ABSTRACT

Title of Thesis: Prediction of Vapor-Liquid Equilibrium From Ternary Liquid-Liquid Equilibrium Data

David Kim Yee, Master of Science, 1982

Thesis directed by: Dimitrios Tassios, Professor of Chemical Engineering

Reasonable estimates of ternary vapor-liquid equilibrium can be obtained by using the corresponding liquid-liquid equilibrium (LLE) data with the NRTL, LEMF and UNIQUAC models. The overall average absolute deviation in vapor phase concentration for seven such systems is 0.028. Use of the UNIFAC method gives erratic predictions suggesting caution when applied to such systems. Combination, however, of the LLE data and the UNIFAC method gives the best results with a deviation of 0.020 Prediction of binary VLE behavior from LLE data yields also reasonably good results.

PREDICTION OF VAPOR-LIQUID EQUILIBRIUM FROM TERNARY LIQUID-LIQUID EQUILIBRIUM DATA

by
David Kim Yee

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
1982

APPROVAL SHEET

Title of Thesis: Prediction of Vapor-Liquid Equilibrium from Ternary Liquid-Liquid Equilibrium Data

Name of Candidate: David Kim Yee
Master of Science, 1982

Thesis and Abstract Approved: ______________ 4/13/82

Dimitrios Tassios — Date
Professor
Chemical Engineering

______________ Mar. 29 1982
Date

______________ 4/13/1982
Date

VITA

Name: David Kim Yee

Permanent address:

Degree and date to be conferred: MS, 1982

Date of birth:

Place of birth:

Secondary education: Verona High School, 1975.

Collegiate institutions attended	Dates	Degree	Date of Degree
New Jersey Institute of Technology	9/75	BS	5/79
New Jersey Institute of Technology	9/79	MS	5/82

Major: Chemical Engineering

Publications: Prediction of Vapor-Liquid Equilibrium from Ternary Liquid-Liquid Equilibrium Data, Ind. Eng. Chem. Process Des. Dev. (submitted for publication, 1982).

Prediction and Correlation of Liquid-Liquid Equilibria, Ind. Eng. Chem. Process Des. Dev., 1982.

This thesis is dedicated to my parents for their love and support.

ACKNOWLEDGEMENTS

I would like to thank Dr. Dimitrios Tassios for the many hours we spent in the preparation of this work. I am also grateful to John Ordaz for the use of some of his computer programs and Jose Simonetty for his assistance in some of the calculations. Finally I would like to thank the Department of Chemical Engineering and Chemistry for awarding me financial support.

TABLE OF CONTENTS

Section Page

LIST OF TABLES

LIST OF TABLES (continued)

LIST OF FIGURES

Figure Page

LIST OF FIGURES (continued)

LIST OF FIGURES (continued)

LIST OF COMPUTER PROGRAMS

1. Introduction

Vapor-Liquid equilibrium (VLE) data are essential in process design calculations, especially distillation. Since such data is not often available, prediction schemes are employed. For binary systems, group contribution techniques, especially the UNIFAC model (Fredenslund et al., 1975), can be used if the necessary interaction parameters are available. For multicomponent systems, good predictions can be achieved if VLE data for the corresponding binary systems are available. If not, the UNIFAC model can be used, with less confidence however, provided again that the appropriate interaction parameters are known.

Another possible prediction scheme involves the use of multicomponent liquid-liquid equilibrium (LLE) data for, in principle at least, one can correlate this data with an appropriate expression for the excess Gibbs free energy to evaluate the parameters for the corresponding binary systems. These parameters can then be used in the prediction of the VLE behavior of the same system; or, combined with parameters obtained from VLE data for other binaries, in the prediction of multicomponent VLE behavior. Since LLE data are plentiful (see for example Stephen and Stephen, 1963; Sorensen and Arlt, 1979) such an approach, if successful, could provide a very helpful scheme for the prediction of vapor-liquid equilibrium.

Joy and Kyle (1970) predicted binary and ternary VLE behavior using binary parameters obtained from the correlation of LLE data for four systems with the NRTL equation. Good results were obtained for three systems while for the fourth one their method failed to provide a set of NRTL parameters capable of approximating either the binodal curve or the solvent selectivity. Newsham and Vahdat (1975) obtained reasonable predictions of ternary VLE behavior from the corresponding LLE data using the Black and NRTL equations. Their data base, however, was limited to systems where one binary is nearly ideal (n-butanol-water with methanol, ethanol and n-propanol).

These two studies are of somewhat limited scope, however, because of the number and type of systems used and, more important, because they have not sufficiently addressed the major problem encountered in evaluating binary parameters from LLE data: how to identify the proper parameter values for, in the typical case, several sets of values can be obtained from different starting values in the regression routine (see for example: Sorensen et al. (1979); DeFre and Verhoeye (1976), Mattelin and Verhoeye (1974); etc.).

In this thesis, a more comprehensive study of the prediction of binary and ternary VLE behavior from LLE data is presented. First, it involves a larger and broader data base of eight systems, all of type I, i.e. containing only one partially miscible binary (Tables I and II), because of their industrial importance.

Furthermore, and for the purpose of evaluating the effect of the binary miscibility gap on the quality of the obtained predictions, they are classified into Type IA, with a small solubility gap between 0.1 and 0.85, and Type IB, with a large solubility gap, outside the aforementioned range. Second, to assist in the determination of the proper binary parameters, three local composition models capable of describing partial miscibility: NRTL (Renon and Prausnitz, 1968), LEMF (Marina and Tassios, 1973) and UNIQUAC (Anderson and Prausnitz, 1978), are considered. Finally the effect of using along with the LLE data binary activity coefficients-experimental or obtained from the UNIFAC model—is examined.

2. Theory

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

$$\hat{f}_i^{\alpha} = \hat{f}_i^{\beta} \qquad (1)$$

where $\hat{f}_i^{\alpha}$ and $\hat{f}_i^{\beta}$ are the fugacities of component i in phases α and β, respectively.

For the case of vapor-liquid equilibrium, equation (1) becomes:

$$\hat{f}_i^{L} = \hat{f}_i^{V} \qquad (2)$$

where $\hat{f}_i^{L}$ and $\hat{f}_i^{V}$ are the fugacities of component i in the liquid phase and vapor phase, respectively. The liquid phase fugacity is defined as:

$$\hat{f}_i^{L} = X_i \gamma_i \phi_i^{s} P_i^{s} \exp \int_{P_i^{s}}^{P} V_i^{L} \frac{dP}{RT} \qquad (3)$$

where X_i = liquid mole fraction of component i

γ_i = activity coefficient of component i

V_i^L = molar liquid volume of component i

P = total pressure

P_i^s = saturated vapor pressure of component i

T = system temperature

ϕ_i^s = fugacity coefficient of pure vapor i at T and saturation pressure P_i^s.

The vapor phase fugacity is defined as:

$$\hat{f}_i^V = \hat{\phi}_i Y_i P \tag{4}$$

where $\hat{\phi}_i$ = the vapor phase fugacity coefficient of component i

Y_i = the vapor phase mole fraction of component i

When equations (3) and (4) are substituted into equation (2), we obtain:

$$\hat{\phi}_i Y_i P = \gamma_i X_i \phi_i^s P_i^s \exp \int_{P_i^s}^{P} V_i^L \frac{dP}{RT} \tag{5}$$

or

$$Y_i = \frac{\gamma_i X_i \phi_i^s P_i^s \exp \dfrac{V_i^L (P - P_i^s)}{RT}}{\hat{\phi}_i P} \tag{6}$$

The vapor fugacity coefficient is given by the virial equation truncated after the second term:

$$\ln \hat{\phi}_i = \frac{2}{V} \sum_{j=1}^{n} Y_j B_{ij} - \ln(Z) \qquad (7)$$

where n = number of components

B_{ij} = second virial coefficient

V = molar volume of the vapor mixture

Z = compressibility factor

The compressibility factor and the molar volume of the vapor mixture are calculated by:

$$Z = \frac{PV}{RT} = 1 + \frac{\sum_{i=1}^{n} \sum_{j=1}^{n} Y_i Y_j B_{ij}}{V} \qquad (8)$$

The second virial coefficients are obtained from the correlation of Tsonopoulos (1974). The saturated vapor pressures are calculated from Antoines's equation with Antoine's constants obtained from Reid et al. (1977). The fugacity coefficient of pure vapor i at saturation pressure, ϕ_i^s, is also calculated with equations (7) and (8). In this case, $Y_i = 1$ and $P = P_i^s$. The activity coefficients are calculated from an activity coefficient equation. In this study, the following equations are used to represent the activity coefficient: NRTL, LEMF and UNIQUAC. For the case of ternary VLE, there are three equations similar to equation (6). In addition to those equations, a fourth relationship exists:

$$Y_1 + Y_2 + Y_3 = 1 \tag{9}$$

By using these four equations, we can solve for the four unknowns, Y_1, Y_2, Y_3, and T or P. The procedure for performing this bubble point calculation is outlined in Figure 1. A more detailed description of this bubble point calculation is given in Prausnitz et al. (1967).

For the case of liquid-liquid equilibrium, equation (1) becomes:

$$\hat{f}_i^{I} = \hat{f}_i^{II} \tag{10}$$

where $\hat{f}_i^{I}$ and $\hat{f}_i^{II}$ are the fugacities of component i in the liquid phases I and II, respectively. When equation (3) is substituted into equation (10), we obtain:

$$(X_i \gamma_i)^{I} = (X_i \gamma_i)^{II} \tag{11}$$

In this study, the binary parameters for the NRTL, LEMF and UNIQUAC equations will be determined from LLE data by using equation (11).

3. The Expressions for the Activity Coefficient

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

$$\ln(\gamma_i) = \frac{\sum_{j=1}^{n} T_{ji} G_{ji} X_j}{\sum_{k=1}^{n} G_{ki} X_k} + \sum_{j=1}^{n} \frac{X_j G_{ij}}{\sum_{k=1}^{n} G_{kj} X_k} \left[T_{ij} - \frac{\sum_{l=1}^{n} X_l T_{lj} G_{lj}}{\sum_{k=1}^{n} G_{kj} X_k} \right] \qquad \text{..........(12)}$$

where n = number of components

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

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

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

$(g_{ij} - g_{jj})$ = binary parameter

X = mole fraction

NRTL: $\alpha_{ij} = 0.2, 0.3, 0.4, 0.47$ (13)

LEMF: $\alpha_{ij} = -1.0$ (13a)

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

for the systems under investigation.

For the UNIQUAC equation:

$$\ln(\gamma_i) = \ln(\Phi_i / x_i) + (z/2) q_i \ln(\theta_i / \Phi_i) + l_i -$$

$$(\Phi_i / x_i) \sum_j x_j l_j - q_i' \ln\left(\sum_j \theta_j' \tau_{ji}\right) + q_i' - q_i' \sum_j \frac{\theta_j' \tau_{ij}}{\sum_k \theta_k' \tau_{kj}}$$

.... (14)

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 (Prausnitz et al. (1980)).

Table IV 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-in principle at least-from multicomponent such as LLE, data.

Activity coefficients from the UNIFAC model were calculated using the interaction parameters of Skjold-Jorgensen et al. (1979).

4. Procedure

Four methods are used for the evaluation of the six binary parameters from the ternary LLE data. In method I, they are obtained by regressing the LLE data with the following minimization function:

$$F = \frac{1}{N} \sum_{i=1}^{N} \left[\frac{K_1^E - K_1^C}{K_1^E} \right]_i^2 + \left[\frac{K_2^E - K_2^C}{K_2^E} \right]_i^2 + \left[\frac{K_3^E - K_3^C}{K_3^E} \right]_i^2 \qquad \text{..........} (15)$$

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

X_i^{I} , X_i^{II} = mole fractions in liquid phases I and II, respectively

I, II = component 1-rich phase and component 2-rich phase, respectively

N = number of tie lines

E, C = experimental and calculated values, respectively

The computer program which performs this regression can be found in the master thesis of Simonetty (1981). The starting values in the regression subroutine for the partially miscible binary, 1-2, are the parameters obtained from the binary mutual solubility data by solving the following two equations of phase equilibrium which were derived in the theory section:

$$(x_1 \gamma_1)^{I} = (x_1 \gamma_1)^{II} \qquad (16)$$

$$(x_2 \gamma_2)^{I} = (x_2 \gamma_2)^{II} \quad (16a)$$

For the NRTL and LEMF equations, these starting values were evaluated with the program found in the Phd Thesis of Marina (1973). For the UNIQUAC model, the parameters were determined with the program found in the Master Thesis of Simonetty (1981).

Our preliminary calculations with method I indicated that inspite of the use of a large number of starting values in the regression subroutine covering the range from -2000 to +2000, in the typical case reasonable parameters were obtained for only one-but not always the same-model. For the remaining two models the parameters for one, or both miscible binaries were unacceptable for they predicted: partial miscibility for one of the completely miscible binaries; or negative deviation from Raoult's Law where they could not be reasonably expected; or positive and negative deviations from Raoult's Law. Consider for example, the activity coefficients for the system water-methanol shown in Figure 2 and predicted from LLE data for the system: water-ethyl acetate-methanol at 70 C by using values of zero as starting parameters in the regression subroutine. The γ values generated from the NRTL and UNIQUAC parameters are obviously incompatible with such a binary system while the LEMF γ's can be considered reasonable. Regression of the LLE data for four parameters by setting the two parameters equal to those obtained from the binary solubility data, was not generally helpfull in ameliorating this problem of converging to unreasonable parameters. The binary parameters and the corresponding predicted binary γ's obtained from method I are shown in Tables V through XI for each model for the following starting values which were found to be the most effective according to our preliminary calculations: zero, +500, -500 and the parameters corresponding to γ values of 1.3 at X = 0.50 for both components of a binary mixture. Close examination of these tables reveals that the majority of these parameters are unreasonable.

It became apparent, therefore, that if reasonable parameters are to be obtained for all models, some additional information must be utilized along with the LLE data. A similar observation was made by Nicolaides and Eckert (1978).

In method II, the additional information is considered to be the binary γ's generated by the model for which acceptable binary parameters were obtained. If we refer to this as model A, for example the LEMF for the aforementioned water-ethyl acetate-methanol system, the binary parameters for the other two models, B and C, are obtained from the following minimization function:

$$D = \frac{1}{M}\sum_{i=1}^{M}\left[\frac{\gamma_1^E - \gamma_1^C}{\gamma_1^E}\right]_i^2 + \left[\frac{\gamma_3^E - \gamma_3^C}{\gamma_3^E}\right]_i^2$$

$$+ \frac{1}{L} \sum_{i=1}^{L} \left[\frac{\gamma_2^E - \gamma_2^C}{\gamma_2^E} \right]_i^2 + \left[\frac{\gamma_3^E - \gamma_3^C}{\gamma_3^E} \right]_i^2$$

+ equation (15) (17)

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

The superscripts E and C stand for experimental and calculated. In this case, experimental γ's are those generated by model A. Binary γ's were generated at the concentrations where actual binary VLE data are available for comparison purposes.

Since this approach always yielded acceptable parameters for the other models B and C, the possibility of further refinement of the parameters was considered. To this purpose, binary γ's generated by models B and C were regressed along with the LLE data to obtain a new set of parameters for model A. This iteration between models A and B and between A and C was continued until the obtained γ's for two successive iterations and for a given model were to within 0.20 %. It should be mentioned that the regressed parameters for a given model and iteration are used as starting values in the following iteration for the same model. This iteration calculation was performed with the program REG-2EQN given in appendix C. This procedure leads often to two sets of parameters for model A. The set that provides the best fit of the ternary LLE data is adopted. An example of the improved parameters thus obtained is presented in Figure 3 for the water-methanol system again. The LEMF γ's are evaluated by using the parameters obtained from the LEMF-NRTL iteration for they provide a better fit of the ternary LLE data.

In method III, the additional information is provided by the binary γ's for the two completely miscible binaries estimated from UNIFAC method whenever the necessary interaction parameters are available (for seven systems in this study). The minimization function given by equation (17) is used again with the γ's from UNIFAC considered as the experimental values.

In method IV, the additional information is the activity coefficients calculated from experimental binary VLE data using the method of Prausnitz et al. (1967) with second virial coefficients obtained from the Tsonopoulos correlation (1974). To facilitate the convergence to reasonable parameters, the starting values for the completely miscible binaries in methods III and IV are those obtained by regressing the binary γ's, UNIFAC or experimental, by using the following minimization function:

$$H = \left[\frac{\sum_{i=1}^{M} \left[\frac{\gamma_1^E - \gamma_1^C}{\gamma_1^E} \right]_i^2 + \left[\frac{\gamma_2^E - \gamma_2^C}{{}^{E}_{2}} \right]_i^2}{2M - 1} \right]^{1/2} \qquad \ldots\ldots\ldots\ldots(18)$$

The starting values for the NRTL and LEMF models were determined with the computer program provided by Ordaz (1978). For the UNIQUAC model, the starting values were evaluated with the computer program found in the Master Thesis of Simonetty (1981). The starting values for the partially miscible binary for methods II, III and IV are, as was the case with method I, the parameters obtained from the mutual solubility data. For both methods III and IV, the six final parameters were obtained with the computer program found in the Master Thesis of Simonetty (1981).

The ternary VLE predictions obtained from these methods are compared to those obtained from the two conventional schemes: from experimental binary data alone (method V); and from the UNIFAC model, if the appropriate interaction parameters are available (method VI). In the former method, the four parameters for the two miscible binaries are obtained from the corresponding VLE data using the minimization function given by equation (18), and the partially miscible binary parameters are evaluated from the binary mutual solubility data. The binary systems used are presented in Table XII. In the latter method, the main groups, subgroups, group volume and area parameters for the components under investigation are shown in Tables XIII and XIV. A summary of the six methods is presented in Table XV.

The quality of the binary VLE data was checked by the "area test" for isothermal systems and by the test of Herington (Herington, 1951) for isobaric systems. The "area test" entails making a plot of ln $\gamma 1/ \gamma 2$ versus X_1 and then calculating the consistency index (C. I.) which is defined as:

$$\text{C. I.} = \left| \frac{|A_p| - |A_n|}{|A_p| + |A_n|} \right| \tag{19}$$

where A_p and A_n are the positive and negative areas, respectively. The consistency index values for the isothermal binary VLE systems used in this study are given in Table XVI. If the consistency index is equal to or less than a specified limit then the binary VLE data is considered to be "good". In this work, the specified limit has been arbitrarily assumed to be 0.04. The reason for choosing this particular value is now discussed. For isothermal data, the Gibbs-Duhem equation takes the form of:

$$\int_{0}^{1} \ln(\gamma 1/\gamma 2)dX_1 = -\int_{X_1=0}^{X_1=1} \frac{v^e}{RT}\, dP \qquad (20)$$

where v^e is the excess volume of the liquid mixture. Since at low pressures, well removed from the critical point, the right-hand side of equation (20) 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. $\leq$ 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:

$$\int_{0}^{1} \ln(\gamma 1/\gamma 2)dX_1 = \int_{X_1=0}^{X_1=1} \frac{h^e}{RT^2}\, dT \qquad (21)$$

where h^e is the excess enthalpy of the liquid mixture. In general, one cannot assume that the right-hand side of equation (21) is zero. Thus $|A_p|$ is not equal to $|A_n|$ and the C.I. is not zero. As a result, one has the problem of making a good estimate of what C. I. should be in a typical situation where no data on the heat of mixing is available. Herington suggests that the C. I. should be compared with the quantity J which is defined as:

$$J \equiv 150(\mathcal{T}/T_{min}) \qquad (22)$$

where T_{min} is the lowest boiling point observed in degrees kelvin

$\mathcal{T}$ is the total boiling point range

The quantity $\mathcal{T}$ is calculated as follows:

$$\mathcal{T} = \left| T_1 - T_2 \right| \qquad (23)$$

where T_1 and T_2 are the boiling points of pure components 1 and 2 in degrees centigrade, respectively

If an azeotrope is formed in the binary mixture, then $\mathcal{T}$ is defined as the absolute difference between the azeotrope temperature and the highest pure component boiling point, for a mixture with a minimum azeotrope; and between the azeotrope temperature and the lowest pure component boiling point, for a mixture with a maximum azeotrope. Herington suggests that a set of isobaric binary VLE data is considered to be consistent if:

$$\left| C.\ I. - J \right| \leq 10$$

The above procedure for checking the quality of a set of isobaric binary VLE data is called the Herington test.

The values of $\left| C.I. - J \right|$ for the isobaric binary VLE systems used in this study are tabulated in Table XVI. Close examination of this Table reveals that the binary VLE data for all the isothermal systems passed the "area test" and the binary VLE data for all the isobaric systems passed the Herington test. Consequently, all of the binary VLE data was considered to be thermodynamically consistent. For the binary systems, n-pentane-benzene and sulfur-dioxide-benzene, consistency index values are not given because these systems have data points only at liquid benzene concentrations greater than X = 0.50. Consequently, a complete curve could not be drawn for those two cases.

The quality of the ternary LLE data was checked with the test of Hand (Hand, 1930) which involves making a plot of $\log_{10}(X_3^{II}/X_2^{II})$ versus $\log_{10}(X_3^{I}/X_1^{I})$. If this plot is linear, then the data is considered to be "good".

The Hand plots for systems 2, 4 and 6 are shown in Figures 4 through 6. A Hand plot for system 8 was not possible because only 1 ternary LLE data point was available. The Hand plots for the other ternary systems can be found in the Master Thesis of Simonetty (1981). Close examination of these plots reveals that in every case, the points seem to lie near a straight line. Consequently, it was not necessary to eliminate any LLE data points.

5. Results and Discussion

The binary parameters from methods I through V for each model are given in Tables V through XI and XVII through XXVIII. These parameters were used along with the bubble point computer program provided by Ordaz (1978) to obtain the binary and ternary vapor phase compositions. For the UNIFAC method, the same bubble point program was used. Average absolute deviations in the vapor phase mole fraction:

$$\Delta\overline{Y} = \frac{1}{3Q} \sum_{i=1}^{Q} \left\{ \left| Y_1^E - Y_1^C \right| + \left| Y_2^E - Y_2^C \right| + \left| Y_3^E - Y_3^C \right| \right\}_i \qquad \text{..........(24)}$$

where Q is the number of experimental data points for each ternary system, are presented in Table XXIX for all six methods. Overall results are presented in Table XXX.

The poor results obtained with method I are expected since "unacceptable parameters" were often used. Of the several starting values in the regression calculation, the ones that lead the most often to reasonable parameters are zero and those that correspond to a value of 1.3 for the activity coefficient of both components at $X_1 = 0.50$ of a binary system. Of the three models used, the LEMF yielded acceptable parameters more often than the other models, in four of the seven systems (1, 2, 6 and 7). For systems 3 and 4, the UNIQUAC model produced acceptable parameters. For system 5, the NRTL model yielded acceptable parameters. These results suggest that the LEMF model has less difficulty obtaining acceptable parameters from LLE data than the other equations. It is worth noticing in Table XXIX that for systems 3 and 5, the LEMF model gave better results than the NRTL model, even though the parameters were unacceptable. Compensating errors are probably responsible for this occurence.

Noticeable improvement is accomplished with method II which uses the same data as method I, but it involves the three models for the excess Gibbs free energy in helping each other towards the evaluation of reasonable binary parameters. As previously mentioned, in method II, iteration calculations are done for two pairs of models. When the iteration calculation is performed for each pair of equations, the quality of the predicted γ's for both binaries improves but not always by the same amount. In some cases, the 1-3 miscible binary experiences a bigger improvement than the 2-3 binary, and in other cases, the 2-3 binary experiences the greater improvement. When the iteration calculation converges for both pairs of equations, we obtain two sets of parameters for the model which yielded acceptable parameters in method I. The parameter set which gave the best fit of the ternary LLE data is used. This criterion is determined by the percentage error in the distribution coefficient. In the typical case, both sets of parameters are similar to each other and predict the VLE with approximately the same quality. For each ternary system, Table XXXI shows both sets of parameters and the corresponding $\Delta\overline{Y}$'s and average percentage errors in distribution coefficient.

For the seven systems where the comparison is possible, method II gave an overall deviation in Y of 0.028 with significantly better results in four of them (systems 1, 2, 5 and 6) and slight improvement for the other three (systems 3, 4 and 7). And it is worth noticing in Table XXIX that improvement is realized over the results obtained by both types of method I parameters, acceptable and unacceptable. This suggests that the iteration among the three models is desirable even for the model where acceptable parameters were obtained with method I. For method II, plots of Y^E versus Y^C are shown in Figures 7 through 13 for seven ternary systems using the models which gave the best $\Delta\overline{Y}$. It should be mentioned that for the systems which have a large number of ternary VLE data points, the plots of Y^E versus Y^C were made by using only 16 carefully chosen data points which cover the entire liquid composition region.

Use of binary γ's generated from the UNIFAC model along with the LLE data, method III, gives still better predictions. The overall average deviation in predicted vapor phase composition, with the three models, is 0.020. On the other hand, the results for method VI suggests that the UNIFAC model may not always provide reliable vapor phase predictions in partially miscible systems.

Combination of binary VLE and ternary LLE data, method IV, and straight predictions from binary data, method V, provide the best results with overall deviations in Y of 0.016 and 0.017, respectively. The overall performance of method V, however is somewhat inferior to that observed in the case of completely miscible ternary systems (see for example Hudson and Van Winkle (1970)), probably because of the uncertainty in the parameter values for the partially miscible binary, obtained from one, and sometimes not very accurate, datum point. And as suggested by the results for method IV, inclusion of the LLE data does not seem to rectify this uncertainty.

For system 7, poor results were obtained with all methods, including methods IV and V which normally give good results. One possible reason for these poor results is that the ternary VLE data is bad since the correlation of that data by Gmehling and Onken (1977) was poor and the quality of the other data (binary VLE and ternary LLE) was found to be good.

A comparison of the results for type IA and IB systems does not suggest the improved performance for type IA systems that was observed in the prediction of ternary LLE behavior from binary data for these type of systems (Simonetty et al. (1982)). And as shown in Table XXX, all models for the excess Gibbs free energy provide similar results. The LEMF model, however, gives somewhat better results with methods II and V and it also has the advantage of using a single value of $\alpha = -1.0$.

In the case of three-phase distillation, it is important that the two sets of predicted vapor phase concentrations resulting from the two liquid phases in equilibrium, are the same or at least very close to each other. The results for the three systems, where such data are available, are presented in Table XXXII and indicate that this is successfully done with parameters obtained from method II. In addition the quality of the predictions as compared to those in the completely miscible region (Table XXIX), suggest that accuracy increases as the binodal curve is approached which is in agreement with the observation of Joy and Kyle (1970) with the NRTL model for the system n-pentane(1)-sulfur dioxide(2)-benzene(3) at 0 F. In order to determine more accurately if this type of behavior is present for all seven ternary systems, plots of $\Delta \overline{Y}$ versus the distance between the binodal curve and a ternary VLE data point (ΔX) were made for each model and system for method II and are shown in Figures 14 through 34. The quantity ΔX was determined in the manner shown in Figure 35. Examination of these plots for all seven systems indicate that while accuracy improves as the binodal curve is approached for systems 3, 6 and 7, no clear trend can be established for the remaining ones. In the typical case, however, best predictions are realized close to the binodal curve.

We turn now to the prediction of binary VLE behavior for the completely miscible binaries. Detailed results for methods I, II and VI are presented in Tables XXXIII and XXXIV and typical ones in Figure 36. A summary of all applicable methods is presented in Table XXXV. As with the prediction of ternary VLE, method I parameters yield poor results and improved performance is realized with method II, with an overall deviation in Y for 14 systems of 0.024. And a comparison of the predictions with method I (Table XXXIII) and method II (Table XXXIV) suggests again that the iteration among models yields better results even for the models where acceptable parameters were obtained with method I. The UNIFAC method, and the combination of LLE data and UNIFAC give the best results with deviations in Y of 0.017 and 0.015, respectively. Finally, of the three models for the activity coefficient, the LEMF gives again somewhat better results.

Prediction of VLE in partially miscible binary systems, however, is less certain, as demonstrated in Table XXXVI for three systems where such data were available. Method V, in this case, involves just the binary mutual solubility data. The LEMF model gives very good results for two of them but not for the third one. Good predictions are also obtained with the UNIFAC model, but not for the water-ethyl acetate system where the results are extremely poor. This observation, combined with the poor ternary predictions for the systems: water-ethyl acetate with methanol and with ethanol, suggests that the interaction parameters for the H_2O - COOC pair are probably unreliable.

The most important use of binary information is, of course, in the prediction of multicomponent VLE behavior such as ternary VLE. For this purpose, in Table XXXVII, we present the prediction results for systems 1, 3, 4 and 7. In this prediction, the parameters for the 1-3 miscible binary was obtained from method II. The parameters for the other two binaries, one completely and the other partially miscible, were obtained from the corresponding binary data. The results are of acceptable quality, but inferior to those obtained by straight prediction from binary data (method V). Plots of Y^E versus Y^C are presented in Figures 37 and 38 for a couple of typical cases.

6. Conclusions

Ternary liquid-liquid equilibrium data can be effectively used in the prediction of vapor-liquid equilibrium.

For ternary predictions, reasonable estimates of vapor phase compositions are obtained by using the LLE data alone. The overall deviation in Y for seven systems is 0.028 but better results are obtained close to the binodal curve, a region important in three phase distillation. If the necessary UNIFAC interaction parameter values are available, improved results are realized by combining the LLE data with the UNIFAC method. The overall deviation in Y for seven such systems is 0.020. Use of the UNIFAC method alone, however, gives erratic predictions suggesting caution when it is applied to such systems.

For the completely miscible binary systems, reasonable estimates of the vapor phase concentrations are again obtained from the LLE data alone. The overall deviation in Y for 14 systems is 0.024. The UNIFAC method, and the LLE data-UNIFAC combination, give the best results with deviations of 0.017 and 0.015, respectively. For the partially miscible binaries, however, predictions are less certain.

Finally, of the three models for the exdess Gibbs free energy, the LEMF appears to give somewhat better results for both binary and ternary VLE predictions.

APPENDIX A

THE FIGURES

This appendix contains Figures 1 through 38.

Figure 1: Block diagram for Bubblepoint Calculation.

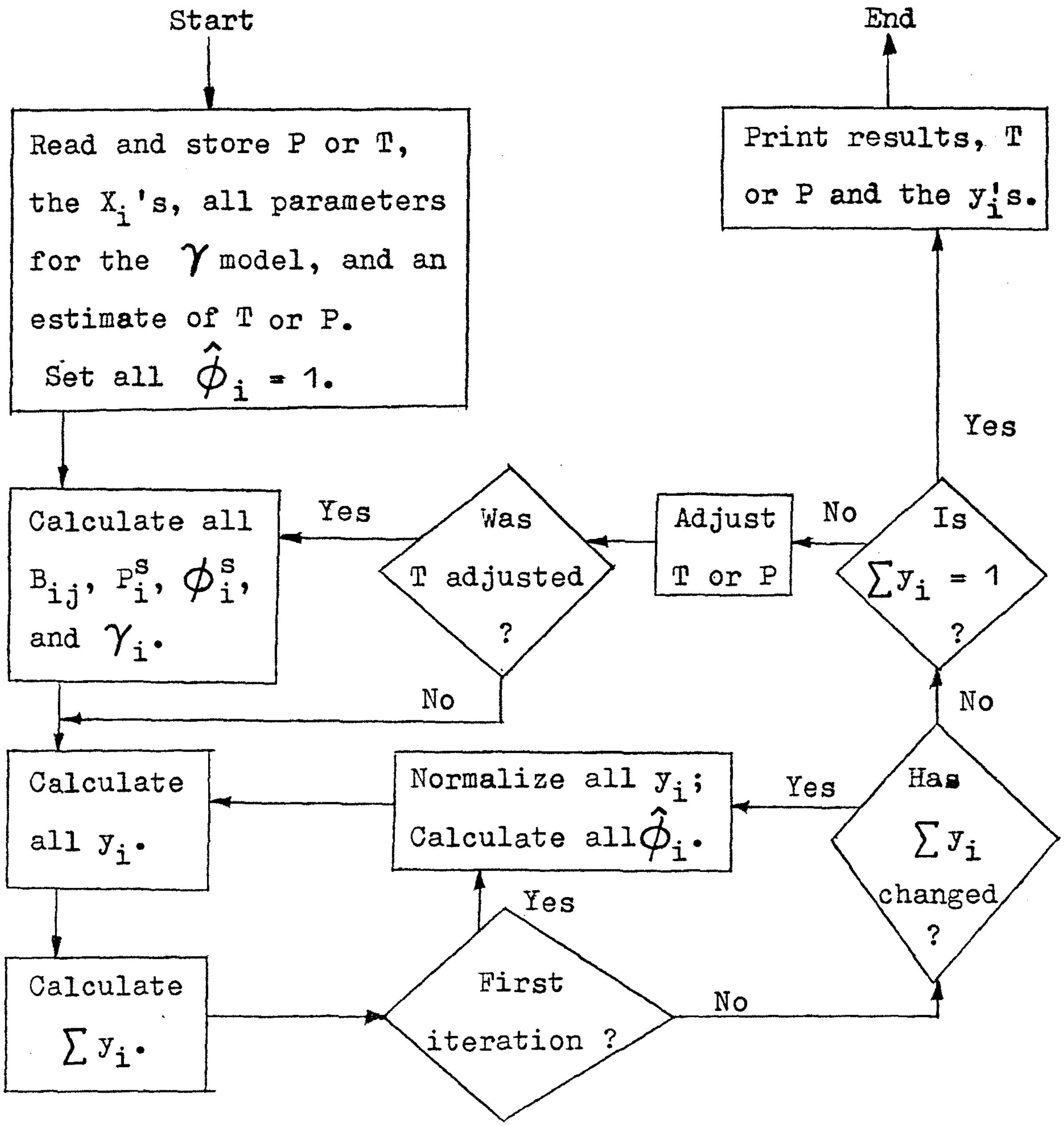


Figure 2: Predicted Activity Coefficients for the System Water(1) - Methanol (3) Using Parameters Obtained from System-2 with Method I. L: LEMF N: NRTL U: UNIQUAC

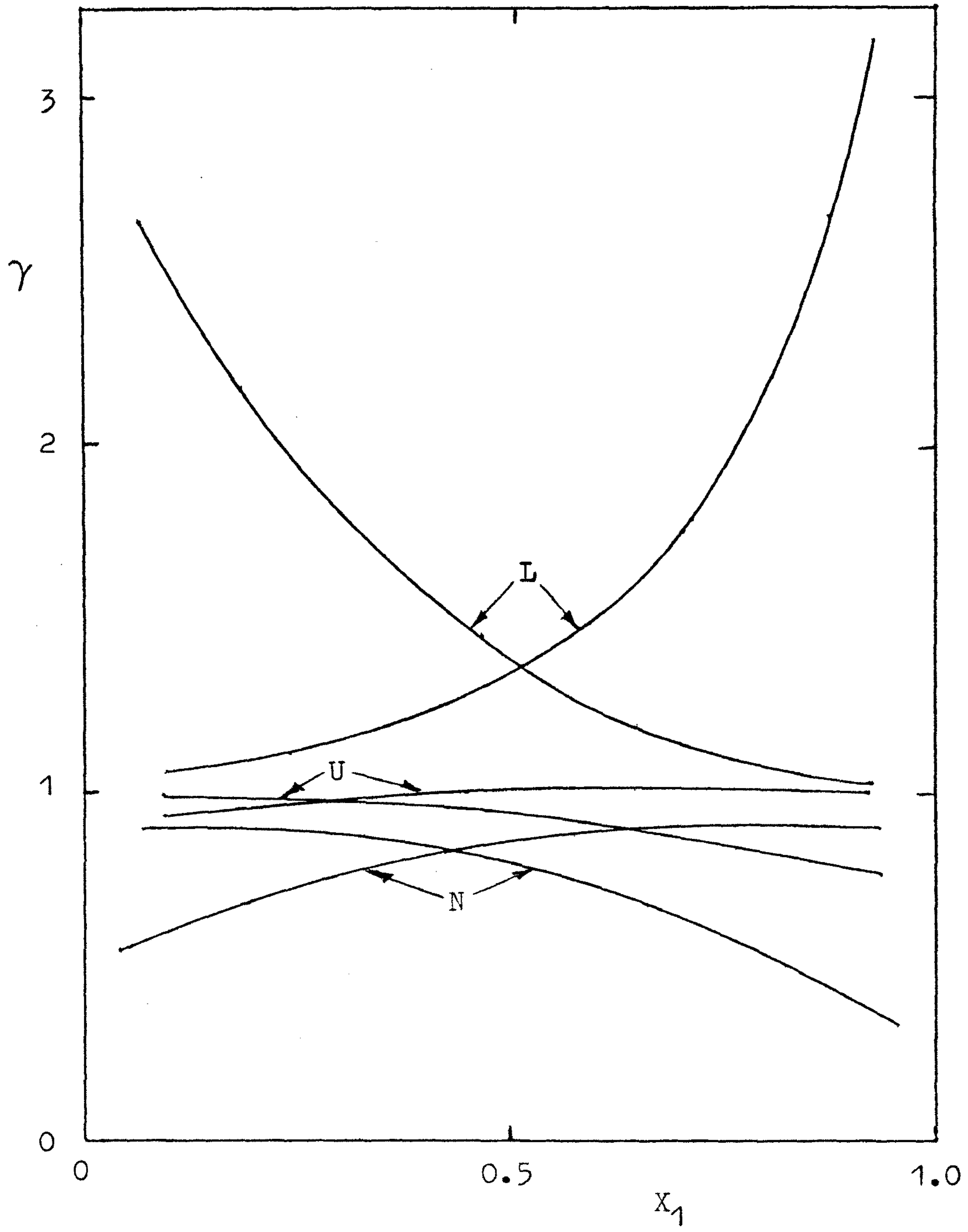


Figure 3: Predicted Activity Coefficients for the System Water(1) - Methanol(3) Using Parameters obtained from System-2 with Method II.

o: experimental at 65 C (McGlashan, 1976)

L: LEMF

N: NRTL

U: UNIQUAC

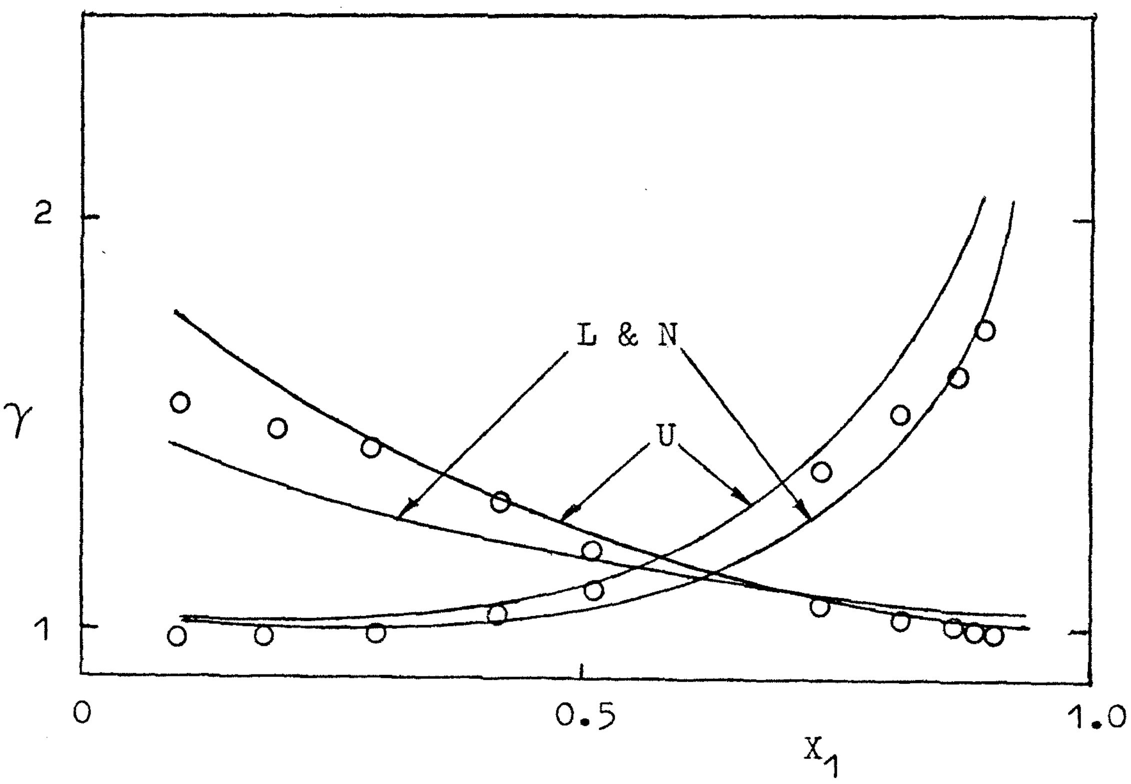


Figure 4: Hand's test for system 2.

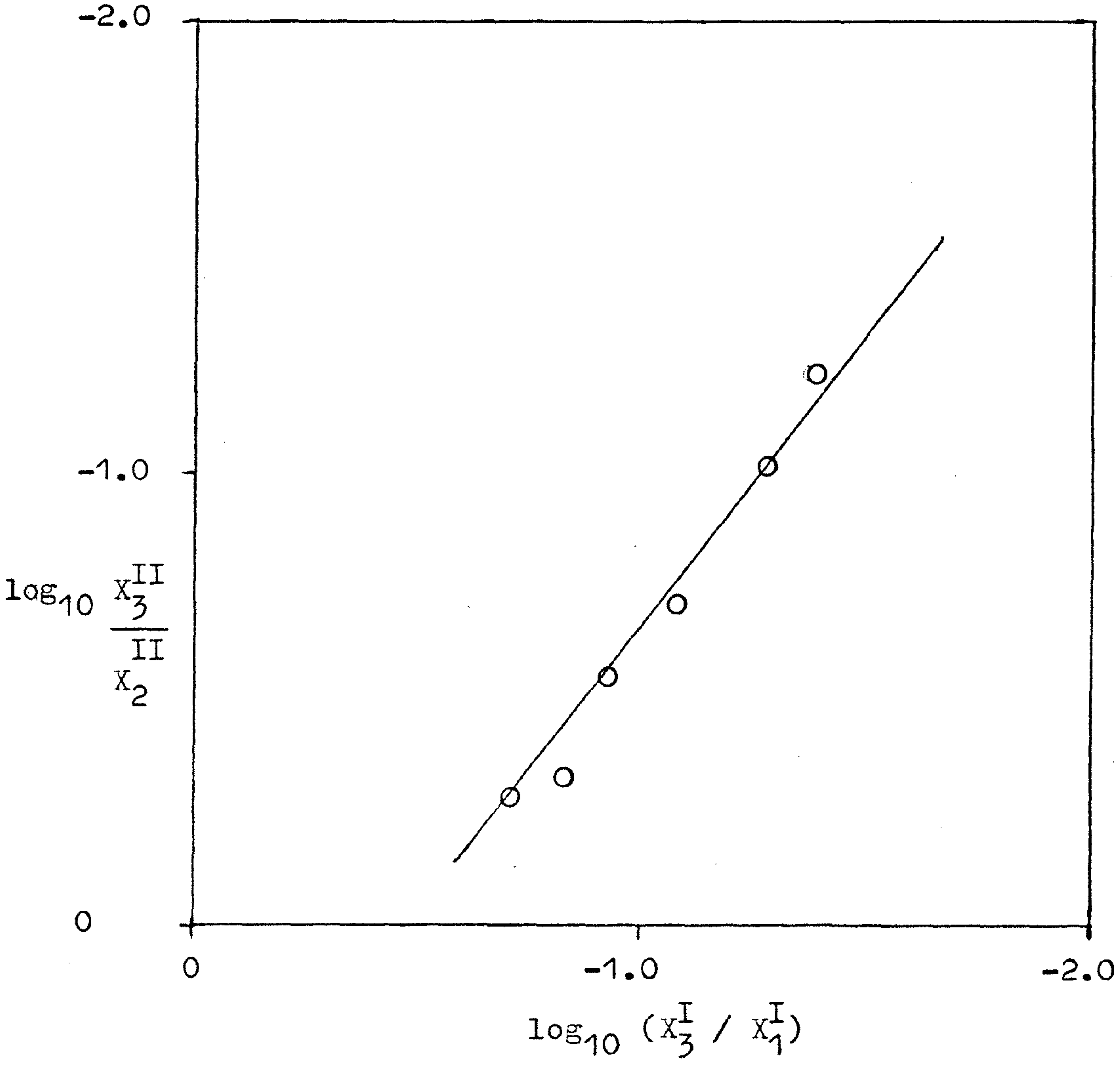


Figure 5: Hand's test for system 4.

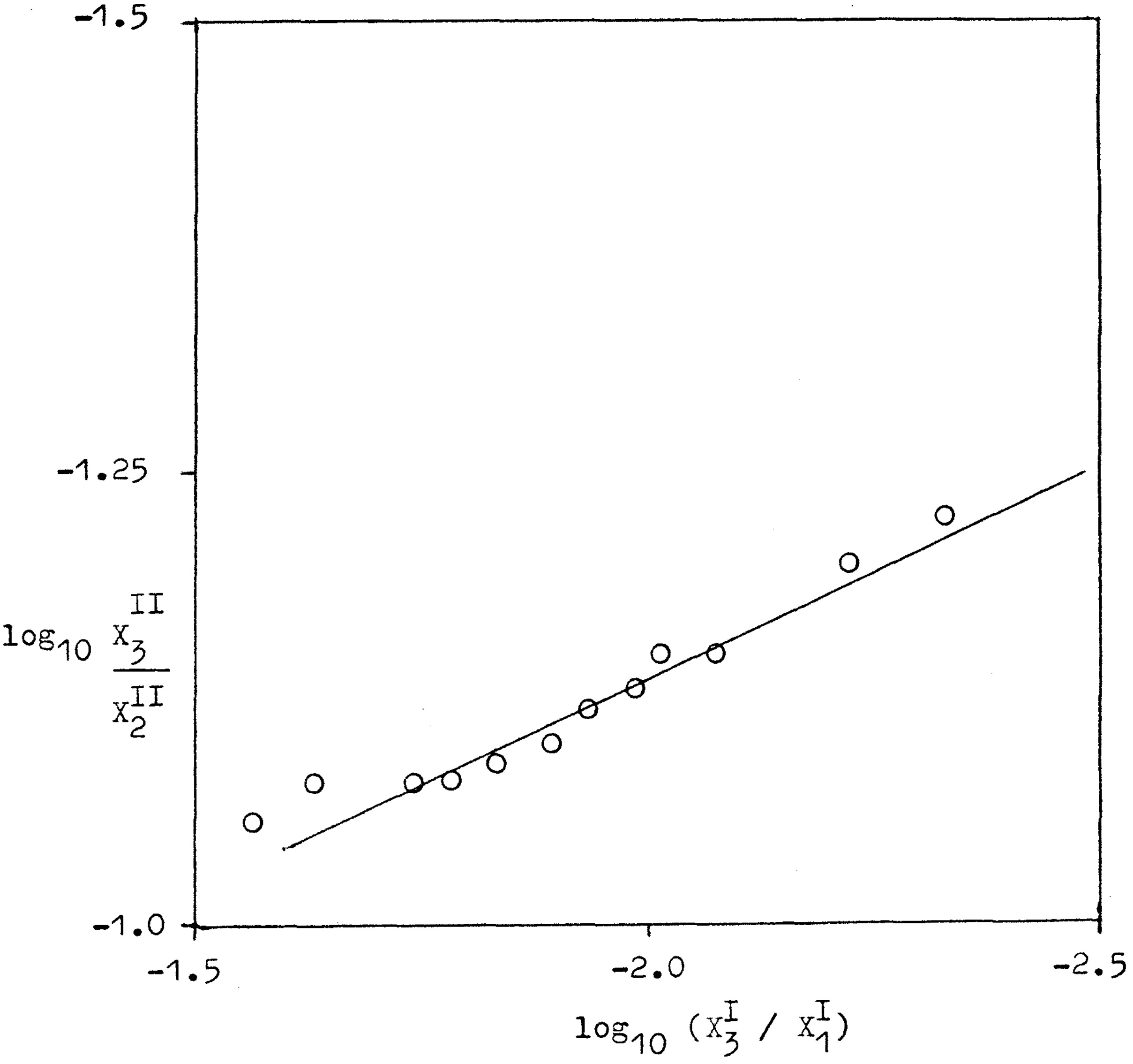


Figure 6: Hand's test for system 6.

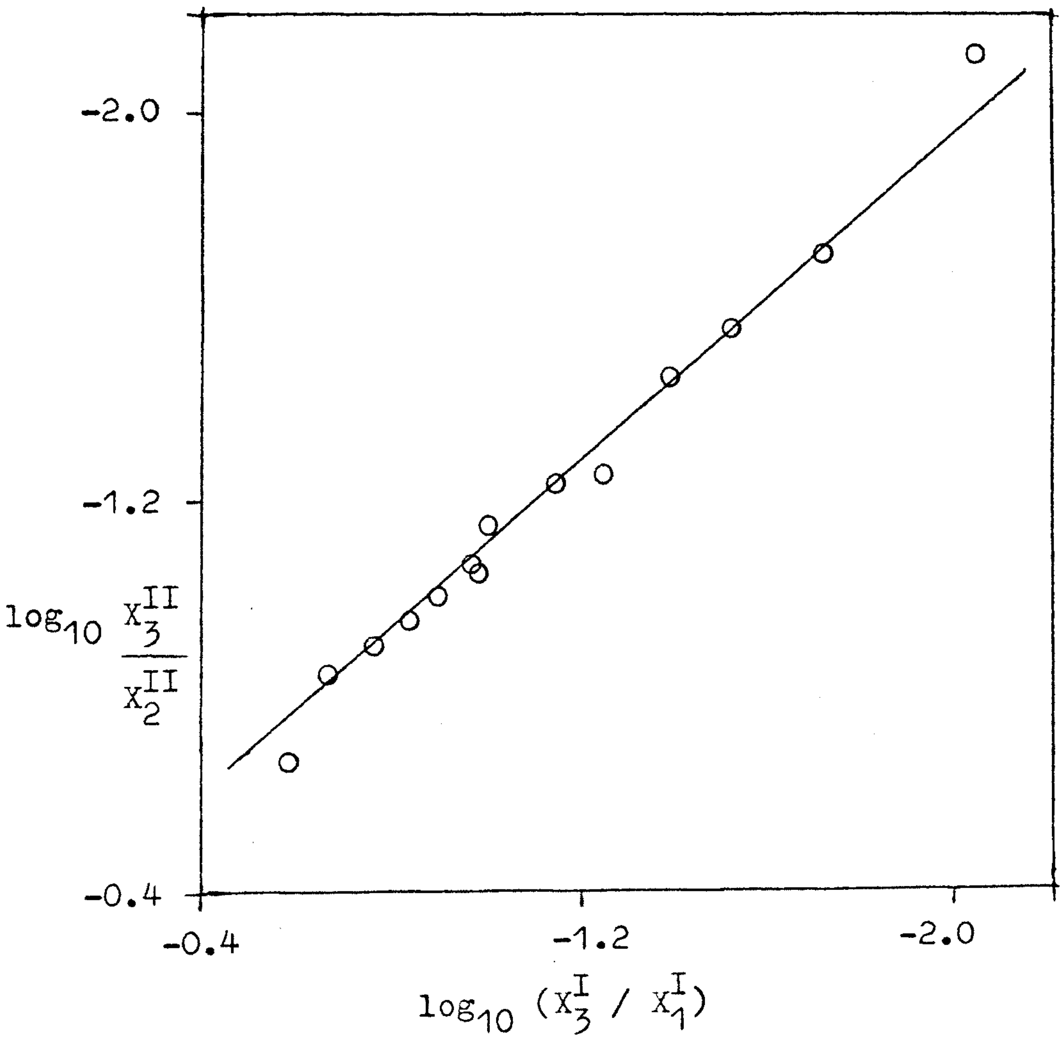


Figure 7: Prediction of Vapor Phase Compositions for system 1 with method II and the LEMF Model.

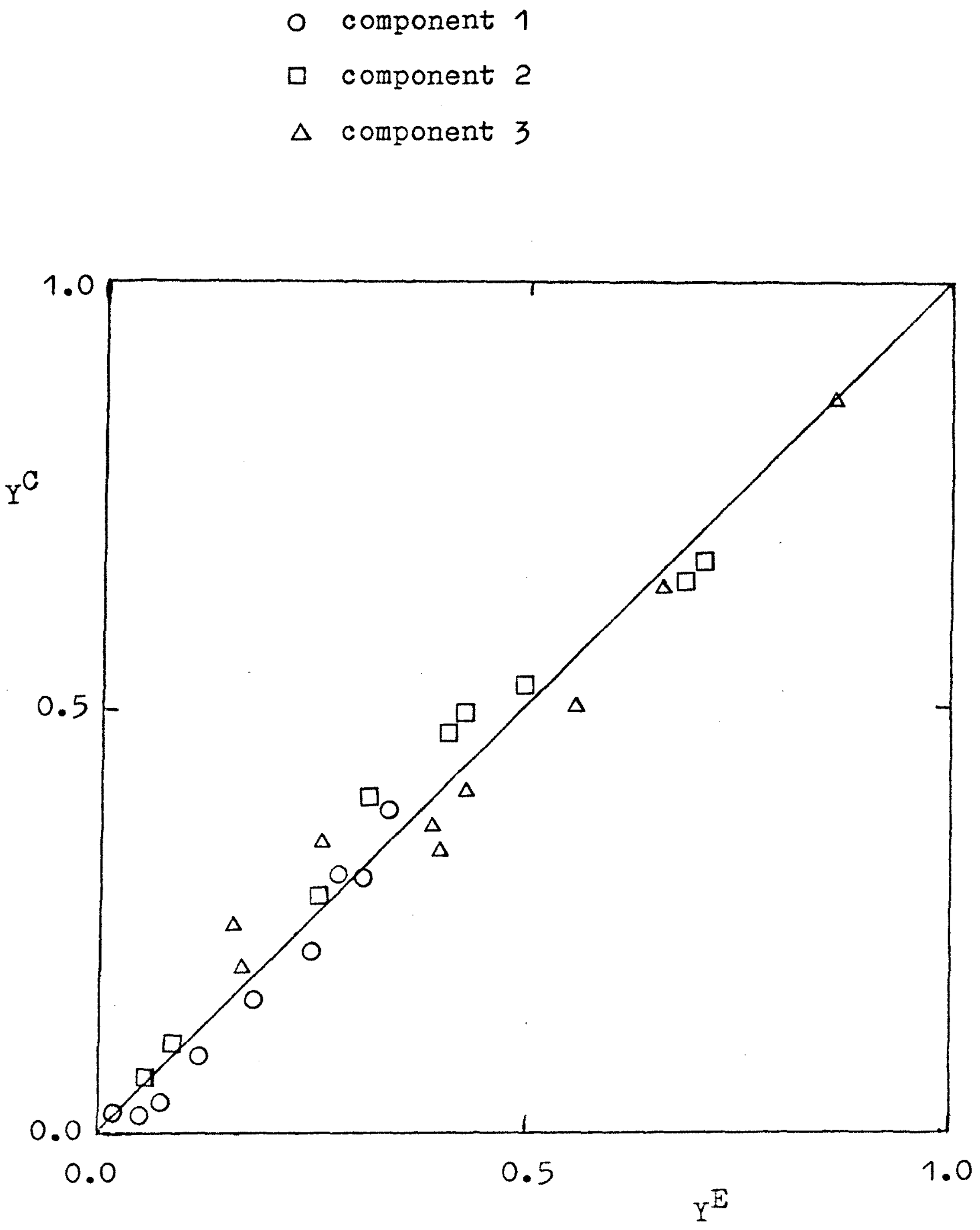


Figure 8: Prediction of Vapor Phase Compositions for system 2 with method II and the UNIQUAC Model.

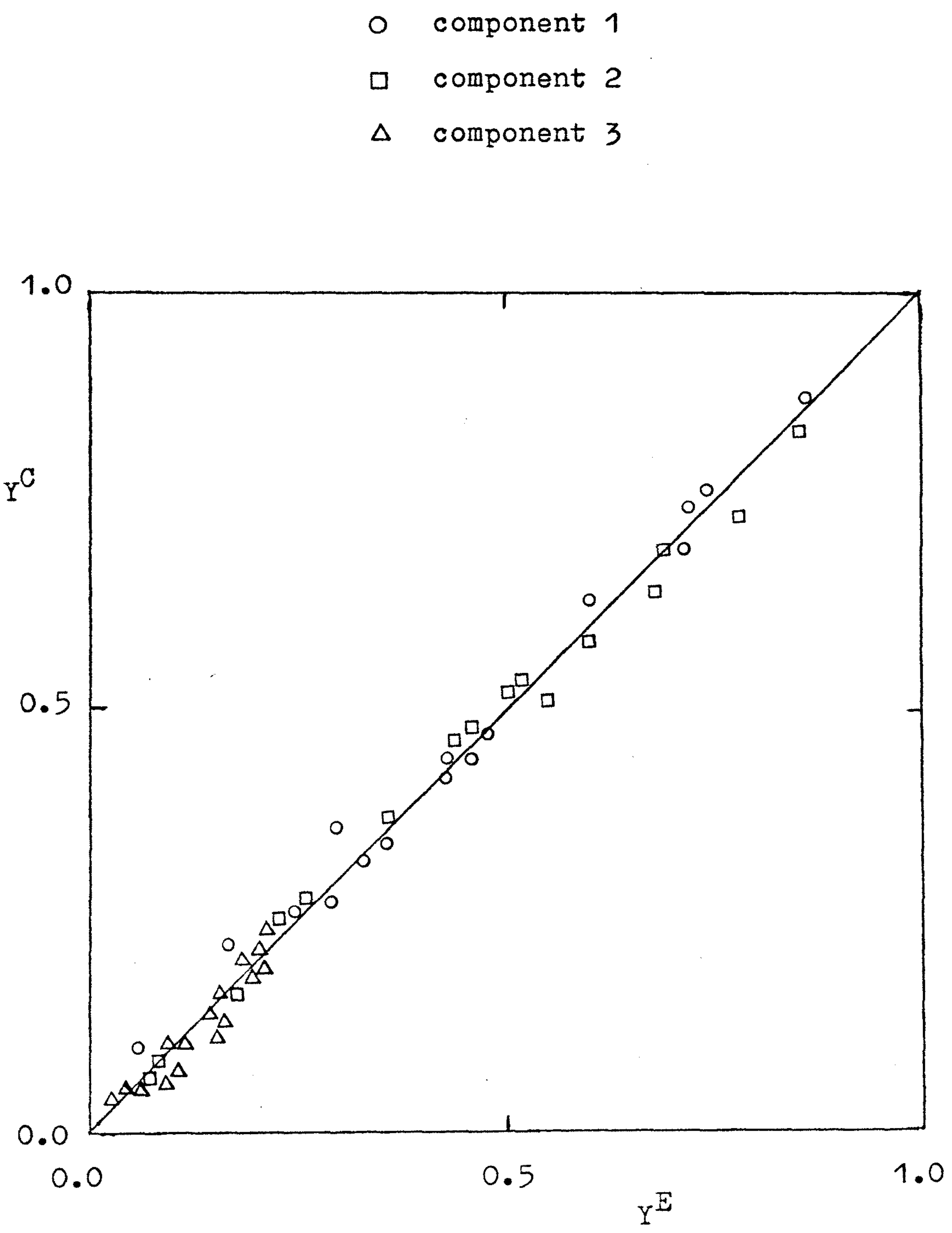


Figure 9: Prediction of Vapor Phase Compositions for system 3 with method II and the NRTL model.

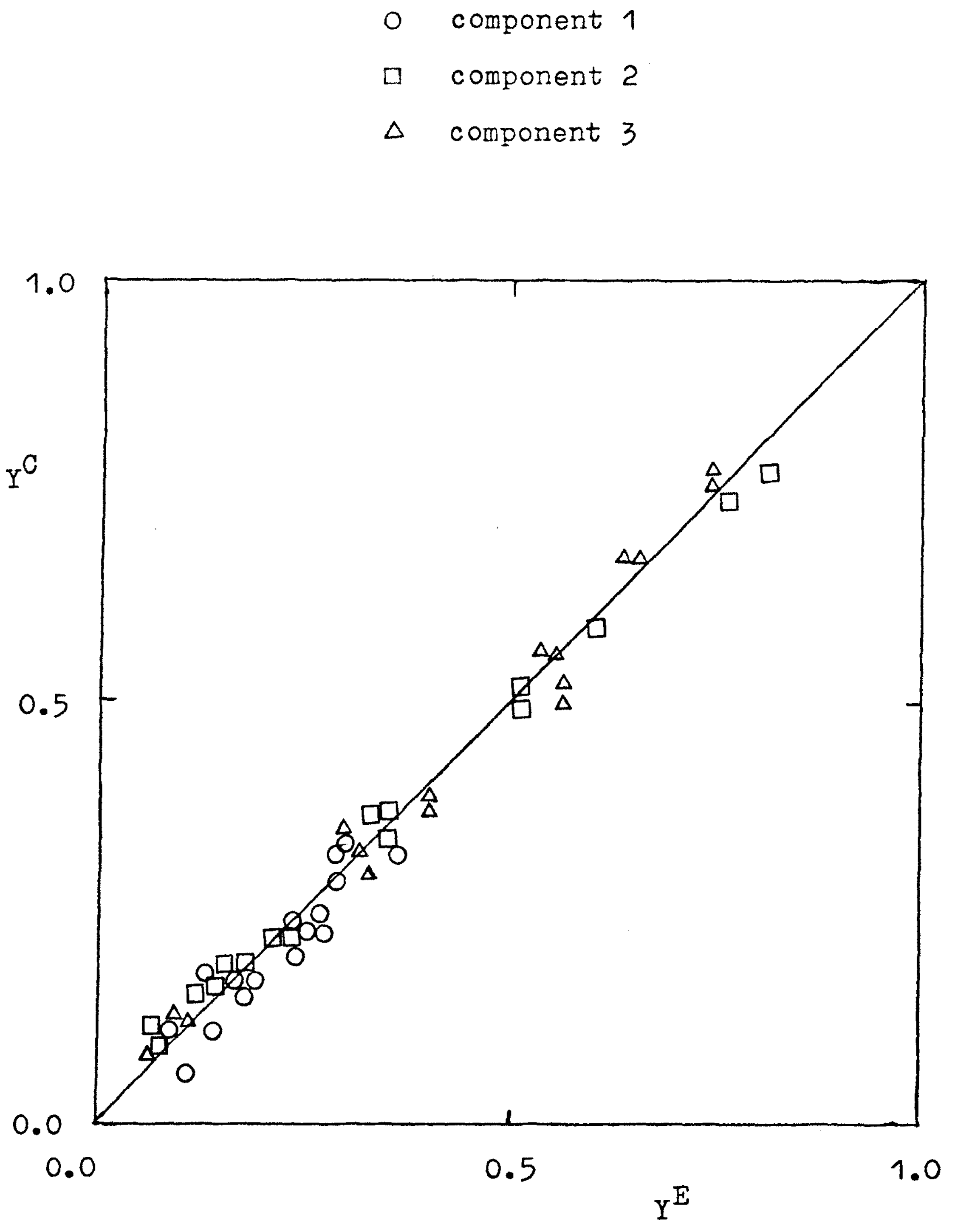


Figure 10: Prediction of Vapor Phase Compositions for system 4 with method II and the UNIQUAC model.

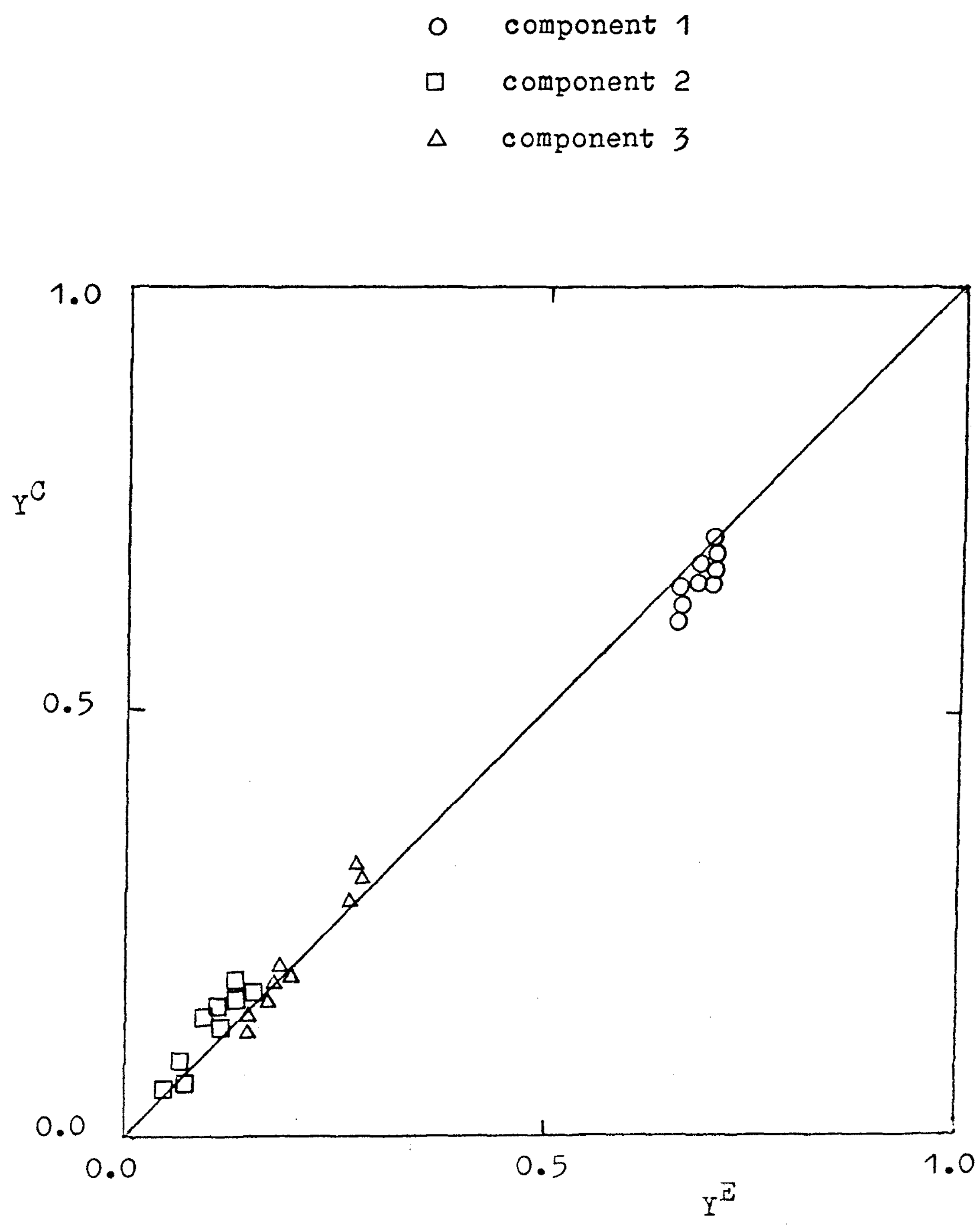


Figure 11: Prediction of Vapor Phase Compositions for system 5 with method II and the LEMF model.

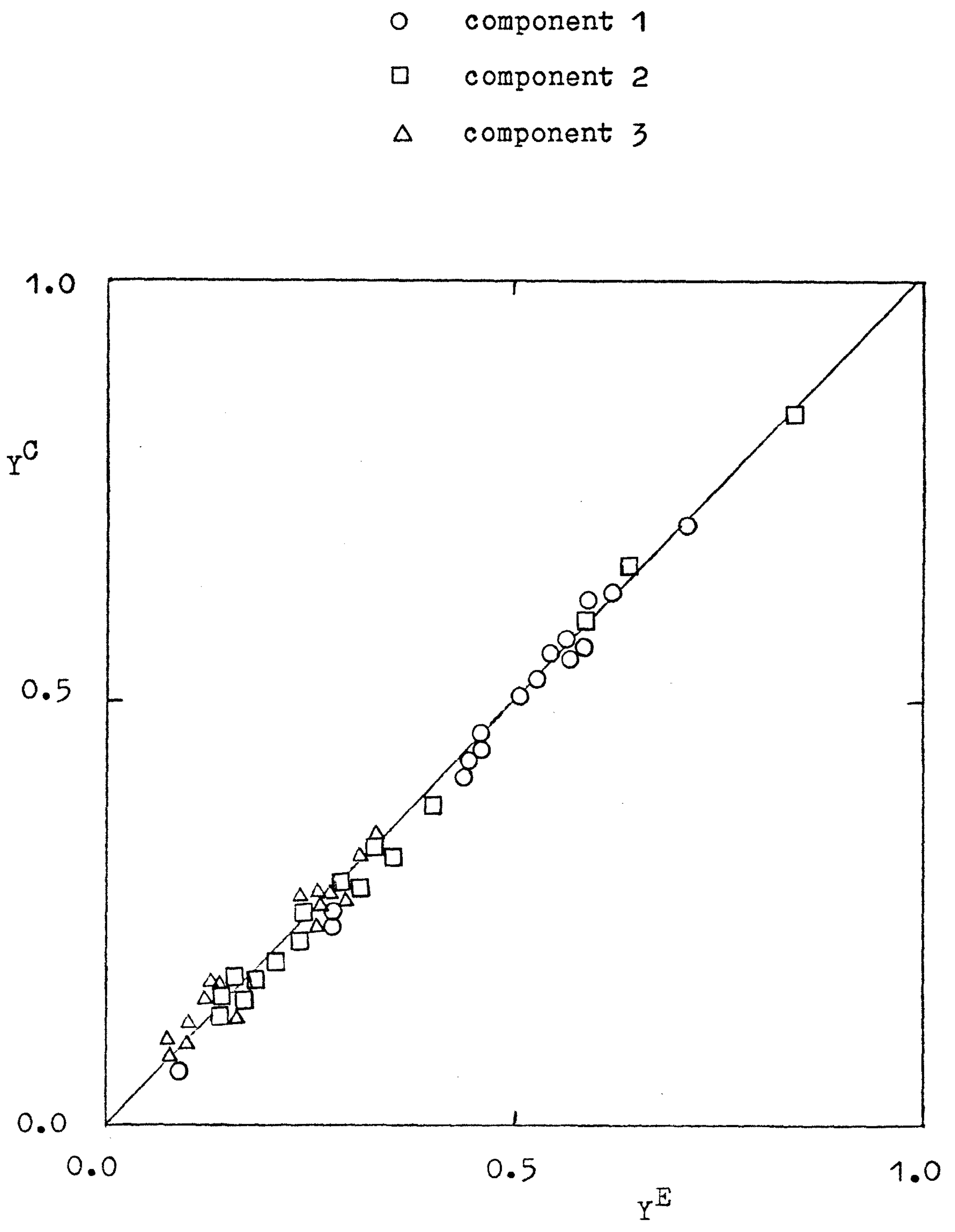


Figure 12: Predictions of Vapor Phase Compositions for system 6 with method II and the UNIQUAC model.

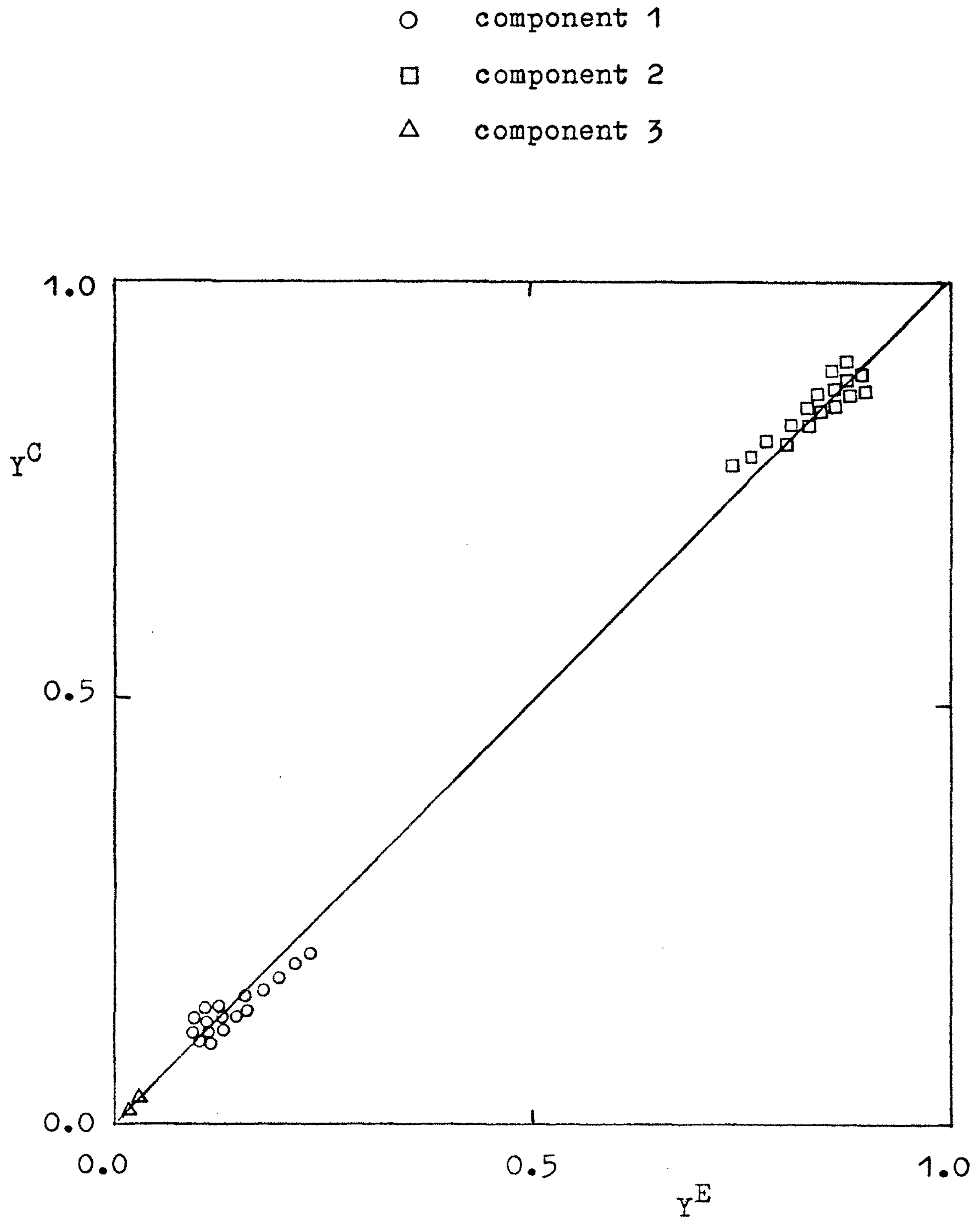


Figure 13: Predictions of Vapor Phase Compositions for system 7 with method II and the LEMF model.

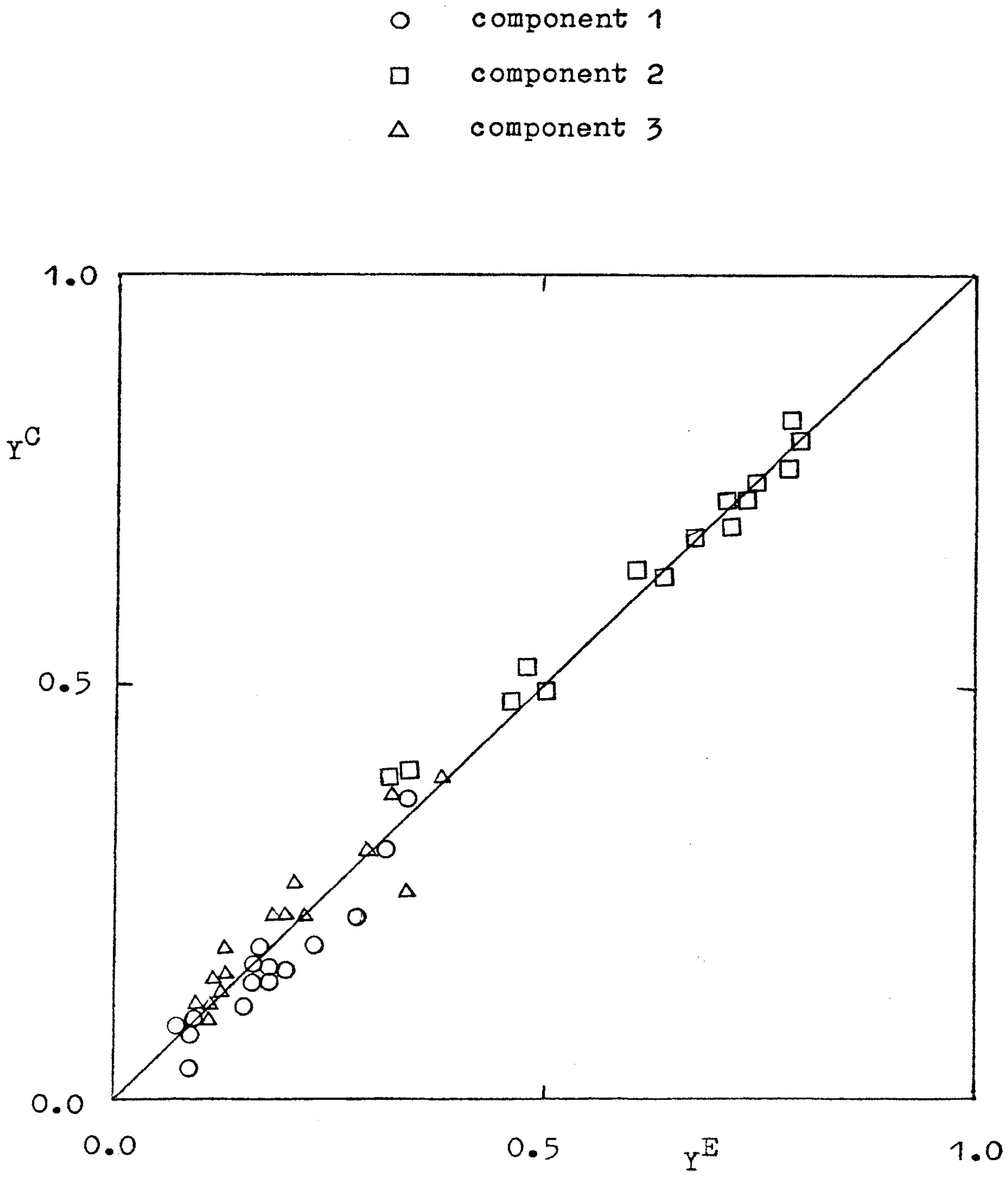


Figure 14: Plot of $\Delta\overline{Y}$ versus ΔX for system 1 using the NRTL (method II).

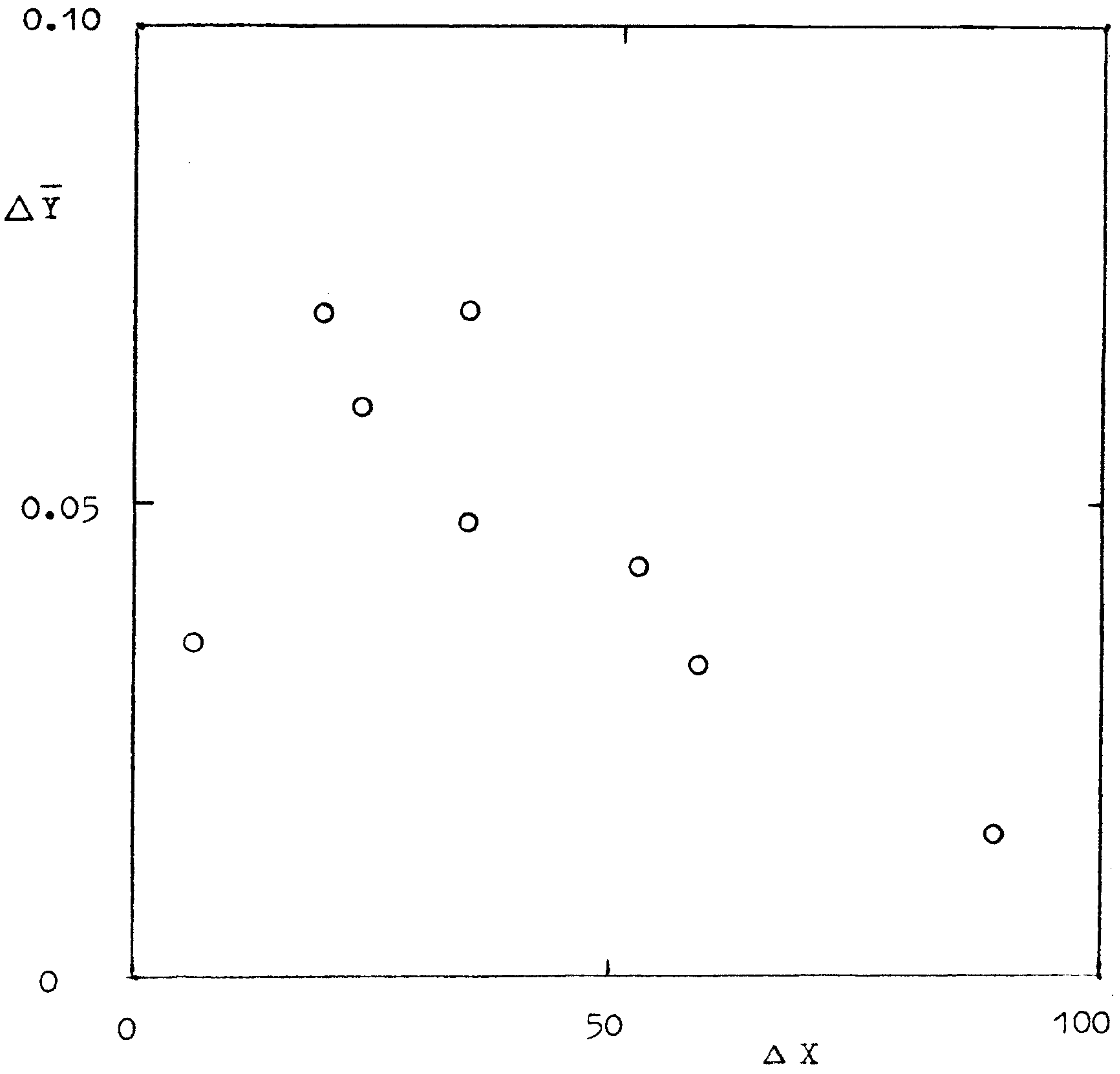


Figure 15: Plot of $\Delta\overline{Y}$ versus ΔX for system 1 using the LEMF (method II).

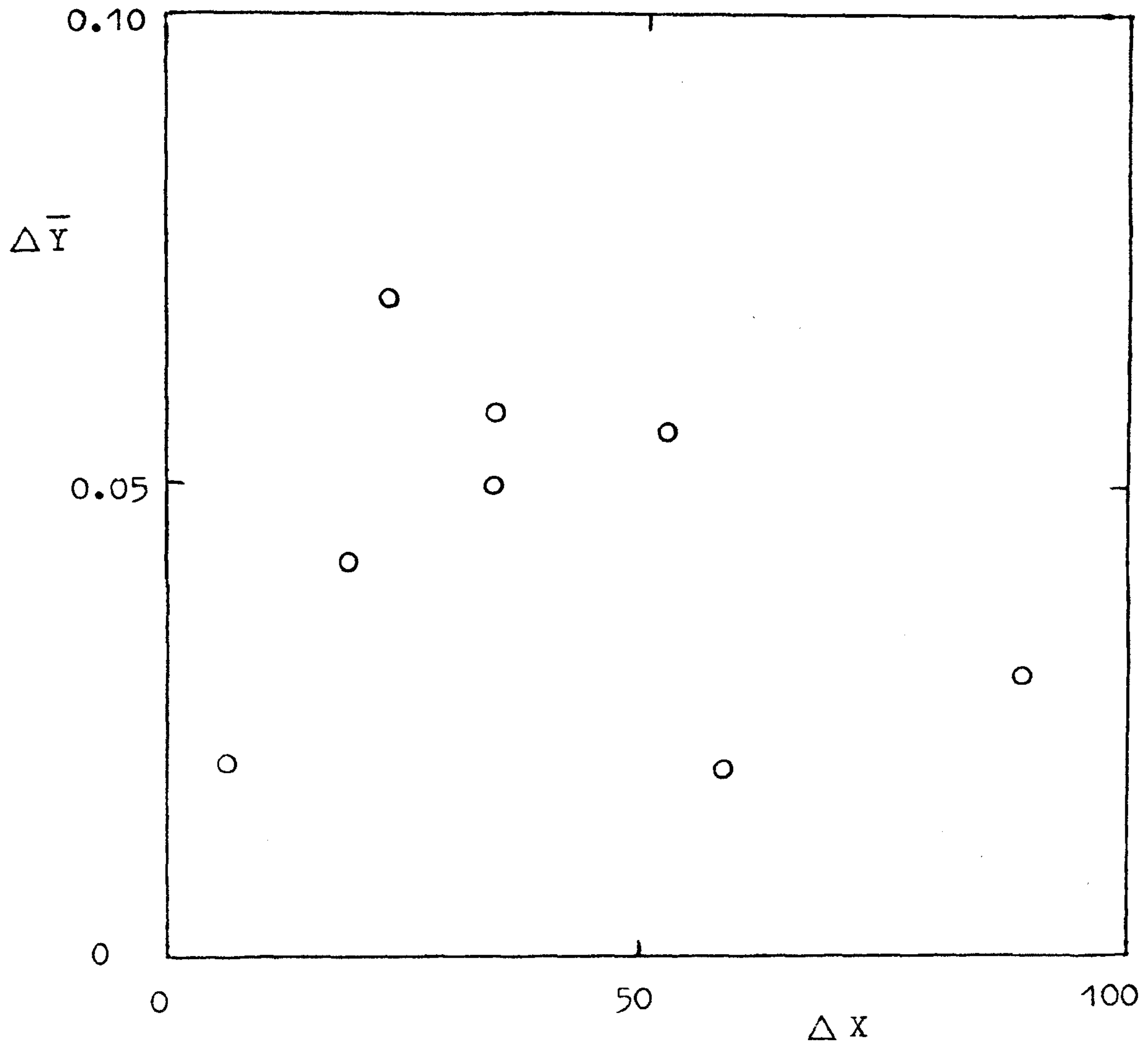


Figure 16: Plot of $\Delta\overline{Y}$ versus ΔX for system 1 using the UNIQUAC (method II).

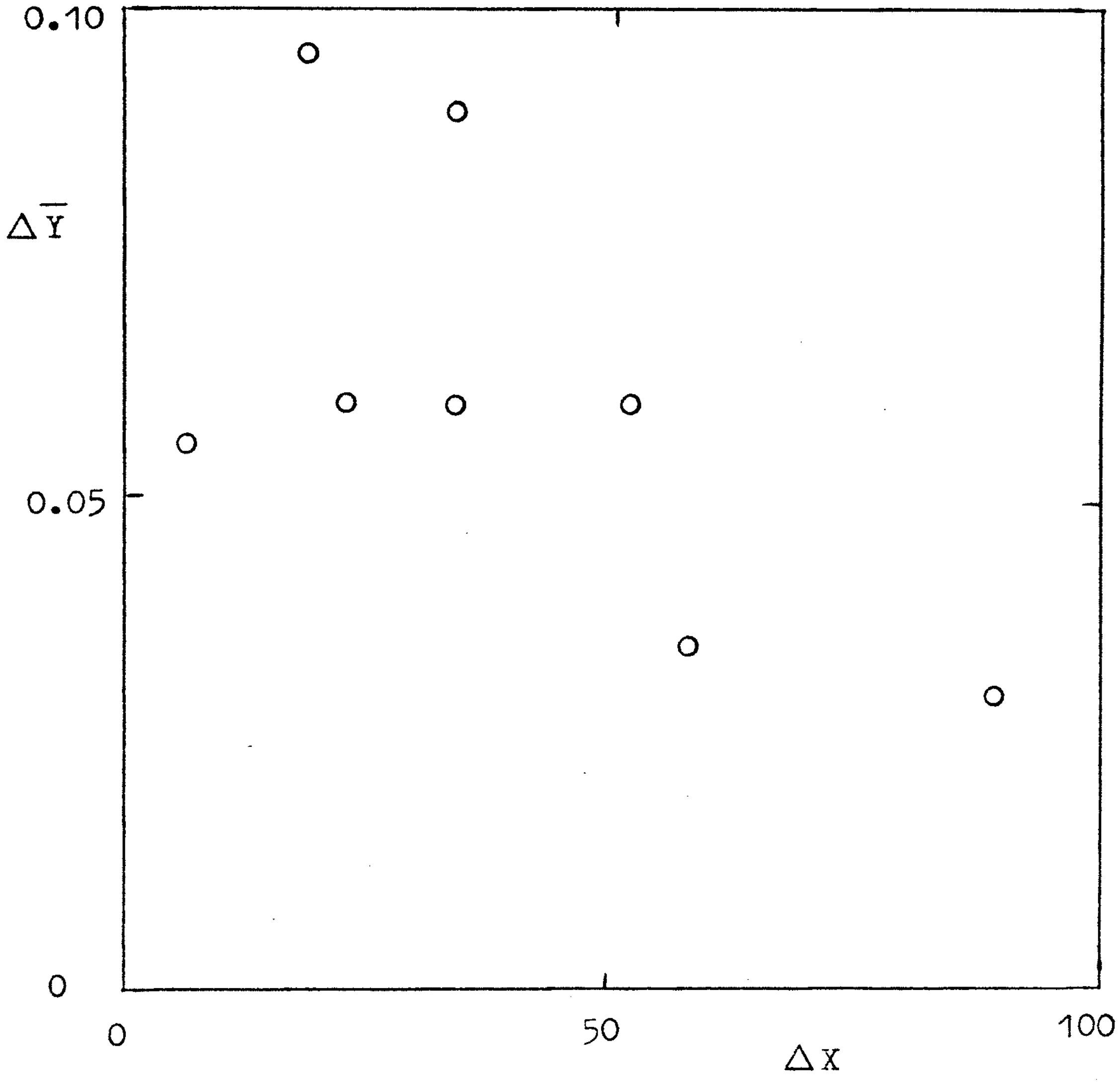


Figure 17: Plot of $\Delta\bar{Y}$ versus ΔX for system 2 using the NRTL (method II).

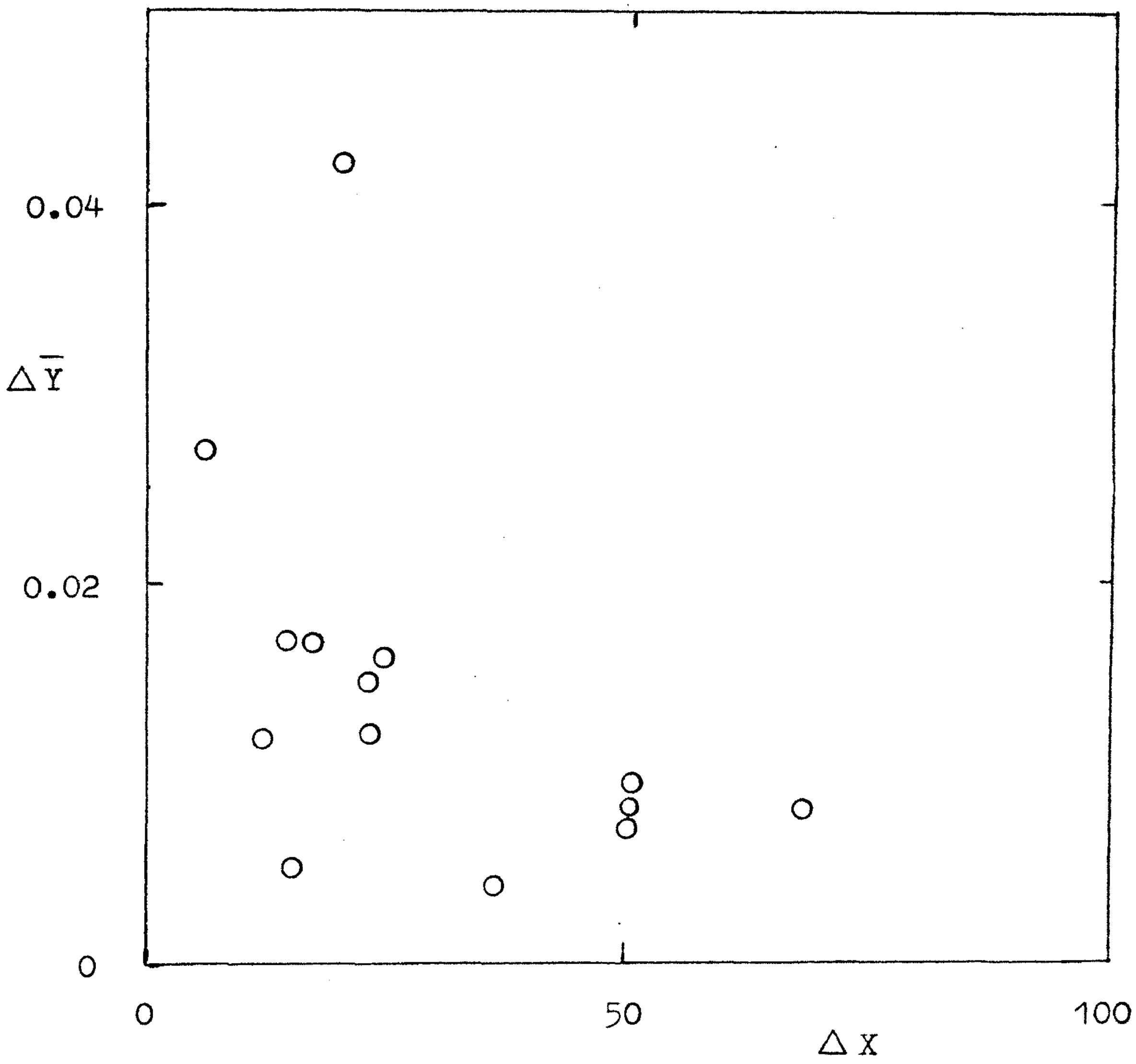


Figure 18: Plot of $\Delta\bar{Y}$ versus ΔX for system 2 using the LEMF (method II).

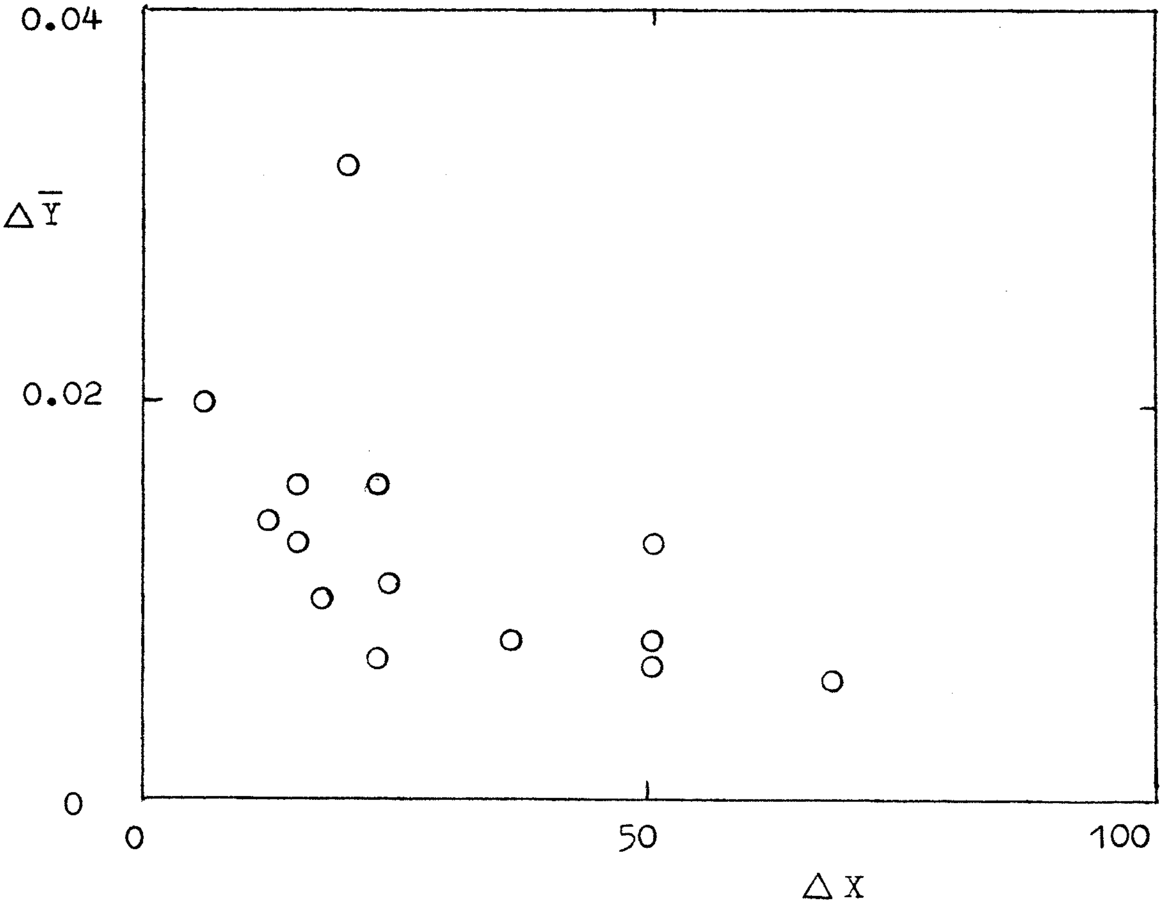


Figure 19: Plot of $\Delta\overline{Y}$ versus ΔX for system 2 using the UNIQUAC (method II).

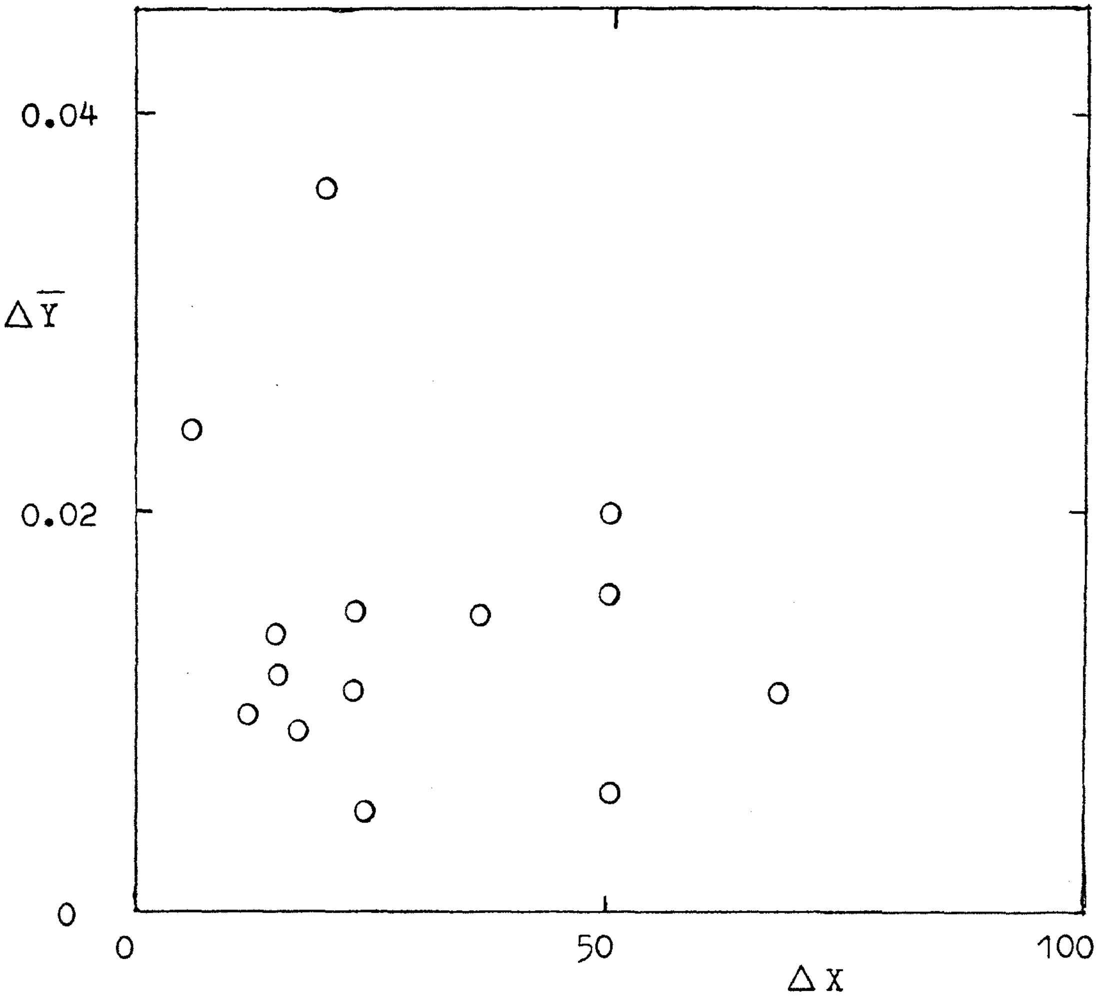


Figure 20: Plot of $\Delta\overline{Y}$ versus ΔX for system 3 using the NRTL (method II).

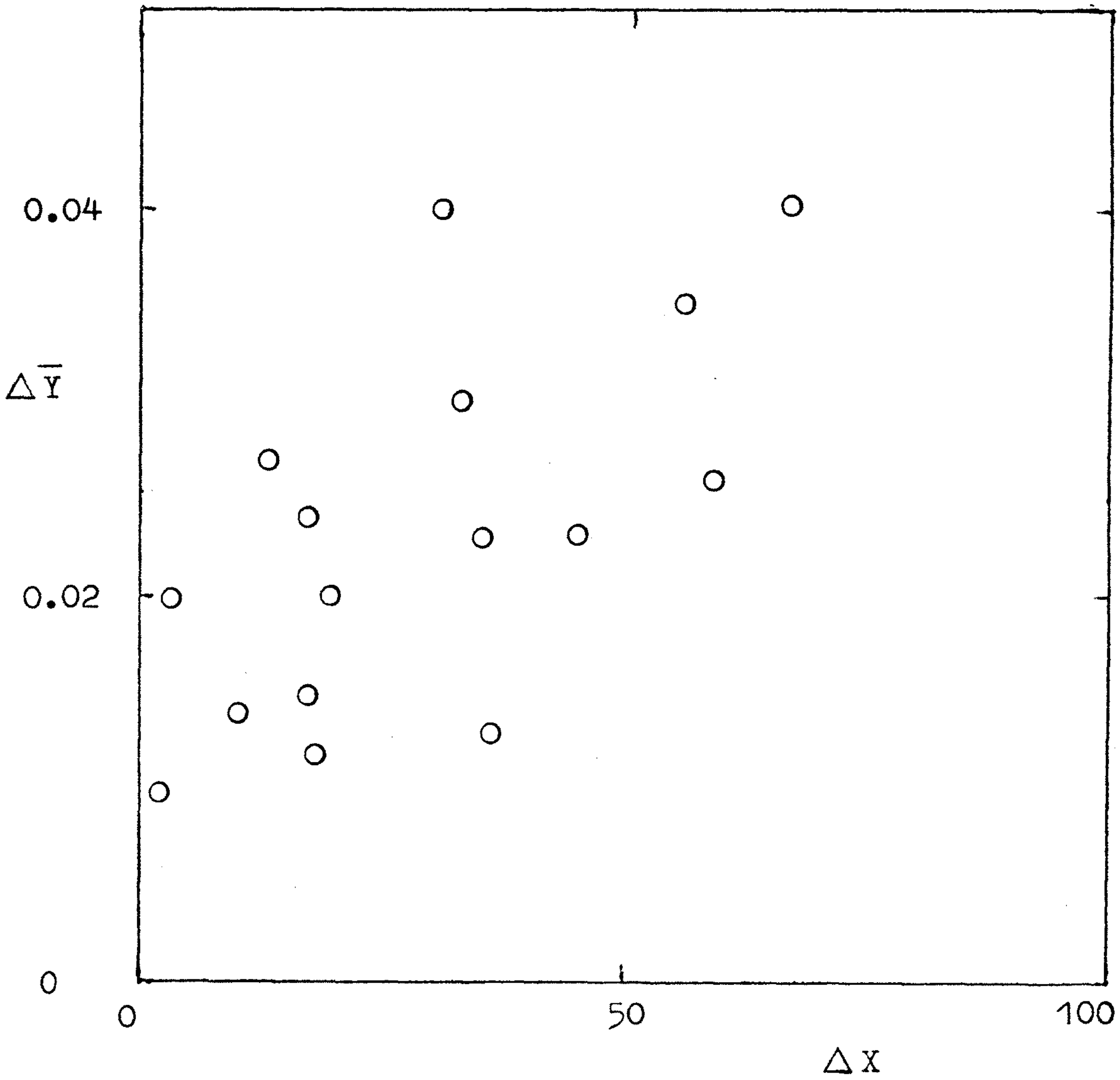


Figure 21: Plot of $\Delta \overline{Y}$ versus ΔX for system 3 using the LEMF (method II).

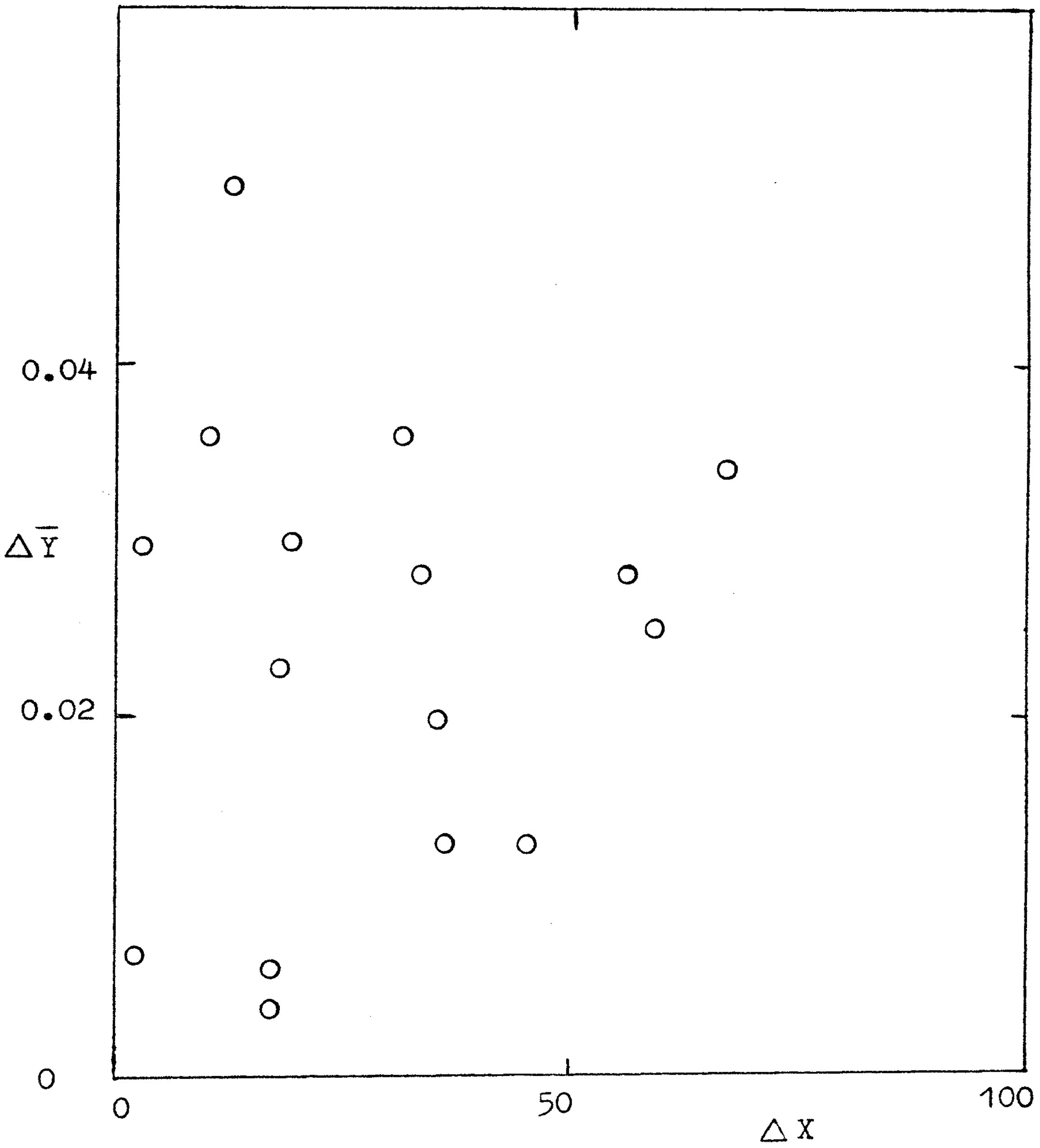


Figure 22: Plot of $\Delta\overline{Y}$ versus ΔX for system 3 using the UNIQUAC (method II).

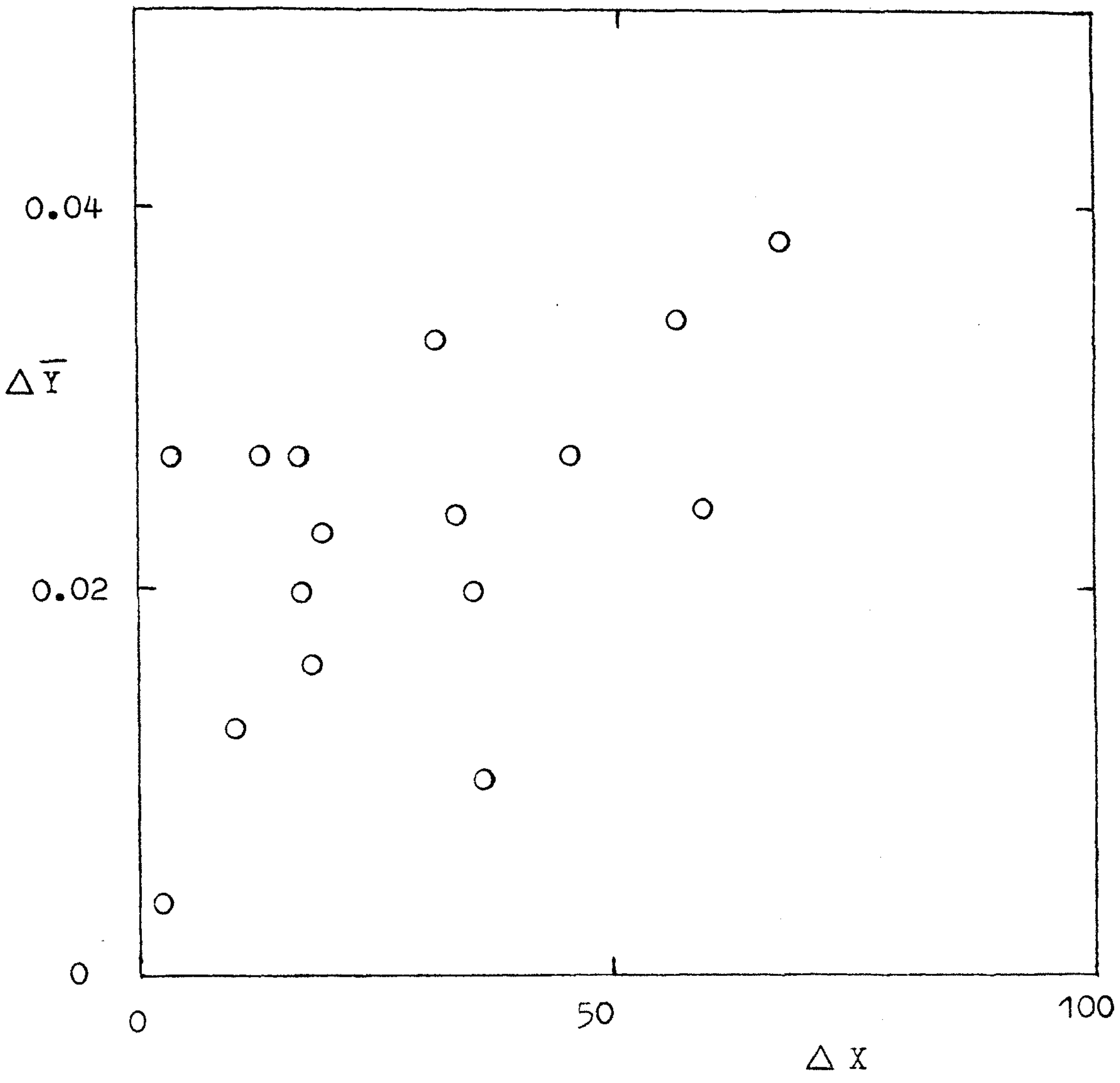


Figure 23: Plot of $\Delta\overline{Y}$ versus ΔX for system 4 using the NRTL (method II).

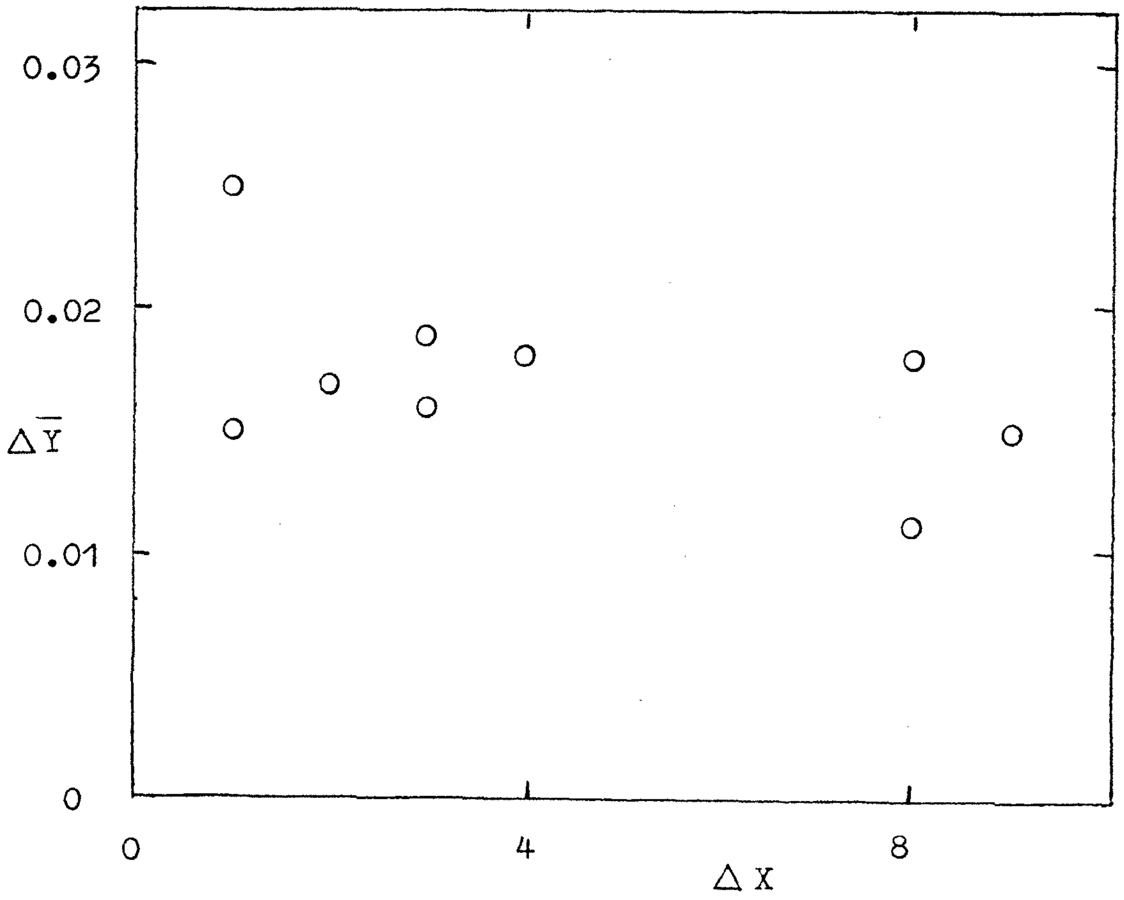
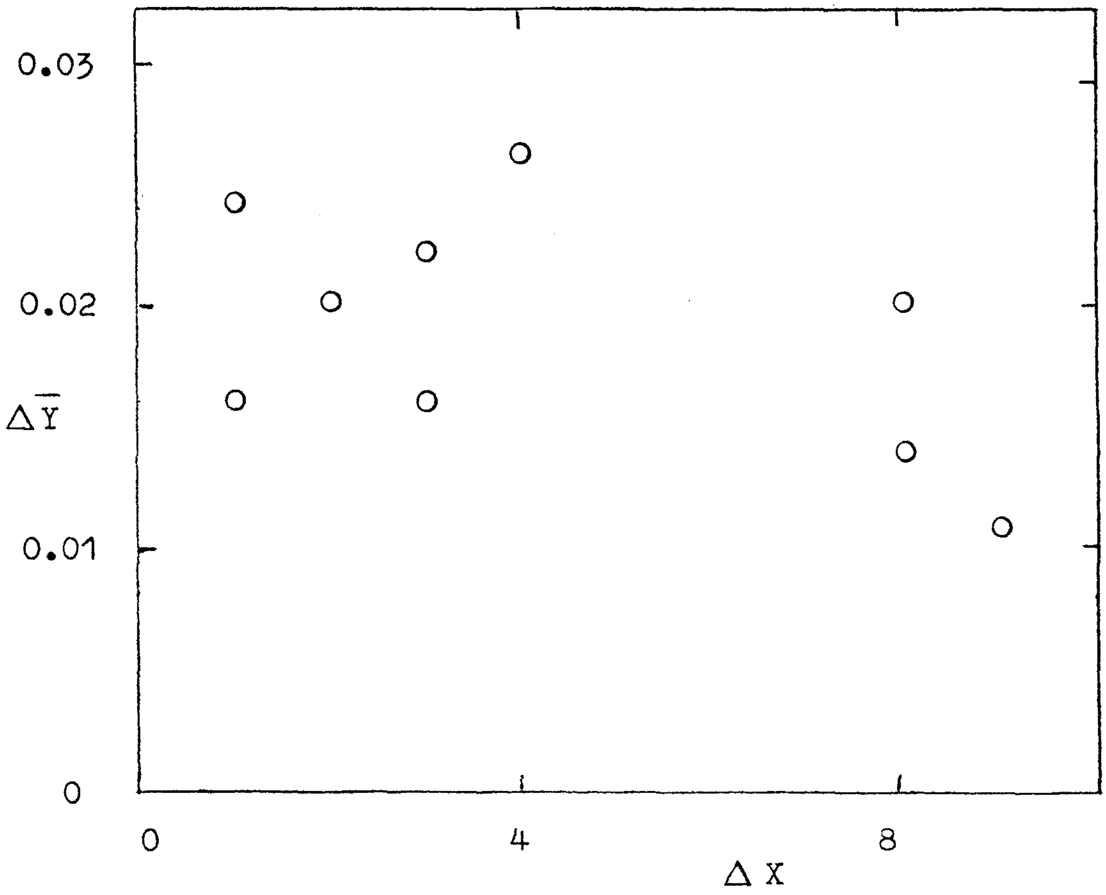


Figure 24: Plot of $\Delta\overline{Y}$ versus ΔX for system 4 using the LEMF (method II).



<u>Figure 25</u>: Plot of $\Delta\overline{Y}$ versus ΔX for system 4 using the UNIQUAC (method II).

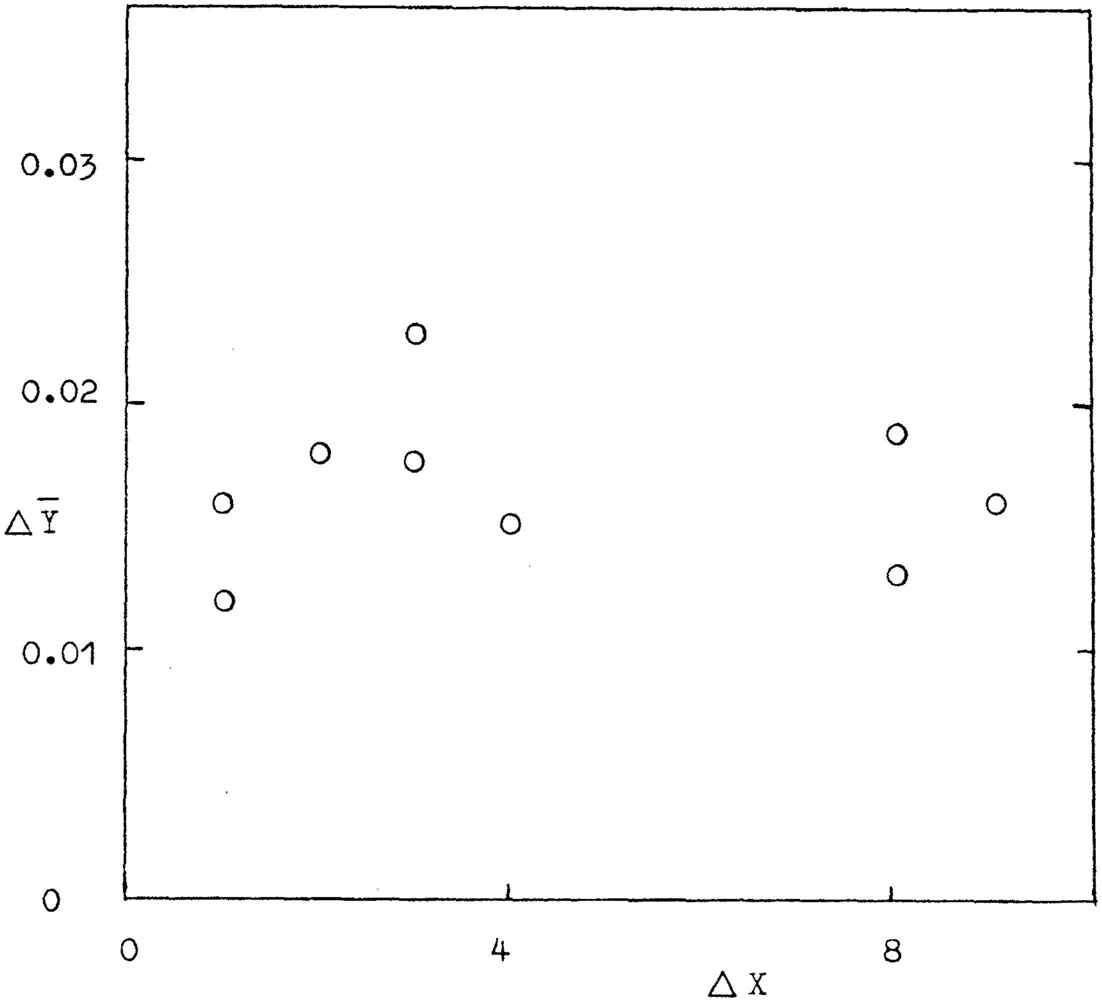


Figure 26: Plot of $\Delta\overline{Y}$ versus ΔX for system 5 using the NRTL (method II).

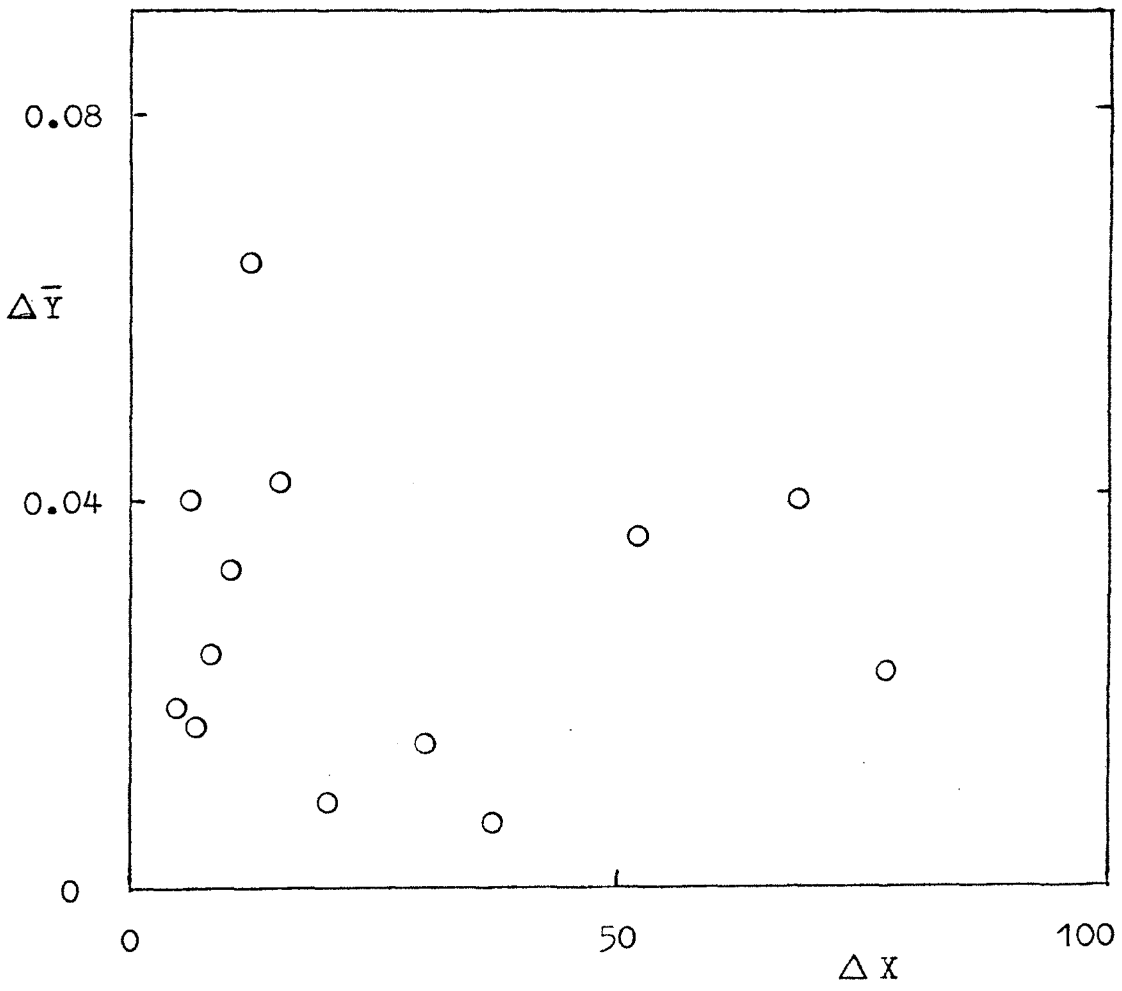
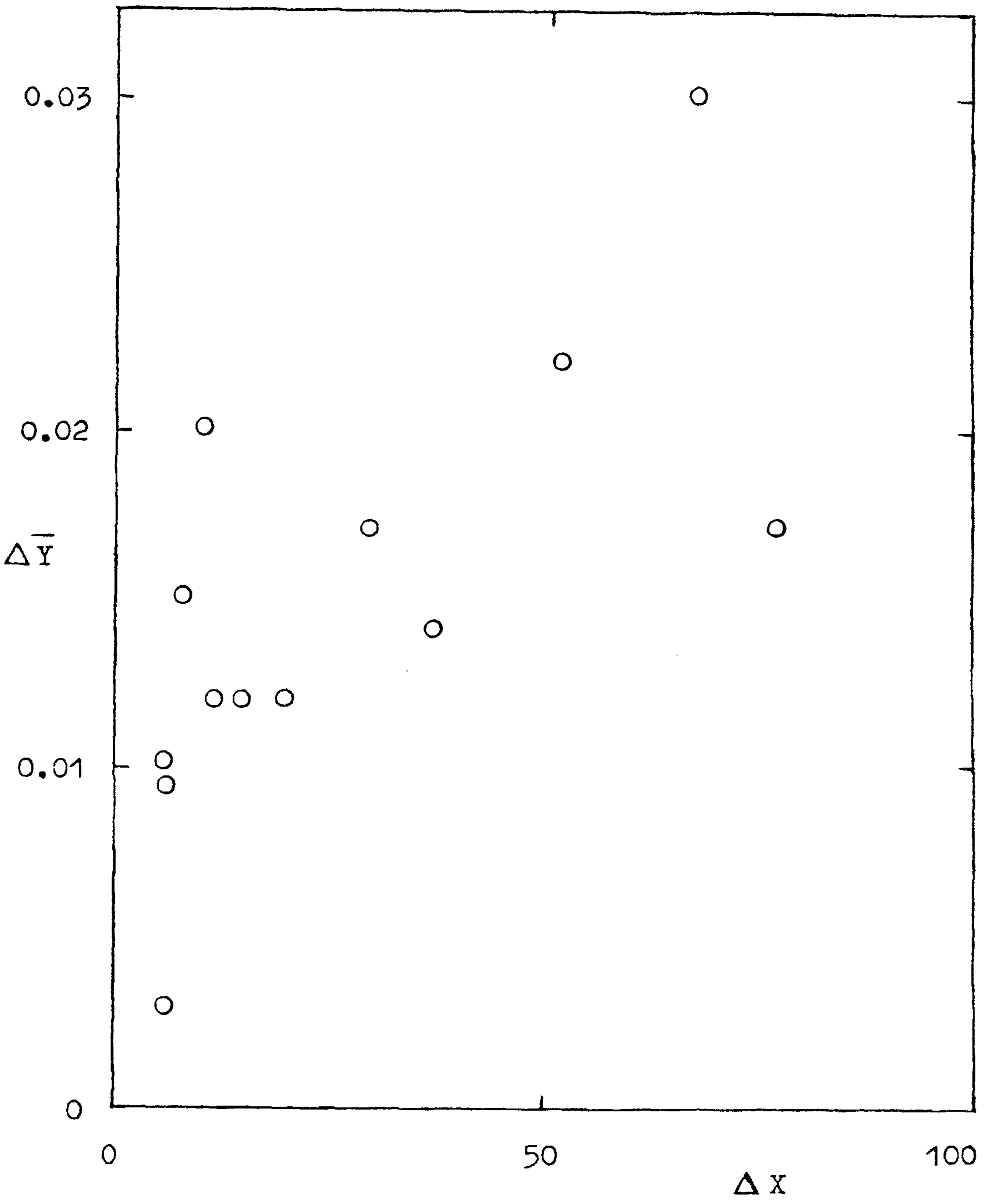


Figure 27: Plot of $\Delta\overline{Y}$ versus ΔX for system 5 using the LEMF (method II).



<u>Figure 28</u>: Plot of $\Delta\overline{Y}$ versus ΔX for system 5 using the UNIQUAC (method II).

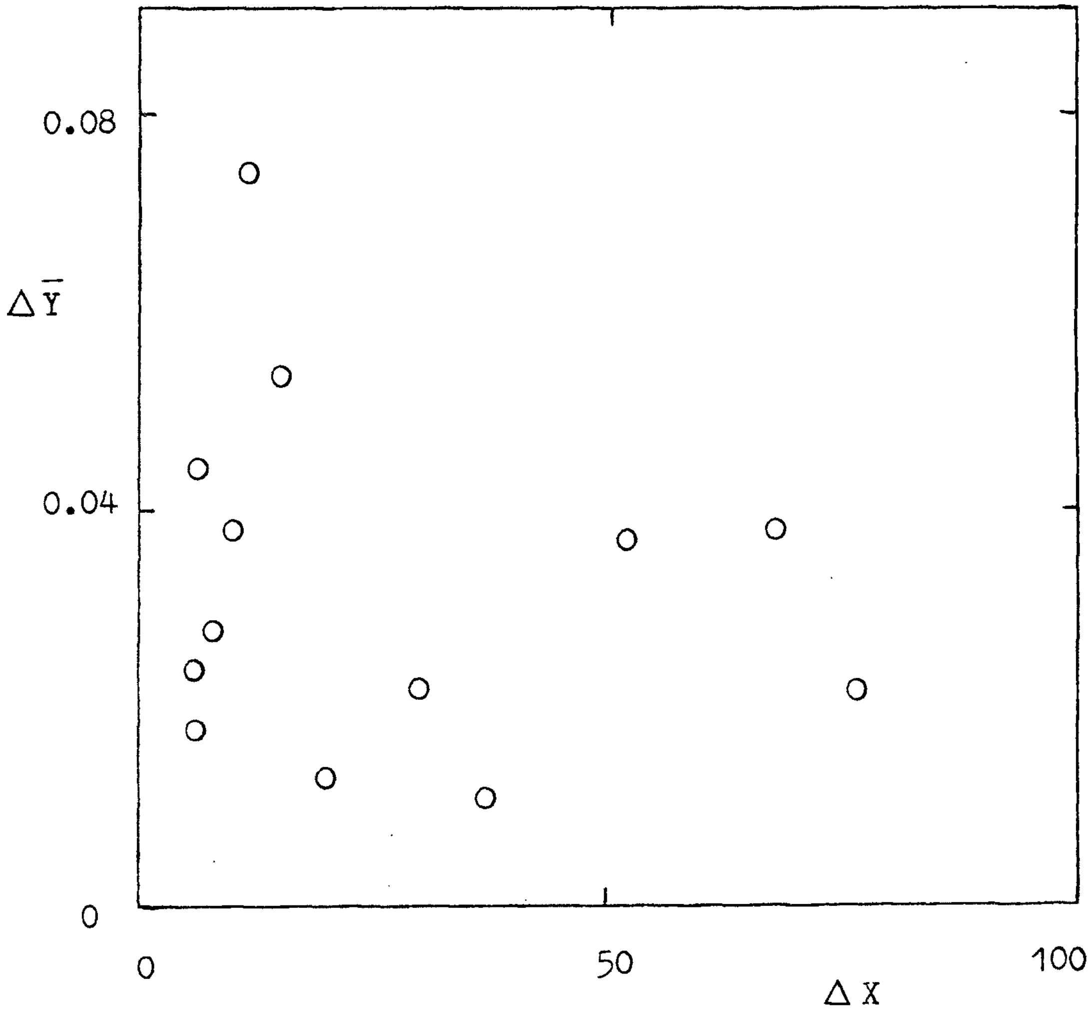


Figure 29: Plot of $\Delta\vec{\overline{Y}}$ versus ΔX for system 6 using the NRTL (method II).

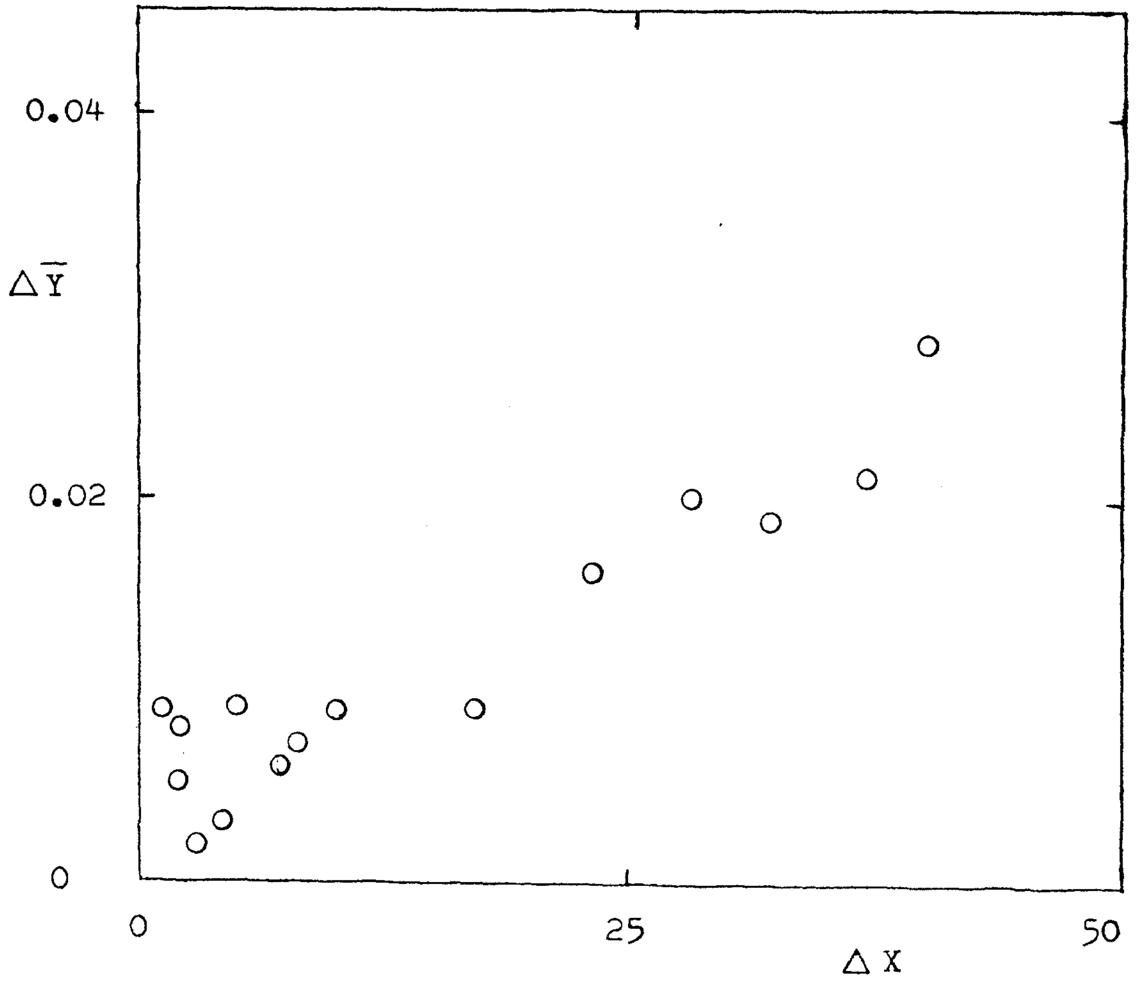


Figure 30: Plot of $\Delta\overline{Y}$ versus ΔX for system 6 using the LEMF (method II).

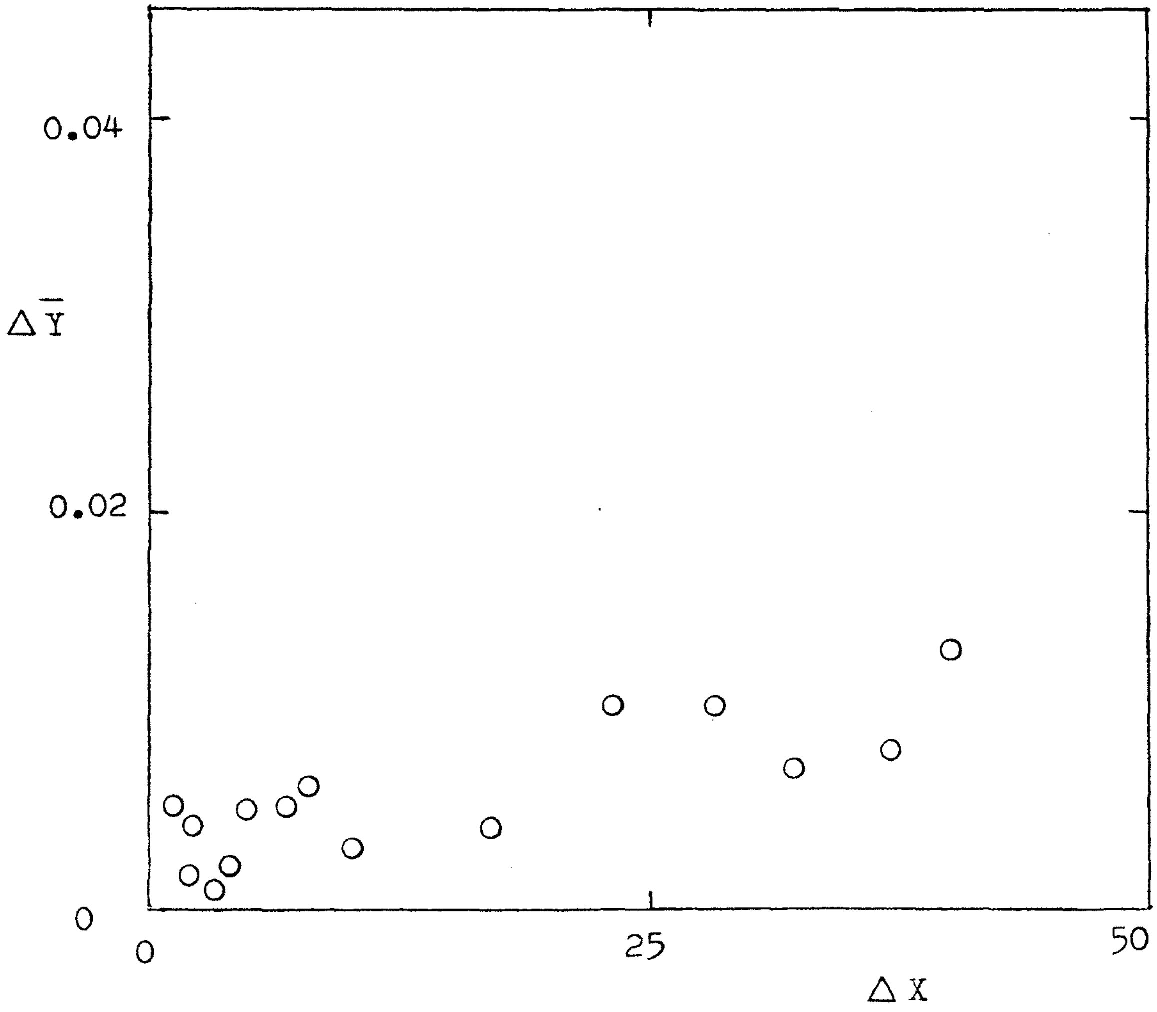


Figure 31: Plot of $\Delta\overline{Y}$ versus ΔX for system 6 using the UNIQUAC (method II).

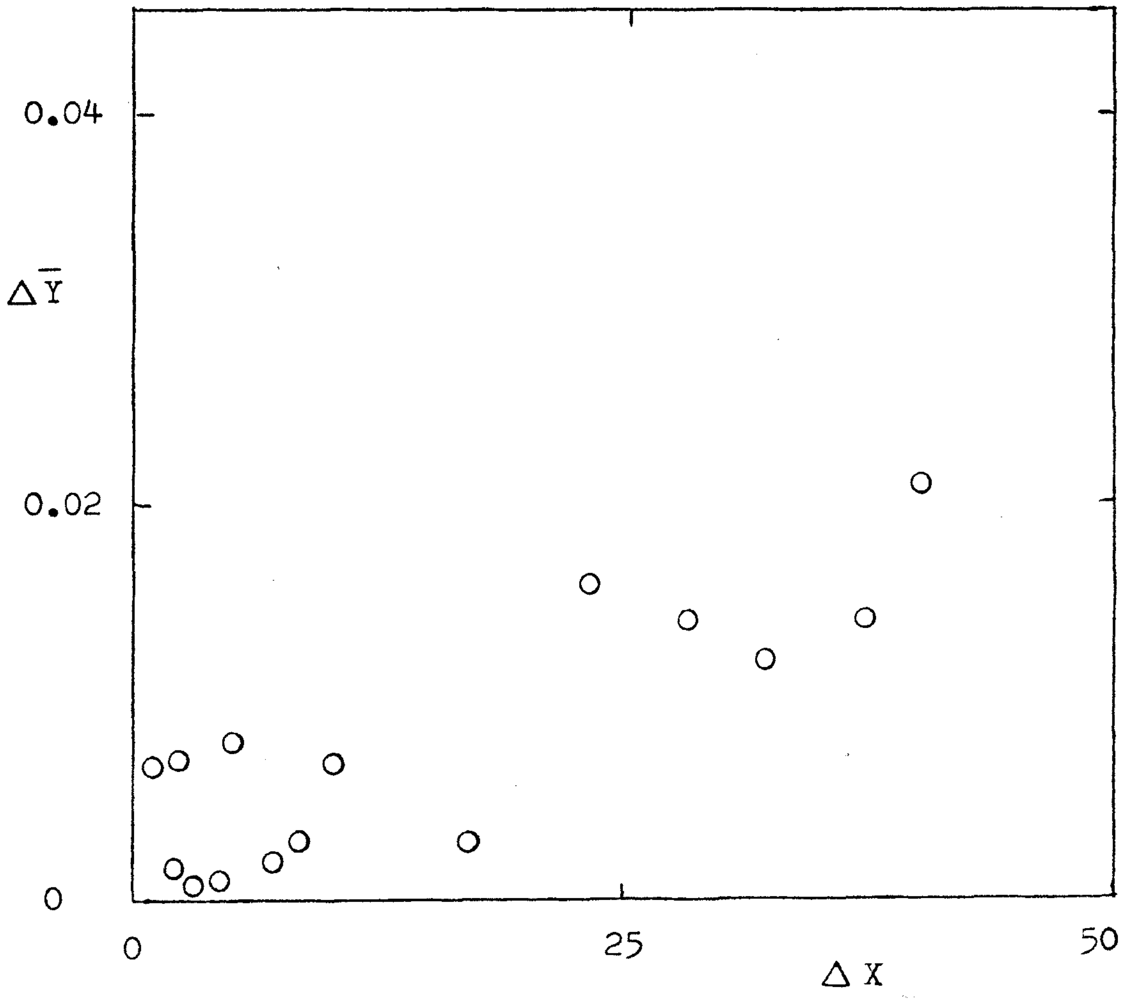


Figure 32: Plot of $\Delta\overline{Y}$ versus ΔX for system 7 using the NRTL (method II).

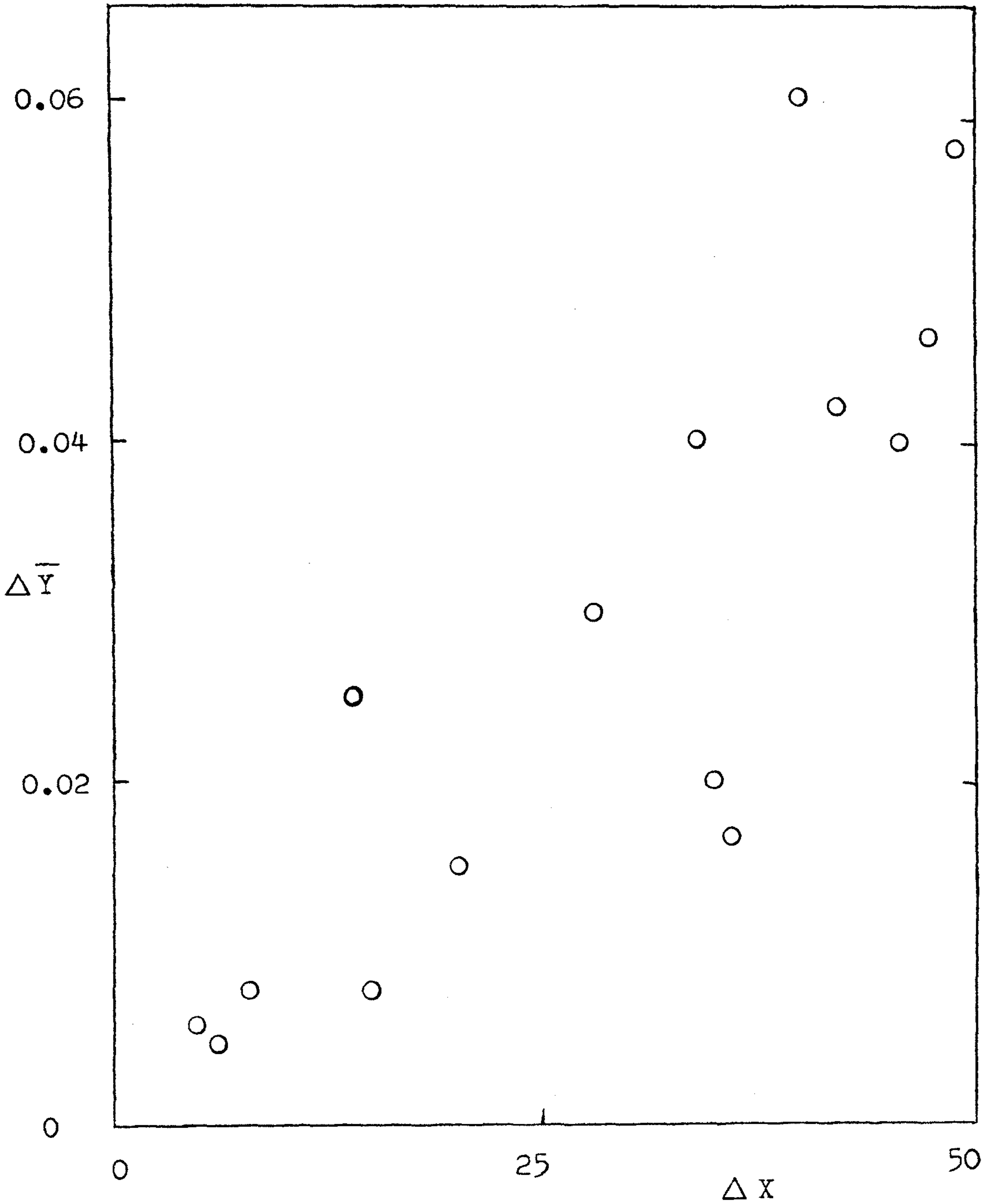


Figure 33: Plot of $\Delta\overline{Y}$ versus ΔX for system 7 using the LEMF (method II).

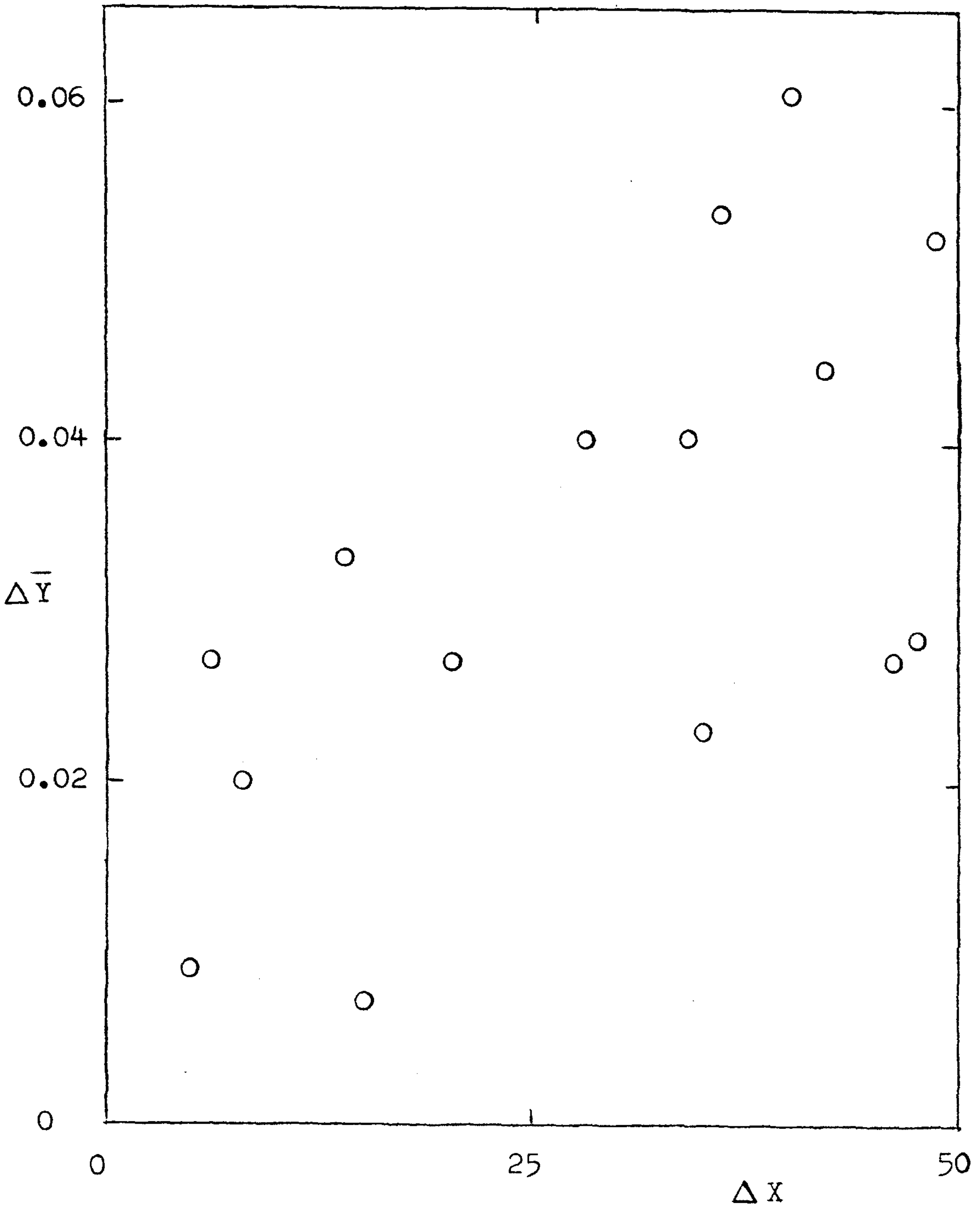


Figure 34: Plot of $\Delta \overline{Y}$ versus ΔX for system 7 using the UNIQUAC (method II).

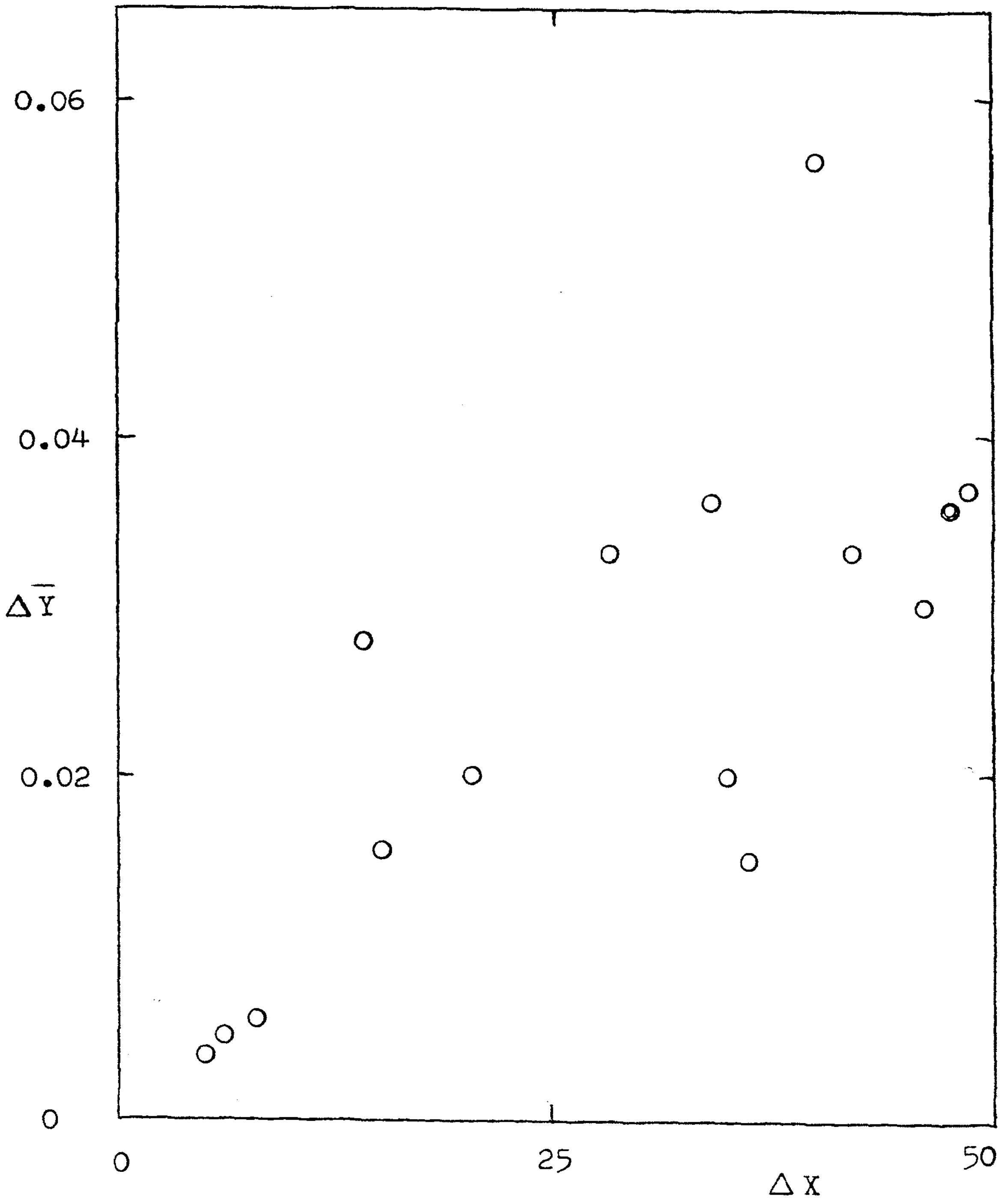


Figure 35: Procedure for Determining the Quantity ΔX.

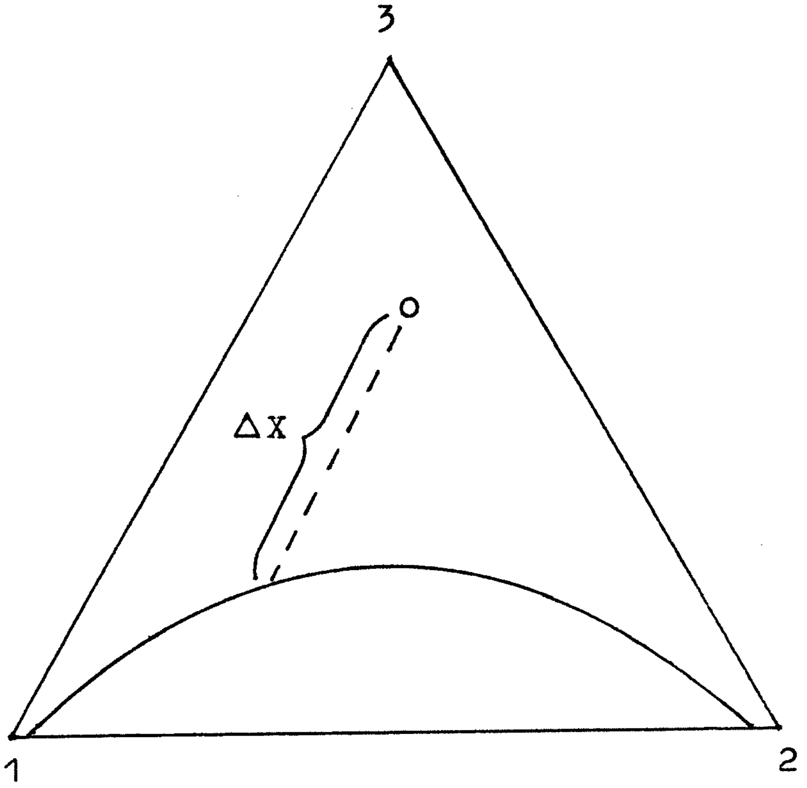


Figure 36: Vapor Phase Prediction for the System Acetonitrile(1) - Benzene(3).

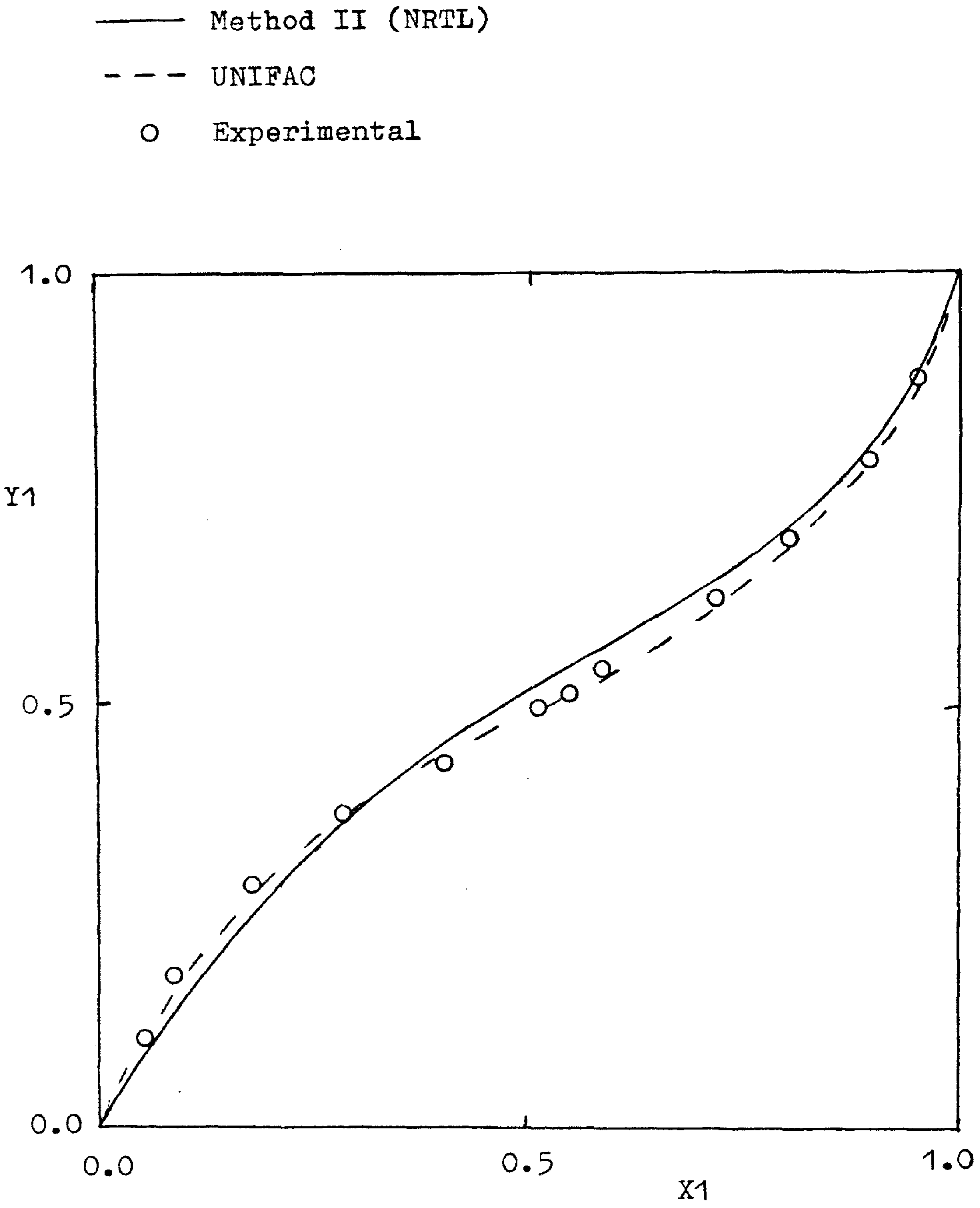


Figure 37: Prediction of Vapor Phase Compositions for system 1 by combining methods II and V (UNIQUAC).

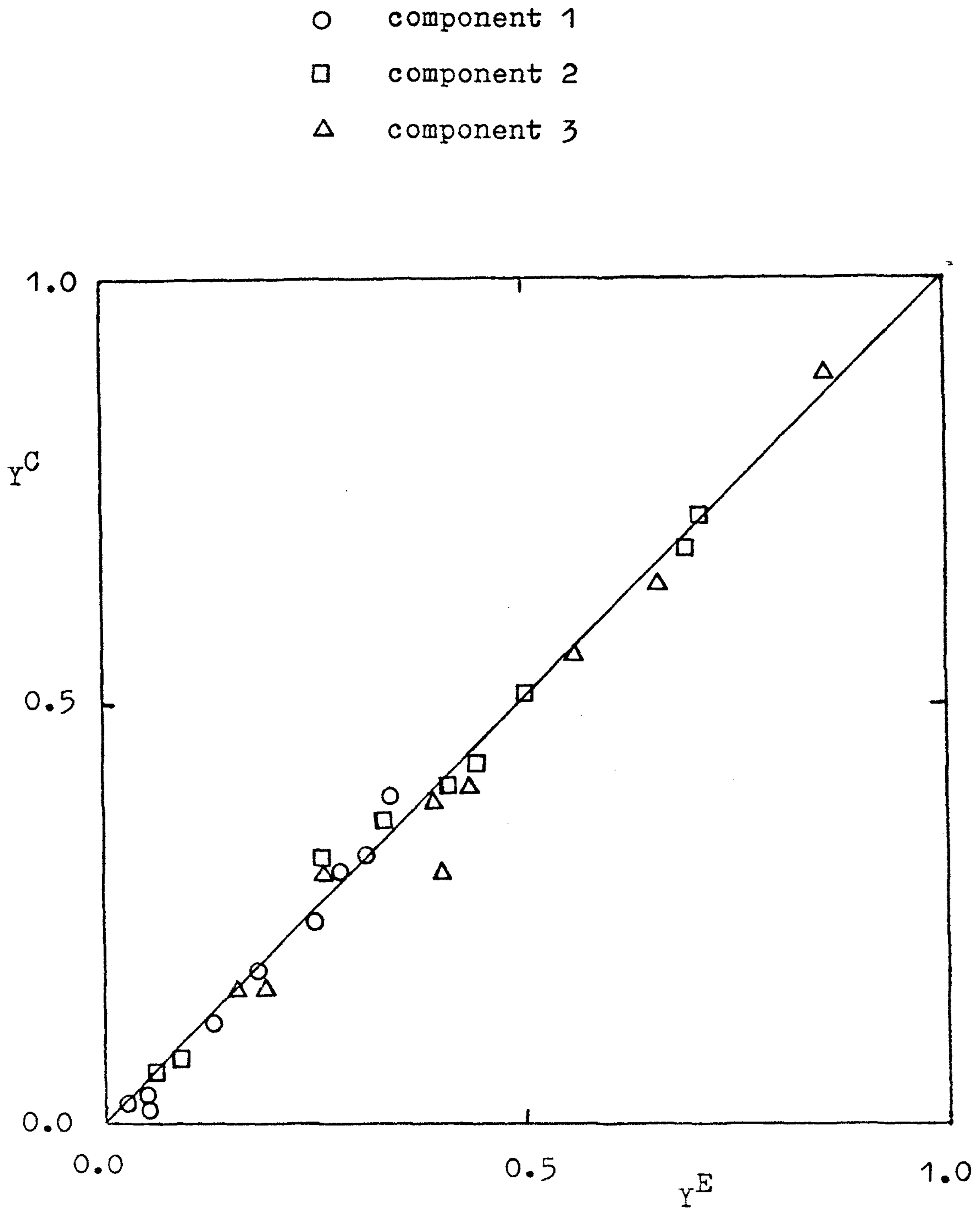
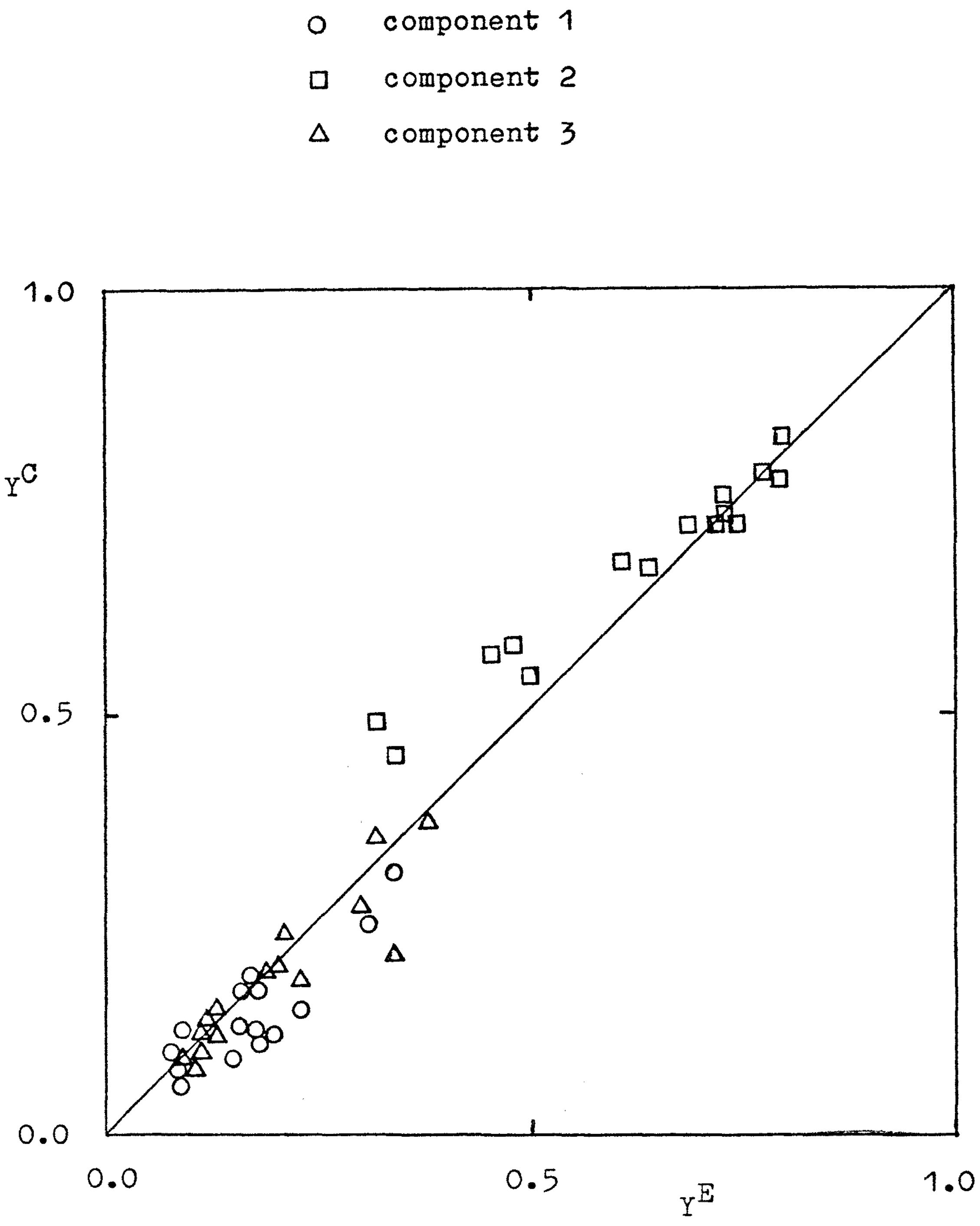


Figure 38: Prediction of Vapor Phase Compositions for system 7 by combining methods II and V (NRTL).



APPENDIX B

THE TABLES

This appendix contains Tables I through XXXVII .

Table I: Ternary LLE Systems.

Systems	Number & Type	T, C	Reference
water(1) ethyl acetate(2) ethanol(3)	1A	70	Griswold and Chu (1949)
water(1) ethyl acetate(2) methanol(3)	2A	70	Akita and Yoshida (1963)
water(1) acrylonitrile(2) acetonitrile(3)	3A	60	Volpicelli (1968)
water(1) n-butanol(2) n-propanol(3)	4A	90-92	Newsham and Vahdat (1977)
acetonitrile(1) n-heptane(2) benzene(3)	5B	45	Palmer and Smith (1972)
n-pentane(1) sulfur dioxide(2) benzene(3)	6B	-17.8	Bowden et al. (1966)
water(1) benzene(2) 1-propanol(3)	7B	37.7	McCants et al. (1953)
water(1) hexane(2) tetrahydrofuran(3)	8B	50	Lampa et al. (1980)

Table II: Ternary VLE Systems.

System #	P or T	# of Points	Reference
1	70 C	9	Griswold and Chu (1949)
2	760 mmHg	65	Akita and Yoshida (1963)
3	760 mmHg	87	Volpicelli (1968)
4	739 mmHg	9	Newsham and Vahdat (1977)
5	45 C	34	Palmer and Smith (1972)
6	-17.8 C	41	Bowden et al. (1966)
7	30 C	22	Udovenko and Mazanko (1975)
8	760 mmHg	21	Lampa et al. (1980)

Table III: Non-randomness Parameter Values for the NRTL model.

System #	α_{12}	α_{13}	α_{23}
1	0.20	0.30	0.30
2	0.20	0.30	0.30
3	0.20	0.30	0.30
4	0.20	0.30	0.30
5	0.20	0.30	0.30
6	0.20	0.30	0.30
7	0.20	0.30	0.47
8	0.20	0.30	0.30

Table IV: Pure Component Constants ^{h} for the UNIQUAC model.

Component	r	q	q'
water	0.92	1.4	1.0
acetonitrile	0.87	1.72	-
benzene	3.19	2.40	-
ethyl acetate	3.48	3.12	-
acrylonitrile	2.09	1.64	-
1-butanol	3.45	3.05	0.88
n-heptane	5.17	4.4	-
n-pentane	3.82	3.31	-
hexane	4.50	3.86	-
ethanol	2.11	1.97	0.92
methanol	1.43	1.43	0.96
1-propanol	2.78	2.51	0.89
sulfur dioxide	1.55	1.45	-
tetrahydrofuran	2.94	2.40	-

[h] Obtained from Prausnitz et al. (1980).

Table V: Parameters from method I for system 1.

Starting Value	Δg_{13} / Δg_{31}	Δg_{23} / Δg_{32}	Δg_{12} / Δg_{21}	Calc. Binary γ Range Binary 1-3: $\gamma 1/\gamma 3$ Binary 2-3: $\gamma 2/\gamma 3$
NRTL				
345	2520	2130	3074	1.0-1.1-0.8/1.2-0.8-0.98 [a]
	-1206	-978	-3	1.0-1.1-0.9/1.1-0.9-0.99 [a]
zero [b]	-390	2886	2977	1.0-1.2/1.2-1.0
	693	-838	77	1.1-1.3-1.0/1.6-0.9-0.99 [a]
+500	872	2320	3063	0.1-1.2/1.4-0.4
	-461	-1000	16	1.1-0.9/1.1-0.99
-500	2000	-4000	5000	1.0-2.0/5.0-1.0
	-1500	850	100	1.0-0.05/1.0-1000
LEMF [c]				
240 [b]	-478	278	431	1.0-1.7/3.7-1.0
	697	622	812	1.1-3.7/4.0-1.0
zero	-461	404	434	1.0-0.8/0.5-1.0
	725	638	812	1.1-5.0/4.8-1.0
+500	-106	903	443	1.0-2.4/8.6-1.0
	788	718	813	1.1-42/12-1.0
-500	3686	-2050	452	1.0-2.4/354-160
	388	-4797	786	0.9-0.86/0.86-0.99
UNIQUAC				
-291 1271 [b]	1757	3000	201	1.0-0.86/0.81-0.99
950 -314	-1090	-1047	1030	1.1-0.3/0.5-0.98
zero	-1625	2070	160	1.0-1.02-0.2/0.3-0.2-0.6 [a]
	67	-790	1098	1.0-1.1-0.6/1.0-0.8-0.99 [a]

Table V, continued

Starting Value	$\frac{\Delta g_{13}}{\Delta g_{31}}$	$\frac{\Delta g_{23}}{\Delta g_{32}}$	$\frac{\Delta g_{12}}{\Delta g_{21}}$	Calc. Binary γ Range Binary 1-3: $\gamma 1/\gamma 3$ Binary 2-3: $\gamma 2/\gamma 3$
		UNIQUAC		
+500	-1800	4000	200	1.0-0.1/0.1-0.9
	500	-1500	1500	1.0-0.5/1.0-0.5
-500	400	-904	273	0.99-0.7/0.44-0.99
	-960	-244	820	0.99-0.02/0.2-0.8

a: Calculated binary γ range exhibits a maximum or minimum.

b: Starting value which gave the best parameters for each model.

c: Model which gave reasonable parameters.

Table VI: Parameters from method I for system 2.

Starting Value	$\frac{\Delta g_{13}}{\Delta g_{31}}$	$\frac{\Delta g_{23}}{\Delta g_{32}}$	$\frac{\Delta g_{12}}{\Delta g_{21}}$	Calc. Binary γ Range Binary 1-3: $\gamma 1/\gamma 3$ Binary 2-3: $\gamma 2/\gamma 3$
		NRTL		
345 [b]	484	416	3222	1.0-1.05/1.06-1.0
	-371	-117	-104	1.0-1.37/1.5-1.0
zero	-627	146	3210	0.9-0.6/0.4-0.9
	408	-116	-77	0.9-0.7/0.6-0.98
+500	373	436	3230	1.0-1.05/1.06-1.0
	-283	-124	-106	1.0-1.37/1.5-1.0
-500	-660	153	3207	0.9-0.6/0.7-0.9
	467	-110	-75	1.0-1.03/1.05-1.0
		LEMF [c]		
240	-896	550	492	1.0-2.3/5.0-1.0
	827	800	817	1.0-12/56-1.0
zero [b]	-451	90	397	1.0-2.5/1.0-3.0
	484	481	830	1.0-2.2/4.0-1.0
+500	120	682	421	1.0-2.5/4.0-1.0
	553	556	836	1.0-16/14-1.0
-500	-741	112	380	0.99-1.3/1.3-1.0
	444	-3725	802	1.0-1.16/1.14-0.98
		UNIQUAC		
24 1237	-8060	6603	209	1.0-0.001/0.0-0.0
397 -239	451	-562	1047	1.0-1.2/12-0.99
zero	1146	50	280	0.99-0.92/0.77-1.0
	-898	220	878	1.0-0.95/0.80-1.0
+500	2790	2381	211	1.0-1.3/1.6-1.0
	-783	-514	967	0.3-1.4/5.5-0.2
-500 [b]	566	1398	210	1.0-1.15/1.13-1.0
	-575	-509	930	1.0-1.2/1.8-0.99

Table VII: Parameters from method I for system 3.

Starting Value	$\frac{\Delta g_{13}}{\Delta g_{31}}$	$\frac{\Delta g_{23}}{\Delta g_{32}}$	$\frac{\Delta g_{12}}{\Delta g_{21}}$	Calc. Binary γ Range Binary 1-3: γ1/ γ3 Binary 2-3: γ2/ γ3
		NRTL		
345[b]	$\frac{1868}{-168}$	$\frac{-610}{1058}$	$\frac{2030}{454}$	1.0-2.6/7.9-1.0 0.9-1.3/1.1-0.9
zero	$\frac{1885}{-110}$	$\frac{-700}{1610}$	$\frac{2047}{421}$	1.0-2.8/8.8-1.0 0.99-0.5/0.7-0.8
+500	$\frac{1824}{-314}$	$\frac{2203}{-1093}$	$\frac{1940}{634}$	1.0-2.1/6.0-1.0 1.0-0.8/1.2-0.99
-500	$\frac{1595}{-225}$	$\frac{-754}{560}$	$\frac{2005}{464}$	1.0-2.3/5.3-1.0 0.99-0.6/0.7-0.99
		LEMF		
240	$\frac{220}{603}$	$\frac{160}{-682}$	$\frac{522}{704}$	1.0-3.5/7.5-1.0 1.0-0.7/0.87-0.99
zero[b]	$\frac{327}{587}$	$\frac{-1200}{255}$	$\frac{491}{705}$	1.0-4.6/8.0-1.0 0.97-1.0/0.7-1.0
+500	$\frac{239}{601}$	$\frac{154}{-830}$	$\frac{518}{704}$	1.0-3.7/7.6-1.0 1.0-0.6/0.86-0.99
-500	$\frac{1422}{565}$	$\frac{-741}{-742}$	$\frac{3267}{756}$	1.0-600,000/33-1.0 0.98-0.4/0.36-0.98
		UNIQUAC[c]		
$\frac{-57}{527}$ $\frac{435}{-209}$[b]	$\frac{554}{37}$	$\frac{-410}{642}$	$\frac{320}{727}$	1.0-3.1/8.2-1.0 1.0-1.3/1.1-1.0
zero	$\frac{815}{-153}$	$\frac{380}{-200}$	$\frac{285}{820}$	1.0-2.7/8.6-1.0 1.0-0.3/0.4-1.0
+500	$\frac{1064}{-240}$	$\frac{-965}{-53}$	$\frac{1320}{214}$	1.0-7.5/4.6-1.0 0.99-0.11/0.4-0.93
-500	$\frac{-26000}{214}$	$\frac{-28000}{40000}$	$\frac{1370}{140}$	1.0-0.0/0.0-0.0 1.0-0.001/0.0-0.0

Table VIII: Parameters from method I for system 4.

Starting Value	Δg_{13} Δg_{31}	Δg_{23} Δg_{32}	Δg_{12} Δg_{21}	Calc. Binary γ Range Binary 1-3: $\gamma 1/ \gamma 3$ Binary 2-3: $\gamma 2/ \gamma 3$
		NRTL		
345	1998	-381	2425	1.0-0.8/1.9-0.99
	-763	-227	-647	0.99-0.7/0.5-0.9
zero	2395	2573	3646	1.0-0.6/1.0-0.7
	-994	-1466	-806	1.0-0.7/0.7-0.9
+500	1426	-790	3260	1.0-1.4/3.1-1.0
	-333	66	-526	0.99-0.62/0.44-0.85
-500 ^{b}	1313	-470	3121	1.0-2.6/6.0-1.2
	5410	116	-390	0.99-0.8/0.7-0.9
		LEMF		
240	-596	-3767	176	1.0-1.9/5.6-1.0
	750	-794	814	0.97-0.8/0.7-0.9
zero ^{b}	-630	-511	180	1.0-1.9/5.1-1.0
	744	11	812	0.99-0.8/0.64-0.98
+500	584	-346	162	1.0-6.7/15-1.0
	657	1066	812	1.1-2.6/11-1.0
-500	-475	-977	175	1.0-1.8/5.4-1.0
	720	-1228	802	0.97-0.66/0.4-0.8
		UNIQUAC ^{c}		
-384 545	3113	1538	1866	1.0-1.1/3.0-0.99
1433 571	-925	552	150	1.0-2.0/4.0-1.1
zero	4478	1176	2640	1.0-1.4/5.7-0.99
	-732	564	145	1.0-1.9/3.5-1.1
+500	836	-134	1848	1.0-5.7/12-1.0
	1018	-256	141	0.99-0.8/0.7-0.95
-500 ^{b}	977	114	1844	1.0-3.4/9.7-1.0
	273	-348	138	0.99-0.95/0.94-0.97

Table IX: Parameters from method I for system 5.

Starting Value	$\frac{\Delta g_{13}}{\Delta g_{31}}$	$\frac{\Delta g_{23}}{\Delta g_{32}}$	$\frac{\Delta g_{12}}{\Delta g_{21}}$	Calc. Binary γ Range Binary 1-3: $\gamma 1/\gamma 3$ Binary 2-3: $\gamma 2/\gamma 3$
		NRTL[c]		
345	$\frac{1114}{-462}$	$\frac{-238}{436}$	$\frac{1378}{840}$	1.0-1.3/1.9-1.0 1.0-1.2/1.1-1.0
zero[b]	$\frac{1392}{-447}$	$\frac{510}{-80}$	$\frac{1360}{835}$	1.0-1.5/3.0-1.0 1.0-1.6/1.8-1.0
+500	$\frac{1252}{-450}$	$\frac{304}{-19}$	$\frac{1390}{820}$	0.6-1.4/2.5-0.7 1.0-1.5/1.5-1.0
-500	$\frac{-364}{196}$	$\frac{-37}{-512}$	$\frac{1390}{807}$	1.0-0.7/0.76-0.99 0.99-0.40/0.4-1.0
		LEMF		
240[b]	$\frac{11}{210}$	$\frac{-103}{-144}$	$\frac{558}{619}$	1.0-1.4/1.6-1.0 0.99-0.7/0.7-1.0
zero[b]	$\frac{14}{215}$	$\frac{-72}{-184}$	$\frac{557}{620}$	1.0-1.4/1.6-1.0 0.99-0.7/0.7-1.0
+500	$\frac{1133}{273}$	$\frac{1207}{-507}$	$\frac{551}{624}$	1.0-996/10-1.0 1.0-8000/4.6-1.0
-500	$\frac{138}{161}$	$\frac{-463}{231}$	$\frac{566}{616}$	1.0-1.6/1.6-1.0 0.99-1.0/0.9-1.0
		UNIQUAC		
$\frac{-57}{434}$ $\frac{527}{-209}$	$\frac{-320}{207}$	$\frac{209}{-382}$	$\frac{47}{1108}$	0.99-0.6/0.6-0.99 0.99-0.3/0.3-0.99
zero	$\frac{775}{17}$	$\frac{926}{-223}$	$\frac{40}{1131}$	1.0-3.5/11-1.0 1.0-6.0/8.0-1.0
+500[b]	$\frac{525}{14}$	$\frac{638}{-200}$	$\frac{40}{1131}$	1.0-2.7/6.0-1.0 1.0-4.0/3.7-1.0
-500	$\frac{-753}{92}$	$\frac{-438}{-304}$	$\frac{42}{1119}$	0.99-0.04/1.0-0.98 0.99-0.003/0.05-0.99

Table X: Parameters from method I for system 6.

Starting Value	Δg_{13}	Δg_{23}	Δg_{12}	Calc. Binary γ Range Binary 1-3: $\gamma 1/\gamma 3$
	Δg_{31}	Δg_{32}	Δg_{21}	Binary 2-3: $\gamma 2/\gamma 3$
		NRTL		
345 [b]	2216	2356	221	1.0-1.7/12-1.0
	-365	-546	1500	1.0-1.4/9.0-0.95
zero	1834	1926	203	1.0-2.5/33-1.4
	438	218	1418	1.0-3.0/30-1.1
+500	2204	2320	220	1.0-1.8/14-1.0
	-297	-471	1491	1.0-1.5/11-0.97
-500	-259	-981	190	0.99-0.85/0.58-0.87
	-30	740	1500	0.99-0.60/0.38-0.77
		LEMF [c]		
240	646	-911	501	1.0-2.7/60-2.4
	585	596	448	1.0-1.9/6.0-1.0
zero	862	-678	497	1.0-2.8/117-3.8
	611	613	466	1.0-1.9/8.7-1.0
-500 [b]	454	588	493	1.0-1.3/2.3-1.5
	-3647	-796	386	1.0-1.5/2.3-1.3
+500	4261	2913	502	1.0-2.2/5000-10000
	626	630	462	1.0-2.7/9000-300
		UNIQUAC		
282 -73 [b]	1181	797	680	1.0-2.6/38-1.4
-76 469	-185	170	233	1.0-3.0/33-1.1
zero	1181	797	680	2.6-1.0/1.4-38
	-185	170	233	1.0-3.0/33-1.1
+500	1120	676	625	1.0-3.4/88-1.8
	6	1234	231	1.0-5.0/95-1.6
-500	1172	632	522	1.0-3.4/76-1.8
	-20	25600	280	1.0-5.0/81-1.9

Table XI: Parameters from method I for system 7.

Starting Value	Δg_{13} Δg_{31}	Δg_{23} Δg_{32}	Δg_{12} Δg_{21}	Calc. Binary γ Range Binary 1-3: γ_1/γ_3 Binary 2-3: γ_2/γ_3
		NRTL		
345 [b]	2844	1745	3403	1.1-1.3/2.8-0.99
	-801	-342	1884	1.0-1.3/4.3-0.98
zero	2815	1674	3392	1.1-1.35/3.0-0.99
	-783	-315	1870	1.0-1.4/4.4-0.99
+500	2700	1500	3100	1.0-2.0/2.0-1.0
	-900	-550	1600	0.7-0.9/0.6-0.8
-500	-3551	-5666	3778	0.97-0.0/0.001-0.4
	-942	7428	1944	1.0-0.5/0.0-0.0
		LEMF [c]		
240 [b]	-577	136	722	1.0-2.1/5.3-1.0
	728	492	895	1.0-1.9/5.3-1.1
zero	-476	851	726	1.1-2.5/10-1.0
	828	494	878	1.0-3.9/17-1.8
+500	503	560	711	1.0-7.4/10-1.0
	577	445	883	1.0-2.8/8.3-1.3
-500	101	-536	737	1.0-2.7/5.6-1.0
	580	645	880	0.7-1.7/5.1-0.6
		UNIQUAC		
-331 940 [b]	2833	5168	497	1.1-1.8/4.2-1.0
1236 -264	-465	-432	3660	1.0-2.0/9.0-1.1
zero	2836	5891	497	1.1-1.8/4.2-1.0
	-466	-432	3665	1.0-2.0/9.0-1.1
+500	-5520	-7200	684	0.99-0.001/0.0-0.006
	-593	15000	9935	1.0-0.6/0.0-0.0
-500	-6306	-8054	684	0.99-0.001/0.0-0.002
	-593	17400	16200	1.0-0.6/0.0-0.0

Table XII: Binary Systems.

System	P or T	Data Points	References
water-ethanol	760 mmHg	20	Hala et al. (1968)
ethyl acetate-ethanol	760 mmHg	9	Griswold and Chu (1949)
water-ethyl acetate	70 C	1	Griswold and Chu (1949)
water-methanol	65 C	10	Mcglashan and Williamson (1976)
ethyl acetate-methanol	760 mmHg	19	Akita and Yoshida (1963)
water-acetonitrile	760 mmHg	11	Blackford and York (1965)
acrylonitrile-acetonitrile	760 mmHg	7	Blackford and York (1965)
water-acrylonitrile	60 C	1	Volpicelli (1968)
water-n-propanol	90 C	12	Ratcliff and Chao (1969)
n-butanol-n-propanol	760 mmHg	6	Gay (1927)
water-n-butanol	92 C	1	Newsham and Vahdat (1977)
acetonitrile-n-heptane	45 C	1	Palmer and Smith (1972)
benzene-n-heptane	45 C	15	Palmer and Smith (1972)
benzene-acetonitrile	45 C	11	Palmer and Smith (1972)
n-pentane-benzene	-17.78 C	18	Bowden et al. (1966)

Table XII, continued

System	P or T	Data Points	References
sulfur dioxide-benzene	-17.78	19	Bowden et al. (1966)
n-pentane-sulfur dioxide	-17.78	1	Bowden et al. (1966)
water-1-propanol	40 C	12	Hala et al. (1968)
benzene-1-propanol	40 C	10	Hala et al. (1968)
water-benzene	37.7 C	1	Stephen and Stephen (1963)
water-tetrahydrofuran	760 mmHg	8	Lampa et al. (1980)
hexane-tetrahydrofuran	760 mmHg	18	Lampa et al. (1980)
water-hexane	40 C	1	Black et al. (1948)

Table XIII: Main groups and subgroups for UNIFAC model.

Component	Group Assignment
water	1 H_2O
acetonitrile	1 MCCN
benzene	6 ACH
ethyl acetate	1 CH_3, 1 CH_2, 1 CH_3COO
acrylonitrile	1 CCN, 1 CH
1-butanol	1 CCOH, 1 CH_2, 1 CH_3
n-heptane	2 CH_3, 5 CH_3
n-pentane	2 CH_3, 3 CH_2
hexane	2 CH_3, 4 CH_2
ethanol	1 CH_2CH_2OH
methanol	1 CH_3OH
1-propanol	1 CCOH, 1 CH_3
tetrahydrofuran	1 CH_2O, 3 CH_2

Table XIV: Group Parameters for UNIFAC model

Main group or subgroup	Group Area R_k	Group Volume Q_k
CH_3	0.9011	0.848
CH_2	0.6744	0.540
CH	0.4469	0.228
ACH	0.5313	0.4
CCOH	2.1055	1.972
CH_3OH	1.4311	1.432
H_2O	0.9200	1.40
CH_2O	0.9183	0.780
CCN	1.6434	1.416
MCCN	1.8701	1.724
COOC	1.9031	1.728

Table XV: Methods Used for the Prediction of VLE Behavior.

Method	Information Used
I	LLE data
II	LLE data plus iteration between the expressions for γ
III	LLE data plus UNIFAC interaction parameters
IV	LLE data plus binary VLE data
V	Binary VLE and binary mutual solubility data
VI	UNIFAC interaction parameters

Table XVI: Consistency Index (C. I.) and Values of $|C.\ I. - J|$ for the Miscible Binary Systems

Binary Systems	C. I.	$\lvert C.\ I. - J \rvert$
water-ethanol at 760 mmHg	-	8.1
ethyl acetate-ethanol at 760 mmHg	-	7.2
water-methanol at 65 C	0.05	-
ethyl acetate-methanol at 760 mmHg	-	6.4
water-acetonitrile at 760 mmHg	-	3.5
acrylonitrile-acetonitrile at 760 mmHg	-	5.2
water-n-propanol at 90 C	0.01	-
n-butanol-n-propanol at 760 mmHg	-	6.7
benzene-n-heptane at 45 C	0.04	-
benzene-acetonitrile at 45 C	0.04	-
n-pentane-benzene at -17.8 C	-	-
sulfur dioxide-benzene at -17.8 C	-	-
water-n-propanol at 40 C	0.01	-
benzene-n-propanol at 40 C	0.04	-
water-tetrahydrofuran at 760 mmHg	-	9.2
hexane-tetrahydrofuran at 760 mmHg	-	7.5

Table XVII: NRTL Parameters From method II

System #	Δg_{12}	Δg_{21}	Δg_{13}	Δg_{31}	Δg_{23}	Δg_{32}
1	2945	-15	1598	-520	1377	-422
2	3172	-93	1336	-542	910	-19
3	2025	424	1728	-53	-613	1037
4	3162	-395	1448	572	-1140	1656
5	1368	790	996	-253	-244	721
6	193	1473	517	103	-128	823
7	3255	1681	2246	-406	1088	117
8 [j]	-	-	-	-	-	-

[j]: Method II is not possible because only 1 ternary LLE tie line is available.

Table XVIII: LEMF Parameters From method II.

System #	Δg_{12}	Δg_{21}	Δg_{13}	Δg_{31}	Δg_{23}	Δg_{32}
1	378	816	-811	640	-311	568
2	354	830	-377	470	158	413
3	560	704	154	628	184	-131
4	172	825	263	668	-333	10
5	575	612	-880	596	315	-62
6	523	371	336	182	88	215
7	720	892	-236	670	182	470
8 [j]	-	-	-	-	-	-

j: Method II is not possible because only 1 ternary LLE tie line is available.

Table XIX: UNIQUAC Parameters From method II.

System #	Δu_{12}	Δu_{21}	Δu_{13}	Δu_{31}	Δu_{23}	Δu_{32}
1	123	1158	2480	-614	2688	-382
2	170	1028	-405	606	1771	-362
3	320	750	570	16	-457	750
4	2110	132	1100	198	267	-448
5	45	1140	348	-62	442	-241
6	668	218	160	61	11	224
7	494	2218	1644	-283	1590	-314
8 [j]	-	-	-	-	-	-

[j]: Method II is not possible because only 1 ternary LLE tie line is available.

Table XX: NRTL Parameters From method III

System #	Δg_{12}	Δg_{21}	Δg_{13}	Δg_{31}	Δg_{23}	Δg_{32}
1	2950	-62	1297	-200	1028	-165
2	3145	-136	945	-317	555	185
3	1705	400	1410	300	-400	800
4	3162	-405	1672	298	-670	958
5	1359	718	415	307	-120	485
6 [k]	-	-	-	-	-	-
7	3221	1630	2064	-258	1030	242
8	3600	-620	990	820	-11	700

k: Method III is not possible because UNIFAC parameters are not available.

Table XXI: LEMF Parameters From method III

System #	Δg_{12}	Δg_{21}	Δg_{13}	Δg_{31}	Δg_{23}	Δg_{32}
1	380	802	110	462	150	404
2	338	820	-54	354	275	297
3	700	756	359	790	125	-210
4	171	835	102	692	-31	36
5	567	624	270	282	303	-95
6 [k]	-	-	-	-	-	-
7	722	888	40	625	212	485
8	-310	750	510	580	210	60

k: Method III is not possible because UNIFAC parameters are not available.

Table XXII: UNIQUAC Parameters From method III

System #	Δu_{12}	Δu_{21}	Δu_{13}	Δu_{31}	Δu_{23}	Δu_{32}
1	120	1140	753	-225	1567	-425
2	162	976	760	-430	1260	-263
3	200	425	300	750	-800	700
4	2135	152	1226	-22	122	-86
5	35	1070	-56	435	300	-164
6 [k]	-	-	-	-	-	-
7	484	2432	1629	-227	1840	-320
8	420	115	-300	1200	210	-31

k: Method III is not possible because UNIFAC parameters are not available.

Table XXIII: NRTL Parameters From method IV.

System #	Δg_{12}	Δg_{21}	Δg_{13}	Δg_{31}	Δg_{23}	Δg_{32}
1	3016	-108	1116	-60	1097	-260
2	3146	-121	907	-310	618	125
3	2001	351	1279	452	-582	920
4	3140	-394	1688	333	-792	1237
5	1325	740	432	266	-300	803
6	203	1433	86	616	796	-338
7	3222	1594	1904	-120	1142	241
8	3750	-595	1234	695	-178	628

Table XXIV: LEMF Parameters From method IV.

System #	Δg_{12}	Δg_{21}	Δg_{13}	Δg_{31}	Δg_{23}	Δg_{32}
1	327	807	184	448	17	437
2	351	818	-72	354	252	313
3	540	697	443	566	145	-67
4	180	837	109	702	170	-222
5	573	620	260	286	331	-115
6	515	393	304	164	35	197
7	730	886	171	605	181	528
8	-285	900	450	603	260	47

Table XXV: UNIQUAC Parameters From method IV.

System #	Δu_{12}	Δu_{21}	Δu_{13}	Δu_{31}	Δu_{23}	Δu_{32}
1	144	1024	573	-72	1580	-463
2	151	1020	490	-310	1254	-270
3	285	636	113	724	-530	900
4	2160	155	1483	-72	323	-257
5	30	1072	-26	373	95	13
6	664	226	157	40	93	68
7	486	2313	1552	-141	2063	-313
8	408	171	-240	1303	195	-46

Table XXVI: NRTL Parameters From Method V

System #	Δg_{12}	Δg_{21}	Δg_{13}	Δg_{31}	Δg_{23}	Δg_{32}
1	2938	20	1388	-174	218	360
2	2938	20	693	-177	448	292
3	2103	366	891	748	-446	688
4	3166	-400	1865	314	178	-168
5	1345	860	388	318	-363	911
6	538	1347	116	562	385	-68
7	3651	2237	1608	54	1316	274
8	6775	3303	1310	673	-140	577

Table XXVII: LEMF Parameters From method V

System #	Δg_{12}	Δg_{21}	Δg_{13}	Δg_{31}	Δg_{23}	Δg_{32}
1	413	805	67	544	240	223
2	413	805	30	303	263	296
3	517	705	470	531	230	-193
4	174	830	78	719	-308	218
5	568	615	256	275	391	-231
6	516	395	303	163	58	181
7	743	913	173	600	138	562
8	805	1140	430	647	262	44

Table XXVIII: UNIQUAC Parameters From method V.

System #	Δu_{12}	Δu_{21}	Δu_{13}	Δu_{31}	Δu_{23}	Δu_{32}
1	170	1050	830	-192	1106	-348
2	170	1050	509	-323	1227	-252
3	383	547	-168	1304	-374	545
4	2148	147	1555	-90	-519	864
5	35	1135	-80	457	-9	118
6	701	228	135	62	-47	233
7	687	2492	1153	63	2184	-332
8	600	1161	-228	1278	178	-31

Table XXIX: Prediction of Ternary Vapor Liquid Equilibrium

	Avg. Abs. Dev. in Y					
	Type A Systems			Type B Systems		
Method	NRTL	LEMF	UNIQUAC	NRTL	LEMF	UNIQUAC
		System 1			System 5	
I	0.050	0.052[d]	0.076	0.032[d]	0.020	0.034
II	0.040	0.040	0.055	0.023	0.015	0.027
III	0.017	0.014	0.023	0.010	0.005	0.009
IV	0.010	0.012	0.015	0.010	0.006	0.009
V	0.016	0.012	0.017	0.007	0.007	0.006
VI		0.060			0.008	
		System 2			System 6	
I	0.036	0.023[d]	0.034	0.035	0.027[d]	0.030
II	0.020	0.017	0.017	0.014	0.016	0.011
III	0.015	0.012	0.014	–[e]	–[e]	–[e]
IV	0.016	0.012	0.013	0.009	0.006	0.008
V	0.015	0.012	0.016	0.018	0.007	0.011
VI		0.062			–[e]	
		System 3			System 7	
I	0.032[d]	0.027	0.028	0.061	0.035[d]	0.038
II	0.027	0.028	0.028	0.038	0.033	0.034
III	0.020	0.021	0.021	0.039	0.035	0.033
IV	0.018	0.017	0.017	0.040	0.041	0.033
V	0.020	0.016	0.020	0.050	0.038	0.038
VI		0.040			0.029	
		System 4			System 8	
I	0.040	0.042	0.034[d]	–[f]	–[f]	–[f]
II	0.035	0.035	0.034	–[f]	–[f]	–[f]
III	0.009	0.010	0.010	0.031	0.030	0.034
IV	0.006	0.006	0.009	0.025	0.026	0.025
V	0.009	0.007	0.010	0.005	0.005	0.007
VI		0.030			0.040	

d : Equation which gave acceptable parameters.

Table XXIX, continued

e: Methods III and VI are not possible because UNIFAC parameters are not available.

f: Methods I and II are not possible because only 1 ternary LLE tie line is available.

Table XXX: Prediction of Ternary Vapor Liquid Equilibrium: Overall Performance

Method	Overall Avg. Abs. Dev. in Y			
	NRTL	LEMF	UNIQUAC	AVERAGE
I	0.037	0.033	0.039	0.036
II	0.029	0.025	0.030	0.028
III	0.020	0.018	0.021	0.020
IV	0.017	0.016	0.016	0.016
V	0.018	0.013	0.016	0.017
VI				0.038

Table XXXI: Relation Between Ternary $\Delta\overline{Y}$ and Fit of Ternary LLE for Model which Obtained Two Sets of Parameters From method II

Avg. % error in Dist. Coeff.	Δg_{12}	Δg_{21}	Δg_{13}	Δg_{31}	Δg_{23}	Δg_{32}	$\Delta\overline{Y}$
System 1, LEMF							
3.0	425	812	-466	664	177	595	0.03
3.4	378	816	-811	640	-311	568	0.04
System 2, LEMF							
3.7	410	830	-377	390	75	413	0.017
3.5	422	817	-320	377	55	493	0.017
System 3, UNIQUAC							
2.3	307	742	543	32	-346	481	0.027
2.2	320	750	570	16	-457	750	0.028
System 4, UNIQUAC							
3.0	1815	2595	917	298	90	-332	0.034
3.2	1998	2400	1100	220	120	-449	0.034
System 5, NRTL							
2.0	1358	817	1080	-290	170	195	0.025
1.6	1368	790	996	-253	244	160	0.023
System 6, LEMF							
3.5	523	371	336	182	88	215	0.007
4.7	518	360	178	270	360	1.2	0.016
System 7, LEMF							
13.9	726	894	-470	703	77	497	0.041
11.1	720	892	-236	670	182	470	0.033

Table XXXII: Prediction of Ternary Vapor Liquid Equilibrium From the Two Liquid Phases in Equilibrium with method II.

System	Model	Avg. Abs. Dev. in Y Phase I	Avg. Abs. Dev. in Y Phase II
4	NRTL	0.011	0.011
	LEMF	0.013	0.016
	UNIQUAC	0.015	0.017
5	NRTL	0.009	0.009
	LEMF	0.004	0.006
	UNIQUAC	0.011	0.012
6	NRTL	0.007	0.005
	LEMF	0.003	0.003
	UNIQUAC	0.006	0.005

Table XXXIII: Prediction of Binary VLE for the Completely Miscible Binaries: method I

System	Equation*	$\Delta\overline{Y}$ binary 1-3	$\Delta\overline{Y}$ binary 2-3
1	N	0.072	0.094
	L	0.06	0.08
	U	0.12	0.13
2	N	0.058	0.045
	L	0.020	0.028
	U	0.065	0.046
3	N	0.052	0.02
	L	0.045	0.016
	U	0.031	0.018
4	N	0.053	0.043
	L	0.072	0.035
	U	0.03	0.033
5	N	0.033	0.017
	L	0.032	0.038
	U	0.05	0.084
6	N	0.029	0.025
	L	0.0095	0.0034
	U	0.07	0.02
7	N	0.09	0.06
	L	0.04	0.04
	U	0.07	0.05

* N: NRTL   L: LEMF   U: UNIQUAC

Table XXXIV: Prediction of Binary VLE for the Completely Miscible Binaries: Method II and UNIFAC

		Avg. Abs. Dev. in Y	
System	Model *	Binary 1-3	Binary 2-3
1	N	0.050	0.028
	L	0.047	0.028
	U	0.063	0.050
	UF	0.013	0.011
2	N	0.011	0.018
	L	0.007	0.018
	U	0.015	0.025
	UF	0.005	0.007
3	N	0.043	0.025
	L	0.041	0.027
	U	0.030	0.027
	UF	0.030	0.045
4	N	0.028	0.030
	L	0.024	0.028
	U	0.030	0.032
	UF	0.011	0.035
5	N	0.024	0.004
	L	0.023	0.003
	U	0.024	0.010
	UF	0.009	0.005
6	N	0.004	0.002
	L	0.005	0.001
	U	0.004	0.001
	UF	-	-
7	N	0.055	0.027
	L	0.038	0.037
	U	0.050	0.043
	UF	0.018	0.026
8	N	-	-
	L	-	-
	U	-	-
	UF	0.013	0.011

N: NRTL L: LEMF U: UNIQUAC UF: UNIFAC

Table XXXV: Prediction of Binary VLE for the Completely Miscible Binaries: Overall Results

	Overall Avg. Abs. Dev. in Y			
Method	NRTL	LEMF	UNIQUAC	AVERAGE
I	0.049	0.037	0.058	0.048
II	0.025	0.023	0.025	0.024
III	0.015	0.014	0.016	0.015
VI				0.017

Table XXXVI: Prediction of Vapor Phase Composition for Partially Miscible Binary System.

System	T(C)	Data Points	Method	Avg. Abs. Dev. in Y NRTL	LEMF	UNIQUAC
water- ethyl acetate	74.1- 75.8	3	II	0.027	0.007	0.027
			V	0.023	0.006	0.025
			VI		0.47	
acetonitrile- n-heptane	45	9	II	0.013	0.006	0.014
			V	0.010	0.004	0.012
			VI		0.010	
water- n-butanol	93.0- 111.5	12	II	0.070	0.039	0.061
			V	0.060	0.033	0.054
			VI		0.020	

Table XXXVII: Prediction of Ternary VLE using Parameters from Method II for the 1-3 Miscible Binary with Parameters from Method V for the Other Binaries.

System	Model*	$\Delta\overline{Y}$
1	N	0.025
	L	0.020
	U	0.020
3	N	0.027
	L	0.027
	U	0.027
4	N	0.009
	L	0.009
	U	0.007
7	N	0.058
	L	0.032
	U	0.040

* N: NRTL L: LEMF U: UNIQUAC

APPENDIX C

THE COMPUTER PROGRAMS

This appendix contains the computer program REG-2EQN (in FORTRAN). This program performs the iteration calculation (method II) for a pair of models for any combination of the following models: NRTL, LEMF and UNIQUAC.

The pages that follow contain, for the program REG-2EQN, the instructions to use it, a sample input, a listing, the information contained in the output, and a glossary.

The Program REG-2EQN

The computer program REG-2EQN performs the iteration calculation (method II) for a pair of models for any combination of the following models: NRTL, LEMF and UNIQUAC. In this calculation, the model which obtained reasonable parameters from method I will be known as model A and the other model will be known as model B; and an iteration is defined as regressing the ternary LLE data and calculated binary γ's from one model to obtain the six binary parameters for the other model. The procedure for using this program is now discussed.

1. System title

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

2. How many iterations and how many tie-lines?

If one is interested in using NTIMES iterations for a system that has NTIE tie-lines then type the following (Format 2I2):

NTIMES NTIE

where NTIMES = number of iterations

NTIE = number of tie-lines

3. 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)

4. 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 and IN2 = number of VLE data points for the 1-3 binary and 2-3 binary, respectively

5. 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      GAMA1E      GAMA2E      TEMP1
```

where X1 = X_1

GAMA1E and GAMA2E = experimental activity coefficient of component 1 and component 3, respectively

TEMP1 = temperature of the binary system, (C)

The binary 1-3 system here is the same as the binary 1-3 in the title.

6. 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 GAMA3E GAMA4E TEMP2

where X3 = X_2

GAMA3E and GAMA4E = experimental activity coefficient of component 2 and component 3, respectively

TEMP2 = temperature of the binary system, (C)

The binary 2-3 system here is the same as the binary 2-3 in the title.

7. Gammas for 1-3 binary system predicted from model A

To read in the predicted gammas for the 1-3 binary system, type the following (Format 2F10.3):

GAMMA1 GAMMA2

where GAMMA1 and GAMMA2 = calculated activity coefficients of component 1 and component 3, respectively

8. Gammas for 2-3 binary system predicted from model A

To read in the predicted gammas for the 2-3 binary system, type the following (Format 2F10.3):

GAMMA3 GAMMA4

where GAMMA3 and GAMMA4 = calculated activity coefficients of component 2 and component 3, respectively

9. The LLE data

To type in the LLE data, 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, DC2 and DC are the experimental distribution coefficients of components 1, 2 and 3, respectively

This is typed beginning on column 1. Do not include the mutual solubility data.

10. Starting values for the miscible binaries for model B

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) starting at column 1:

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}

11. Starting values for the partially miscible binary for model B

To specify a starting value for each parameter in the 1-2 binary, type the following (Format 2F10.2):

G12 G21

where G12 = Δg_{12} or Δu_{12}

G21 = Δg_{21} or Δu_{21}

12. Starting values for the miscible binaries for model A

Follow the instructions given in step 10.

13. Starting values for the partially miscible binary for model A

Follow the instructions given in step 11.

14. Specify Model B

If model B is the NRTL or LEMF equation then let IEQN = 01 (Format I2). If model B is the UNIQUAC equation then let IEQN = 02 (Format I2).

15. α_{13}, α_{23} and α_{12} for model B

If model B is the NRTL or LEMF equation, then the value of α_{13}, α_{23} and α_{12} must be specified. This is done by typing the following (Format 3F10.4):

ALFA13 ALFA23 ALFA12

16. r, q and q' for model B

If model B is the UNIQUAC equation, then the value of r, q and q' must be specified 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 information is typed on 3 lines. Use one line for each component.

17. Specify Model A

Follow the instructions given in step 14.

18. α_{13}, α_{23} and α_{12} for model A

Follow the instructions given in step 15.

19. r, q and q' for model A

Follow the instructions given in step 16.

20. Number of iterations to be used

For every pair of iterations involving models B and A, steps 14 through 19 must be performed. For example, if 4 iterations (2 iterations for each model) are to be performed, then steps 14 through 19 must be performed twice.

All of the input data for the program REG-2EQN are typed beginning on column 1 and, for the ternary LLE and binary VLE data, one line is used for each data point.

A sample input is given in the next page, followed by a listing of the computer program REG-2EQN.

```
ACETONITRILE(1)-NHEPTANE(2)-BENZENE(3) AT 45. C
0409
45.0
1215
0.0455     2.67       1.01       45.0
0.094      2.33       1.02       45.0
0.153      1.916      1.05       45.0
0.291      1.606      1.11       45.0
0.396      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      1.435      45.0
0.7206     1.079      1.677      45.0
0.8145     1.03       1.97       45.0
0.897      1.00       2.3        45.0
0.957      0.99       2.628      45.0
0.9396     0.9895     1.4738     45.0
0.882      1.0        1.4        45.0
0.8565     1.003      1.395      45.0
0.763      1.006      1.3275     45.0
0.7159     1.02       1.3        45.0
0.6895     1.016      1.3        45.0
0.622      1.05       1.24       45.0
0.5905     1.048      1.215      45.0
0.52       1.06       1.207      45.0
0.4144     1.135      1.13       45.0
0.3505     1.17       1.178      45.0
0.3087     1.23       1.08       45.0
0.226      1.308      1.063      45.0
0.082      1.67       1.01       45.0
0.022      2.112      1.012      45.0
1.532      1.0
1.525      1.0
1.501      1.003
1.455      1.013
1.393      1.037
1.315      1.088
1.285      1.117
1.247      1.163
1.144      1.375
1.075      1.695
1.027      2.231
1.005      2.938
1.003      1.778
1.012      1.631
1.017      1.575
1.044      1.435
1.063      1.338
1.074      1.304
1.107      1.231
1.130      1.193
1.168      1.146
1.243      1.085
1.288      1.061
1.332      1.044
1.410      1.022
1.564      1.003
1.636      1.00
```

```
0.9129    0.1167    0.0683    0.8491    0.1278    12.44    1.82
0.8954    0.1451    0.0721    0.7987    0.1621    11.07    1.73
0.8605    0.1642    0.0843    0.7451    0.1908    8.842    1.643
0.8406    0.1711    0.0910    0.7165    0.2035    7.893    1.614
0.7810    0.2225    0.1188    0.632     0.2849    5.32     1.452
0.7529    0.2466    0.1242    0.5807    0.3275    4.673    1.405
0.7235    0.2674    0.1432    0.5617    0.3696    3.92     1.282
0.7025    0.2723    0.1619    0.5506    0.3876    3.4      1.306
0.5903    0.4395    0.2460    0.372     0.7576    1.51     1.083
240.0     240.0     240.0     240.0
568.      615.
345.0     345.0     345.0     345.0
1345.     861.
01
-1.0      -1.0      -1.0
01
0.30      0.30      0.20
01
-1.0      -1.0      -1.0
01
0.30      0.30      0.20
/LOGOFF
```

```
      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/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,EGAM1,EGAM2
      COMMON/COM14/GAMA1E(40),GAMA2E(40),GAMA3E(40),GAMA4E(40)
      DIMENSION XST1(2),XST2(2),XST3(2),XST4(2),XST5(2),XST6(2)
      DIMENSION GAMA11(40),GAMA21(40),GAMA31(40),GAMA41(40)
      DIMENSION GAMA12(40),GAMA22(40),GAMA32(40),GAMA42(40)
      DIMENSION ERRS1C(40),ERRS2C(40),ERRS3C(40),ERRS4C(40)
C
C
C
C     THIS IS THE PROGRAM REG-2EQN
C
C     THIS PROGRAM PERFORMS THE ITERATION CALCULATION (METHOD II)
C     FOR A PAIR OF MODELS FOR ANY COMBINATION OF THE FOLLOWING
C     MODELS:  NRTL, LEMF AND UNIQUAC.
C
C
C
C
C
C
C             FORMAT STATEMENTS FOR THE MAIN PROGRAM
C
C
140   FORMAT(' ','AVG. PERCENTAGE ERROR IN CALC. BINARY GAMMAS')
  363 FORMAT(' ',5X,7F10.4)
 911  FORMAT(2F10.2)
 910  FORMAT(' ',2F10.2)
 909  FORMAT(' ',5X,'G12',7X,'G21',3X,
     1'STARTING VALUES FOR PARTIALLY MISCIBLE BINARY')
 900  FORMAT(I2)
 905  FORMAT('1',5X,'R',10X,'Q',6X,'QPRIME')
 904  FORMAT(3F10.4)
 906  FORMAT(' ',3F10.4)
  102 FORMAT(' ',6F10.2)
   1  FORMAT(60A1)
   2  FORMAT(' ','SYSTEM    ',60A1)
  3   FORMAT(' ',17X,I2,50X,I2)
55    FORMAT(2I2)
   17 FORMAT(2F10.4)
   18 FORMAT(4F10.3)
  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 ITERATIONS',5X,
    1'2ND CHARACTER= # OF TIE-LINES')
 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('1','ALFA13       ALFA23')
 304 FORMAT(' ',5X,'G13',7X,'G31',7X,'G23',7X,'G32',2X,
    1'(STARTING VALUES FOR MISCIBLE  BINARIES)')
 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'STARTING VALUES FOR PARTIALLY MISCIBLE BINARY')
 307 FORMAT(' ',5X,'G13',7X,'G31',7X,'G23',7X,'G32',7X,'G12',
    17X,'G21',2X,'(REGRESSED VALUES)')
 308 FORMAT(' ',5X,'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(' ',8X,'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)
 321 FORMAT(2I2)
 314 FORMAT(' ','NUMBER OF LOOPS USED.  ERROR IN REGRESSION')
 777 FORMAT(' ','AVERAGE PERCENTAGE ERROR IN BINARY GAMMAS')
 778 FORMAT(' ',13X,F10.1)
 779 FORMAT(' ','AVERAGE PERCENTAGE ERROR IN DIST. COEFF.')
750  FORMAT(' ','OVERALL AVG. PERC. ERROR IN CALC. BINARY',2X,
    1'GAMMA FOR 2 ITERATIONS FOR A GIVEN MODEL')
C
C          THIS IS THE MAIN PROGRAM
C
C
C
      NCOMP=3
      READ1,TITLE
      PRINT2,TITLE
      PRINT 300
      READ55,NTIMES,NTIE
      PRINT320,NTIMES,NTIE
      PRINT301
      READ10,TEMP3
```

```
      PRINT322,TEMP3
      PRINT 302
      TK3=273.15+TEMP3
      READ55,IN1,IN2
      PRINT3,IN1,IN2
      DO 117 K=1,IN1
      READ18,X1(K),GAMA1E(K),GAMA2E(K),TEMP1
      TK1(K)=273.15+TEMP1
117   X2(K)=1.0-X1(K)
      DO 118 KK=1,IN2
      READ18,X3(KK),GAMA3E(KK),GAMA4E(KK),TEMP2
      TK2(KK)=273.15+TEMP2
118   X4(KK)=1.0-X3(KK)
      DO 4 K=1,IN1
      READ15,GAMMA1(K),GAMMA2(K)
4     CONTINUE
      DO 6 KK=1,IN2
      READ15,GAMMA3(KK),GAMMA4(KK)
6     CONTINUE
      PRINT305
      DO 41 I=1,NTIE
      READ39,X11(I),X12(I),X21(I),X22(I),DC1(I),DC2(I),DC(I)
      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
      PRINT350,X11(I),X12(I),X21(I),X22(I),X31(I),X32(I),DC1(I),DC2(I)
     1,DC(I)
   41 CONTINUE
      NTOTAL=1
      NFLAG=1
      READ18,XST1(1),XST2(1),XST3(1),XST4(1)
      READ911,XST5(1),XST6(1)
      READ18,XST1(2),XST2(2),XST3(2),XST4(2)
      READ911,XST5(2),XST6(2)
 908  DO 9 I=1,NTIMES
      EPRT1C=0.0
      EPRT2C=0.0
      READ900,IEQN
      IF(IEQN.EQ.2)GO TO 901
      PRINT303
      READ904,ALFA13,ALFA23,ALFA12
      PRINT323,ALFA13,ALFA23
      GO TO 902
901   PRINT905
      DO 903 II=1,NCOMP
      READ904,R(II),Q(II),QP(II)
903   PRINT906,R(II),Q(II),QP(II)
902   PRINT304
      IF(NFLAG.EQ.2)GO TO 136
      PRINT328,XST1(1),XST2(1),XST3(1),XST4(1)
      G12=XST5(1)
      G21=XST6(1)
      GO TO 137
136   CONTINUE
      PRINT328,XST1(2),XST2(2),XST3(2),XST4(2)
      G12=XST5(2)
      G21=XST6(2)
```

```
137   CONTINUE
      IF(IEQN.EQ.2)GO TO 907
      PRINT306
      PRINT379,ALFA12,G12,G21
      GO TO 110
907   CONTINUE
      PRINT909
      PRINT910,G12,G21
110   CONTINUE
      M=6
      L=1000
      E=0.0005
      PRINT2,TITLE
      M1=M+1
      M3=M+3
      DO 27 II=1,M
   27 DX(II)=10.0
      IF(NFLAG.EQ.2)GO TO 130
      XT(1)=XST1(1)
      XT(2)=XST2(1)
      XT(3)=XST3(1)
      XT(4)=XST4(1)
      XT(5)=XST5(1)
      XT(6)=XST6(1)
      DO 460 J=1,IN1
      GAMA12(J)=GAMMA1(J)
      GAMA22(J)=GAMMA2(J)
460   CONTINUE
      DO 461 J=1,IN2
      GAMA32(J)=GAMMA3(J)
      GAMA42(J)=GAMMA4(J)
461   CONTINUE
      GO TO 131
130   CONTINUE
      XT(1)=XST1(2)
      XT(2)=XST2(2)
      XT(3)=XST3(2)
      XT(4)=XST4(2)
      XT(5)=XST5(2)
      XT(6)=XST6(2)
      DO 450 J=1,IN1
      GAMA11(J)=GAMMA1(J)
      GAMA21(J)=GAMMA2(J)
450   CONTINUE
      DO 451 J=1,IN2
      GAMA31(J)=GAMMA3(J)
      GAMA41(J)=GAMMA4(J)
451   CONTINUE
131   CONTINUE
      CALL LSQ2(XT,X,DX,Y,M,M1,M3,L,E,L1C,D)
  101 PRINT307
      PRINT102,XT(1),XT(2),XT(3),XT(4),XT(5),XT(6)
  103 PRINT308
      DO 11 J=1,IN1
   11 PRINT309,X1(J),GAMA1E(J),G1(J),GAMA2E(J),G2(J),ERROR1
     1(J),ERROR2(J)
      IF (NTOTAL.EQ.1)GO TO 540
      IF(NFLAG.EQ.2)GO TO 590
```

```
      DO 510 M=1,IN1
      ERRS1C(M)=(ABS((GAMA11(M)-G1(M))/GAMA11(M)))*100.
      ERRS2C(M)=(ABS((GAMA21(M)-G2(M))/GAMA21(M)))*100.
 510  ERRT1C=ERRT1C+ERRS1C(M)+ERRS2C(M)
      GO TO 530
 500  CONTINUE
      DO 520 J=1,IN1
      ERRS1C(J)=(ABS((GAMA12(J)-G1(J))/GAMA12(J)))*100.
      ERRS2C(J)=(ABS((GAMA22(J)-G2(J))/GAMA22(J)))*100.
 520  ERRT1C=ERRT1C+ERRS1C(J)+ERRS2C(J)
 530  CONTINUE
      ERRT1C=ERRT1C/(2*IN1)
 540  CONTINUE
      DO 115 J=1,IN1
      GAMMA1(J)=G1(J)
      GAMMA2(J)=G2(J)
 115  CONTINUE
      PRINT309
      PRINT13,QQ1
      PRINT777
      PRINT778,EGAM1
      PRINT310
      DO 14 JJ=1,IN2
   14 PRINT389,X3(JJ),GAMA3E(JJ),G3(JJ),GAMA4E(JJ),G4(JJ),
     1ERROR3(JJ),ERROR4(JJ)
      IF(NTOTAL.EQ.1)GO TO 640
      IF(NFLAG.EQ.2)GO TO 600
      DO 610 J=1,IN2
      ERRS3C(J)=(ABS((GAMA31(J)-G3(J))/GAMA31(J)))*100.
      ERRS4C(J)=(ABS((GAMA41(J)-G4(J))/GAMA41(J)))*100.
 610  ERRT2C=ERRT2C+ERRS3C(J)+ERRS4C(J)
      GO TO 630
 600  CONTINUE
      DO 620 J=1,IN2
      ERRS3C(J)=(ABS((GAMA32(J)-G3(J))/GAMA32(J)))*100.
      ERRS4C(J)=(ABS((GAMA42(J)-G4(J))/GAMA42(J)))*100.
 620  ERRT2C=ERRT2C+ERRS3C(J)+ERRS4C(J)
 630  CONTINUE
      ERRT2C=ERRT2C/(2*IN2)
      ERRTC=(ERRT1C+ERRT2C)/2.0
 640  CONTINUE
      DO 116 JJ=1,IN2
      GAMMA3(JJ)=G3(JJ)
      GAMMA4(JJ)=G4(JJ)
 116  CONTINUE
      PRINT311
      PRINT13,QQ2
      PRINT777
      PRINT778,EGAM2
      PRINT312
      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)
      PRINT313
      PRINT13,YY
      PRINT777
      PRINT778,EGAM
      IF(NTOTAL.EQ.1)ERRTC=0.000
```

```
      PRINT750
      PRINT778,ERRTC
      PRINT779
      PRINT778,QDBAR
      PRINT314
      IF(NFLAG.EQ.2)GO TO 132
      XST1(1)=XT(1)
      XST2(1)=XT(2)
      XST3(1)=XT(3)
      XST4(1)=XT(4)
      XST5(1)=XT(5)
      XST6(1)=XT(6)
      GO TO 133
 132  CONTINUE
      XST1(2)=XT(1)
      XST2(2)=XT(2)
      XST3(2)=XT(3)
      XST4(2)=XT(4)
      XST5(2)=XT(5)
      XST6(2)=XT(6)
 133  CONTINUE
      NFLAG=NFLAG+1
      NTOTAL=NTOTAL+1
      IF(NFLAG.EQ.2)GO TO 134
      IF(NFLAG.GT.2)GO TO 135
 135  NFLAG=1
 134  CONTINUE
   9  PRINT100,L10,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/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,EGAM1,EGAM2
      COMMON/COM14/GAMA1E(40),GAMA2E(40),GAMA3E(40),GAMA4E(40)
      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
      YTIE=0.
      NCOMP=2
      EGAM1=0.0
      EGAM2=0.0
      QDEPR=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)/(1.9572*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((GAMA1E(I)-G1(I))/GAMA1E(I)))*100.0
      ERROR2(I)=(ABS((GAMA2E(I)-G2(I))/GAMA2E(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((GAMA3E(I)-G3(I))/GAMA3E(I)))*100.0
```

```
      ERROR4(I)=(ABS((GAMA4E(I)-G4(I))/GAMA4E(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 QQ2=QQ2+YY2
      EGAM2=EGAM2/(2*IN2)
      EGAM=(EGAM1+EGAM2)/2.0
      QQ2=QQ2/IN2
      DO 45 I=1,NCOMP
      GT(I,I)=0.0
   45 CONTINUE
      GT(1,2)=XT(5)
      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 LEMF 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
      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)
  133 YTIE=YTIE+Q6+Q7+Q8
      QDBAR=QDBAR/(3*NTIE)
      YY=(YTIE/NTIE)+QQ1+QQ2
      Y5=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)**E
      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) = (2.0*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 135 J=1,M1
      IF(J.EQ.IL) GO TO 135
      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)
 135  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 REG-2EQN

The output of this program contains the following information for each iteration:

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. Overall average absolute percentage error in binary activity coefficients for each binary.
7. Calculated ternary activity coefficients for each component in both phases.
8. Calculated distribution coefficients for each component.
9. Absolute percentage error in distribution coefficients for each component.
10. Minimum value of the minimization function.
11. Overall average absolute percentage error in binary γ's for both binaries.
12. Overall average absolute percentage error in binary γ's for both binaries for 2 successive iterations for a given model.
13. Overall average absolute percentage error in distribution coefficients for all three components.
14. Number of loops used in the regression.
15. Error in the regression.

Glossary for the Program REG-2EQN

ALFA12 = α_{12}.

ALFA13 = α_{13}.

ALFA23 = α_{23}.

D = error in the regression.

DCC1, DCC2 and DCC = calculated distribution coefficient of components 1, 2 and 3, respectively.

DC1, DC2 and DC = experimental distribution coefficient of components 1, 2 and 3, respectively.

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

EGAM1 and EGAM2 = overall average absolute percentage error in binary activity coefficients for binary 1-3 and binary 2-3, respectively.

ERRTC = overall average absolute percentage error in calculated binary activity coefficients for both binaries for 2 successive iterations for a given model.

ERRTC1 and ERRTC2 = overall average absolute percentage error in binary activity coefficients for 2 successive iterations for a given model for binaries 1-3 and 2-3, respectively.

ERROR1 and ERROR2 = absolute percentage error in binary activity coefficients in the 1-3 binary system for components 1 and 3, respectively.

ERROR3 and ERROR4 = absolute percentage error in binary activity coefficients in the 2-3 binary system for components 2 and 3, respectively.

ERRS1C and ERRS2C = absolute percentage error in binary activity coefficients for 2 successive iterations for a given model for components 1 and 3, respectively.

ERRS3C and ERRS4C = absolute percentage error in binary activity coefficients for 2 successive iterations for a given model for components 2 and 3, respectively.

G1 and G2 = calculated binary activity coefficients in the 1-3 binary system for components 1 and 3, respectively.

G3 and G4 = calculated binary activity coefficients in the 2-3 binary system for components 2 and 3, respectively.

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.

GAMA1E and GAMA2E = experimental activity coefficient in the 1-3 binary system for components 1 and 3, respectively.

GAMA3E and GAMA4E = experimental activity coefficient in the 2-3 binary system for components 2 and 3, respectively.

GAMA11 and GAMA12 = calculated component 1 activity coefficients in binary 1-3 from the latter iteration of 2 successive iterations for model B and model A, respectively.

GAMA21 and GAMA22 = calculated component 3 activity coefficients in binary 1-3 from the latter iteration of 2 successive iterations for model B and model A, respectively.

GAMA31 and GAMA32 = calculated component 2 activity coefficients in binary 2-3 from the latter iteration of 2 successive iterations for model B and model A, respectively.

GAMA41 and GAMA42 = calculated component 3 activity coefficients in binary 2-3 from the latter iteration of 2 successive iterations for model B and model A, respectively.

GAMMA1 and GAMMA2 = activity coefficients predicted by model which obtained reasonable parameters in method I, for binary 1-3 for component 1 and component 3, respectively.

GAMMA3 and GAMMA4 = activity coefficients predicted by model which obtained reasonable parameters in method I, for binary 2-3 for component 2 and component 3, respectively.

IEQN = equation to be used.

IN1 and IN2 = number of VLE data points for the 1-3 and 2-3 binary systems, respectively.

L1C = number of loops used in the regression for each iteration.

NTIMES = number of iterations to be used.

NTIE = number of LLE tie lines.

Q = q in the UNIQUAC model.

QP = q' in the UNIQUAC model.

QQ1 and QQ2 = standard deviation in activity coefficient for the 1-3 and 2-3 binary systems, respectively.

Q_4, Q_5 and Q_3 = absolute percentage error in distribution coefficients for components 1, 2 and 3, respectively.

QDBAR = average of Q_3, Q_4 and Q_5.

R = r in the UNIQUAC model.

TEMP1, TEMP2 and TEMP3 = temperature of the 1-3 binary system, 2-3 binary system and LLE system (C), respectively.

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_n = negative area in the "area test".

A_p = positive area in the "area test".

B_{ij} = second virial coefficient.

C. I. = consistency index.

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

G_{ij} = see equation (12).

g_{ij} = NRTL or LEMF parameters.

Δg_{ij} = $(g_{ij} - g_{jj})$.

h^e = excess enthalpy of the liquid mixture.

J = see equation (22).

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

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

l_j = see equation (14).

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

N = number of tie lines.

n = number of components.

P = total pressure.

P_i^s = saturated vapor pressure of component i.

Q = number of data points in a ternary VLE system.

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

R = gas constant.

r = size parameter in the UNIQUAC model.

T = system temperature.

T_{ij} = see equation (12).

T_{min} = lowest boiling point in a binary VLE system.

T_1, T_2 = boiling points of pure components 1 and 2, respectively.

u_{ij} = UNIQUAC parameter.

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

V = molar volume of the vapor mixture.

v^e = excess volume of the liquid mixture.

V_i^L = molar liquid volume.

X = liquid phase mole fraction.

ΔX = see Figure 35.

Y = vapor phase mole fraction.

$\Delta \overline{Y}$ = see equation (24).

Z = compressibility factor.

z = liquid phase coordination number.

Greek Letters

α = nonrandomness parameter in the NRTL and LEMF models.

γ = activity coefficient.

ϕ_i^s = fugacity coefficient of pure vapor i at T and saturation pressure, P_i^s.

$\hat{\phi}_i$ = vapor phase fugacity coefficient of component i in the mixture.

Φ = segment fraction in the UNIQUAC model.

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

τ = total boiling point range.

τ_{ij} = see equation (14).

Superscripts

C = calculated value.

E = experimental value.

e = excess value.

L = liquid phase.

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

s = saturated.

V = vapor phase.

$\hat{}$ = value for a mixture.

$\bar{}$ = average value.

Subscripts

min = minimum value.

i, j and k = components i, j and k.

LITERATURE CITED

1. Abrams, D. S., Prausnitz, J. M., AIChE J., 21, 116(1975).

2. Akita, K., Yoshida, F., J. Chem. Eng. Data, 8, 484(1963).

3. Anderson, T. F., Prausnitz, J. M., Ind. Eng. Chem. Process Des. Dev., 17, 561(1978).

4. Black, C., Joris, G. G., Taylor, H. S., J. Chem. Phys., 16, 537(1948).

5. Blackford, D. S., York, R., J. Chem. Eng. Data, 10, 313(1965).

6. Bowden, W. W., Staton, J. C., Smith, B. C., J. Chem. Eng. Data, 11, 296(1966).

7. DeFre, R. M., Verhoeye, L. A., J. Appl. Chem. Biotechnol., 26, 469(1976).

8. Fredenslund, A, Jones, R. L., Prausnitz, J. M., AIChE J., 21, 1086(1975).

9. Gay, L., Chim. Ind., 18, 187(1927).

10. Griswold, J., Chu, P. L., Ind. Eng. Chem., 41, 2352(1949).

11. Hala, E., Wichterle, I., Polak, J., Boublik, T., "Vapor-Liquid Equilibrium Data at Normal Pressure", Pergamon Press, New York, N. Y., 1968.

12. Hand, D. B., J. Phys. Chem., 34, 1961(1930).

13. Herington, E. F. G., J. Inst. Petrol., 37, 457(1951).

14. Hudson, J. W., Van Winkle, M., Ind. Eng. Chem. Process Des. Dev., 9, 466(1970).

15. Joy, D. S., Kyle, B. G., Ind. Eng. Chem. Process Des. Dev., 9, 244(1970).

16. Lampa, A., Matous, B., Novak, L., Pick, P., Collection Czechoslov. Chem. Commun., 45, 1159(1980).

17. Marina, J. M., PhD Thesis, New Jersey Institute of Technology, Newark, N. J., 1973.

18. Marina, J. M., Tassios, D. P., Ind. Eng. Chem. Process Des. Dev., 12, 271(1973).

19. Mattelin, A. C., Verhoeye, L. A. J., Chem. Engng. Sci., 30, 193(1975).

20. McCants, J. F., Jones, J. H., Ind. Eng. Chem., 45, 454(1953).

21. Mcglashan, M. L., Williamson, A. G., J. Chem. Eng. Data, 21, 196(1976).

22. Newsham, D. M. T., Vahdat, N. Chem. Eng. J., 13, (Parts I and II), 27(1977).

23. Nicolaides, G. L., Eckert, C. A., Ind. Eng. Chem. Fundam., 17, 331(1978).

24. Ordaz, J., Personal Communication, New Jersey Institue of Technology, Newark, N.J., 1978.

25. Palmer, D. A., Smith, B. D., J. Chem. Eng. Data, 17, 71(1972).

26. Prausnitz, J. M., "Molecular Thermodynamics of Fluid-Phase Equilibria", Prentice Hall, Englewood Cliffs, N. J., 1969.

27. Prausnitz, J. M., Anderson, T. F., Grens, E., Eckert, C. A., Hsieh, R., O'Connell, J., "Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria", Prentice Hall: New Jersey, 1980.

28. Prausnitz, J. M., Eckert, C. A., Orye, R. V., O'Connell, V. P., "Computer Calculations for Multicomponent Vapor-Liquid Equilibria", Prentice Hall: New Jersey, 1967.

29. Ratcliff, G. A., Chao, K. C., Can. J. Chem. Eng., 47, 148(1969).

30. Renon, H., Prausnitz, J. M., AIChE J., 14, 135(1968).

31. Simonetty, J., MS Thesis, New Jersey Institute of Technology, Newark, N. J., 1981.

32. Simonetty, J., Yee, D. K., Tassios, D. P., Ind. Eng. Chem. Process Des. Dev., 21, 174(1982).

33. Skjold-Jorgensen, S., Kolbe, B., Gmehling, J., Rasmussen, P., Ind. Eng. Chem. Process Des. Dev., 18, 714(1979).

34. Sorensen, J. M.,Arlt, W.,"Liquid-Liquid Equilibrium Data Collection", DECHEMA Chemistry Data Series, Vol.5(Parts I-III), Frankfurt, 1979.

35. Sorensen, J. M., Magnussen, T., Rasmussen, P., Fredenslund, A., Fluid Phase Equilibria, 3, (Part II), 47(1979).

36. Stephen, H., Stephen, T., "Solubility of Inorganic and Organic Compounds", Macmillan, New York, N. Y., 1963.

37. Tsonopoulos, C., AIChE J., 20, 263(1974).

38. Udovenko, V. V., Mazanko, T. F., Izv. Vyssh. Ucheb. Zaved. Khim. Khim. Tekhno., 18, 1077(1975).

39. Volpicelli, G., J. Chem. Eng. Data, 13, 150(1968).