Commun. Fac. Sci. Univ. Ank. Serie B
V. 34. pp. 141-158 (1988)

LIMITS ON THE PREDICTION OF ISOBARIC TERNARY PHASE EQUILIBRIA BY NRTL AND LEMF EQUATIONS

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SUMMARY

The isobaric separation of multicomponent mixtures by distillation require reliable vapour-liquid equilibrium data. Therefore, the separation is dependent on the predictive thermodynamic method used for estimation of vapour-liquid equilibria. The abilities of the NRTL and LEMF equations to predict isobaric binary and ternary vapour-liquid equilibria using only two or more lower heats of mixing data were compared. A ternary and three binary systems comprising the ternary were studied. Both equations gave reasonable results for binary systems with intermolecular interactions (H^E max $<$ 200 cal/g.mol). For physical interactions about 235 cal/g.mol the NRTL equation was found to be superior in the prediction of ternary VLE data with standard deviation ranging from 12–17 % whereas the LEMF equation could predict the ternary vapour phase with in the accuracy of 16–21 %.

INTRODUCTION

In the heavy organic chemicals and petroleum industries, reliable vapour liquid equilibria (VLE) data are required in order to design distillation equipment and to determine their optimum operating conditions. Although a great number of methods are available in the literature describing the experiemental techniques suitable for the measurement of equilibrium pressure, temperature and composition of vapour-liquid phases, in many cases, experimental values for the required equilibria are not available at the particular given separation conditions. There is then the choice of performing experimental determination of VLE data or estimating the data with one of the theoretical prediction relationships. Since the experimental determination of binary and especially multicomponent VLE data is laborious and time consuming, designers often prefer prediction methods to estimate the equilibria compositions. With the speedy development of computers, there is

ISSN 0570-1414 A. Üniv. Basımevi

more concern for thermodynamic relations to predict binary and multicomponent VLE data from corresponding binary properties and pure component data because generally binary properties are more readily available. Since, most distillation processes in industry are carried out under isobaric conditions rather than isothermal, it is preferred that the predicting equations should refer to isobaric conditions. The aim of the present study is to see whether NRTL or LEMF method of predicting ternary VLE data is more practical in estimating vapour phase mole fraction values.

THERMODYNAMICS OF PHASE EQUILIBRIA

The fundemental thermodynamic condition for multicomponent phase equilibria is expressed by the equality of fugacities f_i, in all phases for each component (Souders, 1932).

$$f_i^V = f_i^L \text{ ,} \tag{1}$$

The fugacities are related to the experimentally determined quantities x, y, T and P, through two auxiliary functions which contain the fugacity coefficient $\varnothing$, and the activity coefficient γ,

$$f_i^V = \varnothing_i \, y_i \, P \tag{2}$$

$$f_i^L = \gamma_i \, x_i \, f_i^\circ \tag{3}$$

From Eqs. (1), (2) and (3) the equation of multicomponent equilibria becomes

$$y_i = \frac{\gamma_i \, f_i^o}{\varnothing_i \, P} \, X_i \tag{4}$$

When the vapour phase is assumed ideal, the fugacity of each component reduces to its partial pressure

$$y_i = \frac{\gamma_i \, p_i^s}{P} \, X_i \tag{5}$$

The component saturation vapour pressure p_i^s for the required temperature is calculated by the Antoine equation (Holmes and Van Winkle, 1970).

$$\text{Log } (p_i^s) = A - \frac{B}{(C+t)} \tag{6}$$

The composition of a vapour in equilibrium with a liquid can then be calculated with the saturated vapour pressure of component i, p_i^s, and the liquid phase activity coefficient, γ_i by the Eq. (5).

The liquid-phase fugacity of component i, for condensable component is given (Pausnitz, 1969) as,

$$f_i^L = \gamma_i \cdot X_i\, f_i^{oL} \exp \int_{p^r}^{P} \frac{\overline{V}_i^L}{RT}\, dp \tag{7}$$

f_i^{oL} is the fugacity of pure liquid i at the temperature of the solution and at the reference pressure p^r.

The standard-state fugacity is given by

$$f_i^{oL} = p_i^s\ \varnothing_i^s \exp \int_{p_i^s}^{p^r} \frac{V_i^L}{RT}\, dp \tag{8}$$

When the pressure is low, it is common practise to set $p^r = p_i^s$ in Equations (7) and (8).

Taking $\overline{V}_i^L = V_i^L$, one may obtain

$$f_i^L = \gamma_i\, X_i\, (p_i^s\ \varnothing_i^s) \exp \int_{p_i^s}^{p} \frac{V_i^L}{RT}\, dp \tag{9}$$

By rewriting Eq. 9 becomes

$$f_i^L = \gamma_i\, X_i\, p_i^s\ \varnothing_i^s \exp\left(-V_i^L\, p_i^s\ /\ RT\right) \exp\left(V_i^L\, P\ /\ RT\right) \tag{10}$$

where

$$f_{i(p^o)} = p_i^s\ \varnothing_i^s \exp\left(-V_i^L\, p_i^s\ /\ RT\right) = f_{i(oL)} \tag{11}$$

$f_{i(p^o)}$ is the reference fugacity of pure liquid at zero pressure and $\varnothing_i^s$ is the fugacity coefficient at saturation, all at temperature T. When Eq. (10) is rewritten

$$f_i^L = \gamma_i\, X_i\, f_i^{oL} \exp\left(V_i^L\, P\ /\ RT\right) \tag{12}$$

the exponential term is the Poynting correlation which corrects the liquid fugacity to a zero-pressure reference. The liquid molar V_i^L is assumed constant over the range of the integral. This volume is calculated using Rackett's equation as modified by Spencer and Danner (1972). The modified Rackett equation for the saturated-liquid molar volume as used here is

$$V_i^L = \frac{RT_{ci}}{p_{ci}} Za_i^{\tau}, \tau = 1 + (1 - Tr)^{2/7} \text{ for } T/T_0 = Tr \leq 0{,}75 \quad (13)$$

For the liquids used in this work, the quantity Za is tabulated by Spencer and Danner (1972) and given in Table 1. $f_i^{(OL)}$ data, both real and generated, were fit to a function of the form given by Lykman Table (1972) by Prausnitz (1967, 1980).

$$\ln f_i^{oL} = C_{1i} + C_{2i} / T + C_{3i} T + C_{4i} \ln T + C_{5i} T^2 \quad (14)$$

where C's are constant. Eq. (14) excludes any form of the Antoine equation which, although popular for fitting data over a narrow range, extrapolates very poorly over a wide range of temperature.

From Eqs. (3), (4), and (12), for multicomponent vapour-liquid equilibria, the equation of equilibrium for every condensable component i is

$$y_i = \frac{\gamma_i}{\varnothing_i P} X_i f_i^{oL} \exp (P V_i^L/RT) \quad (15)$$

The vapour phase fugacity coefficient is a function of temperature, total pressure, and the composition of the vapour phase; it can be calculated from the equation of state using the thermodynamic relation (Bealtie, 1949).

$$\ln \varnothing_{i,p} - \ln \varnothing_{i,p_i^s} = B_{ii} \frac{(P - p_i^s)}{RT} \quad (16)$$

The detailed derivation of Eq. (16) from the virial expansion in terms of pressure is given by Hayden (1975).

When experimental values of the second virial coefficients are not available, the equation of Pitzer and Curl (1957) is used for pure nonpolar gases.

$$\frac{B_{ii} P_{ci}}{R T_{ci}} = (0.1445 + 0.073 w) - (0{,}33 - 0{,}46 w) Tr^{-1} - (0{,}1385 + 0{,}5 w) Tr - (0{,}0121 + 0{,}097 w) Tr^{-3} - (0{,}0073 w) Tr^{-8} \quad (17)$$

where w is the acentric factor calculated from

$$w = -1 - \log \frac{P'_{0\cdot7}}{P_{ci}} \quad (18)$$

and $P'_{0\cdot7}$ is the vapour pressure at $T/T_{ci} = Tr = 0{,}7$.

Table 1. Pure Component Data.

Component Name	T_c °K	P_c Bars	Z_{RA}	Antoine Constants			Constants for Standart-State Fugacity Equation				
				A	B	C	C_1	C_2	C_3	C_4	C_5
Benzene	562.16	48.98	0.2696	6.90565	1211.033	220.79	97.209	-6976.1	$1.9082.10^{-2}$	-14.212	$-6.7182.10^{-6}$
Toluene	591.79	41.09	0.2646	6.95334	1343.943	219.377	20.899	-5790.2	$-2.0741.10^{-2}$	71.440	$1.151\ .10^{-5}$
n.Heptane	540.26	27.36	0.2611	6.90240	1268.115	216.900	-17.613	-4669.8	$-3.5093.10^{-2}$	6.9580	$1.4503.10^{-5}$

The composition of a vapour in equilibrium with a liquid can then be calculated by the Eq. (15) with the knowledge of the liquid phase activity coefficient, γ_i.

Although assuming liquid phase activity coefficient equals to unity, VLE data for ideal systems can be easily calculated by Raults and Dalton's Law, VLE data for real solutions which are subject to distillation can not be valuated so easily. In order to overcome the difficulties met in design and operation of the equipment, the estimation methods for non-ideal systems have become subject to many investigators. In the past 25 years two major group methods have developed to calculate the activity coefficient of component i in a multicomponent mixture. Generally, these methods can be divided into those which require binary pair interactions, and those which split the component molecules into fundamental groups.

The well known binary interaction methods are the NRTL equation (Renon 1968), the LEMF equation (Marina, 1973, Hanks, 1978), and the UNIQUAC equation (Abrams, 1975).

The major group contribution methods are ASOG (Derr, 1969) and UNIFAC (Fredenslund, 1975).

Determination of Activity Coefficients

In a liquid mixture, all activity coefficients are directly related to the molar excess Gibbs energy G^E which was proposed by Scatchard (1937).

$$G^E = RT \sum_{i=1}^{N} X_i \ln \gamma_i \qquad (19)$$

If VLE data measured at some low temperature, say T_o, together with several sets of heat of mixing data covering the entire temperature range over which the extrapolation is to be made are available, one can estimate the G^E, at the temperature of interest by means of the integrated Gibbs-Helmholtz relation (Prausnitz, 1969).

$$G^E(T) = \frac{T}{T_o} G^E(T_o) - T \int_{T_o}^{T} \frac{H^E(T)}{T^2} \, dT \qquad (20)$$

where $H^E(T)$ represents the heat of mixing of the system as a function of temperature and $G^E(T_o)$ is the low temperature reference set of data.

Since it is difficult to obtain experimental H^E data covering the entire temperature range Hanks et al (1971) determined the parameters of a given model by fitting the algebraic expression for H^E, derived from the G^E model by application of the Gibbs-Helmholtz relation, to a set of experimental H^E data

$$H^E = -T^2 \left[\frac{\partial (G^E/T)}{\partial T}\right]_{p,\,x} \tag{21}$$

Using the parameters thus obtained to calculate activity coefficients from G^E model, one may then compute activity coefficients, γ_i, by applying the relation

$$\ln \gamma_i = \frac{\partial}{\partial X_i} (n_T\, G^E)\ T,\ p,\ x_k = i \tag{22}$$

and hence VLE data from Eq. (15).

There are numerous semitheoretical and empirical models of G^E, which involve empirical constants which must be determined by fitting the equations to experimental data.

If one applies Eq. (21) to the function G^E $(X_i, A_1, A_2 \ldots A_k)$ one obtains another algebraic function H^E $(X_i, A_1, A_2, \ldots A_k)$ which for models of practical interest, contains the same set of adjustable parameters, A_k. Since H^E data can easily be measured at moderate temperatures, this method simplifies the prediction of VLE data.

WILSON Equation

Wilson (1964) proposed the following logaritmic function as an expression for the molar-excess free-energy for multicomponent systems

$$\frac{G^E}{RT} = - \sum_{i=1}^{N} X_i \ln \left[\sum_{j=1}^{N} \Lambda_{ij} X_j\right] \tag{23}$$

When Eq. (22) is applied to the expression above, the Wilson equation for a multicomponent system becomes

$$\ln \gamma_i = 1 - \ln \left(\sum_{j=1}^{N} X_j \Lambda_{ij}\right) - \sum_{k=1}^{N} \frac{X_{ki}}{\sum\limits_{j=1} X_j \Lambda_{kj}} \tag{24}$$

The heat of mixing for binary solution can be calculated from Eq. (21) and (23).

$$H^E = X_1 X_2 \left[\frac{\Lambda_{12}(g_{12}-g_{11})}{X_1 + \Lambda_{12}X_2} + \frac{\Lambda_{21}(g_{12}-g_{22})}{X_2 + \Lambda_{21}X_1} \right] \tag{25}$$

where

$$\Lambda_{12} = \frac{V_2}{V_1} \exp\left(- \frac{g_{12} - g_{11}}{RT} \right) \tag{26}$$

$$\Lambda_{21} = \frac{V_1}{V_2} \exp\left(- \frac{g_{21} - g_{22}}{RT} \right) \tag{27}$$

If Eq. (25) in curve-fitted to a set of experimental $H^E(X_i)$ data by the regression analysis methods, the values of $(g_{12} - g_{11})$ and $(g_{21} - g_{22})$ can be determined for binary mixture (Orje 1965). Wilson's equation gives a good representation of G^E data for many completely miscible mixtures, but it has two disadvantages: first it can not predict the occurence of partial miscibility, and second Wilson H^E equation is shown to break down to ideal solution models in the limit of large intermolecular interactions $| H^E_{max} | > 120$ cal/mol (Hanks, 1971). Wilson's equation, therefore, can be reliably used only for completely miscible systems.

NRTL Equation

Renon and Prausnitz (1968) used the Wilson's local composition concept in their derivation of the Nonrandom two-liquid (NRTL) equation. The NRTL equation, on the contrary to Wilson's is applicable to partially miscible as well as completely miscible systems. Renon and Prausnitz's equation for the excess free energy for multicomponent systems is

$$\frac{G^E}{RT} = \sum_{i=1}^{N} X_i \frac{\sum_{j=1}^{N} \tau_{ji} G_{ji} X_j}{\sum_{k=1}^{N} G_{ki} X_i} \tag{28}$$

$$\ln \gamma_i = \frac{\sum_{j=1}^{N} \tau_{ji} G_{ji} X_j}{\sum_{k=1}^{N} G_{ki} X_k} + \sum_{j=1}^{N} \frac{X_i G_{ij}}{\sum_{k=1}^{N} G_{kj} X_k} \left(\tau_{ij} - \frac{\sum_{r=1}^{N} X_r \tau_{rj} G_{rj}}{\sum_{k=1}^{N} G_{kj} X_k} \right) \tag{29}$$

where

$$\tau_{ji} = (g_{ji} - g_{ii})/RT, \; G_{ji} = \exp(-\alpha_{ji}\,\tau_{ji})$$

$$\alpha_{ij} = \alpha_{ji}, \; g_{ij} = g_{ji}, \; G_{kk} = 1, \; \tau_{kk} = 0. \tag{30}$$

The parameters in Eqs. (28) and (29) can be determined from binary H^E data for the binary systems comprising the ternary.

$$H^E = \frac{X_1X_2(g_{21}-g_{11})G_{21}}{(X_1+X_2G_{21})}\left[1 - \frac{\alpha\tau_{21}\,X_1}{(X_1+X_2G_{21})}\right]$$

$$+ X_1X_2\,\frac{(g_{12}-g_{22})G_{12}}{(X_2+X_1G_{12})}\left[1 - \frac{\alpha\tau_{12}X_2}{(X_2+X_1G_{12})}\right] \tag{31}$$

When deriving H^E expression from G^E model, parameters are assumed independent of temperature otherwise equations become very complicated (Asselineau 1970). When Hanks et al (1978) used a three-parameter model of NRTL equation, they did not observe any systematic temperature dependence of parameters. But, when the NRTL equation was used as a two-parameter model (α was set to a constant value of 0.3 as recommended by Renon and Prausnitz (1968) the parameters showed a clear temperature dependence.

LEMF Equation

Marina and Tossios (1973) studied the parametric behaviour of the NRTL equation by setting $\alpha = -1$ and called the new expression as the LEMF model.

The LEMF model for multicomponent systems is described by the Equations (32) and (22).

$$\frac{G^E}{RT} = \sum_{i=1}^{N} X_i \;\frac{\Sigma\,\tau_{ji}\,X_i}{\sum\limits_{k=1}^{N} G_{ki}X_i} \tag{32}$$

where

$$\tau_{ij} = (g_{ij} - g_{jj})/RT \text{ and } G_{ij} = \exp(-\tau_{ij})$$

and

$$\tau_{ii} = \tau_{jj} = \tau_{kk} = 0, \; G_{ii} = G_{jj} = G_{kk} = 1.0$$

The parameters in Eq. (32) can be calculated from the experimental binary H^{E}' data, by the following equation.

$$H^E = \frac{X_1X_2RT\tau_1}{X_1+X_2G_1}\left(1 + \frac{\tau_1G_1X_2}{X_1+X_2G_1}\right) + \frac{X_1X_2RT\tau_2}{X_2+X_1G_2}\left(1 + \frac{\tau_2G_2X_1}{X_2+X_1G_2}\right) \tag{33}$$

Both the NRTL and the LEMF equations require the determination of two parameters for each binary system comprising the ternary.

SELECTION OF THE TERNARY MIXTURE FOR THIS WORK

While choosing the ternary system for this work, the following requirements were kept in mind:

1- Two or more sets of H^E data each measured at a different temperature for each of the binary comprising the ternary system must be available in the literature.

2- Max. heat of mixing of each binary mixture must differ from each other.

3- The experimental isobaric ternary vapour-liquid equilibrium data must be available in the literature.

With these considerations Benzene(1)/Toluene (2)/n.Heptane (3) (Park and Nam, 1986) has been chosen to study the prediction of isobaric ternary vapour-liquid equilibria from two or more isothermal low temperature heat of mixing data.

CALCULATION PROCEDURE

Expressions for H^E, for the NRTL model, Eq. (31), (The α parameter was fixed at 0.3 in calculations) and the LEMF model, Eq. (33), were fitted to experimental binary H^E data (Rastogi 1967, Lundberg 1964, Brown 1955) to determine the numerical values of the parameters at given temperatures for the three binary systems which comprise the ternary system studied in this work. Determination of $(g_{ij} - g_{jj})$ values require many iterations and for practical purposes, the Quasi-Newton fit program has been developed to evaluate the parameters by minimizing the function given by Eq. (34).

$$S_e^2 = \frac{1}{n} \Sigma (H^E{}_{cal} - H^E{}_{exp})^2 \tag{34}$$

The values of $(g_{ij} - g_{jj})$ and $(g_{ji} - g_{ii})$ parameters thus obtained were used to predict the istohermal heat fo mixing data. The error between the calculated and the experimental values of H^E for a given system composition, X_1, was expressed as the Root Mean Square Deviation (R.M.S.D.) and Percent Standart Deviation.

$$\text{R.M.S.D.} = \left[\frac{1}{n} \Sigma \left(H^E_{cal} - H^E_{exp} \right)^2 \right]^{1/2}$$

$$\text{S.D. \%} = \left\{ \frac{1}{n-1} \Sigma \left(H^E_{cal} - H^E_{exp} \right) / H^E_{exp} \right)^2 \right\}^{1/2} \times 100$$

Two or more sets of H^E data, each at a different temperature were fitted in this way and the values of $(g_{ij} - g_{jj})$ and $(g_{ji} - g_{ii})$ thus obtained were extrapolated as a linear function of temperature, to the boiling point of the ternary mixtures. The values of $(g_{ij} - g_{jj})$ and $(g_{ji} - g_{ii})$ determined by this extrapolation technique were used in Eqs (29) and (22) to evaluate the activity coefficients for the first and the second component of the ternary system. The respective parameters obtained are shown in Tables (2) and (3) .How well the NRTL and the LEMF equation fits heat of mixing data is demonstrated by R.M S.D. and S.D. % reported in Tables (2) and (3).

The vapour phase fugacity coefficients were calculated by using the virial equation. The self viral coefficients were computed where necessary, by the Pitzer and Curl (1957) method. Liquid molar volumes of the pure components were required for calculation of the Poynting correction factor. These were obtained from the Eq. (13) at the required ternary boiling point. Pure component vapour pressures P_i^s were computed by means of Antonie equation. Antoine constants were obtained from Holmes (1970). The necessary constants for the calculations are given in Table 1.

The calculated γ_i's in turn was used in Eq. (15) to evaluate y_1 and y_2 values at 1 atm. Then y_3 was otained from the relation given below.

$$\Sigma y_i = 1.0 \tag{35}$$

For practical purposes, a detailed computer program was prepared for each of the two equations to predict the isobaric ternary equilibrium data. In the computer programs the liquid composition, the boiling

Table 2. Binary Systems: Parameters for NRTL Equation Determined From H^E Data And Statistical Measures Of Fits Of H^E And VLE Data.

System	VLE Data	NRTL		Parameters		Statistical Measures of fit of H^E		Statistical Measures of VLE Predictions		Sourse of Exptl. Data Ref.	
		°C	α	$g_{12}g_{22}$	$g_{21}-g_{11}$	S_e^2	S.D.%	R.M.S.D.	S.D.%	H^E Data	VLE Data
Benzene(1) / Toluene(2)	Isobaric 1 atm 80.1–110°C	15 25 35	0.3 0.3 0.3	-142.756 -112.516 -127.525	242.916 187.956 203.288	0.2891 0.8515 0.5777	2.39 7.97 5.71	0.0258	5.25	Rastogi (1967) Rastori (1967) Rastogi (1967)	Marsan (1966)
Heptane(1) / Toluene(2)	Isobaric 1 atm 98.5–110°C	25 20	0.3 0.3	490.255 417.304	174.600 143.219	0.2354 0.3862	0.33 0.39	0.0346	11.7	Lundberg (1964) Özalp (1987) Lundberg (1964) Özalp (1987)	Rose (1955)
Benzene(1) / n.Heptane(2)	Isobaric 1 atm 80–98.5°C	20 25 50	0.3 0.3 0.3	523.038 499.950 380.010	980.14 940.10 769.90	3.8033 2.0180 3.267	2.26 1.20 1.99	0.0847	23.76	Brown (1955) Lundberg (1964) Özalp (1987) Lundberg (1964) Özalp (1987)	Sieg (1950)

Table 3. Binary Systems: Parameters For LEMF Equation Determine From H^E Data And Statistical Measures Of Fits Of H^E And VLE Data.

	VLE Data	LEMF °C	Parameters		Statistical Measures of fit of H^E		Statistical Measures of VLE Predictions		Source of Exptl. Data Ref.	
			$g_{12}-g_{22}$	$g_{21}-g_{11}$	R.M.S.D.	S.D.%	R.M.S.D.	S.D.%	H^E Data	VLE
Toluene(2)	Isobaric 1 atm. 80.1–110°C	15 25 35	264.888 255.902 251.671	−401.291 −371.375 −354.776	0.2100 0.7487 0.5140	1.71 7.03 4.98	0.0145	2.43	Rastogi (1967) Rastogi (1967) Rastogi (1967)	Marcan (1966)
Heptane(1)/ Toluene(2)	Isobaric 1 atm. 98.5–110°C	25 50	356.739 303.649	129.419 116.663	0.1229 0.2373	0.19 0.21	0.0322	11.42	Lundberg (1964) Özalp (1987) Lundberg (1964) Özalp (1987)	Rose (1955)
Benzene(1)/ Heptane(2)	Isdbaric 1 atm. 80.1–98.5°C	20 25 50	212.929 219.335 116.432	469.345 458.378 467.729	3.1733 1.4096 0.1929	1.90 0.80 0.10	0.1218	31.72	Brown (1955) Lundberg (1964) Özalp (1987) Lundberg (1964) Özalp (1987)	Sieg (1950)

point and the total pressure were fixed by the experimental data and the solution models were used to predict the vapour compositions.

Vapour compositions predicted by the NRTL and the LEMF equations are given in Table (4). The R.M.S.D. s and S.D. % of the experimental and the calculated vapour mol fractions were tabulated in Table (5) for comparison.

RESULTS AND CONCLUSIONS

The separation of multicomponent mixtures by distillation require reliable VLE data. Experimental data for binary mixtures are frequently available, but data for multicomponent mixtures almost never available, and must be calculated. For that reason the separation is dependent on the predictive thermodynamic method used for estimation of the VLE data. The limitations of these predictive methods must be considered in the design and operation of distillation columns. There would appear to be a major difficulty in selecting one thermodynamic models as "the best" as the choice may be system dependent.

Tables (2) and (3) summarizes the results of Quasi-Newton fit programme for binary systems It can be seen from these tables that the NRTL equation can predict the isobaric binary VLE data with standard deviation ranging from to 5 to 24 %, whereas the LEMF equation could estimate the vapour phase within the accuracy of 2–31 %.

Table 5. summarizes the results of testing the NRTL and LEMF equations using the published ternary VLE and binary heats of mixing data. Although NRTL and LEMF equations were originally derived for prediction of isothermal VLE, the predictions show that Isobaric ternary VLE data can be estimated as accurate as isothermal VLE data using NRTL parameter constants obtained from two or more low temperature heats of mixing data. The NRTL equation was found to be superior to the LEMF equation, in the prediction of ternary VLE data with standart deviation ranging from 12–17 %, whereas the LEMF equation could predict the vapour phase within the accuracy of 16–21 %. An examination of the ternary VLE errors in the predicted vapour phase compositions (Table (5)) show R.M.S.D.'s of the order of 0.027–0.035 mole fractions with the NRTL equation and R.M.S.D.'s of the order of 0.028–0.062 mole fractions with the LEMF equation Park et al (1986) correlated their experimental ternary isobaric VLE data by means of the NRTL parameters obtained from only binary VLE data

Table 4. Ternary vapour-liquid Equilibrium Predictions from NRTL and LEMF Equations for Benzene (1)/Toluene (2)/n.Heptane (3) at 1 atm.

No	Temp °K	Liquid Composition			Exptl Vapour Compn.			Calcd. by NRTL			Calcd. by LEMF		
		X_1	X_2	X_3	y_1	y_2	y_3	y_1	y_2	y_3	y_1	y_2	y_3
1	378.15	0.083	0.866	0.051	0.212	0.697	0.091	0.1554	0.7271	0.1175	0.1738	0.7275	0.0987
2	376.65	0.085	0.786	0.129	0.197	0.632	0.171	0.1559	0.6395	0.2045	0.1765	0.6404	0.1831
3	374.95	0.089	0.729	0.182	0.207	0.529	0.264	0.1597	0.5722	0.2681	0.1814	0.5735	0.2451
4	373.15	0.103	0.614	0.283	0.206	0.452	0.342	0.1852	0.4730	0.3418	0.2113	0.4750	0.3137
5	371.45	0.105	0.505	0.390	0.220	0.342	0.438	0.1933	0.3888	0.4178	0.2207	0.3907	0.3886
6	370.15	0.114	0.387	0.499	0.232	0.261	0.507	0.2205	0.3055	0.4740	0.2502	0.3062	0.4436
7	370.05	0.111	0.279	0.610	0.219	0.199	0.582	0.2344	0.2371	0.5285	0.2644	0.2361	0.4996
8	368.15	0.123	0.133	0.744	0.243	0.098	0.659	0.2850	0.1192	0.5958	0.3129	0.1170	0.5700
9	374.65	0.195	0.750	0.055	0.325	0.588	0.087	0.3383	0.5707	0.0910	0.3664	0.5724	0.0612
10	372.95	0.209	0.627	0.119	0.345	0.482	0.173	0.3529	0.4907	0.1563	0.3855	0.4918	0.1227
11	370.75	0.220	0.584	0.196	0.358	0.385	0.257	0.3618	0.4067	0.2315	0.3982	0.4078	0.1940
12	369.15	0.232	0.477	0.291	0.372	0.295	0.333	0.3838	0.3276	0.2894	0.4257	0.3280	0.2463
13	367.15	0.240	0.367	0.393	0.373	0.226	0.401	0.4033	0.2478	0.3488	0.4480	0.2489	0.3031
14	366.15	0.245	0.255	0.500	0.384	0.154	0.462	0.4353	0.1775	0.3872	0.4825	0.1779	0.3396
15	365.05	0.256	0.132	0.612	0.404	0.078	0.518	0.4887	0.0958	0.4155	0.5363	0.0954	0.3682
16	371.05	0.282	0.658	0.060	0.475	0.439	0.086	0.4501	0.4513	0.0985	0.4781	0.4537	0.0681
17	369.65	0.297	0.576	0.127	0.499	0.336	0.165	0.4654	0.3820	0.1526	0.4993	0.3833	0.1174
18	367.15	0.310	0.481	0.209	0.505	0.261	0.234	0.4709	0.3012	0.2279	0.5096	0.3023	0.1881
19	365.15	0.318	0.375	0.307	0.504	0.197	0.299	0.4834	0.2282	0.2884	0.5272	0.2292	0.2435
20	363.95	0.329	0.256	0.415	0.508	0.133	0.359	0.5206	0.1576	0.3217	0.5701	0.1583	0.2715
21	362.15	0.339	0.133	0.528	0.519	0.067	0.414	0.5621	0.0826	0.3552	0.6121	0.0828	0.3051
22	368.05	0.379	0.559	0.062	0.608	0.313	0.079	0.5625	0.3507	0.0868	0.5879	0.3537	0.0584
23	366.05	0.379	0.489	0.132	0.611	0.240	0.149	0.5445	0.2909	0.1646	0.5759	0.2923	0.1317
24	363.95	0.421	0.362	0.217	0.575	0.223	0.202	0.5920	0.2052	0.2028	0.6313	0.2060	0.1627
25	362.15	0.438	0.246	0.316	0.622	0.113	0.265	0.6194	0.1359	0.2447	0.6664	0.1365	0.1971
26	360.65	0.447	0.128	0.425	0.623	0.061	0.316	0.6543	0.0707	0.2750	0.7072	0.0710	0.2217
27	364.35	0.493	0.444	0.063	0.703	0.223	0.074	0.6657	0.2489	0.854	0.6859	0.2520	0.0621
28	362.95	0.510	0.353	0.137	0.704	0.158	0.138	0.6766	0.1905	0.1329	0.7055	0.1917	0.1028
29	360.95	0.533	0.243	0.224	0.705	0.102	0.193	0.6939	0.1250	0.1811	0.7317	0.1254	0.1428
30	359.15	0.555	0.124	0.321	0.702	0.055	0.243	0.7248	0.0619	0.2133	0.7716	0.0621	0.1662
31	361.35	0.596	0.339	0.065	0.778	0.151	0.071	0.7429	0.1732	0.0840	0.7586	0.1758	0.0656
32	359.25	0.623	0.235	0.142	0.779	0.090	0.131	0.7484	0.1126	0.1389	0.7728	0.1134	0.1138
33	357.65	0.647	0.122	0.231	0.771	0.048	0.181	0.7702	0.0562	0.1735	0.8051	0.0564	0.1385
34	358.65	0.706	0.227	0.067	0.840	0.091	0.069	0.8165	0.1065	0.0770	0.8282	0.1084	0.0635
35	356.65	0.740	0.115	0.145	0.843	0.037	0.120	0.8251	0.0505	0.1243	0.8458	0.0509	0.1033
36	356.15	0.819	0.112	0.069	0.902	0.036	0.062	0.8815	0.0485	0.0699	0.8897	0.0494	0.0608
37	355.05	0.913	0.053	0.034	0.952	0.018	0.030	0.9465	0.2230	0.0312	0.9488	0.0230	0.0281
38	369.85	0.077	0.062	0.861	0.139	0.050	0.811	0.2077	0.0651	0.7272	0.2260	0.0629	0.7111
39	381.25	0.039	0.936	0.025	0.076	0.884	0.040	0.0779	0.8542	0.0679	0.0884	0.8543	0.0573

Table 5. Comparison of NRTL and LEMF eEquations in the Prediction of İsobaric Ternary Vapour-Liquid Equilibrium Data.

Equation	R.M.S.D.			S.D. %		
	y_1	y_2	y_3	y_1	y_2	y_3
NRTL	0.0342	0.0268	0.0353	12.50	17.80	16.08
LEMF	0.0488	0.0277	0.0619	16.12	18.21	21.61

Park's (1986) correlation was in the order of 0.021–0.025 mole fractions. Comparing our predictions with their correlations, it can be detected that our predictions obtained with the NRTL parameters are quite reasonable eventhough the correlation values are little better. If Table (4) in closely observed, one may find out that standart deviations highly increases when the composition of one of the component is $y_i < 0.05$. In table (4) if the experimental runs, 15, 21 and 38 are excluded from the calculations than S.D. % drops below 12 % which makes the results comparable to those obtained for isothermal conditions with NRTL equation. This feature provides an important economic advantage since the amount of experimental work required to characterize a multicomponent solution is thereby very much reduced. And the sensitivity variables in the calculations are the thermodynamic models used and the cause of the prediction errors is the lack of reliable low temperature heats of mixing data in the literature. The limitations of these predictive methods must be considered in the design of distillation columns.

ACKNOWLEDGEMENT

The author is grateful to the Computer Center, Faculty of Science, Uludağ University for the use of its facilities.

SYMBOLS

A_k	Parameter
A.B.C.D.	Antoine constants
B_{ii}	Viral coefficient
C_1, C_2	Standart-state Fugacity Eq. Constants
f	Fugacity
G^E	Gibb's Excess Free Energy.
$g_{ij} - g_{jj}$	NRTL or LEMF Equation parameter
H^E	Heat of mixing (cal/g.mol)

N	Number of components in a multicomponent system
n	Number of experimental points
P	Total pressure (mm Hg)
p_{ci}	Critical pressure of component i
p_i^s	Vapour pressure of component i at the system boiling point (mm Hg)
Pr	Reducaed pressure (p_i / p_{ci})
R	Ideal gas constant (cal /g.mol °K
T	Absolute temperature (°K)
T_{ci}	Critical temperature of component i
T_{ri}	Reduced temperature (T / T_{ci})
V_i^L	Liquid molar volume of component i
W	Acentric factor
X_i	Mole fraction of component i in liquid phase
y_i	Mole fraction of component i in vapour phase
Z_{ai}	Modified Rackett number

GREEK LETTERS

α	NRTL Equation parameter
γ_i	Liquid phase activity coefficient of compoenent i
Λ_{12}	Wilson Equation parameter
τ_{12}	NRTL and LEMF equation parameter
$\varnothing$	fugacity coefficient

SUPERSCRIPTS and SUBSCRIPTS

i, j, k	component, i, j, k in a multicomponent system
L	Liquid phase
o	Standart state
r	Reduced
v	Vapour phase

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