	26.5	22.4	35.2	35.2	62.4

[a] Components and phases are defined below.

1) Component 1 is the component with the larger mutual solubility.
2) Components 1 and 2 are partially miscible.
3) Phase I is the phase rich in component 1, and phase II is the phase rich in component 2, based on the mutual solubility.

[b] Average of the three equations.

Table X: Performance of the NRTL, LEMF, and UNIQUAC Equations in the Prediction of Distribution Coefficients From Binary Data.

System #	NRTL	LEMF	UNIQUAC
		Q	
1	15.3	19.2	14.2
2	37.3	30.0	20.8
3	11.3	9.1	6.8
4	19.1	27.7	19.0
5	21.8	36.6	19.2
6	7.6	2.9	5.5
7	13.1	6.0	32.6
8	35.5	32.1	29.3
9	45.0	25.3	74.1
10	23.5	6.5	25.3
Overall	23.0	19.5	24.7

Table XI: Summary of the Methods.

Method	Number of Parameters	Data Required
I	4	VLE, mutual solubility, and K_3^{∞}
II	4	VLE, mutual solubility, and LLE
III	4	mutual solubility and LLE
IV	6	LLE
V	6	VLE and LLE

Table XII: NRTL Parameters From Method I.

System #	Δg_{12}	Δg_{21}	Δg_{13}	Δg_{31}	Δg_{23}	Δg_{32}
1	2938	20	919	14	1699	-423
2	3975	2971	549	245	1832	13
3	1344	860	261	438	-337	872
4	1390	1245	-775	1773	1030	11
5	3426	1836	827	373	855	-818
6	1799	34	395	841	-64	200
7	2288	313	966	254	508	-382
8	3002	556	-722	3497	128	244
9	3650	2236	1874	-16	1214	298
10	2103	366	1283	483	-728	1223

Table XIII: NRTL Parameters From Method II.

System #	Δg_{12}	Δg_{21}	Δg_{13}	Δg_{31}	Δg_{23}	Δg_{32}
1	2938	20	1013	-1	1294	-355
2	3975	2971	718	-132	-0.5	1747
3	1344	860	564	144	236	98
4	1390	1245	70	186	1200	-182
5	3426	1836	901	312	-121	-101
6	1799	34	664	520	538	-347
7	2288	313	746	433	728	-486
8	3002	556	197	1083	771	-290
9	3650	2236	1168	2	2152	-501
10	2103	366	1252	480	1010	-645

Table XIV: NRTL Parameters From Method III.

System #	Δg_{12}	Δg_{21}	Δg_{13}	Δg_{31}	Δg_{23}	Δg_{32}
1	2938	20	574	19	1752	-707
2	3975	2971	-691	-420	-1054	1934
3	1344	860	1278	-421	243	118
4	1390	1245	656	-1049	-476	871
5	3426	1836	1033	249	-153	14
6	1799	34	4202	-528	1975	1457
7	2288	313	809	141	492	-513
8	3002	556	2819	-261	2007	423
9	3650	2236	2206	-851	2210	-735
10	2103	366	1984	-108	-646	1827

Table XV: NRTL Parameters From Method IV.

System #	Δg_{12}	Δg_{21}	Δg_{13}	Δg_{31}	Δg_{23}	Δg_{32}
1	3074	-3	2519	-1205	2128	-978
2	5577	3002	-4111	105	-3968	1374
3	1377	839	1114	-461	-237	435
4	1441	1188	1306	62	2329	-266
5	3514	1747	891	351	-82	-177
6	1852	27	4099	-970	2022	-118
7	2271	346	762	182	618	-590
8	3066	701	632	770	1982	-542
9	3402	1884	2844	-801	1745	-342
10	2029	453	1868	-167	-609	1058

Table XVI: NRTL Parameters From Method V.

System #	Δg_{12}	Δg_{21}	Δg_{13}	Δg_{31}	Δg_{23}	Δg_{32}
1	3042	-126	1104	-49	1113	-271
2	5393	2754	335	320	225	1278
3	1324	739	431	266	-299	802
4	1302	1184	-390	852	964	-24
5	3516	1752	849	373	-36	-190
6	1822	-15	684	501	424	-270
7	2308	287	758	423	681	-459
8	3042	606	197	1080	930	-384
9	3221	1594	1903	-120	1142	241
10	2001	351	1278	451	-581	920

Table XVII: LEMF Parameters From Method I.

System #	Δg_{12}	Δg_{21}	Δg_{13}	Δg_{31}	Δg_{23}	Δg_{32}
1	413	805	323	348	-1135	646
2	742	879	248	313	148	611
3	568	615	262	281	307	-68
4	598	614	184	-85	-7	531
5	672	867	373	398	-515	99
6	425	591	430	356	-491	335
7	455	693	298	446	-37	88
8	476	799	822	-1381	-1095	516
9	743	912	132	628	160	547
10	517	704	432	580	99	-18

Table XVIII: LEMF Parameters From Method II.

System #	Δg_{12}	Δg_{21}	Δg_{13}	Δg_{31}	Δg_{23}	Δg_{32}
1	413	805	186	466	-1091	653
2	742	879	343	246	128	589
3	568	615	264	281	348	-152
4	598	614	182	-0.7	249	377
5	672	867	226	478	-337	87
6	425	591	364	401	-237	235
7	455	694	333	420	37	50
8	476	799	450	369	-1057	554
9	743	912	-826	780	32	598
10	517	704	438	570	184	-121

Table XIX: LEMF Parameters From Method III.

System #	Δg_{12}	Δg_{21}	Δg_{13}	Δg_{31}	Δg_{23}	Δg_{32}
1	413	805	-296	558	-515	694
2	742	879	-278	235	-903	641
3	568	615	68	169	-286	92
4	598	614	-666	160	-30	378
5	672	867	317	474	-288	211
6	425	591	-576	787	1166	660
7	455	693	122	460	111	-439
8	476	799	597	425	-793	650
9	743	912	-928	762	-263	613
10	517	704	290	595	-966	326

Table XX: LEMF Parameters From Method IV.

System #	Δg_{12}	Δg_{21}	Δg_{13}	Δg_{31}	Δg_{23}	Δg_{32}
1	430	812	-478	696	277	621
2	692	951	17	459	95	578
3	558	619	10	209	-103	-144
4	629	565	619	-568	260	513
5	621	874	282	484	20	-85
6	437	596	574	551	-1071	589
7	442	695	119	465	78	-1015
8	444	815	2572	498	593	673
9	721	895	-576	727	136	492
10	521	703	220	603	159	-682

Table XXI: LEMF Parameters From Method V.

System #	Δg_{12}	Δg_{21}	Δg_{13}	Δg_{31}	Δg_{23}	Δg_{32}
1	326	807	183	447	14	438
2	689	947	107	447	201	558
3	572	620	259	286	330	-114
4	612	599	225	-58	229	394
5	615	866	269	463	-312	37
6	430	585	380	391	-48	122
7	466	688	344	414	28	57
8	444	795	474	355	-1038	538
9	729	885	170	604	181	527
10	540	697	443	565	145	-66

Table XXII: UNIQUAC Parameters From Method I.

System #	Δu_{12}	Δu_{21}	Δu_{13}	Δu_{31}	Δu_{23}	Δu_{32}
1	169	1050	814	-216	2567	-559
2	711	2616	446	13	2514	-253
3	34	1135	-58	427	-37	148
4	1078	181	179	-116	615	-144
5	558	2402	-302	1278	528	-453
6	28	933	-412	2106	-8	74
7	79	1299	-249	1039	401	-287
8	468	1681	-946	3444	-164	196
9	687	2492	1449	-9	2098	-324
10	382	546	170	662	-554	952

Table XXIII: UNIQUAC Parameters From Method II.

System #	Δu_{12}	Δu_{21}	Δu_{13}	Δu_{31}	Δu_{23}	Δu_{32}
1	169	1050	576	-76	1727	-492
2	711	2616	1212	-331	2328	-224
3	34	1135	43	275	303	-155
4	1078	181	-215	386	289	61
5	558	2402	-258	1111	-44	-41
6	28	933	-335	1454	227	-157
7	79	1299	-301	1267	258	-182
8	468	1681	-509	2968	151	-113
9	687	2492	883	-29	9032	-601
10	382	546	236	487	-530	922

Table XXIV: UNIQUAC Parameters From Method III.

System #	Δu_{12}	Δu_{21}	Δu_{13}	Δu_{31}	Δu_{23}	Δu_{32}
1	169	1050	187	-442	9432	-878
2	711	2616	-85	-819	-575	703
3	34	1135	-347	148	59	-328
4	1078	181	227	-469	-272	247
5	558	2402	-197	1040	-49	29
6	28	933	1349	219	870	6225
7	79	1299	-289	865	142	-152
8	468	1681	2878	381	1892	504
9	687	2492	607	-270	6314	-845
10	382	546	395	298	-675	6488

Table XXV: UNIQUAC Parameters From Method IV.

System #	Δu_{12}	Δu_{21}	Δu_{13}	Δu_{31}	Δu_{23}	Δu_{32}
1	201	1029	1757	-1090	2999	-1046
2	1291	2494	-968	1423	1820	-527
3	47	1108	-320	207	209	-382
4	1148	180	-21	259	532	-38
5	583	2541	-201	1028	6	-44
6	7	966	582	2430	492	1422
7	88	1272	-338	1167	227	-218
8	452	1966	3101	339	1949	486
9	597	3659	2832	-465	5168	-432
10	319	727	554	37	-409	642

Table XXVI: UNIQUAC Parameters From Method V.

System #	Δu_{12}	Δu_{21}	Δu_{13}	Δu_{31}	Δu_{23}	Δu_{32}
1	142	1028	554	-59	1568	-461
2	999	2326	2359	-448	3333	-351
3	30	1071	-26	372	95	13
4	1122	163	-136	267	291	57
5	593	2388	-262	1137	25	-108
6	24	919	-333	1436	202	-139
7	90	1246	-325	1477	315	-224
8	486	1651	-507	2984	188	-142
9	485	2311	1551	-140	2062	-313
10	284	636	113	724	-531	903

Table XXVII: Performance of Method I.

System #	NRTL		LEMF		UNIQUAC	
	Q	G	Q	G	Q	G
1	8.3	7.0	11.4	6.0	7.0	6.1
2	27.0	6.6	31.7	6.2	26.1	2.2
3	11.2	1.3	5.7	1.5	11.1	1.3
4	12.7	8.0	15.1	8.8	20.2	8.5
5	26.6	7.3	23.9	6.9	32.7	7.4
6	5.4	6.2	6.6	4.8	6.0	6.9
7	22.0	6.1	14.3	5.8	11.8	6.0
8	22.0	26.0	49.5	14.9	23.4	27.6
9	31.9	4.0	60.8	3.4	47.8	3.5
10	29.0	7.2	11.2	5.7	19.6	7.5
Overall	19.6	8.0	23.0	6.4	20.6	7.7

Table XXVIII: Performance of Method II.

System #	NRTL		LEMF		UNIQUAC	
	Q	G	Q	G	Q	G
1	3.0	4.9	3.9	4.3	7.3	4.0
2	47.1[a]	18.0	42.1	7.1	28.3	4.4
3	7.2	3.5	7.3	1.5	3.3	2.8
4	12.5	4.7	17.2	3.4	12.3	4.0
5	7.9	7.6	6.8	8.4	9.1	7.7
6	4.5	4.2	3.6	3.9	5.2	4.4
7	8.8	5.0	11.0	4.9	3.5	4.8
8	16.8	12.2	18.9	10.8	17.7	14.2
9	24.2	21.2	7.7	7.6	55.1	14.8
10	16.1	7.5	5.5	5.4	8.0	7.0
Overall	14.8	8.9	12.4	5.7	15.0	6.8

[a] Fix X_1^{II}

Table XXIX: Performance of Method III.

System #	NRTL Q	LEMF Q	UNIQUAC Q
1	1.9	3.7	3.3
2	35.3[a]	31.6	26.8[a]
3	3.0	3.0	3.2
4	5.2	19.9	5.8
5	7.4	8.4	9.7
6	1.7	2.5	3.0
7	6.7	2.6	3.3
8	27.7	21.7	6.5
9	15.1	36.0[b]	36.8
10	1.6	1.1	6.5
Overall	10.6	13.1	10.5

a Fix X_1^{II}

b Fix X_1^{I}

Table XXX: Performance of Method IV.

System #	NRTL Q	LEMF Q	UNIQUAC Q
1	1.7	2.6	2.3
2	12.3[a,b]	18.2	13.7[a]
3	2.8	0.8	2.2
4	4.4	11.0	9.4
5	7.2	4.8	6.2
6	3.8	2.2	5.2
7	4.6	2.5	2.0
8	14.4[c]	7.2[d]	12.2
9	15.1	4.8	4.7
10	1.1	1.1	1.2
Overall	6.7	5.5	5.9

[a] Fix X_1^{II}

[b] Starting value = -2000

[c] Starting value = 0

[d] Starting value = 1000

Table XXXI: Performance of Method V.

System #	NRTL		LEMF		UNIQUAC	
	Q	G	Q	G	Q	G
1	6.2	4.1	4.6	4.6	5.9	3.5
2	20.3[a]	12.8	20.7	2.7	18.3	8.9
3	6.2	1.6	3.9	1.6	4.4	1.6
4	8.6	4.1	14.9	3.7	9.5	3.6
5	7.1	7.4	4.5	8.0	8.7	7.5
6	4.2	4.1	3.1	3.9	4.2	4.3
7	8.8	4.9	7.5	4.7	2.6	5.0
8	13.9	12.2	14.6	10.3	18.6	14.3
9	21.9	6.2	4.5	3.5	13.4	5.3
10	15.7	6.5	3.3	5.4	16.4	6.9
Overall	11.3	6.4	8.2	4.8	10.2	6.1

[a] Fix X_1^{II}

APPENDIX C

THE COMPUTER PROGRAMS

This appendix contains the following computer programs (in FORTRAN):

1. TLLE
2. REGRESS-UNIQUAC
3. OTILIA-UNIQUAC
4. TREG

The program TLLE calculates ternary LLE compositions with the NRTL, LEMF, or UNIQUAC equations. The program REGRESS-UNIQUAC calculates the binary parameters in the UNIQUAC equation from binary VLE data. The program OTILIA-UNIQUAC determines the binary parameters in the UNIQUAC equation from the mutual solubility data. Finally, the program TREG evaluates the binary parameters in the NRTL, LEMF, or UNIQUAC equations from ternary LLE data alone, or from binary VLE and ternary LLE data together.

The pages that follow contain, for each computer program, the instructions to use it, a sample input, a listing, the information contained in the output, and a dictionary.

The Program TLLE

The computer program TLLE calculates ternary LLE compositions with the NRTL, LEMF, or UNIQUAC equations. The procedure for using this program is now discussed.

1. Which equation?

To specify the NRTL or LEMF equations let IEQN = 01 (Format I2). For the UNIQUAC equation IEQN = 02 (Format I2). This is typed on line 1 starting on column 1.

2. How many jobs to be run?

If one desires to run several jobs let JK = N (Format I2), where N = number of jobs to be run. This is typed on line 2 starting on column 1.

3. How many tie-lines for the system?

To specify the number of ternary tie-lines (do not include the mutual solubility data), let NPOINT = N (Format I2), where N = number of tie-lines in the system. This is typed on line 3 starting on column 1.

4. How many components?

Since we are calculating ternary LLE only, NCOMP = 03 (Format I2). This is typed on line 4 starting on column 1.

5. Molecular weights of each component

If the tie-line data is in mole fraction let AMW1 = AMW2 = AMW3 = 1.0 (Format 3F10.4). If the tie-line data is in weight fraction let AMW1 = MW1, AMW2 = MW2, and AMW3 = MW3, where MW1, MW2, and MW3 are the molecular weights for each component. Again Format 3F10.4 is used. This is typed on line 5 starting on column 1.

6. Title of the system

Here the title of the system is typed. It should not exceed 60 spaces in lenght. When typing the title note that the order of the components must correspond to that for the molecular weights typed above. This is typed on line 6 starting on column 1.

7. The LLE data

Here the LLE data is typed (Format 5F10.4). For each tie-line one must specify the following:

AT AX11 AX12 AX21 AX22

where AT = temperature of the system, (C)

AX11 = X_1^I

AX12 = X_1^{II}

AX21 = X_2^I

AX22 = X_2^{II}

This is typed on line 7 starting on column 1. Note that we use one line per tie-line. Since X_1^I is the first composition given, this composition

is specified when performing the calculations. If one desires to specify a different composition it must be put in the place of X_1^I. For example, if X_2^I is to be specified, the data is typed as follow:

AT AX21 AX22 AX11 AX12

8. Read in r, q, and q' if using the UNIQUAC equation

If the UNIQUAC equation was specified we must read in the values of r, q, and q' for each component. The order of the components must correspond to the order used in the title. For each component, starting with component 1, we must type the following (Format 3F10.4):

R Q QP

where R = r

Q = q

QP = q'

And similarly for components 2 and 3. This is typed starting on column 1, and using one line for each component.

9. The binary parameters in the UNIQUAC equation

The binary parameters (CACTCO(I,J) or Δu_{ij}) in the UNIQUAC equation are now specified. They are read in matrix form (Format 3F10.2) as follow:

$$\begin{matrix} \Delta u_{11} & \Delta u_{12} & \Delta u_{13} \\ \Delta u_{21} & \Delta u_{22} & \Delta u_{23} \\ \Delta u_{31} & \Delta u_{32} & \Delta u_{33} \end{matrix}$$

If more than one job are to be run, simply type the next set of parameters after the above set. This is typed starting on column 1. Note that one can run either all jobs using the UNIQUAC equation only, or all jobs using the NRTL and LEMF equations only. But never should try to run NRTL or LEMF and UNIQUAC jobs together.

10. The binary parameters and α for the NRTL and LEMF equations

If one is interested in using the NRTL or the LEMF equations, one must type in Δg_{ij} and α_{ij} in matrix form as shown below (Format 3F10.2):

$$\begin{array}{ccc} \Delta g_{11} & \Delta g_{12} & \Delta g_{13} \\ \Delta g_{21} & \Delta g_{22} & \Delta g_{23} \\ \Delta g_{31} & \Delta g_{32} & \Delta g_{33} \\ \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{array}$$

This is typed starting on column 1. If more than one set of parameters are to be used, they are typed after the above set. Notice that Δg_{ij} = CACTCO(I,J), and α_{ij} = ALFA(I,J).

A sample input is given on the next page, and followed by a listing of the computer program TLLE.

Sample Input for the Program TLLE

```
02
01
04
03
1.0         1.0         1.0
METHYL ACETATE(1)-WATER(2)-ACETONE(3) AT 30 C
30.0        0.628       0.0796      0.3581      0.9153
30.0        0.5814      0.0845      0.3883      0.9047
30.0        0.4964      0.0916      0.4403      0.8877
30.0        0.3972      0.1126      0.5283      0.8513
2.8042      2.576       2.576
0.92        1.4         1.0
2.57        2.34        2.34
0.0         933.6       227.85
28.2        0.0         -335.77
-157.65     1454.52     0.0
```

```
      DIMENSION CACTCO(3,3),ALFA(3,3),SYS(20)
      DIMENSION XT(3),X(3,6),Y(4)
      COMMON/COM1/T,X11,X12,X21,X22,X31,X32,CACTCO,ALFA,NCOMP,
     1YY,IEQN
      COMMON/COM2/R(3),Q(3),QP(3),INK
      COMMON/COM3/GAM11(20),GAM12(20),GAM21(20),GAM22(20),GAM31(20),
     1GAM32(20)
      DIMENSION BX11(20),BX12(20),BX21(20),BX22(20),BX31(20),BX32(20)
      DIMENSION X11C(20),X12C(20),X21C(20),X22C(20),X31C(20),X32C(20)
      DIMENSION AT(20),AX11(20),AX12(20),AX21(20),AX22(20),
     1AX31(20),AX32(20)
C
C
C
C
C     THIS IS THE PROGRAM TLLE
C
C
C
C
C  FORMAT STATEMENTS
C
C
600   FORMAT('0','BINARY INTERACTION PARAMETERS')
 312  FORMAT(' ',5X,'GAM11',5X,'GAM12',5X,'GAM21',5X,'GAM22',5X,
     1'GAM31',5X,'GAM32')
  16  FORMAT(' ',6F10.3)
 905  FORMAT(' ',6X,'R',10X,'Q',6X,'QPRIME')
 902  FORMAT(3F10.4)
 904  FORMAT(' ',3F10.4)
601   FORMAT('0','BINARY SYSTEM 1-2 IS PARTIALLY MISCIBLE')
 150  FORMAT(' ',6F10.4)
602   FORMAT('0',17X,'COMPONENT MOLECULAR WEIGHTS')
603   FORMAT(' ',11X,'MW1',15X,'MW2',15X,'MW3')
604   FORMAT(' ',8X,F7.3,11X,F7.3,11X,F7.3)
605   FORMAT('0','EXP. TIE LINE DATA IN WEIGHT OR MOLE FRACTION')
606   FORMAT(' ','FIRST DIGIT=COMPONENT',
     ,15X,'SECOND DIGIT=PHASE')
607   FORMAT('0',1X,'TEMP.',7X,'EX11',6X,'EX12',6X,'EX21',
     ,6X,'EX22',6X,'EX31',6X,'EX32')
608   FORMAT('0',20X,'EXP. TIE LINE DATA IN MOLE FRACTION')
609   FORMAT(' ',10X,F8.4,2X,F8.4,2X,F8.4,2X,F8.4,2X,F8.4,
     ,2X,F8.4)
610   FORMAT('0',20X,'CALC. TIE LINE DATA IN MOLE FRACTION')
611   FORMAT('0',13X,'CX11',6X,'CX12',6X,'CX21',6X,'CX22',
     ,6X,'CX31',6X,'CX32')
612   FORMAT('1','DIFFERENCE BETWEEN EXP. AND CALC. MOLE',
     ,1X,'FRACTION')
613   FORMAT('0',2X,'CALC. AND EXP. COMP. DIST. COEFF.',
     ,40X,'PERCENTAGE ERROR IN COMP. DIST. COEFF.')
614   FORMAT('0',5X,'CK1',9X,'CK2',9X,'CK3',9X,'EK1',9X,
     ,'EK2',9X,'EK3',9X,'QD1',9X,'QD2',9X,'QD3')
 12   FORMAT(F8.4,3X,F8.4,2X,F8.4,2X,F8.4,2X,F8.4,2X,F8.4,2X,F8.4)
 27   FORMAT('0',1X,'DIF12',6X,'DIF21',5X,'DIF22',
     ,5X,'DIF31',5X,'DIF32')
 13   FORMAT(F10.4,2X,F10.4,2X,F10.4,2X,F10.4,2X,F10.4,2X,F10.4,
     12X,F10.4,2X,F10.4,2X,F10.4)
```

```
    1  FORMAT(5F10.4)
  999  FORMAT(3F10.2)
    2  FORMAT(I2)
    4  FORMAT(20A4)
    8  FORMAT(1H1,////,T10,20A4)
  650 FORMAT('0',5X,'AVERAGE PERCENTAGE ERROR IN COMP. DIST. COEFF.',
     ,10X,'OVERALL AVERAGE PERCENTAGE ERROR IN DIST. COEFF.')
  651 FORMAT('0',6X,'QD1AVG',12X,'QD2AVG',12X,'QD3AVG',26X,'QDOAVG')
  652 FORMAT('0',6X,F6.1,12X,F6.1,12X,F6.1,26X,F6.1)
C
C
C  THIS PROGRAM CALCULATES TERNARY LIQUID-LIQUID EQUILIBRIUM
C  COMPOSITIONS WITH THE NRTL, LEMF, AND MODIFIED UNIQUAC
C  EQUATION.
C
C
      READ2,IEQN
      READ 2,JK
      READ 2 ,NPOINT
      READ 2,NCOMP
      READ1,AMW1,AMW2,AMW3
      READ 6 ,(SYS(I),I=1,20)
      DO 99 I=1,NPOINT
      READ1,AT(I),AX11(I),AX12(I),AX21(I),AX22(I)
      AX31(I)=1.0-AX11(I)-AX21(I)
   99 AX32(I)=1.0-AX12(I)-AX22(I)
      IF(IEQN.EQ.2)GO TO 900
      GO TO 901
  900 DO 907 I=1,NCOMP
  907 READ902,R(I),Q(I),QP(I)
      PRINT905
      DO 908 I=1,NCOMP
  908 PRINT904,R(I),Q(I),QP(I)
  901 CONTINUE
      DO 450 NT=1,JK
      SUM=0.
      SUM1=0.
      SUM2=0.
      PRINT 8,(SYS(I),I = 1,20)
      PRINT600
      PRINT601
      DO 20 I = 1,NCOMP
C
C  READ BINARY PARAMETERS IN MATRIX FORM. FIRST
C  SUBSCRIPT INDICATES ROW SECOND SUBSCRIPT INDICATES COLUMN
C
      READ 999,(CACTCO(I,J),J = 1,NCOMP)
20    PRINT 999,(CACTCO(I,J),J=1,NCOMP)
      IF(IEQN.EQ.2)GO TO 23
      DO 21 I = 1,NCOMP
C
C  READ ALFA VALUES IN MATIX FORM.  FOR THE LEMF
C  EQUATION ALFA = -1.0
C
      READ 999,(ALFA(I,J),J=1,NCOMP)
   21 PRINT 999,(ALFA(I,J),J=1,NCOMP)
      DO 22 I = 1,NCOMP
      CACTCO(I,I) = 0.0
   22 CONTINUE
   23 CONTINUE
      PRINT602
      PRINT603
      PRINT604,AMW1,AMW2,AMW3
      PRINT605
      PRINT606
      PRINT607
```

```
      DO 17 I=1,NPOINT
   17 PRINT12,AT(I),AX11(I),AX12(I),AX21(I),AX22(I),AX31(I),AX32(I)
      PRINT 608
      DO 19 I=1,NPOINT
      SMF1=(AX11(I)/AMW1)+(AX21(I)/AMW2)+(AX31(I)/AMW3)
      SMF2=(AX12(I)/AMW1)+(AX22(I)/AMW2)+(AX32(I)/AMW3)
      BX11(I)=(AX11(I)/AMW1)/SMF1
      BX31(I)=(AX31(I)/AMW3)/SMF1
      BX21(I)=1.0-BX11(I)-BX31(I)
      BX12(I)=(AX12(I)/AMW1)/SMF2
      BX32(I)=(AX32(I)/AMW3)/SMF2
      BX22(I)=1.0-BX12(I)-BX32(I)
   19 PRINT609,BX11(I),BX12(I),BX21(I),BX22(I),BX31(I),BX32(I)
      PRINT610
      PRINT611
      DO 404 INK=1,NPOINT
      K = 0
      I = 0
C
C  READ THE TEMPERATURE OF THE SYSTEM AND INITIAL GUESSES
C  FOR THE COMPOSITIONS IN EQUILIBRIUM. FIRST SUBSCRIPT
C  INDICATES COMPONENT SECOND SUBSCRIPT INDICATES PHASE
C
      T=AT(INK)
      IF(AT(INK) .LT. -273.2)GO TO 450
      X11=BX11(INK)
      X12=BX12(INK)
      X21=BX21(INK)
      X22=BX22(INK)
      X11REF=X11
      X12REF=X12
      X21REF=X21
      X22REF=X22
      T = 273.2 + T
      DX = 0.00001
      M = 3
      M1 = M+1
      M3 = M+3
      L = 1000
      E = 0.00000000005
      KINC = 0
      MSIGN = 1
  405 CONTINUE
      XT(1) = X12REF
      XT(2) = X21REF
      XT(3) = X22REF
      CALL LSQ2(XT,X,DX,Y,M,M1,M3,L,E)
  101 X11C(INK)=X11
      X12C(INK)=X12
      X21C(INK)=X21
      X22C(INK)=X22
      X31C(INK)=X31
      X32C(INK)=X32
  404  PRINT609,X11C(INK),X12C(INK),X21C(INK),X22C(INK),
     1X31C(INK),X32C(INK)
      PRINT312
      DO 700 I=1,NPOINT
  700  PRINT16,GAM11(I),GAM12(I),GAM21(I),GAM22(I),GAM31(I),
     1GAM32(I)
      PRINT612
      PRINT27
      DO 66 I=1,NPOINT
      DIF12=BX12(I)-X12C(I)
      DIF21=BX21(I)-X21C(I)
      DIF22=BX22(I)-X22C(I)
      DIF31=BX31(I)-X31C(I)
```

```
      DIF32=BX32(I)-X32C(I)
   66 PRINT12,DIF12,DIF21,DIF22,DIF31,DIF32
      PRINT613
      PRINT614
      QD1SUM=0.0
      QD2SUM=0.0
      QD3SUM=0.0
      DO 28 I=1,NPOINT
      IF(X11C(I) .EQ. 0.0)GO TO 30
      CK1=X12C(I)/X11C(I)
      GO TO 31
   30 CK1=-0.0
   31 IF(X21C(I) .EQ. 0.0)GO TO 32
      CK2=X22C(I)/X21C(I)
      GO TO 33
   32 CK2=-0.0
   33 IF(X31C(I) .EQ. 0.0)GO TO 34
      CK3=X32C(I)/X31C(I)
      GO TO 35
   34 CK3=-0.0
   35 IF(BX11(I) .EQ. 0.0)GO TO 37
      EK1=BX12(I)/BX11(I)
      GO TO 38
   37 EK1=-0.0
   38 IF(BX21(I) .EQ. 0.0 )GO TO 39
      EK2=BX22(I)/BX21(I)
      GO TO 40
   39 EK2=-0.0
   40 IF(BX31(I) .EQ. 0.0) GO TO 41
      EK3=BX32(I)/BX31(I)
      GO TO 42
   41 EK3=-0.0
   42 IF(X11C(I) .EQ. 0.0)GO TO 45
      IF(BX11(I) .EQ. 0.0)GO TO 45
      QDF1=(ABS((EK1-CK1)/EK1))*100.0
      QD1SUM=QD1SUM+QDF1
      GO TO 43
   45 QDF1=-0.0
   43 IF(X21C(I) .EQ. 0.0)GO TO 44
      IF(BX21(I) .EQ. 0.0)GO TO 44
      QDF2=(ABS((EK2-CK2)/EK2))*100.0
      QD2SUM=QD2SUM+QDF2
      GO TO 46
   44 QDF2=-0.0
   46 IF(X31C(I) .EQ. 0.0) GO TO 47
      IF(BX31(I) .EQ. 0.0)GO TO 47
      QDF3=(ABS((EK3-CK3)/EK3))*100.0
      QD3SUM=QD3SUM+QDF3
      GO TO 28
   47 QDF3=-0.0
   28 PRINT13,CK1,CK2,CK3,EK1,EK2,EK3,QDF1,QDF2,QDF3
      QD1AVG=QD1SUM/NPOINT
      QD2AVG=QD2SUM/NPOINT
      QD3AVG=QD3SUM/NPOINT
      QD0AVG=(QD1AVG+QD2AVG+QD3AVG)/3.0
      PRINT650
      PRINT651
      PRINT652,QD1AVG,QD2AVG,QD3AVG,QD0AVG
  450 CONTINUE
  500 CONTINUE
      STOP
      END
      SUBROUTINE FN(Y,XT)
      DIMENSION XR(3)
      REAL SUMTXT(3),SUM(3),SUMTT(3)
      REAL L(3),PHI(3),B(3),THETA(3),THETAP(3)
```

```
      DIMENSION CACTCO(3,3),ALFA(3,3),GX(3,2),XT(3),DELX(3)
      DIMENSION TAOU(3,3),GT(3,3),G(3,3),GAMT(5),A(3),W(3),C(3),
     1D(3),CC(3),AA(3),BB(3),GLC(3)
      COMMON/COM1/T,X11,X12,X21,X22,X31,X32,CACTCO,ALFA,
     1NCOMP,YY,IEQN
      COMMON/COM2/R(3),Q(3),QP(3),INK
      COMMON/COM3/GAM11(20),GAM12(20),GAM21(20),GAM22(20),
     1GAM31(20),GAM32(20)
      NFLAG = 0
      XR(1)=X11
      XR(2)=XT(2)
      IF(XR(2).GT.1.0)XR(2)=0.9999999999
      IF(XR(2).LE.0.0)XR(2)=0.00000000001
      IF((X11+XR(2)).GT.1.0)XR(2)=1.0-X11
      XT(2)=XR(2)
      XR(3)=1.0-X11-XR(2)
      IF(XR(3).LE.0.0)XR(3)=0.00000000001
      X21=XR(2)
      X31=XR(3)
      GO TO 40
   30 CONTINUE
      XR(1)=XT(1)
      IF(XR(1).LE.0.0)XR(1)=0.00000000001
      IF(XR(1).GT.1.0)XR(1)=0.9999999999
      XT(1)=XR(1)
      XR(2)=XT(3)
      IF(XR(2).LE.0.0)XR(2)=0.00000000001
      IF(XR(2).GT.1.0)XR(2)=0.9999999999
      IF((XR(1)+XR(2)).GT.1.0)XR(2)=1.0-XR(1)
      XT(3)=XR(2)
      XR(3)=1.0-XR(1)-XR(2)
      IF(XR(3).LE.0.0)XR(3)=0.00000000001
      X12=XR(1)
      X22=XR(2)
      X32=XR(3)
   40 CONTINUE
   60 CONTINUE
C
C     THIS ROUTINE EVALUATES TERNARY GAMMAS USING BINARY CONSTANTS
C     FROM THE NRTL EQUATION.
C
      GMIX = 0.0
      YY = 0.0
      Y = 0.0
      DO 70 I = 1,NCOMP
      DO 70 J = 1,NCOMP
      GT(I,J) = CACTCO(I,J)
   70 CONTINUE
      RT=1.987*T
      IF(IEQN.EQ.2)GO TO 900
      DO 298 I = 1,NCOMP
      DO 298 J = 1,NCOMP
      ALFA(J,J) = 0.
      ALFA(J,I) = ALFA(I,J)
      TAOU(J,I) = (GT(J,I) - GT(I,I))/RT
      G(J,I) = EXP(-ALFA(J,I)*TAOU(J,I))
  298 CONTINUE
      DO 302 I = 1,NCOMP
      CC(I) = 0
      A(I) = 0.
      W(I) = 0.
      DO 301 J = 1,NCOMP
      C(J) = 0
      D(J) = 0
      DO 300 K = 1,NCOMP
      IF(J .GE. 2) GO TO 299
```

```
      A(I) = A(I) + TAOU(K,I)*G(K,I)*XR(K)
      W(I) = W(I) + G(K,I)*XR(K)
  299 C(J) = C(J) +XR(K)*TAOU(K,J)*G(K,J)
      D(J) = D(J) + G(K,J)*XR(K)
  300 CONTINUE
      AA(I) = A(I)/W(I)
      BB(J) = C(J)/D(J)
      CC(I) = CC(I) +((XR(J)*G(I,J))/D(J))*(TAOU(I,J) - BB(J))
  301 CONTINUE
      GLC(I) = AA(I) + CC(I)
      GAMT(I) = EXP(GLC(I))
  302 CONTINUE
      GO TO 911
  900 CONTINUE
C
C   THIS ROUTINE CALCULATES TERNARY GAMMAS WITH THE MODIFIED
C   UNIQUAC EQUATION.
C
      Z=10.0
      DO 77 I=1,NCOMP
      DO 88 J=1,NCOMP
      GT(J,J)=0.0
   88 TAOU(J,I)=EXP(-GT(J,I)/RT)
   77 CONTINUE
      SUMQX=0.0
      SUMRX=0.0
      SUMQPX=0.0
      SUMXL=0.0
      DO 607 I=1,NCOMP
      SUMTXT(I)=0.0
      SUM(I)=0.0
  607 SUMTT(I)=0.0
      DO 600 I=1,NCOMP
      SUMRX=SUMRX+R(I)*XR(I)
      SUMQX=SUMQX+Q(I)*XR(I)
  600 SUMQPX=SUMQPX+QP(I)*XR(I)
      DO 601 I=1,NCOMP
      PHI(I)=(R(I)*XR(I))/SUMRX
      THETA(I)=(Q(I)*XR(I))/SUMQX
      THETAP(I)=(QP(I)*XR(I))/SUMQPX
  601 L(I)=(Z/2.0)*(R(I)-Q(I))-R(I)+1.0
      DO 604 I=1,NCOMP
  604 SUMXL=SUMXL+XR(I)*L(I)
      DO 606 I=1,NCOMP
      DO 606 J=1,NCOMP
  606 SUMTT(I)=SUMTT(I)+THETAP(J)*TAOU(J,I)
      DO 608 J=1,NCOMP
      DO 608 K=1,NCOMP
  608 SUMTXT(J)=SUMTXT(J)+THETAP(K)*TAOU(K,J)
      DO 609 I=1,NCOMP
      DO 609 J=1,NCOMP
  609 SUM(I)=SUM(I)+(THETAP(J)*TAOU(I,J))/SUMTXT(J)
      DO 611 I=1,NCOMP
      AA(I)=ALOG(PHI(I)/XR(I))+(Z/2.0)*Q(I)*ALOG(THETA(I)/PHI(I))
     1+L(I)
      B(I)=-(PHI(I)/XR(I))*SUMXL-QP(I)*ALOG(SUMTT(I))+QP(I)-
     1(QP(I)*SUM(I))
  611 GAMT(I)=EXP(AA(I)+B(I))
  911 CONTINUE
      NFLAG = NFLAG + 1
      DO 100 I=1,NCOMP
      IF(NFLAG.EQ.2)GO TO 150
      GAM11(INK)=GAMT(1)
      GAM21(INK)=GAMT(2)
      GAM31(INK)=GAMT(3)
      GO TO 100
```

```
150   GAM12(INK)=GAMT(1)
      GAM22(INK)=GAMT(2)
      GAM32(INK)=GAMT(3)
 100  GX(I,NFLAG)=XR(I)*GAMT(I)
      IF(NFLAG .LT. 2)GO TO 30
      DELX(1) = X11 - X12
      DELX(2) = X21 - X22
      DELX(3) = X31 - X32
      IF(DELX(1) .EQ. 0.0)DELX(1) = 1.0E-10
      IF(DELX(2) .EQ. 0.0)DELX(2) = 1.0E-10
      IF(DELX(3) .EQ. 0.0)DELX(3) = 1.0E-10
      DO 110 I = 1,NCOMP
      YY = YY + ABS(GX(I,1) - GX(I,2))
      Y = Y + ABS((GX(I,1) - GX(I,2))/DELX(I))
 110  CONTINUE
 500  CONTINUE
      RETURN
      END
      SUBROUTINE LSQ2(XT,X,DX,Y,M,M1,M3,L,E)
      REAL XT(3),X(3,6),Y(4),JJ(3),A(3,3)
      IH=0
      IL=0
      L1C=0
      IF(L.LE.0) GO TO 50
      IHC = M1+1
      EN = M
      EN = EN*1.5
      L1 = L
      L = -L
      L2 = (3*M)/2+5
      K3 = 2
      IF(M.GE.3) K3=3
      K4 = K3-1
      G = K3*2
      G = 1.0/G
      DO 100 I=1,M
100   X(I,1) = XT(I)
      CALL FN(Y(1),XT)
      DO 106 J=2,M1
      XT(J-1) = XT(J-1)+DX
      DO 104 I=1,M
104   X(I,J) = XT(I)
      CALL FN(Y(J),XT)
      XT(J-1) = X(J-1,1)
106   CONTINUE
      L2C = 0
      FLG = 1.0
      GO TO 50
108   L1C = L1C +1
      IF(L1C.GE.L1) GO TO 400
50    YL = 1.0E38
      YH = -YL
      Y2 = YH
      Y3 = YL
      DO 110 J=1,M1
      IF(Y(J).LT.YH) GO TO 1091
      Y2 = YH
      I2 = IH
      YH = Y(J)
      IH = J
      GO TO 109
1091  IF(Y(J).LT.Y2) GO TO 109
      Y2 = Y(J)
      I2 = J
109   IF(Y(J).GT.YL) GO TO 1101
      Y3 = YL
```

```
      I3 = IL
      IL = J
      YL = Y(J)
      GO TO 110
 1101 IF(Y(J).GT.Y3) GO TO 110
      Y3 = Y(J)
      I3 = J
  110 CONTINUE
      L2C = L2C+1
      IF(L2C.LT.L2) GO TO 111
      L2C = 0
      JJ(1) = IL
      JJ(2) = I2
      JJ(3) = I3
      DO 60 K1=1,K3
      J1 = JJ(K1)
      DO 60 K2=K1,K3
      J2 = JJ(K2)
      S = 0.0
      DO 55 I=1,M
   55 S = S+(X(I,J1)-X(I,IH))*(X(I,J2)-X(I,IH))
   60 A(K1,K2) = S
      IF(A(1,1) .EQ. 0.0)A(1,1) = 1.0E-10
      D = A(1,1)*A(2,2)-A(1,2)**2
      GO TO(62,61),K4
   61 D1 = A(1,1)*A(2,3)-A(1,2)*A(1,3)
      D = ((A(1,1)*A(3,3)-A(1,3)**2)*D-D1*D1)/(A(1,1)*9.0)
   62 IF(D .EQ. 0.0)GO TO 65
      IF(D .LE. 0.)D = ABS(D)
      D = (D/4.0)**G
      IF(D.LT.E) GO TO 65
      FLG = 1.0
      GO TO 111
   65 IF(FLG.LT.0.0) GO TO 400
      FLG = -1.0
  111 DO 115 I=1,M
      XT(I) = 0.0
      DO 112 J=1,M1
      IF(J.NE.IH) XT(I) = XT(I)+X(I,J)
  112 CONTINUE
  115 XT(I) = (3.0*XT(I)+X(I,I2)-X(I,IL))/EN-X(I,IH)
  121 CALL FN(YT,XT)
      IF(YT.GE.Y2) GO TO 167
      IHC = M1+1
      IF(YT.GE.YL) GO TO 140
      YTT = YT
      DO 135 I=1,M
  135 XT(I) = 1.5*XT(I)-0.5*X(I,IH)
      CALL FN(YT,XT)
      IF(YT.LE.YL ) GO TO 140
      DO 138 I=1,M
  138 X(I,IH) = (2.0*XT(I)+X(I,IH))/3.0
      Y(IH) = YTT
      GO TO 108
  140 DO 142 I=1,M
  142 X(I,IH) = XT(I)
      Y(IH) = YT
      GO TO 108
  167 IHC = IHC-1
      IF(IHC.EQ.0) GO TO 300
      IF(YT.GE.YH) GO TO 173
      DO 168 I=1,M
      XS = XT(I)
      XT(I) = X(I,IH)
  168 X(I,IH) = XS
  173 DO 174 I=1,M
```

```
174   XT(I)    = 0.75*X(I,IH)+0.25*XT(I)
      CALL FN(YT,XT)
      IF(YT.GT.YH) GO TO 180
      Y(IH) = YT
      DO 175 I=1,M
175   X(I,IH) = XT(I)
      GO TO 108
180   DO 185 J=1,M1
      IF(J.EQ.IL) GO TO 185
      DO 182 I=1,M
      XT(I) = (X(I,J)+X(I,IL))/2.0
182   X(I,J) = XT(I)
      CALL FN(Y(J),XT)
185   CONTINUE
      GO TO 108
300   IHC = 2*M1
      IF(M.GE.3) GO TO 350
      S = 0.0
      DO 302 I=1,M
      X(I,M+2) = X(I,IH)-X(I,IL)
      X(I,M+3) = X(I,IH)-X(I,I3)
302   S = S+X(I,M+2)**2
303   S = SQRT(S)
      IF(S .EQ. 0.0)S = 1.0E-5
304   U = -X(2,M+2)/S
      X(2,M+2) = X(1,M+2)/S
      X(1,M+2) = U
      S = X(1,M+2)*X(1,M+3)+X(2,M+2)*X(2,M+3)
      DO 305 I=1,M
305   X(I,M+2) = X(I,M+2)*S
306   DO 307 I=1,M
307   XT(I) = X(I,IH)+X(I,M+2)
      CALL FN(YT,XT)
      DO 309 I=1,M
309   XT(I) = X(I,IH)-X(I,M+2)
      CALL FN(YTT,XT)
      IF(YTT.LE.YT) GO TO 320
      DO 311 I=1,M
311   XT(I) = X(I,IH)+X(I,M+2)
      YTT = YT
320   Y(IH) = YTT
      DO 321 I=1,M
321   X(I,IH) = XT(I)
      GO TO 108
350   DO 352 I=1,M
      XT(I) = X(I,IH) - X(I,IL)
      X(I,M+2) = X(I,IH) - X(I,I2)
352   X(I,M+3) = X(I,IH) - X(I,I3)
      S = 0.0
      S1 = 0.0
      DO 355 I=1,M
      S = S+XT(I)**2
355   S1 = S1+X(I,M+3)**2
      S  = SQRT(S )
      IF(S .EQ. 0.0)S = 1.0E-5
      S1 = SQRT(S1)
      IF(S1 .EQ. 0.0)S1 = 1.0E-5
      S2 = 0.0
      DO 357 I=1,M
      XT(I) = XT(I)/S
      S2 = S2+XT(I)*X(I,M+2)
357   X(I,M+3) = X(I,M+3)/S1
      DO 360 I=1,M
360   X(I,M+2) = X(I,M+2)-XT(I)*S2
      S1 = 0.0
      DO 362 I=1,M
```

```
362   S1 = S1+X(I,M+2)**2
      S1 = SQRT(S1)
      IF(S1 .EQ. 0.0)S1 = 1.0E-10
      DO 365 I=1,M
365   X(I,M+2) = X(I,M+2)/S1
      S1 = 0.0
      S2 = 0.0
      DO 367 I=1,M
      S1 = S1+XT(I)*X(I,M+3)
367   S2 = S2+X(I,M+2)*X(I,M+3)
      DO 370 I=1,M
370   X(I,M+2) = S*(S1*XT(I)+S2*X(I,M+2)-X(I,M+3))
      GO TO 306
400   S = Y(1)
      Y(1) = Y(IL)
      Y(IL) = S
      DO 402 I=1,M
      XT(I) = X(I,IL)
      X(I,IL) = X(I,1)
402   X(I,1) = XT(I)
      RETURN
      END
```

Output from the Program TLLE

The output from this program contains the following information:

1. All of the input data.
2. Calculated LLE compositions for each component in both phases.
3. Activity coefficients for each component in both phases.
4. Deviation in compositions.
5. Calculated distribution coefficients for each component.
6. Experimental distribution coefficients for each component.
7. Absolute percentage error in distribution coefficients for each component.
8. Average absolute percentage error in distribution coefficients for each component.
9. Overall average absolute percentage error in distribution coefficients.

Dictionary for the Program TLLE

ALFA = α in the NRTL and LEMF equations.

AMW1 = molecular weight of component 1.

AMW2 = molecular weight of component 2.

AMW3 = molecular weight of component 3.

AT = temperature of the LLE system, (C).

AX11 = experimental X_1^I.

AX12 = experimental X_1^{II}.

AX21 = experimental X_2^I.

AX22 = experimental X_2^{II}.

BX11 = experimental X_1^I in mole fraction.

BX12 = experimental X_1^{II} in mole fraction.

BX21 = experimental X_2^I in mole fraction.

BX22 = experimental X_2^{II} in mole fraction.

BX31 = experimental X_3^I in mole fraction.

BX32 = experimental X_3^{II} in mole fraction.

CACTCO = NRTL, LEMF, or UNIQUAC binary parameter, Δg_{ij} or Δu_{ij}.

CK1 = calculated distribution coefficient of component 1.

CK2 = calculated distribution coefficient of component 2.

CK3 = calculated distribution coefficient of component 3.

DIF12 = difference between experimental and calculated X_1^{II}.

DIF21 = difference between experimental and calculated X_2^I.

DIF22 = difference between experimental and calculated X_2^{II}.

DIF31 = difference between experimental and calculated X_3^I.

DIF32 = difference between experimental and calculated X_3^{II}.

EK1 = experimental distribution coefficient of component 1.

EK2 = experimental distribution coefficient of component 2.

EK3 = experimental distribution coefficient of component 3.

GAM11 = γ_1^I.

GAM12 = γ_1^{II}.

GAM21 = γ_2^I.

GAM22 = γ_2^{II}.

GAM31 = γ_3^I.

GAM32 = γ_3^{II}.

IEQN = equation to be run.

JK = number of jobs to be run.

NCOMP = number of components in the LLE system.

NPOINT = number of tie-lines.

Q = parameter q in the UNIQUAC model.

QDF1 = absolute percentage error in distribution coefficients for component 1.

QDF2 = absolute percentage error in distribution coefficients for component 2.

QDF3 = absolute percentage error in distribution coefficients for component 3.

QD1AVG = average of QDF1.

QD2AVG = average of QDF2.

QD3AVG = average of QDF3.

QDOAVG = average of QD1AVG, QD2AVG, and QD3AVG.

QP = parameter q' in the UNIQUAC model.

R = parameter r in the UNIQUAC model.

SYS = system name.

X11C = calculated X_1^I in mole fraction.

X12C = calculated X_1^{II} in mole fraction.

X21C = calculated X_2^I in mole fraction.

X22C = calculated X_2^{II} in mole fraction.

X31C = calculated X_3^I in mole fraction.

X32C = calculated X_3^{II} in mole fraction.

The Program REGRESS-UNIQUAC

The computer program REGRESS-UNIQUAC calculates the binary parameters in the UNIQUAC equation from the binary VLE data. The procedure for using this program is now discussed.

1. Title of the system

Here the title of the system is typed. It should not exceed 60 spaces in lenght. This is typed on line 1 beginning on column 1.

2. How many data points?

To specify the number of VLE data points let IN1 = N (Format I2), where N = number of VLE data points. This is typed on line 2 starting on column 1.

3. Starting values

Now it is necessary to give a starting value for each parameter so that the data regression may be started. It is recommended to use 0.0 as the starting value for both parameters. Therefore, let XST1 = XST2 = 0.0 (Format 2F10.1). This is typed on line 3 beginning on column 1.

4. Read in r, q, and q'

To specify the values of r, q, and q' for each component, type the following (Format 6F10.5):

R1 Q1 Q1PRIM R2 Q2 Q2PRIM

where R1 = r_1

Q1 = q_1

Q1PRIM = q_1'

R2 = r_2

Q2 = q_2

Q2PRIM = q_2'

The first component here must correspond to the first component in the title. This is typed on line 4 starting on column 1.

5. The binary VLE data

To read in the binary VLE data, type the following (Format 4F10.5):

X1 GAMMA1 GAMMA2 TEMP

where X1 = X_1

GAMMA1 = γ_1

GAMMA2 = γ_2

TEMP = T(C)

The first component here must correspond to the first component in the title. This is typed starting on line 5 and column 1. Use one line per data point.

A sample input is given in the next page, followed by a listing of the computer program REGRESS-UNIQUAC.

Sample Input for the Program REGRESS-UNIQUAC

```
ACETONITRILE(1)-BENZENE(2) AT 45 C
12
0.0         0.0
1.87        1.72        1.72        3.19        2.4         2.4
0.0455      2.67        1.01        45.0
0.094       2.33        1.02        45.0
0.183       1.916       1.05        45.0
0.291       1.606       1.11        45.0
0.398       1.41        1.19        45.0
0.507       1.263       1.304       45.0
0.546       1.22        1.354       45.0
0.594       1.174       1.425       45.0
0.7206      1.079       1.677       45.0
0.8145      1.03        1.95        45.0
0.897       1.00        2.3         45.0
0.957       0.99        2.628       45.0
```

```
      REAL XT(2),X(10,13),DX(2),Y(11)
      INTEGER TITLE(60)
      COMMON/COM1/IN1,R1,Q1,Q1PRIM,R2,Q2,Q2PRIM
      COMMON/COM2/X1(40),X2(40),GAMMA1(40),GAMMA2(40),TEMP(40),TK(40)
      COMMON/COM3/G1(40),G2(40),ERROR1(40),ERROR2(40),YY
C
C
C
C
C     THIS IS THE PROGRAM REGRESS-UNIQUAC
C
C
C
C
C     FORMAT STATEMENTS
C
C
  1   FORMAT(60A1)
  2   FORMAT('1','SYSTEM IS  ',60A1)
  5   FORMAT(' ',12X,'U12',9X,'U21',3X,'(STARTING VALUES)')
  4   FORMAT(2F10.1)
  6   FORMAT(' ',5X,F10.1,2X,F10.1)
  7   FORMAT(6F10.5)
  8   FORMAT(' ',6X,'R1',8X,'Q1',6X,'Q1PRIME',5X,'R2',
     18X,'Q2',6X,'Q2PRIME')
 17   FORMAT(' ',3F10.4,F10.2)
  9   FORMAT(' ',6F10.4)
 11   FORMAT(I2)
 12   FORMAT(' ','NUMBER OF DATA POINTS')
 13   FORMAT(' ',9X,I2)
 15   FORMAT(' ',6X,'X1',6X,'G1(EXP)',3X,'G2(EXP)',4X,'T(C)')
 14   FORMAT(4F10.5)
 18   FORMAT(' ',6X,'U12',12X,'U21',3X,'(REGRESSED VALUES)')
 19   FORMAT(' ',F10.1,5X,F10.1)
 20   FORMAT(' ',6X,'X1',6X,'G1(EXP)',3X,'G1(CAL)',3X,
     1'G2(EXP)',3X,'G2(CAL)',3X,'ERROR1(%)',3X,'ERROR2(%)')
 23   FORMAT(' ',2X,'LOOPS USED',7X,'ERROR YY',6X,
     1'ERROR IN REGESSION')
 24   FORMAT(' ',4X,I5,8X,F10.6,10X,F10.7)
 22   FORMAT(' ',5F10.4,F10.1,2X,F10.1)
C
C
C     THIS PROGRAM REGRESSES FOR THE BINARY PARAMETERS IN
C     THE MODIFIED UNIQUAC EQUATION
C
C
      READ1,TITLE
      PRINT2,TITLE
      READ11,IN1
      PRINT12
      PRINT13,IN1
      READ4,XST1,XST2
      PRINT5
      PRINT6,XST1,XST2
      READ7,R1,Q1,Q1PRIM,R2,Q2,Q2PRIM
      PRINT8
```

```
      PRINT9,R1,Q1,Q1PRIM,R2,Q2,Q2PRIM
       DO 10 I=1,IN1
      READ14,X1(I),GAMMA1(I),GAMMA2(I),TEMP(I)
      X2(I)=1.0-X1(I)
10    TK(I)=273.15+TEMP(I)
      PRINT15
      DO 16 I=1,IN1
16    PRINT17,X1(I),GAMMA1(I),GAMMA2(I),TEMP(I)
      XT(1)=XST1
      XT(2)=XST2
      M=2
      M1=M+1
      M3=M+3
      L=1000
      E=0.00005
      DX(1)=50.0
      DX(2)=50.0
      CALL LSQ2(XT,X,DX,Y,M,M1,M3,L,E,L1C,D)
      PRINT18
      PRINT19,XT(1),XT(2)
      PRINT20
      DO 21 K=1,IN1
21    PRINT22,X1(K),GAMMA1(K),G1(K),GAMMA2(K),G2(K),
     1ERROR1(K),ERROR2(K)
      PRINT23
      PRINT24,L1C,YY,D
      STOP
      END
      SUBROUTINE FN(YS,XT)
      REAL L1,L2
      REAL XT(2)
      COMMON/COM1/IN1,R1,Q1,Q1PRIM,R2,Q2,Q2PRIM
      COMMON/COM2/X1(40),X2(40),GAMMA1(40),GAMMA2(40),TEMP(40),
     1TK(40)
      COMMON/COM3/G1(40),G2(40),ERROR1(40),ERROR2(40),YY
      YS=0.0
      Z=10.0
      DO 13 K=1,IN1
      R=1.9872
      L1=(Z/2.0)*(R1-Q1)-(R1-1.0)
      L2=(Z/2.0)*(R2-Q2)-(R2-1.0)
      PHI1=(X1(K)*R1)/(X1(K)*R1+X2(K)*R2)
      PHI2=1.0-PHI1
      THETA1=(X1(K)*Q1)/(X1(K)*Q1+X2(K)*Q2)
      THETA2=1.0-THETA1
      THET1P=(X1(K)*Q1PRIM)/(X1(K)*Q1PRIM+X2(K)*Q2PRIM)
      THET2P=1.0-THET1P
      TAOU12=EXP(-XT(1)/(R*TK(K)))
      TAOU21=EXP(-XT(2)/(R*TK(K)))
      GC1=ALOG(PHI1/X1(K))+(Z/2.0)*Q1*(ALOG(THETA1/PHI1))+
     1PHI2*(L1-(R1*L2/R2))
      GC2=ALOG(PHI2/X2(K))+(Z/2.0)*Q2*(ALOG(THETA2/PHI2))+
     1PHI1*(L2-(R2*L1/R1))
      GR1=-Q1PRIM*(ALOG(THET1P+THET2P*TAOU21))+
     1(THET2P*Q1PRIM)*((TAOU21/(THET1P+THET2P*TAOU21))-
     1(TAOU12/(THET2P+THET1P*TAOU12)))
      GR2=-Q2PRIM*(ALOG(THET2P+THET1P*TAOU12))+
     1(THET1P*Q2PRIM)*((TAOU12/(THET2P+THET1P*TAOU12))-
     1(TAOU21/(THET1P+THET2P*TAOU21)))
      G1(K)=EXP(GC1+GR1)
      G2(K)=EXP(GC2+GR2)
      ERROR1(K)=(ABS((GAMMA1(K)-G1(K))/GAMMA1(K)))*100.0
      ERROR2(K)=(ABS((GAMMA2(K)-G2(K))/GAMMA2(K)))*100.0
      FY1=(ABS((GAMMA1(K)-G1(K))/GAMMA1(K)))**2.0
      FY2=(ABS((GAMMA2(K)-G2(K))/GAMMA2(K)))**2.0
      Y=FY1+FY2
```

```
      YS=YS+Y
   13 CONTINUE
      YS=YS/(2.0*IN1-1.0)
      YS=SQRT(YS)
      YY=YS
      RETURN
      END
      SUBROUTINE LSQ2(XT,X,DX,Y,M,M1,M3,L,E,L1C,D)
      REAL XT(6),X(10,13),JJ(10),A(10,10),DX(6),Y(11)
      IH=0
      IL=0
      L1C = 0
      IF(L.LE.0) GO TO 50
      IHC = M1+1
      EN = M
      EN = EN*1.5
      L1 = L
      L = -L
      L2 = (3*M)/2+5
      K3 = 2
      IF(M.GE.3) K3=3
      K4 = K3-1
      G = K3*2
      G = 1.0/G
      DO 100 I=1,M
  100 X(I,1) = XT(I)
      CALL FN(Y(1),XT)
      DO 106 J=2,M1
      XT(J-1) = XT(J-1)+DX(J-1)
      DO 104 I=1,M
  104 X(I,J) = XT(I)
      CALL FN(Y(J),XT)
      XT(J-1) = X(J-1,1)
  106 CONTINUE
      L2C = 0
      FLG = 1.0
      GO TO 50
  108 L1C = L1C +1
      IF(L1C.GE.L1) GO TO 400
   50 YL = 1.0E38
      YH = -YL
      Y2 = YH
      Y3 = YL
      DO 110 J=1,M1
      IF(Y(J).LT.YH) GO TO 1091
      Y2 = YH
      I2 = IH
      YH = Y(J)
      IH = J
      GO TO 109
 1091 IF(Y(J).LT.Y2) GO TO 109
      Y2 = Y(J)
      I2 = J
  109 IF(Y(J).GT.YL) GO TO 1101
      Y3 = YL
      I3 = IL
      IL = J
      YL = Y(J)
      GO TO 110
 1101 IF(Y(J).GT.Y3) GO TO 110
      Y3 = Y(J)
      I3 = J
  110 CONTINUE
      L2C = L2C+1
      IF(L2C.LT.L2) GO TO 111
      L2C = 0
```

```
      JJ(1) = IL
      JJ(2) = I2
      JJ(3) = I3
      DO 60 K1=1,K3
      J1 = JJ(K1)
      DO 60 K2=K1,K3
      J2 = JJ(K2)
      S = 0.0
      DO 55 I=1,M
 55   S = S+(X(I,J1)-X(I,IH))*(X(I,J2)-X(I,IH))
 60   A(K1,K2) = S
      D = A(1,1)*A(2,2)-A(1,2)**2
      GO TO(62,61),K4
 61   D1 = A(1,1)*A(2,3)-A(1,2)*A(1,3)
      IF (A(1,1).EQ.0.0) A(1,1) =1. E-5
      D = ((A(1,1)*A(3,3)-A(1,3)**2)*D-D1*D1)/(A(1,1)*9.0)
62    IF (D.EQ.0.0) GO TO 65
      IF (D.LE.0.0) D=ABS (D)
      D=(D/4.0)**G
      IF(D.LT.E) GO TO 65
      FLG = 1.0
      GO TO 111
 65   IF(FLG.LT.0.0) GO TO 400
      FLG = -1.0
 111  DO 115 I=1,M
      XT(I) = 0.0
      DO 112 J=1,M1
      IF(J.NE.IH) XT(I) = XT(I)+X(I,J)
 112  CONTINUE
 115  XT(I) = (3.0*XT(I)+X(I,I2)-X(I,IL))/EN-X(I,IH)
 121  CALL FN(YT,XT)
      IF(YT.GE.Y2) GO TO 167
      IHC = M1+1
      IF(YT.GE.YL) GO TO 140
      YTT = YT
      DO 135 I=1,M
 135  XT(I) = 1.5*XT(I)-0.5*X(I,IH)
      CALL FN(YT,XT)
      IF(YT.LE.YL ) GO TO 140
      DO 138 I=1,M
 138  X(I,IH) = (2.0*XT(I)+X(I,IH))/3.0
      Y(IH) = YTT
      GO TO 108
 140  DO 142 I=1,M
 142  X(I,IH) = XT(I)
      Y(IH) = YT
      GO TO 108
 167  IHC = IHC-1
      IF(IHC.EQ.0) GO TO 300
      IF(YT.GE.YH) GO TO 173
      DO 168 I=1,M
      XS = XT(I)
      XT(I) = X(I,IH)
 168  X(I,IH) = XS
 173  DO 174 I=1,M
 174  XT(I)   = 0.75*X(I,IH)+0.25*XT(I)
      CALL FN(YT,XT)
      IF(YT.GT.YH) GO TO 180
      Y(IH) = YT
      DO 175 I=1,M
 175  X(I,IH) = XT(I)
      GO TO 108
 180  DO 185 J=1,M1
      IF(J.EQ.IL) GO TO 185
      DO 182 I=1,M
      XT(I) = (X(I,J)+X(I,IL))/2.0
```

```
 182  X(I,J) = XT(I)
      CALL FN(Y(J),XT)
 185  CONTINUE
      GO TO 108
 300  IHC = 2*M1
      IF(M.GE.3) GO TO 350
      S = 0.0
      DO 302 I=1,M
      X(I,M+2) = X(I,IH)-X(I,IL)
      X(I,M+3) = X(I,IH)-X(I,I3)
 302  S = S+X(I,M+2)**2
 303  S = SQRT(S)
      IF  (S.EQ.0.0) S=1.0 E-5
 304  U = -X(2,M+2)/S
      X(2,M+2) = X(1,M+2)/S
      X(1,M+2) = U
      S=X(1,M+2)*X(1,M+3)+X(2,M+2)*X(2,M+3)
      DO 305 I=1,M
 305  X(I,M+2) = X(I,M+2)*S
 306  DO 307 I=1,M
 307  XT(I) = X(I,IH)+X(I,M+2)
      CALL FN(YT,XT)
      DO 309 I=1,M
 309  XT(I) = X(I,IH)-X(I,M+2)
      CALL FN(YTT,XT)
      IF(YTT.LE.YT) GO TO 320
      DO 311 I=1,M
 311  XT(I) = X(I,IH)+X(I,M+2)
      YTT = YT
 320  Y(IH) = YTT
      DO 321 I=1,M
 321  X(I,IH) = XT(I)
      GO TO 108
 350  DO 352 I=1,M
      XT(I) = X(I,IH) - X(I,IL)
      X(I,M+2) = X(I,IH) - X(I,I2)
 352  X(I,M+3) = X(I,IH) - X(I,I3)
      S = 0.0
      S1 = 0.0
      DO 355 I=1,M
      S = S+XT(I)**2
 355  S1 = S1+X(I,M+3)**2
      S  = SQRT(S )
      S1 = SQRT(S1)
      S2 = 0.0
      DO 357 I=1,M
      IF(S.EQ.0.) S=1.E-5
      XT(I) = XT(I)/S
      S2 = S2+XT(I)*X(I,M+2)
      IF (S1.EQ.0.0)S1=1.0 E-5
 357  X(I,M+3) = X(I,M+3)/S1
      DO 360 I=1,M
 360  X(I,M+2) = X(I,M+2)-XT(I)*S2
      S1 = 0.0
      DO 362 I=1,M
 362  S1 = S1+X(I,M+2)**2
      S1 = SQRT(S1)
      DO 365 I=1,M
      IF (S1.EQ.0.0)S1=1.0 E-5
 365  X(I,M+2) = X(I,M+2)/S1
      S1 = 0.0
      S2 = 0.0
      DO 367 I=1,M
      S1 = S1+XT(I)*X(I,M+3)
 367  S2 = S2+X(I,M+2)*X(I,M+3)
      DO 370 I=1,M
```

```
370   X(I,M+2) = S*(S1*XT(I)+S2*X(I,M+2)-X(I,M+3))
      GO TO 306
400   S = Y(1)
      Y(1) = Y(IL)
      Y(IL) = S
      DO 402 I=1,M
      XT(I) = X(I,IL)
      X(I,IL) = X(I,1)
402   X(I,1) = XT(I)
      RETURN
      END
```

Output From the Program REGRESS-UNIQUAC

The output from this program contains the following information:

1. The input data.
2. Δu_{12} and Δu_{21}.
3. Calculated activity coefficients for each component.
4. Absolute percentage error in activity coefficients for each component.
5. Number of iterations used.
6. Minimum value of the minimization function.
7. Error in the regression.

Dictionary for the Program REGRESS-UNIQUAC

D = error in the regression.

ERROR1 = absolute percentage error in activity coefficients for component 1.

ERROR2 = absolute percentage error in activity coefficients for component 2.

GAMMA1 = experimental activity coefficient of component 1.

GAMMA2 = experimental activity coefficient of component 2.

G1 = calculated activity coefficient of component 1.

G2 = calculated activity coefficient of component 2.

IN1 = number of data points.

LIC = number of iterations used in the regression.

Q1 = q_1.

Q1PRIM = q_1'.

Q2 = q_2.

Q2PRIM = q_2'.

R1 = r_1.

R2 = r_2.

TEMP = temperature, (C).

TITLE = title of the system.

XST1 = starting value for Δu_{12}.

XST2 = starting value for Δu_{21}.

XT(1) = Δu_{12}.

XT(2) = Δu_{21}.

X1 = X_1.

YY = minimum value of the minimization function.

The Program OTILIA-UNIQUAC

The computer program OTILIA-UNIQUAC calculates the binary parameters in the UNIQUAC equation from the mutual solubility data. The procedure for using this program is now discussed.

1. Title of the system

Here the title of the system is specified. It should not exceed 60 spaces in lenght. This is typed on line 1 starting on column 1.

2. Starting values

To begin the regression for Δu_{12} and Δu_{21} it is necessary to specify a starting value for each parameter. It is recommended to use 0.0 as the starting value for both parameters. Therefore, let XST1 = XST2 = 0.0 (Format 2F10.1). This is typed on line 2 starting on column 1.

3. Read in r, q, and q'

To specify the values of r, q, and q' for each component, type the following (Format 6F10.4):

R1 Q1 Q1PRIM R2 Q2 Q2PRIM

where R1 = r_1

Q1 = q_1

Q1PRIM = q_1'

R2 = r_2

$Q2 = q_2$

$Q2PRIM = q_2'$

Note that the first component here must correspond to the first component in the title. This is typed on line 3 starting with column 1.

4. Read in the molecular weights and the temperature

To read in the molecular weights for both components and the temperature of the system, type the following (Format 3F10.2):

MW1 MW2 TEMP

where MW1 = molecular weight of component 1.

MW2 = molecular weight of component 2.

TEMP = temperature, (C).

If the mutual solubility data is in mole fraction let MW1 = MW2 =1.0. This is typed on line 4 starting on column 1.

5. Read in X_1^I

To specify X_1^I let X1(1) = N (Format F10.5), where $N = X_1^I$. This is typed on line 5 starting on column 1.

6. Read in X_1^{II}

To specify X_1^{II} let X1(2) = N (Format F10.5), where $N = X_1^{II}$. This is typed on line 6 starting on column 1.

A sample input is given on the next page, followed by a listing of the computer program OTILIA-UNIQUAC.

Sample Input for the Program OTILIA-UNIQUAC

```
CYCLOHEXANE(1)-NITROMETHANE(2) AT 25 C
0.0         0.0
4.0464      3.24        3.24        2.0086      1.868       1.868
1.0         1.0         25.0
0.9699
0.0375
```

```
      REAL XT(2),X(10,13),DX(2),Y(11)
      REAL MW1,MW2
      INTEGER TITLE(60)
      COMMON/COM1/R1,Q1,Q1PRIM,R2,Q2,Q2PRIM,TK(2)
      COMMON/COM2/X1(2),X2(2),G1(2),G2(2),TEMP,YY
      COMMON/COM3/U12,U21
C
C
C
C
C     THIS IS THE PROGRAM OTILIA-UNIQUAC
C
C
C
C
C     FORMAT STATEMENTS
C
C
  1   FORMAT(60A1)
  2   FORMAT('1','SYSTEM IS   ',60A1)
  8   FORMAT(' ',5X,F10.1,2X,F10.1)
  6   FORMAT(2F10.1)
  7   FORMAT(' ',12X,'U12',9X,'U21',3X,'(STARTING VALUES)')
  11  FORMAT(' ',6F10.4)
  10  FORMAT(' ',6X,'R1',8X,'Q1',6X,'Q1PRIME',5X,'R2',
     18X,'Q2',6X,'Q2PRIME')
  9   FORMAT(6F10.4)
  12  FORMAT(3F10.2)
  13  FORMAT(' ',6X,'MW1',7X,'MW2',6X,'T(C)')
  14  FORMAT(' ',3F10.2)
  16  FORMAT(F10.5)
  17  FORMAT(' ',6X,'U12',12X,'U21',3X,'(REGRESSED VALUES)')
  18  FORMAT(' ',F10.1,5X,F10.1)
  19  FORMAT(' ',6X,'X1',8X,'X2',9X,'GAMMA1',7X,
     1'GAMMA2',7X,'TEMP(C)')
  21  FORMAT(' ',2F10.4,3X,F10.3,3X,F10.3,3X,F10.1)
  23  FORMAT(' ',2X,'LOOPS USED',7X,'ERROR YY',6X,
     1'ERROR IN REGRESSION')
  24  FORMAT(' ',4X,I5,8X,F10.6,10X,F10.7)
C
C
C     THIS PROGRAM USES THE MUTUAL SOLUBILITY DATA TO
C     OBTAIN THE BINARY PARAMETERS IN THE MODIFIED
C     UNIQUAC EQUATION
C
C
      READ1,TITLE
      PRINT2,TITLE
      READ6,XST1,XST2
      PRINT7
      PRINT8,XST1,XST2
      READ9,R1,Q1,Q1PRIM,R2,Q2,Q2PRIM
      PRINT10
      PRINT11,R1,Q1,Q1PRIM,R2,Q2,Q2PRIM
      READ12,MW1,MW2,TEMP
      PRINT13
      PRINT14,MW1,MW2,TEMP
```

```
      DO 15 I=1,2
      TK(I)=273.15+TEMP
      READ16,X1(I)
      X2(I)=1.0-X1(I)
      X1(I)=X1(I)/MW1
      X2(I)=X2(I)/MW2
      X1(I)=X1(I)/(X1(I)+X2(I))
15    X2(I)=1.0-X1(I)
      XT(1)=XST1
      XT(2)=XST2
      M=2
      M1=M+1
      M3=M+3
      L=1000
      E=0.0001
      DX(1)=50.0
      DX(2)=50.0
      CALL LSQ2(XT,X,DX,Y,M,M1,M3,L,E,L1C,D)
      PRINT17
      PRINT18,U12,U21
      PRINT19
      DO 20 J=1,2
20    PRINT21,X1(J),X2(J),G1(J),G2(J),TEMP
      PRINT23
      PRINT24,L1C,YY,D
      STOP
      END
      SUBROUTINE FN(YS,XT)
      REAL XT(2)
      REAL L1,L2
      COMMON/COM1/R1,Q1,Q1PRIM,R2,Q2,Q2PRIM,TK(2)
      COMMON/COM2/X1(2),X2(2),G1(2),G2(2),TEMP,YY
      COMMON/COM3/U12,U21
      DIMENSION ACT1(2),ACT2(2)
      Z=10.0
      R=1.9872
      DO 13 K=1,2
      L1=(Z/2.0)*(R1-Q1)-(R1-1.0)
      L2=(Z/2.0)*(R2-Q2)-(R2-1.0)
      PHI1=(X1(K)*R1)/(X1(K)*R1+X2(K)*R2)
      PHI2=1.0-PHI1
      THETA1=(X1(K)*Q1)/(X1(K)*Q1+X2(K)*Q2)
      THETA2=1.0-THETA1
      THET1P=(X1(K)*Q1PRIM)/(X1(K)*Q1PRIM+X2(K)*Q2PRIM)
      THET2P=1.0-THET1P
      TAOU12=EXP(-XT(1)/(R*TK(K)))
      TAOU21=EXP(-XT(2)/(R*TK(K)))
      GC1=ALOG(PHI1/X1(K))+(Z/2.0)*Q1*(ALOG(THETA1/PHI1))+
     1PHI2*(L1-(R1*L2/R2))
      GC2=ALOG(PHI2/X2(K))+(Z/2.0)*Q2*(ALOG(THETA2/PHI2))+
     1PHI1*(L2-(R2*L1/R1))
      GR1=-Q1PRIM*(ALOG(THET1P+THET2P*TAOU21))+
     1(THET2P*Q1PRIM)*((TAOU21/(THET1P+THET2P*TAOU21))-
     1(TAOU12/(THET2P+THET1P*TAOU12)))
      GR2=-Q2PRIM*(ALOG(THET2P+THET1P*TAOU12))+
     1(THET1P*Q2PRIM)*((TAOU12/(THET2P+THET1P*TAOU12))-
     1(TAOU21/(THET1P+THET2P*TAOU21)))
      G1(K)=EXP(GC1+GR1)
      G2(K)=EXP(GC2+GR2)
      ACT1(K)=X1(K)*G1(K)
13    ACT2(K)=X2(K)*G2(K)
      FY1=(ABS(ACT1(1)-ACT1(2)))**2.0
      FY2=(ABS(ACT2(1)-ACT2(2)))**2.0
      YS=FY1+FY2
      YS=SQRT(YS/2.0)
      YY=YS
```

```
      U12=XT(1)
      U21=XT(2)
      RETURN
      END
      SUBROUTINE LSQ2(XT,X,DX,Y,M,M1,M3,L,E,L1C,D)
      REAL XT(2),X(2,5),JJ(3),A(3,3),DX(2),Y(3)
      IH=0
      IL=0
      L1C = 0
      IF(L.LE.0) GO TO 50
      IHC = M1+1
      EN = M
      EN = EN*1.5
      L1 = L
      L = -L
      L2 = (3*M)/2+5
      K3 = 2
      IF(M.GE.3) K3=3
      K4 = K3-1
      G = K3*2
      G = 1.0/G
      DO 100 I=1,M
100   X(I,1) = XT(I)
      CALL FN(Y(1),XT)
      DO 106 J=2,M1
      XT(J-1) = XT(J-1)+DX(J-1)
      DO 104 I=1,M
104   X(I,J) = XT(I)
      CALL FN(Y(J),XT)
      XT(J-1) = X(J-1,1)
106   CONTINUE
      L2C = 0
      FLG = 1.0
      GO TO 50
108   L1C = L1C +1
      IF(L1C.GE.L1) GO TO 400
50    YL = 1.0E38
      YH = -YL
      Y2 = YH
      Y3 = YL
      DO 110 J=1,M1
      IF(Y(J).LT.YH) GO TO 1091
      Y2 = YH
      I2 = IH
      YH = Y(J)
      IH = J
      GO TO 109
1091  IF(Y(J).LT.Y2) GO TO 109
      Y2 = Y(J)
      I2 = J
109   IF(Y(J).GT.YL) GO TO 1101
      Y3 = YL
      I3 = IL
      IL = J
      YL = Y(J)
      GO TO 110
1101  IF(Y(J).GT.Y3) GO TO 110
      Y3 = Y(J)
      I3 = J
110   CONTINUE
      L2C = L2C+1
      IF(L2C.LT.L2) GO TO 111
      L2C = 0
      JJ(1) = IL
      JJ(2) = I2
      JJ(3) = I3
```

```
      DO 60 K1=1,K3
      J1 = JJ(K1)
      DO 60 K2=K1,K3
      J2 = JJ(K2)
      S = 0.0
      DO 55 I=1,M
 55   S = S+(X(I,J1)-X(I,IH))*(X(I,J2)-X(I,IH))
 60   A(K1,K2) = S
      D = A(1,1)*A(2,2)-A(1,2)**2
      GO TO(62,61),K4
 61   D1 = A(1,1)*A(2,3)-A(1,2)*A(1,3)
      IF (A(1,1).EQ.0.0) A(1,1) =1. E-5
      D = ((A(1,1)*A(3,3)-A(1,3)**2)*D-D1*D1)/(A(1,1)*9.0)
 62   IF (D.EQ.0.0) GO TO 65
      IF (D.LE.0.0) D=ABS (D)
      D=(D/4.0)**G
      IF(D.LT.E) GO TO 65
      FLG = 1.0
      GO TO 111
 65   IF(FLG.LT.0.0) GO TO 400
      FLG = -1.0
 111  DO 115 I=1,M
      XT(I) = 0.0
      DO 112 J=1,M1
      IF(J.NE.IH) XT(I) = XT(I)+X(I,J)
 112  CONTINUE
 115  XT(I) = (3.0*XT(I)+X(I,I2)-X(I,IL))/EN-X(I,IH)
 121  CALL FN(YT,XT)
      IF(YT.GE.Y2) GO TO 167
      IHC = M1+1
      IF(YT.GE.YL) GO TO 140
      YTT = YT
      DO 135 I=1,M
 135  XT(I) = 1.5*XT(I)-0.5*X(I,IH)
      CALL FN(YT,XT)
      IF(YT.LE.YL ) GO TO 140
      DO 138 I=1,M
 138  X(I,IH) = (2.0*XT(I)+X(I,IH))/3.0
      Y(IH) = YTT
      GO TO 108
 140  DO 142 I=1,M
 142  X(I,IH) = XT(I)
      Y(IH) = YT
      GO TO 108
 167  IHC = IHC-1
      IF(IHC.EQ.0) GO TO 300
      IF(YT.GE.YH) GO TO 173
      DO 168 I=1,M
      XS = XT(I)
      XT(I) = X(I,IH)
 168  X(I,IH) = XS
 173  DO 174 I=1,M
 174  XT(I)   = 0.75*X(I,IH)+0.25*XT(I)
      CALL FN(YT,XT)
      IF(YT.GT.YH) GO TO 180
      Y(IH) = YT
      DO 175 I=1,M
 175  X(I,IH) = XT(I)
      GO TO 108
 180  DO 185 J=1,M1
      IF(J.EQ.IL) GO TO 185
      DO 182 I=1,M
      XT(I) = (X(I,J)+X(I,IL))/2.0
 182  X(I,J) = XT(I)
      CALL FN(Y(J),XT)
 185  CONTINUE
```

```
      GO TO 108
  300 IHC = 2*M1
      IF(M.GE.3) GO TO 350
      S = 0.0
      DO 302 I=1,M
      X(I,M+2) = X(I,IH)-X(I,IL)
      X(I,M+3) = X(I,IH)-X(I,I3)
  302 S = S+X(I,M+2)**2
  303 S = SQRT(S)
      IF  (S.EQ.0.0) S=1.0 E-5
  304 U = -X(2,M+2)/S
      X(2,M+2) = X(1,M+2)/S
      X(1,M+2) = U
      S=X(1,M+2)*X(1,M+3)+X(2,M+2)*X(2,M+3)
      DO 305 I=1,M
  305 X(I,M+2) = X(I,M+2)*S
  306 DO 307 I=1,M
  307 XT(I) = X(I,IH)+X(I,M+2)
      CALL FN(YT,XT)
      DO 309 I=1,M
  309 XT(I) = X(I,IH)-X(I,M+2)
      CALL FN(YTT,XT)
      IF(YTT.LE.YT) GO TO 320
      DO 311 I=1,M
  311 XT(I) = X(I,IH)+X(I,M+2)
      YTT = YT
  320 Y(IH) = YTT
      DO 321 I=1,M
  321 X(I,IH) = XT(I)
      GO TO 108
  350 DO 352 I=1,M
      XT(I) = X(I,IH) - X(I,IL)
      X(I,M+2) = X(I,IH) - X(I,I2)
  352 X(I,M+3) = X(I,IH) - X(I,I3)
      S = 0.0
      S1 = 0.0
      DO 355 I=1,M
      S = S+XT(I)**2
  355 S1 = S1+X(I,M+3)**2
      S  = SQRT(S )
      S1 = SQRT(S1)
      S2 = 0.0
      DO 357 I=1,M
      IF(S.EQ.0.) S=1.E-5
      XT(I) = XT(I)/S
      S2 = S2+XT(I)*X(I,M+2)
      IF (S1.EQ.0.0)S1=1.0 E-5
  357 X(I,M+3) = X(I,M+3)/S1
      DO 360 I=1,M
  360 X(I,M+2) = X(I,M+2)-XT(I)*S2
      S1 = 0.0
      DO 362 I=1,M
  362 S1 = S1+X(I,M+2)**2
      S1 = SQRT(S1)
      DO 365 I=1,M
      IF (S1.EQ.0.0)S1=1.0 E-5
  365 X(I,M+2) = X(I,M+2)/S1
      S1 = 0.0
      S2 = 0.0
      DO 367 I=1,M
      S1 = S1+XT(I)*X(I,M+3)
  367 S2 = S2+X(I,M+2)*X(I,M+3)
      DO 370 I=1,M
  370 X(I,M+2) = S*(S1*XT(I)+S2*X(I,M+2)-X(I,M+3))
      GO TO 306
  400 S = Y(1)
```

```
      Y(1) = Y(IL)
      Y(IL) = S
      DO 402 I=1,M
      XT(I) = X(I,IL)
      X(I,IL) = X(I,1)
402   X(I,1) = XT(I)
      RETURN
      END
```

Output From the Program OTILIA-UNIQUAC

The output of this program contains the following information:

1. Input data.
2. Δu_{12} and Δu_{21}.
3. Calculated activity coefficients for each component in both phases.
4. Number of iterations used in the regression.
5. The minimum value of the minimization function.
6. The error in the regression.

Dictionary for the Program OTILIA-UNIQUAC

D = error in the regression.

G1(1) = γ_1^I.

G1(2) = γ_1^{II}.

G2(1) = γ_2^I.

G2(2) = γ_2^{II}.

L1C = number of iterations used in the regression.

MW1 = molecular weight of component 1.

MW2 = molecular weight of component 2.

Q1 = q_1.

Q1PRIM = q_1'.

Q2 = q_2.

Q2PRIM = q_2'.

R1 = r_1.

R2 = r_2.

TEMP = temperature, (C).

TITLE = title of the system.

U12 = Δu_{12}.

U21 = Δu_{21}.

XST1 = starting value for Δu_{12}.

XST2 = starting value for Δu_{21}.

X1(1) = X_1^I.

X1(2) = X_1^{II}.

X2(1) = X_2^I.

X2(2) = X_2^{II}.

YY = minimum value of the minimization function.

The Program TREG

The computer program TREG calculates the binary parameters in the NRTL, LEMF, and UNIQUAC equations from LLE data alone, or from binary VLE data plus ternary LLE data together. The procedure for using this program is now discussed.

1. Which equation?

To specify the NRTL or the LEMF equations let IEQN = 01 (Format I2). To specify the UNIQUAC equation let IEQN = 02 (Format I2). This is typed on line 1 starting on column 1.

2. System title

Here the title of the system is typed. The title should not be more than 60 spaces in lenght. The 1-2 binary must be the partially miscible binary.

3. How many runs, how many tie-lines, and which method?

If one is interested in running NTIMES jobs (where NTIMES = 1, 2, 3, and 4) for a system that has NTIE tie-lines, and want to run Method NOPT first (where NOPT = 2, 3, 4, and 5), type the following (Format 3I2):

NTIMES NTIE NOPT

where NTIMES = number of jobs to be run

NTIE = number of tie-lines

NOPT = method to be run first

This is typed on line 3 starting on column 1. With this program one can only use a particular equation at a time. Whenever using Method I, NTIMES must be set equal to 01.

4. Temperature of the LLE system

To read in the temperature of the LLE system, type the following (Format F10.3):

TEMP3

where TEMP3 = temperature of the LLE system, (C). This is typed on line 4 starting on column 1.

5. How many binary VLE data points?

To specify the number of binary VLE data points for the 1-3 and 2-3 binaries, type the following (Format 2I2):

IN1 IN2

where IN1 = number of VLE data points for the 1-3 binary.

IN2 = number of VLE data points for the 2-3 binary

This is typed on line 5 starting on column 1.

6. α_{13} and α_{23}

If using the NRTL or LEMF equations, the value of α_{13} and α_{23} must be specified. This is done by typing the following (Format 2F10.4):

ALFA13 ALFA23

This is typed on line 6 starting on column 1.

7. r, q, and q'

If using the UNIQUAC equation we must specify r, q, and q' for each component. The order of the components here must correspond to that used in the title. This is done by typing for each component the following (Format 3F10.4):

R Q QP

where R = r

Q = q

QP = q'

This is typed on lines 6, 7, and 8, starting on column 1. Use one line for each component.

8. VLE data for the 1-3 binary

To read in the VLE data for the 1-3 binary, type the following (Format 4F10.3):

X1 GAMMA1 GAMMA2 TEMP1

where X1 = X_1

GAMMA1 = experimental activity coefficient of component 1.

GAMMA2 = experimental activity coefficient of component 3

TEMP1 = temperature of the binary system, (C).

The binary 1-3 system here is the same as the binary 1-3 in the title. This is typed starting on column 1. Use one line per data point.

9. VLE data for the 2-3 binary

To read in the VLE data for the 2-3 binary system, type the following (Format 4F10.3):

X3 GAMMA3 GAMMA4 TEMP2

where X3 = X_2

GAMMA3 = experimental activity coefficient of component 2

GAMMA4 = experimental activity coefficient of component 3

TEMP2 = temperature of the binary system, (C)

The binary 2-3 system here is the same as the binary 2-3 in the title. This is typed starting on column 1. Use one line per data point.

10. Starting values

Here it is necessary to specify a starting value for each parameter in the 1-3 and 2-3 binaries. This is done by typing the following (Format 4F10.2):

XST1 XST2 XST3 XST4

where XST1 = starting value for Δg_{13} or Δu_{13}

XST2 = starting value for Δg_{31} or Δu_{31}

XST3 = starting value for Δg_{23} or Δu_{23}

XST4 = starting value for Δg_{32} or Δu_{32}

This is typed starting on column 1.

11. The LLE data (for Method I only)

To type in the LLE data for Method I, type the following (Format 5F10.4):

X11 X12 X21 X22 DC

where X11 = X_1^I

X12 = X_1^{II}

X21 = X_2^I

X22 = X_2^{II}

DC = K_3^∞

This is typed starting on column 1.

12. The LLE data (for Methods II through V)

To type in the LLE data for Methods II through V, type the following (Format 7F10.4):

X11 X12 X21 X22 DC1 DC2 DC

where X11 = X_1^I

X12 = X_1^{II}

X21 = X_2^I

X22 = X_2^{II}

DC1 = experimental distribution coefficient of component 1

DC2 = experimental distribution coefficient of component 2

DC = experimental distribution coefficient of component 3

This is typed beginning on column 1. Do not include the mutual solubility data. Use one line per data point.

13. α_{12}, Δg_{12}, Δg_{21}

If the NRTL or the LEMF equation is being used, one has to specify α_{12}, Δg_{12}, and Δg_{21}, as obtained from the mutual solubility data. This is done by typing the following (Format 3F10.2):

ALFA12 G12 G21

where ALFA12 = α_{12}

G12 = Δg_{12}

G21 = Δg_{21}

This is typed starting on column 1.

14. Δu_{12} and Δu_{21}

If using the UNIQUAC equation one has to specify Δu_{12} and Δu_{21} as obtained from the mutual solubility data. This is done by typing the following (Format 2F10.2):

G12 G21

where G12 = Δu_{12}

G21 = Δu_{21}

This is typed beginning on column 1.

A sample input is given in the next page, followed by a listing of the computer program TREG.

Sample Input for the Program TREG

```
01
WATER(1)-N-PROPYL ACETATE(2)-ACETONE(3) AT 30 C
010804
30.0
0912
0.3         0.3
0.9667      1.11        4.966       30.0
0.928       1.158       4.69        30.0
0.883       1.072       4.031       30.0
0.829       1.272       3.244       30.0
0.764       1.202       2.713       30.0
0.682       1.616       2.093       30.0
0.58        1.579       1.718       30.0
0.446       1.421       1.429       30.0
0.263       2.528       1.127       30.0
0.04        1.271       0.976       57.7
0.155       1.227       1.021       59.3
0.255       1.128       0.998       62.8
0.39        1.099       1.029       63.3
0.445       1.063       1.028       68.6
0.495       1.039       1.025       70.5
0.595       1.047       1.075       72.2
0.725       1.054       1.094       78.7
0.785       1.036       1.129       83.3
0.855       1.016       1.129       88.7
0.915       1.009       1.147       93.2
0.97        1.012       1.182       98.2
-500.0      -500.0      -500.0      -500.0
0.9843      0.0935      0.0037      0.892       0.095       242.15      1.211
0.9772      0.1012      0.0037      0.8438      0.1036      225.42      2.852
0.9678      0.0997      0.004       0.8121      0.103       202.63      3.139
0.9542      0.1176      0.0053      0.7131      0.1233      134.27      4.194
0.9303      0.1412      0.0062      0.6151      0.1518      99.305      3.036
0.9144      0.1718      0.0085      0.511       0.1879      59.774      4.119
0.8197      0.2846      0.0205      0.3102      0.3472      15.147      2.536
0.8003      0.3236      0.0247      0.2611      0.4044      10.578      2.373
0.2         3002.8      556.8
```

```
      REAL XT(6),X(10,13),DX(6),Y(11)
      INTEGER TITLE(60)
      COMMON/COM1/ALFA13,ALFA23
      COMMON/COM2/ERROR1(40),ERROR2(40),ERROR3(40),ERROR4(40)
      COMMON/COM3/IN1,IN2,IEQN,R(3),Q(3),QP(3)
      COMMON/COM4/X1(40),X2(40),X3(40),X4(40)
      COMMON/COM5/GAMMA1(40),GAMMA2(40),GAMMA3(40),GAMMA4(40)
      COMMON/COM6/X11(40),X12(40),X21(40),X22(40),X31(40),X32(40)
      COMMON/COM7/TK1(40),G1(40),G2(40),TK2(40),G3(40),G4(40)
      COMMON/COM8/ALFA12,G12,G21,TK3,DC(40)
      COMMON/COM9/YY,QQ1,QQ2,Q3(40)
      COMMON/COM10/G5(40),G6(40),DCC(40),NTIE
      COMMON/COM11/NOPT,G7(20),G8(20),G9(20),G10(20),DCC1(20),DCC2(20)
      COMMON/COM12/Q4(20),Q5(20),DC1(20),DC2(20)
      COMMON/COM13/EGAM,QDBAR
C
C
C
C
C
C
C     THIS IS THE PROGRAM TREG
C
C
C
C
C
C     THIS PROGRAM REGRESSES FOR THE BINARY PARAMETERS IN
C     THE NRTL, LEMF, AND MODIFIED UNIQUAC EQUATION.
C
C
C
C
C
C
C
C          FORMAT STATEMENTS FOR THE MAIN PROGRAM
C
C
  360 FORMAT(' ',5X,7F10.4)
  911 FORMAT(2F10.2)
  910 FORMAT(' ',2F10.2)
  909 FORMAT(' ',5X,'G12',7X,'G21',3X,
     1'AS OBTAINED FROM THE MUTUAL SOLUBILITY DATA')
  900 FORMAT(I2)
  905 FORMAT(' ',6X,'R',10X,'Q',6X,'QPRIME')
  904 FORMAT(3F10.4)
  906 FORMAT(' ',3F10.4)
  701 FORMAT(' ','EXP.',6X,'X11',7X,'X12',7X,'X21',7X,'X22',7X,
     1'X31',7X,'X32',8X,'K3',2X,'K3=X32/X31')
  102 FORMAT(' ',6F10.2)
    1 FORMAT(60A1)
    2 FORMAT('1','SYSTEM   ',60A1)
    3 FORMAT(' ',17X,I2,50X,I2)
   55 FORMAT(2I2)
   17 FORMAT(2F10.4)
   18 FORMAT(4F10.2)
    8 FORMAT(5F10.4)
```

```
   16  FORMAT(' ',9F10.3,2X,3F10.1)
   13  FORMAT(' ',F10.6)
   15  FORMAT(' ',3F10.3,2X,F10.1)
    10 FORMAT(F10.3)
    19 FORMAT(3F10.2)
   89  FORMAT(7F10.4)
  100 FORMAT(' ',I4,20X,F10.6)
  300 FORMAT(' ','1ST CHARACTER= # OF OPTIONS',5X,
     1'2ND CHARACTER= # OF TIE-LINES',5X,'3RD CHARACTER= OPTION #')
  301 FORMAT(' ','TEMPERATURE(C) OF THE LLE SYSTEM')
  302 FORMAT(' ','FIRST CHARACTER= # OF VLE POINTS FOR 1-3 BINARY',
     18X,'SECOND CHARACTER= FOR THE 2-3 BINARY')
  303 FORMAT(' ','ALFA13       ALFA23')
  304 FORMAT(' ',5X,'G13',7X,'G31',7X,'G23',7X,'G32',2X,
     1'(STARTING VALUES)')
  305 FORMAT(' ','EXP.',6X,'X11',7X,'X12',7X,'X21',7X,'X22',7X,
     1'X31',7X,'X32',8X,'K1',8X,'K2',8X,'K3',2X,'K1=X12/X11')
  306 FORMAT(' ',10X,'ALFA12',5X,'G12',7X,'G21',2X,
     1'AS OBTAINED FROM THE MUTUAL SOLUBILITY DATA')
  307 FORMAT(' ',5X,'G13',7X,'G31',7X,'G23',7X,'G32',7X,'G12',
     17X,'G21',2X,'(REGRESSED VALUES)')
  308 FORMAT(' ',8X,'X1(EXP)',6X,'G1(EXP)',3X,'G1(CAL)',3X,'G2(EXP)',
     13X,'G2(CAL)',5X,'%ERRORG1',3X,'%ERRORG2',2X,'FOR THE 1-3 BINARY'
     1)
  309 FORMAT(' ','REGRESSION ERROR IN GAMMA FOR THE 1-3 BINARY')
  310 FORMAT(' ',9X,'X1(EXP)',6X,'G1(EXP)',3X,'G1(CAL)',3X,'G2(EXP)',
     13X,'G2(CAL)',5X,'%ERRORG1',3X,'%ERRORG2',2X,'FOR THE 2-3 BINARY'
     1)
  311 FORMAT(' ','REGRESSION ERROR IN GAMMA FOR THE 2-3 BINARY')
  312 FORMAT(' ',5X,'GAM11',5X,'GAM12',5X,'GAM21',5X,'GAM22',5X,
     1'GAM31',5X,'GAM32',6X,'KC1',7X,'KC2',7X,'KC3',10X,'QD1',7X,
     1'QD2',7X,'QD3')
  313 FORMAT(' ','ERROR YY')
  380 FORMAT(' ',5X,9F10.4)
  322 FORMAT(' ',5X,F10.1)
  323 FORMAT(' ',F5.2,9X,F5.2)
  328 FORMAT(' ',4F10.2)
  333 FORMAT(' ',5X,'GAM31',5X,'GAM32',6X,'KC3',10X,'QD3')
  379 FORMAT(' ',5X,3F10.1)
  389 FORMAT(' ',5X,F10.4,2X,4F10.3,2X,2F10.1)
  320 FORMAT(' ',10X,I2,37X,I2,30X,I2)
  321 FORMAT(3I2)
  314 FORMAT(' ','NUMBER OF LOOPS USED.  ERROR IN REGRESSION')
  315 FORMAT(' ',5X,'G13',7X,'G31',7X,'G23',7X,'G32',2X,
     1'(REGRESSED VALUES)')
  777 FORMAT(' ','AVERAGE PERCENTAGE ERROR IN BINARY GAMMAS')
  778 FORMAT(' ',13X,F10.1)
  779 FORMAT(' ','AVERAGE PERCENTAGE ERROR IN DIST. COEFF.')
C
C          THIS IS THE MAIN PROGRAM
C
C
C
      NCOMP=3
      READ900,IEQN
      READ1,TITLE
      PRINT2,TITLE
      PRINT 300
      READ321,NTIMES,NTIE,NOPT
      PRINT320,NTIMES,NTIE,NOPT
      PRINT301
      READ10,TEMP3
      PRINT322,TEMP3
      PRINT 302
      TK3=273.15+TEMP3
      READ55,IN1,IN2
```

```
      PRINT3,IN1,IN2
      IF(IEQN.EQ.2)GO TO 901
      PRINT303
      READ17,ALFA13,ALF423
      PRINT323,ALFA13,ALFA23
      GO TO 902
  901 PRINT905
      DO 903 I=1,NCOMP
      READ904,R(I),Q(I),QP(I)
  903 PRINT906,R(I),Q(I),QP(I)
  902 PRINT304
      DO 4 K=1,IN1
      READ18,X1(K),GAMMA1(K),GAMMA2(K),TEMP1
      TK1(K)=273.15+TEMP1
    4 X2(K)=1.0-X1(K)
      DO 6 KK=1,IN2
      READ18,X3(KK),GAMMA3(KK),GAMMA4(KK),TEMP2
      TK2(KK)=273.15+TEMP2
    6 X4(KK)=1.0-X3(KK)
      READ18,XST1,XST2,XST3,XST4
      PRINT328,XST1,XST2,XST3,XST4
      IF(NOPT.EQ.1)GO TO 700
      PRINT305
      GO TO 702
  700 PRINT701
  702 DO 41 I=1,NTIE
      IF(NOPT.GE.2)GO TO 205
      READ8,X11(I),X12(I),X21(I),X22(I),DC(I)
      GO TO 202
  205 READ89,X11(I),X12(I),X21(I),X22(I),DC1(I),DC2(I),DC(I)
  202 X31(I)=1.0-X11(I)-X21(I)
      X32(I)=1.0-X12(I)-X22(I)
      IF(X31(I).EQ.0.0)X31(I)=1.0E-20
      IF(X32(I).EQ.0.0)X32(I)=1.0E-20
      IF(NOPT.GE.2)GO TO 203
      PRINT360,X11(I),X12(I),X21(I),X22(I),X31(I),X32(I),DC(I)
      GO TO 41
  203 PRINT380,X11(I),X12(I),X21(I),X22(I),X31(I),X32(I),DC1(I),DC2(I)
     1,DC(I)
   41 CONTINUE
      IF(IEQN.EQ.2)GO TO 907
      PRINT306
      READ19,ALFA12,G12,G21
      PRINT379,ALFA12,G12,G21
      GO TO 908
  907 READ911,G12,G21
      PRINT909
      PRINT910,G12,G21
  908 DO 9 I=1,NTIMES
      M=4
      L=1000
      E=0.0005
      IF(I.EQ.1)GO TO 500
      PRINT2,TITLE
      NOPT=NOPT+1
  500 IF(NOPT.EQ.4)M=NOPT+2
      IF(NOPT.EQ.5)M=NOPT+1
      M1=M+1
      M3=M+3
      DO 27 II=1,M
   27 DX(II)=10.0
      XT(1)=XST1
      XT(2)=XST2
      XT(3)=XST3
      XT(4)=XST4
      IF(NOPT.GT.3)XT(5)=G12
```

```
      IF(NOPT.GT.3)XT(6)=G21
      CALL LSQ2(XT,X,DX,Y,M,M1,M3,L,E,L1C,D)
      IF(NOPT.GT.3)GO TO 101
      PRINT315
      PRINT328,XT(1),XT(2),XT(3),XT(4)
      GO TO 103
  101 PRINT307
      PRINT102,XT(1),XT(2),XT(3),XT(4),XT(5),XT(6)
  103 PRINT308
      DO 11 J=1,IN1
   11 PRINT389,X1(J),GAMMA1(J),G1(J),GAMMA2(J),G2(J),ERROR1
     1(J),ERROR2(J)
      PRINT309
      PRINT13,QQ1
      PRINT310
      DO 14 JJ=1,IN2
   14 PRINT389,X3(JJ),GAMMA3(JJ),G3(JJ),GAMMA4(JJ),G4(JJ),
     1ERROR3(JJ),ERROR4(JJ)
      PRINT311
      PRINT13,QQ2
      IF(NOPT.EQ.1)GO TO 200
      PRINT312
      GO TO 201
  200 PRINT333
      DO 42 LL=1,NTIE
   42 PRINT15,G5(LL),G6(LL),DCC(LL),Q3(LL)
      GO TO 400
  201 DO 43 LL=1,NTIE
   43 PRINT16,G7(LL),G8(LL),G9(LL),G10(LL),G5(LL),G6(LL),DCC1(LL),
     1DCC2(LL),DCC(LL),Q4(LL),Q5(LL),Q3(LL)
  400 PRINT313
      PRINT13,YY
      PRINT777
      PRINT778,EGAM
      PRINT779
      PRINT778,QDBAR
      PRINT314
    9 PRINT100,L1C,D
      STOP
      END
      SUBROUTINE FN(YS,XT)
      REAL XT(6)
      REAL SUMTXT(3),SUM(3),SUMTT(3)
      REAL PHI(3),B(3),THETA(3),THETAP(3)
      REAL L(3),L1,L2
      COMMON/COM1/ALFA13,ALFA23
      COMMON/COM2/ERROR1(40),ERROR2(40),ERROR3(40),ERROR4(40)
      COMMON/COM3/IN1,IN2,IEQN,R(3),Q(3),QP(3)
      COMMON/COM4/X1(40),X2(40),X3(40),X4(40)
      COMMON/COM5/GAMMA1(40),GAMMA2(40),GAMMA3(40),GAMMA4(40)
      COMMON/COM6/X11(40),X12(40),X21(40),X22(40),X31(40),X32(40)
      COMMON/COM7/TK1(40),G1(40),G2(40),TK2(40),G3(40),G4(40)
      COMMON/COM8/ALFA12,G12,G21,TK3,DC(40)
      COMMON/COM9/YY,QQ1,QQ2,Q3(40)
      COMMON/COM10/G5(40),G6(40),DCC(40),NTIE
      COMMON/COM11/NOPT,G7(20),G8(20),G9(20),G10(20),DCC1(20),DCC2(20)
      COMMON/COM12/Q4(20),Q5(20),DC1(20),DC2(20)
      COMMON/COM13/EGAM,QDBAR
      DIMENSION TAOU(3,3),ALFA(3,3),GT(3,3),G(3,3),GAMT(6),
     1A(3),W(3)
      DIMENSION C(3),D(3),CC(3),AA(3),BB(3),GLC(6),XR(6)
C
C
C
C
C
```

```
C           THIS IS THE SUBROUTINE FN
C
C
C
C
C
      YTIE=0.
      NCOMP=3
      EGAM1=0.0
      EGAM2=0.0
      QQBAR=0.0
      QQ1=0.0
      QQ2=0.0
      DO 270 J=1,NTIE
      Q3(J)=0.0
      Q4(J)=0.0
  270 Q5(J)=0.0
      DO 30 I=1,IN1
      IF(IEQN.EQ.2)GO TO 900
      TAU13=XT(1)/(TK1(I)*1.9872)
      TAU31=XT(2)/(TK1(I)*1.9872)
      G13=EXP(-ALFA13*TAU13)
      G31=EXP(-ALFA13*TAU31)
      S01=X1(I)+X2(I)*G31
      S02=X2(I)+X1(I)*G13
      S1=G31/S01
      S2=G13/S02
      S1S=S1**2.0
      S2S=S2**2.0
      S44=X2(I)**2.0*(TAU31*S1S+TAU13*G13/S02**2.0)
      G1(I)=EXP(S44)
      S55=X1(I)**2.0*(TAU13*S2S+TAU31*G31/S01**2.0)
      G2(I)=EXP(S55)
      GO TO 901
  900 Z=10.0
      R1=R(1)
      Q1=Q(1)
      Q1PRIM=QP(1)
      R2=R(3)
      Q2=Q(3)
      Q2PRIM=QP(3)
      L1=(Z/2.0)*(R1-Q1)-(R1-1.0)
      L2=(Z/2.0)*(R2-Q2)-(R2-1.0)
      PHI1=(X1(I)*R1)/(X1(I)*R1+X2(I)*R2)
      PHI2=1.0-PHI1
      THETA1=(X1(I)*Q1)/(X1(I)*Q1+X2(I)*Q2)
      THETA2=1.0-THETA1
      THET1P=(X1(I)*Q1PRIM)/(X1(I)*Q1PRIM+X2(I)*Q2PRIM)
      THET2P=1.0-THET1P
      TAOU12=EXP(-XT(1)/(1.9872*TK1(I)))
      TAOU21=EXP(-XT(2)/(1.9872*TK1(I)))
      GC1=ALOG(PHI1/X1(I))+(Z/2.0)*Q1*(ALOG(THETA1/PHI1))+
     1PHI2*(L1-(R1*L2/R2))
      GC2=ALOG(PHI2/X2(I))+(Z/2.0)*Q2*(ALOG(THETA2/PHI2))+
     1PHI1*(L2-(R2*L1/R1))
      GR1=-Q1PRIM*(ALOG(THET1P+THET2P*TAOU21))+
     1(THET2P*Q1PRIM)*((TAOU21/(THET1P+THET2P*TAOU21))-
     1(TAOU12/(THET2P+THET1P*TAOU12)))
      GR2=-Q2PRIM*(ALOG(THET2P+THET1P*TAOU12))+
     1(THET1P*Q2PRIM)*((TAOU12/(THET2P+THET1P*TAOU12))-
     1(TAOU21/(THET1P+THET2P*TAOU21)))
      G1(I)=EXP(GC1+GR1)
      G2(I)=EXP(GC2+GR2)
  901 ERROR1(I)=(ABS((GAMMA1(I)-G1(I))/GAMMA1(I)))*100.0
      ERROR2(I)=(ABS((GAMMA2(I)-G2(I))/GAMMA2(I)))*100.0
      EGAM1=EGAM1+ERROR1(I)+ERROR2(I)
      YY1=(ABS((GAMMA1(I)-G1(I))/GAMMA1(I)))**2+(ABS((GAMMA2(I)-
```

```
     1G2(I))/GAMMA2(I)))**2
  30  GQ1=GQ1+YY1
      EGAM1=EGAM1/(2*IN1)
      GQ1=GQ1/IN1
      DO 31 I=1,IN2
      IF(IEQN.EQ.2)GO TO 903
      TAU23=XT(3)/(TK2(I)*1.9872)
      TAU32=XT(4)/(TK2(I)*1.9872)
      G23=EXP(-ALFA23*TAU23)
      G32=EXP(-ALFA23*TAU32)
      S03=X3(I)+X4(I)*G32
      S04=X4(I)+X3(I)*G23
      S3=G32/S03
      S4=G23/S04
      S3S=S3**2.0
      S4S=S4**2.0
      S66=X4(I)**2.0*(TAU32*S3S+TAU23*G23/S04**2.0)
      G3(I)=EXP(S66)
      S77=X3(I)**2.0*(TAU23*S4S+TAU32*G32/S03**2.0)
      G4(I)=EXP(S77)
      GO TO 904
 903  CONTINUE
      R1=R(2)
      Q1=Q(2)
      Q1PRIM=QP(2)
      R2=R(3)
      Q2=Q(3)
      Q2PRIM=QP(3)
      L1=(Z/2.0)*(R1-Q1)-(R1-1.0)
      L2=(Z/2.0)*(R2-Q2)-(R2-1.0)
      PHI1=(X3(I)*R1)/(X3(I)*R1+X4(I)*R2)
      PHI2=1.0-PHI1
      THETA1=(X3(I)*Q1)/(X3(I)*Q1+X4(I)*Q2)
      THETA2=1.0-THETA1
      THET1P=(X3(I)*Q1PRIM)/(X3(I)*Q1PRIM+X4(I)*Q2PRIM)
      THET2P=1.0-THET1P
      TAOU12=EXP(-XT(3)/(1.9872*TK2(I)))
      TAOU21=EXP(-XT(4)/(1.9872*TK2(I)))
      GC1=ALOG(PHI1/X3(I))+(Z/2.0)*Q1*(ALOG(THETA1/PHI1))+
     1PHI2*(L1-(R1*L2/R2))
      GC2=ALOG(PHI2/X4(I))+(Z/2.0)*Q2*(ALOG(THETA2/PHI2))+
     1PHI1*(L2-(R2*L1/R1))
      GR1=-Q1PRIM*(ALOG(THET1P+THET2P*TAOU21))+
     1(THET2P*Q1PRIM)*((TAOU21/(THET1P+THET2P*TAOU21))-
     1(TAOU12/(THET2P+THET1P*TAOU12)))
      GR2=-Q2PRIM*(ALOG(THET2P+THET1P*TAOU12))+
     1(THET1P*Q2PRIM)*((TAOU12/(THET2P+THET1P*TAOU12))-
     1(TAOU21/(THET1P+THET2P*TAOU21)))
      G3(I)=EXP(GC1+GR1)
      G4(I)=EXP(GC2+GR2)
 904  ERROR3(I)=(ABS((GAMMA3(I)-G3(I))/GAMMA3(I)))*100.0
      ERROR4(I)=(ABS((GAMMA4(I)-G4(I))/GAMMA4(I)))*100.0
      EGAM2=EGAM2+ERROR3(I)+ERROR4(I)
      YY2=(ABS((GAMMA3(I)-G3(I))/GAMMA3(I)))**2+(ABS((GAMMA4(I)-
     1G4(I))/GAMMA4(I)))**2
  31  GQ2=GQ2+YY2
      EGAM2=EGAM2/(2*IN2)
      EGAM=(EGAM1+EGAM2)/2.0
      GQ2=GQ2/IN2
      IF(NOPT.EQ.3)GQ1=0.0
      IF(NOPT.EQ.3)GQ2=0.0
      IF(NOPT.EQ.4)GQ1=0.0
      IF(NOPT.EQ.4)GQ2=0.0
      DO 45 I=1,NCOMP
      GT(I,I)=0.0
  45  CONTINUE
```

```
      GT(1,2)=G12
      GT(2,1)=G21
      IF(NOPT.GT.3)GT(1,2)=XT(5)
      IF(NOPT.GT.3)GT(2,1)=XT(6)
      GT(1,3)=XT(1)
      GT(3,1)=XT(2)
      GT(2,3)=XT(3)
      GT(3,2)=XT(4)
      DO 133 NT=1,NTIE
      NFLAG=0
      XR(1)=X11(NT)
      XR(2)=X21(NT)
      XR(3)=X31(NT)
      GO TO 40
3     CONTINUE
      XR(1)=X12(NT)
      XR(2)=X22(NT)
      XR(3)=X32(NT)
40    CONTINUE
      RT=1.9872*TK3
      IF(IEQN.EQ.2)GO TO 905
      ALFA(1,1)=0.0
      ALFA(1,2)=ALFA12
      ALFA(2,1)=ALFA12
      ALFA(2,2)=0.0
      ALFA(3,3)=0.0
      ALFA(1,3)=ALFA13
      ALFA(3,1)=ALFA13
      ALFA(2,3)=ALFA23
      ALFA(3,2)=ALFA23
C
C   THIS ROUTINE CALCULATES TERNARY GAMMAS WITH THE NRTL
C   AND LENF EQUATION.
C
      DO 298 I=1,NCOMP
      DO 298 J=1,NCOMP
      TAOU(J,I)=(GT(J,I)-GT(I,I))/RT
      G(J,I)=EXP(-ALFA(J,I)*TAOU(J,I))
298   CONTINUE
      DO 302 I=1,NCOMP
      CC(I)=0
      A(I)=0.
      W(I)=0.
      DO 301 J=1,NCOMP
      C(J)=0
      D(J)=0
      DO 300 K=1,NCOMP
      IF(J.GE.2)GO TO 299
      A(I)=A(I)+TAOU(K,I)*G(K,I)*XR(K)
      W(I)=W(I)+G(K,I)*XR(K)
299   C(J)=C(J)+XR(K)*TAOU(K,J)*G(K,J)
      D(J)=D(J)+G(K,J)*XR(K)
300   CONTINUE
      AA(I)=A(I)/W(I)
      BB(J)=C(J)/D(J)
      CC(I)=CC(I)+((XR(J)*G(I,J))/D(J))*(TAOU(I,J)-BB(J))
301   CONTINUE
      GLC(I)=AA(I)+CC(I)
      GAMT(I)=EXP(GLC(I))
302   CONTINUE
      GO TO 906
C
C   THIS ROUTINE CALCULATES TERNARY GAMMAS WITH THE MODIFIED
C   UNIQUAC EQUATION.
C
 905  Z=10.0
```

```
      DO 77 I=1,NCOMP
      DO 88 J=1,NCOMP
      GT(J,J)=0.0
   88 TAOU(J,I)=EXP(-GT(J,I)/RT)
   77 CONTINUE
      SUMQX=0.0
      SUMRX=0.0
      SUMQPX=0.0
      SUMXL=0.0
      DO 607 I=1,NCOMP
      SUMTXT(I)=0.0
      SUM(I)=0.0
  607 SUMTT(I)=0.0
      DO 600 I=1,NCOMP
      SUMRX=SUMRX+R(I)*XR(I)
      SUMQX=SUMQX+Q(I)*XR(I)
  600 SUMQPX=SUMQPX+QP(I)*XR(I)
      DO 601 I=1,NCOMP
      PHI(I)=(R(I)*XR(I))/SUMRX
      THETA(I)=(Q(I)*XR(I))/SUMQX
      THETAP(I)=(QP(I)*XR(I))/SUMQPX
  601 L(I)=(Z/2.0)*(R(I)-Q(I))-R(I)+1.0
      DO 604 I=1,NCOMP
  604 SUMXL=SUMXL+XR(I)*L(I)
      DO 606 I=1,NCOMP
      DO 606 J=1,NCOMP
  606 SUMTT(I)=SUMTT(I)+THETAP(J)*TAOU(J,I)
      DO 608 J=1,NCOMP
      DO 608 K=1,NCOMP
  608 SUMTXT(J)=SUMTXT(J)+THETAP(K)*TAOU(K,J)
      DO 609 I=1,NCOMP
      DO 609 J=1,NCOMP
  609 SUM(I)=SUM(I)+(THETAP(J)*TAOU(I,J))/SUMTXT(J)
      DO 611 I=1,NCOMP
      AA(I)=ALOG(PHI(I)/XR(I))+(Z/2.0)*Q(I)*ALOG(THETA(I)/PHI(I))
     1+L(I)
      B(I)=-(PHI(I)/XR(I))*SUMXL-QP(I)*ALOG(SUMTT(I))+QP(I)-
     1(QP(I)*SUM(I))
  611 GAMT(I)=EXP(AA(I)+B(I))
  906 NFLAG=NFLAG+1
      IF(NFLAG.GT.1)GO TO 800
      G5(NT)=GAMT(3)
      G7(NT)=GAMT(1)
      G9(NT)=GAMT(2)
      GO TO 3
  800 G6(NT)=GAMT(3)
      G8(NT)=GAMT(1)
      G10(NT)=GAMT(2)
      DCC(NT)=G5(NT)/G6(NT)
      DCC1(NT)=G7(NT)/G8(NT)
      DCC2(NT)=G9(NT)/G10(NT)
      Q3(NT)=(ABS((DC(NT)-DCC(NT))/DC(NT)))*100.0
      Q6=(ABS((DC(NT)-DCC(NT))/DC(NT)))**2.0
      IF(NOPT.EQ.1)GO TO 801
      Q4(NT)=(ABS((DC1(NT)-DCC1(NT))/DC1(NT)))*100.0
      Q5(NT)=(ABS((DC2(NT)-DCC2(NT))/DC2(NT)))*100.0
      Q7=(ABS((DC1(NT)-DCC1(NT))/DC1(NT)))**2.0
      Q8=(ABS((DC2(NT)-DCC2(NT))/DC2(NT)))**2.0
      QDBAR=QDBAR+Q3(NT)+Q4(NT)+Q5(NT)
      GO TO 133
  801 Q4(NT)=0.0
      Q5(NT)=0.0
      Q7=0.0
      Q8=0.0
      QDBAR=Q3(NT)
  133 YTIE=YTIE+Q6+Q7+Q8
```

```
      QDBAR=QDBAR/(3*NTIE)
      IF(NOPT.EQ.1)QDBAR=QDBAR*3.0
      YY=(YTIE/NTIE)+QQ1+QQ2
      YS=YY
      RETURN
      END
      SUBROUTINE LSQ2(XT,X,DX,Y,M,M1,M3,L,E,L1C,D)
      REAL XT(6),X(6,9),JJ(3),A(3,3),DX(6),Y(7)
      IH=0
      IL=0
      L1C = 0
      IF(L.LE.0) GO TO 50
      IHC = M1-1
      EN = M
      EN = EN*1.5
      L1 = L
      L = -L
      L2 = (3*M)/2+5
      K3 = 2
      IF(M.GE.3) K3=3
      K4 = K3-1
      G = K3*2
      G = 1.0/G
      DO 100 I=1,M
100   X(I,1) = XT(I)
      CALL FN(Y(1),XT)
      DO 106 J=2,M1
      XT(J-1) = XT(J-1)+DX(J-1)
      DO 104 I=1,M
104   X(I,J) = XT(I)
      CALL FN(Y(J),XT)
      XT(J-1) = X(J-1,1)
106   CONTINUE
      L2C = 0
      FLG = 1.0
      GO TO 50
108   L1C = L1C +1
      IF(L1C.GE.L1) GO TO 400
50    YL = 1.0E38
      YH = -YL
      Y2 = YH
      Y3 = YL
      DO 110 J=1,M1
      IF(Y(J).LT.YH) GO TO 1091
      Y2 = YH
      I2 = IH
      YH = Y(J)
      IH = J
      GO TO 109
1091  IF(Y(J).LT.Y2) GO TO 109
      Y2 = Y(J)
      I2 = J
109   IF(Y(J).GT.YL) GO TO 1101
      Y3 = YL
      I3 = IL
      IL = J
      YL = Y(J)
      GO TO 110
1101  IF(Y(J).GT.Y3) GO TO 110
      Y3 = Y(J)
      I3 = J
110   CONTINUE
      L2C = L2C+1
      IF(L2C.LT.L2) GO TO 111
      L2C = 0
      JJ(1) = IL
```

```
      JJ(2) = I2
      JJ(3) = I3
      DO 60 K1=1,K3
      J1 = JJ(K1)
      DO 60 K2=K1,K3
      J2 = JJ(K2)
      S = 0.0
      DO 55 I=1,M
 55   S = S+(X(I,J1)-X(I,IH))*(X(I,J2)-X(I,IH))
 60   A(K1,K2) = S
      D = A(1,1)*A(2,2)-A(1,2)**2
      GO TO(62,61),K4
 61   D1 = A(1,1)*A(2,3)-A(1,2)*A(1,3)
      IF (A(1,1).EQ.0.0) A(1,1) =1. E-5
      D = ((A(1,1)*A(3,3)-A(1,3)**2)*D-D1*D1)/(A(1,1)*9.0)
 62   IF (D.EQ.0.0) GO TO 65
      IF (D.LE.0.0) D=ABS (D)
      D=(D/4.0)**G
      IF(D.LT.E) GO TO 65
      FLG = 1.0
      GO TO 111
 65   IF(FLG.LT.0.0) GO TO 400
      FLG = -1.0
 111  DO 115 I=1,M
      XT(I) = 0.0
      DO 112 J=1,M1
      IF(J.NE.IH) XT(I) = XT(I)+X(I,J)
 112  CONTINUE
 115  XT(I) = (3.0*XT(I)+X(I,I2)-X(I,IL))/EN-X(I,IH)
 121  CALL FN(YT,XT)
      IF(YT.GE.Y2) GO TO 167
      IHC = M1+1
      IF(YT.GE.YL) GO TO 140
      YTT = YT
      DO 135 I=1,M
 135  XT(I) = 1.5*XT(I)-0.5*X(I,IH)
      CALL FN(YT,XT)
      IF(YT.LE.YL ) GO TO 140
      DO 138 I=1,M
 138  X(I,IH) = (2.0*XT(I)+X(I,IH))/3.0
      Y(IH) = YTT
      GO TO 108
 140  DO 142 I=1,M
 142  X(I,IH) = XT(I)
      Y(IH) = YT
      GO TO 108
 167  IHC = IHC-1
      IF(IHC.EQ.0) GO TO 300
      IF(YT.GE.YH) GO TO 173
      DO 168 I=1,M
      XS = XT(I)
      XT(I) = X(I,IH)
 168  X(I,IH) = XS
 173  DO 174 I=1,M
 174  XT(I)   = 0.75*X(I,IH)+0.25*XT(I)
      CALL FN(YT,XT)
      IF(YT.GT.YH) GO TO 180
      Y(IH) = YT
      DO 175 I=1,M
 175  X(I,IH) = XT(I)
      GO TO 108
 180  DO 185 J=1,M1
      IF(J.EQ.IL) GO TO 185
      DO 182 I=1,M
      XT(I) = (X(I,J)+X(I,IL))/2.0
 182  X(I,J) = XT(I)
```

```
      CALL FN(Y(J),XT)
  185 CONTINUE
      GO TO 108
  300 INC = 2*M1
      IF(M.GE.3) GO TO 350
      S = 0.0
      DO 302 I=1,M
      X(I,M+2) = X(I,IH)-X(I,IL)
      X(I,M+3) = X(I,IH)-X(I,I3)
  302 S = S+X(I,M+2)**2
  303 S = SQRT(S)
      IF  (S.EQ.0.0) S=1.0 E-5
  304 U = -X(2,M+2)/S
      X(2,M+2) = X(1,M+2)/S
      X(1,M+2) = U
      S=X(1,M+2)*X(1,M+3)+X(2,M+2)*X(2,M+3)
      DO 305 I=1,M
  305 X(I,M+2) = X(I,M+2)*S
  306 DO 307 I=1,M
  307 XT(I) = X(I,IH)+X(I,M+2)
      CALL FN(YT,XT)
      DO 309 I=1,M
  309 XT(I) = X(I,IH)-X(I,M+2)
      CALL FN(YTT,XT)
      IF(YTT.LE.YT) GO TO 320
      DO 311 I=1,M
  311 XT(I) = X(I,IH)+X(I,M+2)
      YTT = YT
  320 Y(IH) = YTT
      DO 321 I=1,M
  321 X(I,IH) = XT(I)
      GO TO 108
  350 DO 352 I=1,M
      XT(I) = X(I,IH) - X(I,IL)
      X(I,M+2) = X(I,IH) - X(I,I2)
  352 X(I,M+3) = X(I,IH) - X(I,I3)
      S = 0.0
      S1 = 0.0
      DO 355 I=1,M
      S = S+XT(I)**2
  355 S1 = S1+X(I,M+3)**2
      S  = SQRT(S )
      S1 = SQRT(S1)
      S2 = 0.0
      DO 357 I=1,M
      IF(S.EQ.0.) S=1.E-5
      XT(I) = XT(I)/S
      S2 = S2+XT(I)*X(I,M+2)
      IF (S1.EQ.0.0)S1=1.0 E-5
  357 X(I,M+3) = X(I,M+3)/S1
      DO 360 I=1,M
  360 X(I,M+2) = X(I,M+2)-XT(I)*S2
      S1 = 0.0
      DO 362 I=1,M
  362 S1 = S1+X(I,M+2)**2
      S1 = SQRT(S1)
      DO 365 I=1,M
      IF (S1.EQ.0.0)S1=1.0 E-5
  365 X(I,M+2) = X(I,M+2)/S1
      S1 = 0.0
      S2 = 0.0
      DO 367 I=1,M
      S1 = S1+XT(I)*X(I,M+3)
  367 S2 = S2+X(I,M+2)*X(I,M+3)
      DO 370 I=1,M
  370 X(I,M+2) = S*(S1*XT(I)+S2*X(I,M+2)-X(I,M+3))
```

```
      GO TO 306
400   S = Y(1)
      Y(1) = Y(IL)
      Y(IL) = S
      DO 402 I=1,M
      XT(I) = X(I,IL)
      X(I,IL) = X(I,1)
402   X(I,1) = XT(I)
      RETURN
      END
```

Output From the Program TREG

The output of this program contains the following information:

1. Input data.
2. The regressed parameters.
3. Calculated binary activity coefficients for each component in the 1-3 and 2-3 binaries.
4. Absolute percentage error in binary activity coefficients for each component in the 1-3 and 2-3 binaries.
5. Standard deviation in binary activity coefficients for the 1-3 and 2-3 binaries.
6. Calculated ternary activity coefficients for each component in both phases.
7. Calculated distribution coefficients for each component.
8. Absolute percentage error in distribution coefficients for each component.
9. Overall average absolute percentage error in distribution coefficients for all three components.
10. Overall average absolute percentage error in binary activity coefficients.
11. Number of iterations used in the regression.
12. Minimum value of the minimization function.
13. Error in the regression.

Dictionary for the Program TREG

ALFA12 = α_{12}.

ALFA13 = α_{13}.

ALFA23 = α_{23}.

D = error in the regression.

DCC1 = calculated distribution coefficient of component 1.

DCC2 = calculated distribution coefficient of component 2.

DCC = calculated distribution coefficient of component 3.

DC1 = experimental distribution coefficient of component 1.

DC2 = experimental distribution coefficient of component 2.

DC = experimental distribution coefficient of component 3.

EGAM = overall average absolute percentage error in binary activity coefficients.

ERROR1= absolute percentage error in binary activity coefficients for component 1 in the 1-3 binary system.

ERROR2 = absolute percentage error in binary activity coefficients for component 3 in the 1-3 binary system.

ERROR3 = absolute percentage error in binary activity coefficients for component 2 in the 2-3 binary system.

ERROR4 = absolute percentage error in binary activity coefficients for component 3 in the 2-3 binary system.

G1 = calculated binary activity coefficients for component 1 in the 1-3 binary system.

G2 = calculated binary activity coefficients for component 3 in the 1-3 binary system.

G3 = calculated binary activity coefficients for component 2 in the 2-3 binary system.

G4 = calculated binary activity coefficients for component 3 in the 2-3 binary system.

G5 = γ_3^I.

G6 = γ_3^{II}.

G7 = γ_1^I.

G8 = γ_1^{II}.

G9 = γ_2^I.

G10 = γ_2^{II}.

G12 = Δg_{12} or Δu_{12}, from the mutual solubility data.

G21 = Δg_{21} or Δu_{21}, from the mutual solubility data.

GAMMA1 = experimental activity coefficient of component 1 in the 1-3 binary system.

GAMMA2 = experimental activity coefficient of component 3 in the 1-3 binary system.

GAMMA3 = experimental activity coefficient of component 2 in the 2-3 binary system.

GAMMA4 = experimental activity coefficient of component 3 in the 2-3 binary system.

IEQN = equation to be used.

IN1 = number of VLE data points for the 1-3 binary system.

IN2 = number of VLE data points for the 2-3 binary system.

L1C = number of iterations used in the regression.

NTIMES = number of jobs to be run.

NTIE = number of tie-lines.

NOPT = Method to be used.

Q = q in the UNIQUAC model.

QP = q' in the UNIQUAC model.

QQ1 = standard deviation in activity coefficient for the 1-3 binary system.

QQ2 = standard deviation in activity coefficient for the 2-3 binary system.

Q4 = absolute percentage error in distribution coefficients for component 1.

Q5 = absolute percentage error in distribution coefficients for component 2.

Q3 = absolute percentage error in distribution coefficients for component 3.

QDBAR = average of Q3, Q4, and Q5.

R = r in the UNIQUAC model.

TEMP1 = temperature of the 1-3 binary system, (C).

TEMP2 = temperature of the 2-3 binary system, (C).

TEMP3 = temperature of the LLE system, (C).

TITLE = title of the system.

X1 = X_1 for the 1-3 binary system.

X2 = X_3 for the 1-3 binary system.

X3 = X_2 for the 2-3 binary system.

X4 = X_3 for the 2-3 binary system.

X11 = X_1^I.

X12 = X_1^{II}.

X21 = X_2^I.

X22 = X_2^{II}.

X31 = X_3^I.

X32 = X_3^{II}.

XST1 = starting value for Δg_{13} or Δu_{13}.

XST2 = starting value for Δg_{31} or Δu_{31}.

XST3 = starting value for Δg_{23} or Δu_{23}.

XST4 = starting value for Δg_{32} or Δu_{32}.

XT(1) = Δg_{13} or Δu_{13}.

XT(2) = Δg_{31} or Δu_{31}.

XT(3) = Δg_{23} or Δu_{23}.

XT(4) = Δg_{32} or Δu_{32}.

XT(5) = Δg_{12} or Δu_{12}.

XT(6) = Δg_{21} or Δu_{21}.

YY = minimum value of the minimization function.

NOMENCLATURE

A_p = positive area in the "area test".

A_n = negative area in the "area test".

c_H = constant in the Hand correlation.

C.I. = consistency index.

F = degrees of freedom.

$\hat{f}_i$ = fugacity of component i in the mixture.

f_i^o = standard state fugacity of component i.

G = average absolute percentage error in binary activity coefficients for the 1-3 and 2-3 binary systems.

$\bar{G}_1$, $\bar{G}_2$ = average absolute percentage error in binary activity coefficients for the 1-3 and 2-3 binary systems, respectively.

G_{ij} = see equation (1-1).

g_{ij} = NRTL or LEMF parameter.

$\Delta g_{ij} = (g_{ij} - g_{jj})$.

h^e = excess enthalpy of the liquid mixture.

$K = X^{II}/X^{I}$, distribution coefficient.

k_H = constant in the Hand correlation.

L = number of VLE data points for the 2-3 binary system.

l_j = see equation (1-3).

M = number of VLE data points for the 1-3 binary system.

N = number of ternary tie-lines.

n = number of components.

P = pressure.

Q = average absolute percentage error in distribution coefficients for components 1, 2, and 3.

$\bar{Q}_i$ = average absolute percentage error in distribution coefficients for component i.

q, q' = surface parameters in the UNIQUAC model.

R = gas constant.

r = size parameter in the UNIQUAC model.

T = absolute temperature.

T_{ij} = see equation (1-1).

u_{ij} = UNIQUAC parameter.

$\Delta u_{ij} = (u_{ij} - u_{jj})$.

v^e = excess volume of the liquid mixture.

X = liquid phase mole fraction.

z = liquid phase coordination number.

Greek Letters

α = nonrandomness parameter in the NRTL model.

γ = activity coefficient.

ϕ = number of phases.

Φ = segment fraction in the UNIQUAC model.

θ, θ' = area fraction in the UNIQUAC model.

τ_{ij} = see equation (1-3).

Superscripts

cal = calculated value.

e = excess value.

exp = experimental value.

I, II = liquid phases I and II, respectively.

o = standard state value.

∞ = infinite dilution value.

$\frown$ = value for a mixture.

$\overline{}$ = average value.

Subscripts

i = component i.

j = component j.

k = component k.

l = component l.

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