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UNIVERSAL LIQUID MIXTURE MODEL FOR VAPOR-LIQUID AND LIQUID-LIQUID EQUILIBRIA IN HEXANE-BUTANOL-WATER SYSTEM OVER THE TEMPERATURE RANGE 10 - 100 °C

Akand W. Islam* and Vinayak N. Kabadi

Department of Chemical Engineering, North Carolina A&T State University
1601 East Market Street, Greensboro, North Carolina 27411, USA

This is an extended research of the paper (Islam et al., 2011) conducted to obtain a universal set of interaction parameters of the model NRTL over the temperature range 10 – 100 °C for hexane–butanol–water system; meaning for binary pairs hexane–butanol, butanol–water and hexane–water; and for ternary system hexane–butanol–water. Thorough investigations of data selections for all binary pairs (Vapor–Liquid Equilibrium (VLE), Liquid–Liquid Equilibrium (LLE)), infinite dilution activity coefficient (γ^{∞}), infinite dilution distribution coefficient (D_{sw}), excess enthalpy (H^E), and for ternary system (LLE of hexane–butanol–water) were carried out. Finally quadratic temperature dependent interaction parameters were estimated regressing all the mentioned data and in each case calculated results were compared with literature values. The comparisons showed an overall percentage of error within 15% for the mentioned phase equilibrium calculations.

Keywords: NRTL, single set of parameters, reasonable error

1. INTRODUCTION

In previous investigations (Islam et al., 2011) it had been possible to attain a universal liquid mixture model in hexane–butanol–water system; implying that separate sets of parameters are not needed to calculate different types of phase equilibrium data. In that study two two-parameter models (UNIQUAC and LSG) and two three-parameter models (NRTL and GEM-RS) were analyzed against experimental or literature phase equilibrium data (binary VLE, binary LLE, γ^{∞}, and infinite dilution distribution coefficient) of binary pairs hexane–butanol, butanol–water, and hexane–water; and ternary LLE data of hexane–butanol–water system in order to obtain a universal liquid mixture model which would compute the above mentioned data types within fair deviation by only a single set of parameters.

We concluded that NRTL was such a model, and was validated only at 25 °C. As an extension, following the same procedures the aim of this work is also to obtain a unique set of parameters of NRTL for a wide temperature range 10 - 100 °C.

Studies on temperature dependent parameters of activity coefficient models (Abrams and Prausnitz, 1975; Hashemi et al., 2004; Renon and Prausnitz, 1968; Wang and Vera, 1995) in literature are limited. The models give a good representation of VLE or LLE data using adjustable interaction parameters which describe the energy of interactions between molecules for each binary pair. These parameters are temperature independent. Therefore, the set of parameters calculated by fitting the original models to isothermal VLE or LLE data should make it possible to predict for a wide range of temperatures. In

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*Corresponding author, e-mail: amislam@ncat.edu practice, the accuracy of such a prediction is poor. A more accurate prediction can be obtained by introduction of temperature dependent parameters (Anderson and Prausnitz, 1978; Murthy and Zudkevitch, 1979). Skjold-Jørgensen et al. (1980) modified the interaction parameter a_{ij} of the UNIQUAC model as follows:

$$a_{ij} = \frac{Z}{2} a_{mn}^{'} \tag{1}$$

A polynomial was chosen to represent $Z(T)$:

$$Z\left(T\right) = A + BT + CT^2 + ... \tag{2}$$

According to Nagata et al. (1991) the linear temperature dependence of the energy parameters could not yield a quantitive agreement with experimental data. Hence, quadratic functions similar to Eq. 1 were suggested.

$$a_{ij} = A_{ij} + B_{ij}T + C_{ij}T^2 \tag{3}$$

Demirel et al. (1992), Demirel (1993) used the following alterations

$$a_{12} = d_1 + d_2 / \left(T - T^*\right) \tag{4}$$

$$a_{21} = d_3 + d_4 / \left(T - T^*\right) \tag{5}$$

Nagata and Yamada (1972) first studied temperature dependence on the NRTL model parameters and showed linear correlation was capable of representing both VLE and H^E (excess enthalpy) data with a single set of parameters.

$$a_{12} = c_1 + c_2 / \left(T - T^*\right) \tag{6}$$

$$a_{21} = c_3 + c_4 / \left(T - T^*\right) \tag{7}$$

$$\alpha = \alpha_{12} = \alpha_{21} = c_5 + c_6 / \left(T - T^*\right) \tag{8}$$

Nagata and Yamada (1973) then added quadratic terms with the above a_{12} and a_{21} relations to obtain better results. Introducing empirical temperature dependencies into the original version of the NRTL model improves the performance considerably, especially for highly non-ideal mixtures. Demirel et al. (1993) also used the same relations as in Eqs. 6 - 8. Mato et al. (1989) proposed $\alpha_{ij} = 1/(2+G_{ij}G_{ji})$ for modifying the original three–parameter NRTL equation to make it a true two–parameter model for VLE systems that are completely miscible in a liquid phase. Their results suggested α parameter should be set not only according to the chemical nature of mixture components but also to the temperature. Therefore, following the linear reciprocal absolute temperature dependence for the logarithm of it α was recommended that

$$\ln \alpha = A + B / T \tag{9}$$

In this study, we assumed quadratic temperature dependence for the NRTL interaction parameters and compared performances of this model with respect to the experimental data.

2. DATA SELECTION

Similar to methods applied in Islam et al. (2011) an extensive literature search was carried out to obtain mutual solubility, γ^∞, and VLE data of hexane–water, butanol–water, and butanol–hexane pairs; D_{sw} and LLE data of hexane–butanol–water; vapor pressure, and liquid density of hexane, butanol, and water within temperature range from 10 to 100 °C. Most of the solubility (binary LLE), γ^∞ and H^E data were taken from DECHEMA Chemistry Data Series (Christensen et al., 1984; Gmehling and Menke, 1994, 2007; Gmehling and Onken, 1977; 2003; Gmehling et al., 1987; Sorensen and Arlt, 1979, 1980). The data which were selected finally for our regression purpose are shown in Appendix A. Complete descriptions of the data selections are discussed in the following sections.

2.1. Hexane - water

In the literature (Chapoy et al., 2008; Deal and Derr, 1964; Leinonen and Mackay, 1973; Macauliffe, 1963; Mackay and Shiu, 1981; Polak and Lu, 1973; Roddy and Coleman, 1968; Sorensen and Arlt, 1979; Sugi and Katayama, 1977; Tsonopoulos and Wilson, 1983) numerous values for solubility were found at several temperatures for this pair. However, in most cases values varied from source to source and thus consistent trends were not found. Generally the solubility of oil in water increases with temperature and the data points were selected using this criterion. Tsonopoulos and Wilson's (1983) data were our final selection because they followed a non–erratic trend throughout. The solubility data of water in hexane at 293.15 K did not follow the trend with other temperatures, such as 298.15, 303.15 and 313.15 K (Sorensen and Arlt, 1979). Hence data at 293.15 K was disregarded.

2.2. Water - butanol

There are plentiful solubility and γ^∞ data available for this pair (Butler et al., 1933; Fischer and Gmehling, 1994; Gmehling et al., 1926; Kinoshita et al. 1958; Loblein and Prausnitz, 1982; Menke, 1994, 2007; Sorensen and Arlt, 1979; Yaws et al. 1997). Some data points were discarded due to discontinuity. The solubility data for water in butanol at different temperatures do not differ much from source to source. The data trend indicates solubility of water in butanol increases with temperature. Hill and Malisoff (1926) showed solubility data from a lower temperature to a higher temperature which were consistent and these data were taken for our final selection. Many references in DECHEMA (Gmehling and Menke, 1994) showed a decline of solubility of butanol in water with temperature; however, one source (Lesteva et al.'s data reported in Sorensen and Arlt, 1979) showed reverse behavior. Fuehner et al.'s data reported in Sorensen and Arlt (1979) showed a smooth trend from a lower to a higher temperature range and this dataset was finally selected. γ^∞ of water in butanol reported in Loblein and Prausnitz (1982) was finally selected because those data were consistent with values at 25 °C. References (Gmehling and Menke, 1994, 2007; Thomas et al. 1982; Tochigi and Kojima, 1976; Vrbka et al., 2005) show different trends of γ^∞ data of butanol in water at different temperatures. Tochigi and Kojima (1976)'s data showed γ^∞ of butanol in water decreases with temperature whereas other sources showed an opposite manner. Because Vrbka et al. (2005) reported from a lower temperature to a higher temperature, his dataset was used for our calculations.

For VLE, x–y values were generated by the previously mentioned procedure (Islam et al., 2011). Second virial coefficients (B_{ii}), saturated liquid volume (V_i^L) and saturated vapor pressure (p_i^{sat}) data or empirical correlations were chosen carefully by thorough studies of literature (Ambrose and Ghiasse, 1987; ASME Steam Tables, 1993; Daubert and Danner, 1992; Garriza et al., 2002; Hansch and Leo, 1979; Harvey and Lemon, 2004; Reid et al. 1987; Rodriguez et al. 1993; Tsonopoulos, 1974).

V_i^L and p_i^{sat} of hexane and butanol were calculated from the temperature dependent correlation by Daubert and Danner (1992), and of water from the ASME Tables (1993). The equation for calculating V_i^L and p_i^{sat} is reported as

$$V_i^L = A/\left(B^{\left(1+(1-T/C)^D\right)}\right)\cdot 1000 \; (V_i^L \text{ is in cm}^3\text{/mol}) \tag{10}$$

$$p_i^{sat} = \exp\left[A + B/T + C\log T + DT^E\right] \div 1000 \; (p_i^{sat} \text{ in kPa}) \tag{11}$$

B_{ii} of hexane and butanol, mixed virial coefficient (*Bij*) of hexane–butanol/water–butanol pairs were calculated by the Tsonopoulos (1974) correlation. water's B_{ii} was taken from Harvey and Lemon (2004). The Harvey and Lemon correlation is as follows:

$$B(T)/B^o = \sum_{i=1}^{4} a_i (T^*)^{b_i} \tag{12}$$

All the parameters of the above equation are shown in Table 1.

Table 1. Parameters of Daubert and Danner (1992), Harvey and Lemon (2004)

Parameters of Daubert and Danner (1992)	V_i^L		p_i^{sat}		Parameters of Harvey and Lemon (2004)	B_i	
	hexane	butanol	hexane	butanol	i	water	
						a_i	b_i
A	0.7147	0.9677	165.47	96.23	1	0.34	-0.5
B	0.265	0.2664	-8353.3	-9214.30	2	-0.76	-0.8
C	507.43	562.93	-23.972	-10.295	3	-24.22	-3.35
D	0.2781	0.2457	0.0295	0.000002	4	3978.2	-8.3
E	0	0	1.0	2.0			

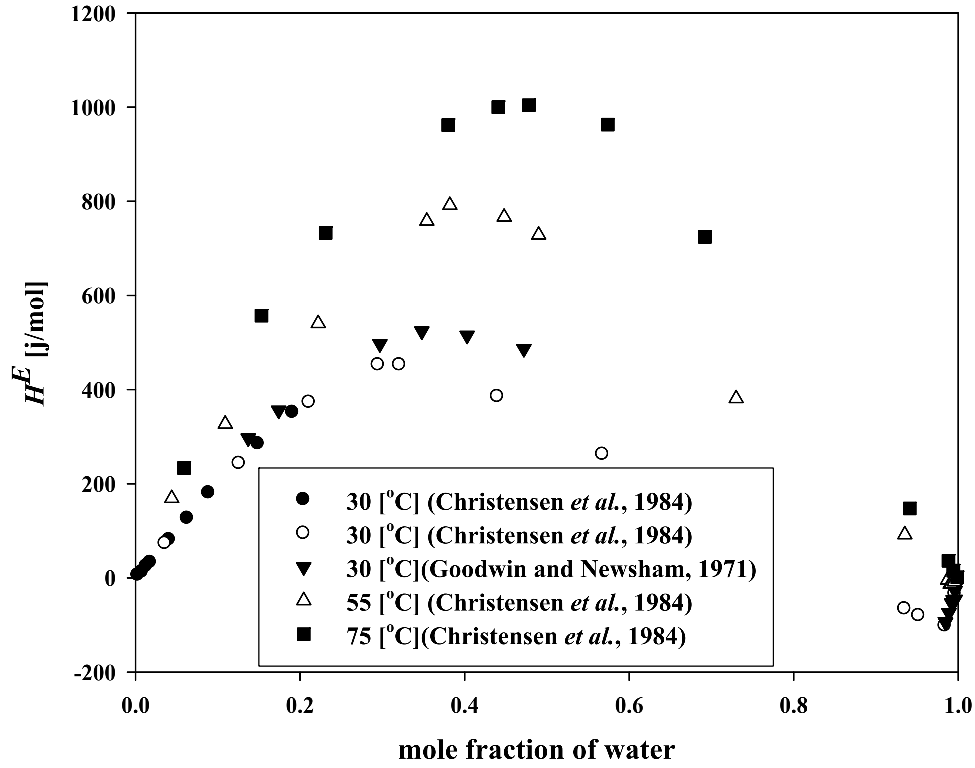

Fig.1. Excess enthalpy of water–butanol at different temperatures

Five H^E datasets were found for water–butanol. These are shown in Fig. 1. Data from Ponner et al. reported in Christensen et al. (1984) were not selected because the dataset did not show a solubility gap between water and butanol. Therefore, Pannov's data reported in Christensen et al. (1984), and

Goodwin and Newsham (1971)'s datasets were used finally. H^E data are very important to validate an activity coefficient model because excess enthalpy is the first derivative of the activity coefficient at a constant pressure and composition. H^E expression for NRTL is shown in Appendix B.

2.3. Hexane - butanol

Large amounts of VLE data of hexane-butanol over the temperature range were found (Chapoy et al., 2008; Christensen et al., 1984; Gmehling and Onken, 2003; Gmehling et al., 1981; Gracia et al., 1992). Barker's method (Barker, 1953) was also applied following the excess Gibbs energy expression from Marsh (1977) in order to get vapor composition (y) data, and to generate corresponding γ 's for whose datasets were in P-x form. Coefficients that were calculated to use in Barker's method are listed in Table 2. Matlab® (The MathWorks, version 2009a) programming was used to estimate these coefficients. A brief description of this method is stated in Appendix C.

Five excess enthalpy datasets for this pair were collected from Christensen et al. (1984), and Nguyen and Ratcliff (1975). Brown et al.'s datasets at temperatures 25, 35 and 45 °C were reported in Christensen et al. (1984). Those datasets were our selected data. Mukrami's data reported by Christensen et al. (1984), and Nguyen and Ratcliff (1975)'s datasets were inconsistent. All the datasets are shown in Fig. 2.

γ^∞ data of hexane in butanol and that of butanol in hexane in the literature over the temperature range were scant. Thomas et al. (1982) and Dobrjakov et al. (2001) reported very few γ^∞'s at different temperatures and we had not many choices of sorting these data.

Table 2. Coefficients for use in Barker's method

T [K]	A_0	A_1	A_2	B_1
288.15	1.8698	-1.1973	-0.0527	-0.8453
293.15	1.8553	-1.1564	-0.0348	-0.8254
298.15	1.8374	-1.1080	-0.0234	-0.8047
303.15	1.8204	-1.1015	-0.0310	-0.8025
308.15	1.8049	-1.0658	-0.0182	-0.7852
313.15	1.7880	-1.0416	-0.0310	-0.7745
318.15	1.7741	-1.0031	0.0118	-0.7487
323.15	1.7538	-0.9645	0.0163	-0.7305

2.4. Hexane - butanol - water

Two ternary data sets of hexane–butanol–water system; one from Sugi and Katayama (1977), and another from our own measurements (Islam et al., 2011) were used in computations. These were at 25 °C and no ternary data at other temperatures for this system could be found in other sources.

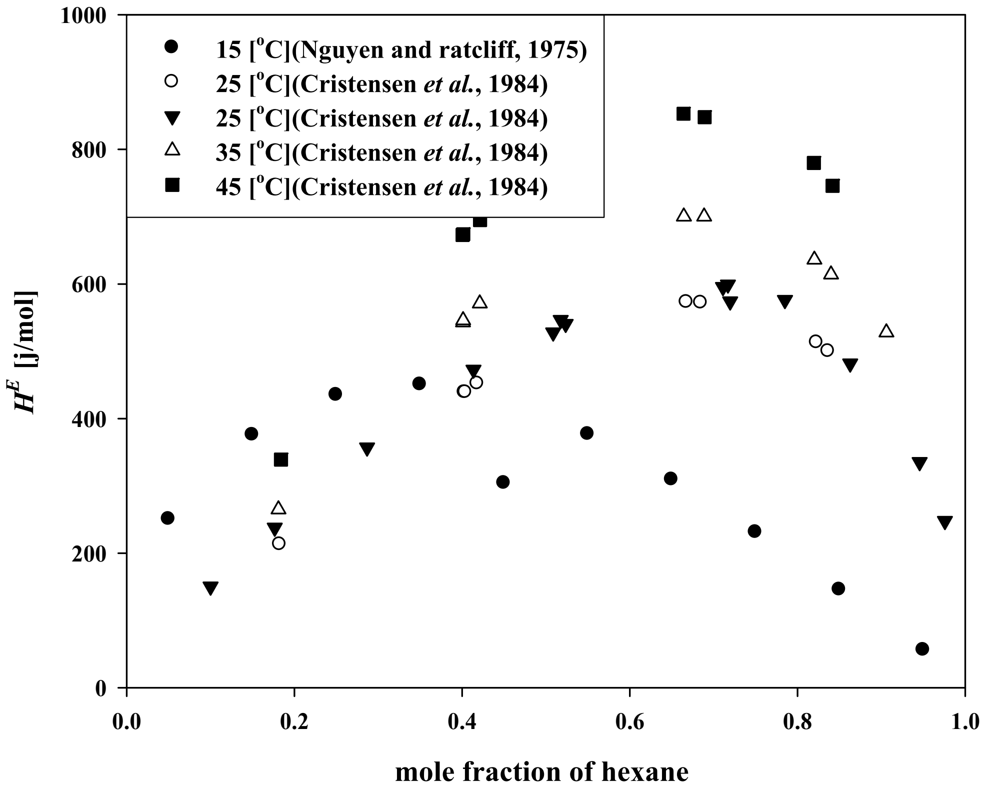

Fig.2. Excess enthalpy of hexane–butanol

3. PARAMETERS ESTIMATION AND RESULTS

As mentioned earlier, quadratic temperature dependent functions were used for NRTL parameters estimation. The expressions

$$a_{12} = A_{12} + B_{12}(T - 298.15) + C_{12}(T - 298.15)^2 \tag{13}$$

$$a_{21} = A_{21} + B_{21}(T - 298.15) + C_{21}(T - 298.15)^2 \tag{14}$$

298 K (25 °C) were taken as the reference temperature. NRTL parameters were estimated by regressing all the finally selected binary data (LLE, VLE, γ^{∞} and H^E) of hexane–butanol, butanol–water and hexane–water pairs. A_{12}, A_{21}, and α were kept fixed equal to the values for 25 °C (obtained from Islam et al., 2011) and only four parameters B_{12}, B_{21}, C_{12}, *and* C_{21} were estimated. Regression computations were done by IMSL FORTRAN Numerical Library 5.1. In all cases, the objective function was set as:

$$F_i(obj) = \sum_{k}^{N_k} \sum_{i}^{N_i} \frac{1}{N} w_k \frac{F_{i,k}(\exp) - F_{i,k}(cal)}{F_{i,k}(\exp)} \tag{15}$$

where,

$N = N_k \times N_i$

N_i = number of data points,

N_k = total number of property (like, $k = 1$ (γ^{∞}), $k = 2$ (binary LLE), $k = 3$ (binary VLE) and $k = 4$ (H^E),

w_k = weightage.

Based on the work done for 25 °C (Islam et al., 2011), several combinations of weights for different properties in the above objective functions were applied to obtain the best parameters for each pair (hexane–water, hexane–butanol, water–butanol). In every case the percentage of error of each data point as well as overall average percentage of error from the selected literature data of each property was recorded. Errors were calculated by the following relation:

$$\text{Error of data point } i \text{ of property } k,\ Err_{i,k}(\text{in }\%) = \frac{\left(V_{exp,i} - V_{cal,i}\right)\cdot 100}{V_{exp,i}} \tag{16}$$

$$\text{Over all error} = \frac{\sum_{i=1}^{N} Err_{i,k}}{N_T} \tag{17}$$

Here, N_T means total number of data points.

Our target was to minimize the error of each data point of binary LLE, binary VLE, γ^{∞} and H^E, and finally to obtain parameters which will predict data with an overall average percentage of error not more than 15%. After data regression with several combinations of weights the desired parameters were successfully obtained. During the data regression process error estimations for different weights are shown in Tables 3 and 4 for water–butanol and hexane–butanol pairs respectively. In these tables w_1, w_2, w_3, and w_4 represent weight on binary LLE, γ^{∞}, binary VLE, and on H^E data respectively. For hexane–water these calculations are not necessary to show because this pair exhibits only binary LLE computation.

The desired parameters which showed optimum results in terms of the least average percentage of error from experimental or literature data are shown in Table 5. The average percentages of error in calculating different properties of three pairs are reported in Table 6.

The parameters that we have obtained finally can be referred to as universal parameters because these can predict data within fair deviation (≤15%) regardless of VLE, LLE, binary or ternary datasets. Upon obtaining a universal set of parameters a ternary diagram was plotted with the calculated results at 25 °C as well as at 75 °C. These are shown in Fig. 3. In the figure L_1 and L_2 represent hexane and water rich phase respectively. The calculated results also clearly show the phase split just as clearly as the experimental data. The experimental ternary data are shown only at 25 °C because no other data are available in the literature at higher temperatures; however, a prediction can be made based on calculated results. From this figure it is observed that at higher temperatures the water–rich phase behaves the same as in 25 °C; however, the hexane-rich phase behaves differently. At higher temperatures there is more butanol in the hexane–rich phase than in 25 °C. The calculated ternary data at 40, 60 and 75 °C are also shown in this figure. Variations of butanol concentrations in the hexane–rich phase at higher temperatures are shown in Fig. 4. The calculated D_{sw} at 40, 60 and 75 °C are reported as 1.81, 2.31 and 2.98 respectively.

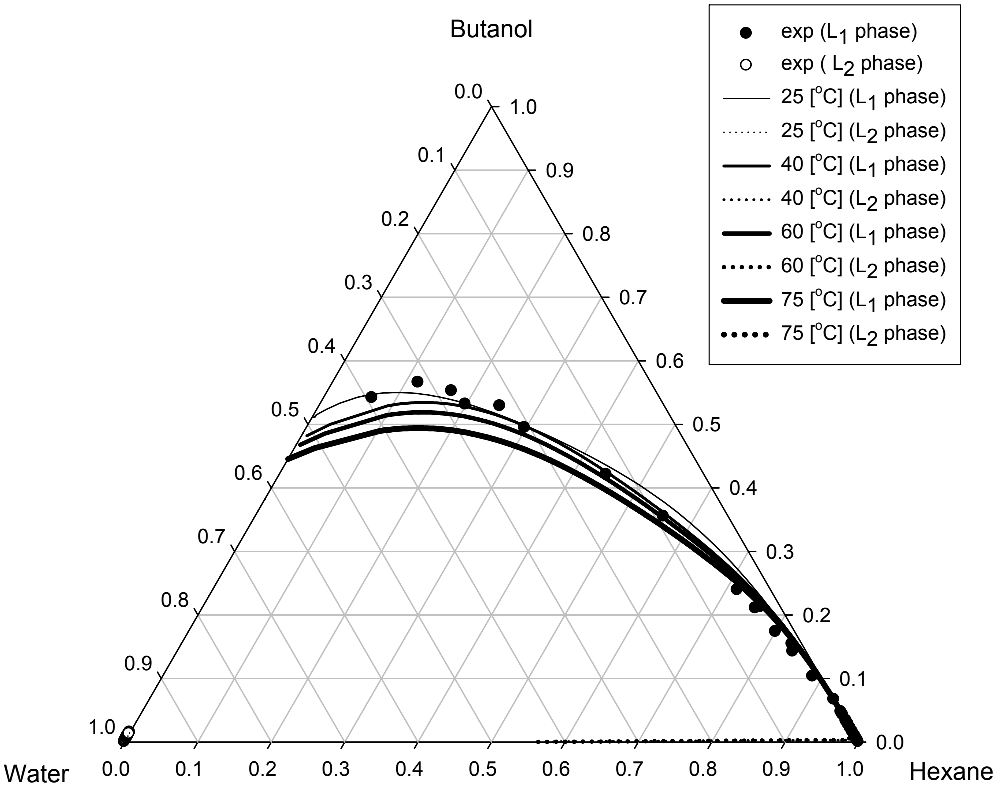

Fig.3. Ternary diagram for hexane–butanol–water at higher temperatures (L_1 is hexane-rich phase and L_2 is water rich phase)

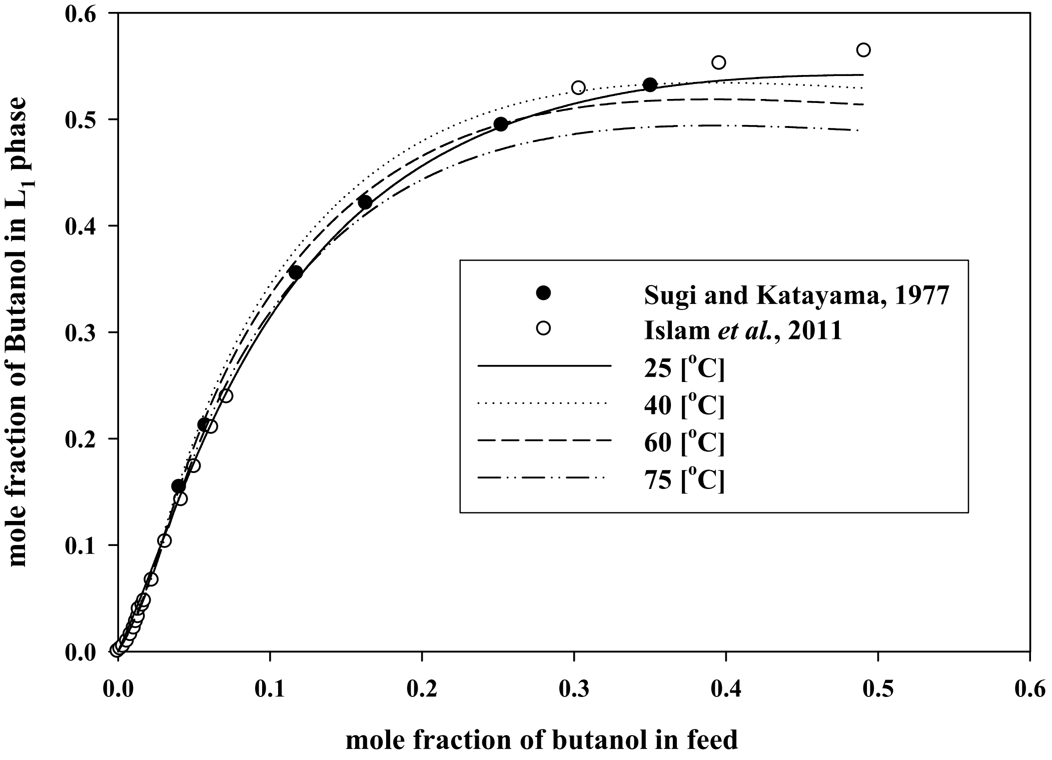

Fig.4. Variation of butanol concentration in L_1 (hexane-rich) phase at higher temperatures

Table 3. Parameter estimations for water-butanol

weights	average error in solubility [%]		average error in γ^∞ [%]		average error in γ [%]		average error in H^E [%]
	i in *j*	*i* in *j*	*i* in *j*	*j* in *i*	*i* in *j*	*j* in *i*	
$w_1 = 1, w_2 = 1, w_3 = 1, w_4 = 1$	12.61	4.1	5.89	4.37	3.7	4.43	14.41
$w_4 = 10$	23.38	36.21	15.58	13.37	7.18	11.02	8.92
$w_2 = 4.5$	18.36	4.82	2.99	5.99	2.44	3.88	16.73
$w_1 = 10$	18.51	5.99	3.02	4.5	2.47	4.04	15.9
$w_2 = 10$	1.21	4.86	2.81	7.51	5.39	4.48	19.0
$w_2 = 10, w_4 = 5$	4.34	6.38	10.14	2.4	13.04	6.99	12.91
$w_2 = 5, w_4 = 10$	14.6	26.43	6.5	10.68	9.52	9.82	9.75
$w_4 = 10, w_2 = 10$	8.69	17.9	9.75	7.37	113.65	8.83	10.89
$w_4 = 5, w_2 = 5$	4.94	9.84	4.78	7.31	4.4	5.9	16.32
$w_2 = 10, w_4 = 8, w_1 = 5$	8.41	11.46	6.16	4.74	5.85	6.69	13.67
$w_2 = 10, w_1 = 5$	8.57	4.33	3.97	3.19	6.46	5.52	14.04
$w_1 = 10, w_4 = 15, w_2 = 5$	10.9	7.73	7.78	1.09	6.72	6.16	12.54

Table 4. Parameter estimations for hexane-butanol

weights	average error in H^E [%]	average error in γ^∞ [%]		average error in γ [%]	
		i in *j*	*j* in *i*	*i* in *j*	*j* in *i*
$w_2 = 1, w_3 = 1, w_4 = 1$	8.95	10.02	14.08	3.41	5.17
$w_2 = 2$	7.48	11.7	15.51	3.83	6.19
$w_3 = 3$	6.42	12.39	17.14	4.06	6.93
$w_4 = 5$	6.05	12.43	11.49	4.33	7.64
$w_2 = 2, w_4 = 5$	9.18	9.48	13.69	2.48	3.51
$w_2 = 5, w_4 = 5$	8.82	10.31	12.97	2.73	3.85
$w_2 = 2.5, w_4 = 5$	8.53	11.02	12.13	2.57	3.52

Table 5. Best fitted parameters for all three pairs

Pair (*i* - *j*)		*A*	*B*	*C*	α
hexane-water	*i, j*	3381.10	7.478	-0.0167	0.22
	j, i	2013.86	-17.886	0.1527	
water-butanol	*i, j*	1031.46	6.315	0.00096	0.41
	j, i	229.43	0.585	-0.0387	
hexane-butanol	*i, j*	910.21	-0.307	-0.003	0.56
	j, i	323.42	-2.157	0.018	

Table 6. Calculated results by NRTL model using best fitted parameters for all three pairs

Pair (i-j)	average error in solubility [%]		average error in γ^{∞} [%]		average error in γ [%]		average error in H^E [%]
	i in *j*	*j* in *i*	*i* in *j*	*j* in *i*	*i*	*j*	
hexane - water	1.13	5.49					
water - butanol	5.52	12.01	8.47	8.98	3.14	6.49	12.21
hexane - butanol			11.02	2.13	2.57	3.52	8.53

5. CONCLUSIONS

It can be concluded that it is possible to obtain a single set of parameters of the so–called universal model to calculate the earlier mentioned phase equilibrium data within a reasonable error (<15%) over the temperature range 10-100 °C provided data selections are very thorough and parameters are estimated by regressing all possible data types of each binary pair. These parameters are also able to calculate ternary data with an appropriate phase split at higher temperatures. As future suggestions, this proposed method of attaining a universal model for a wide temperature range can be further validated on other non-ideal ternary systems addressed by Islam and Kabadi (2009).

SYMBOLS

a	energy parameter of UNIQUAC/NRTL
c_1, c_2, c_3, c_4	constants
d_1, d_2, d_3, d_4	constants
A, B, C, D, E	constants
T^*	reference temperature, K
Z	coordination number ($Z = 10$ in this study)
x-γ	activity coefficient(γ_i) values for corresponding mole fraction (x_i) of binary VLE system
P-x	saturated vapor pressure (P_i) for mole fraction (x_i) of binary VLE system (P, kPa)
α	nonrandomness factor of NRTL
subscripts	
i, j	interaction between *i* and *j*
m, n	interaction between *m* and *n*

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APPENDIX A: FINAL DATA

The data which were finally used for parameters estimation after painstaking data selection process are shown in Table A1.

Table A1. Final data used in regression over the temperature range 10-100 °C

Binary pair	Type of data	Temp. [°C]	Data (ref.)
hexane - water	solubility of hexane in water	25	2.57E-06 (Islam et al., 2011)
		35	2.69E-06 (Tsonopoulos and Wilson,1983)
		93	5.73E-06 (Tsonopoulos and Wilson,1983)
		100	6.21E-06 (Tsonopoulos and Wilson,1983)
	solubility of water in hexane	25	4.7E-04 (Islam et al., 2011)
		40	1.5E-03 (Tsonopoulos and Wilson,1983)
		93	5.95E-03 (Tsonopoulos and Wilson,1983)
		100	7.09E-03 (Tsonopoulos and Wilson,1983)
water-butanol	solubility of water in butanol	15	0.021(Hill and Malisoff, 1926)
		25	0.0187 (Islam et al., 2011)
		30	0.0181 (Hill and Malisoff, 1926)
		35	0.0175 (Hill and Malisoff, 1926)
		40	0.0168 (Hill and Malisoff, 1926)
		50	0.0165 (Hill and Malisoff, 1926)
		60	0.0162(Sorensen and Arlt, 1980)
	solubility of butanol in water	15	0.5048 (Hill and Malisoff, 1926)
		25	0.506 (Islam et al., 2011)
		30	0.511 (Hill and Malisoff, 1926)
		35	0.516 (Hill and Malisoff, 1926)
		40	0.523 (Hill and Malisoff, 1926)
		50	0.528 (Hill and Malisoff, 1926)
		60	0.543 (Hill and Malisoff, 1926)
		70	0.559 (Hill and Malisoff, 1926)
		80	0.581 (Hill and Malisoff, 1926)
		92	0.597 (Hill and Malisoff, 1926)
	γ^{∞} of water	25	5.06 (Islam et al., 2011)
		70	3.27 (Loblein and Prausnitz, 1982)
		80	3.12 (Loblein and Prausnitz, 1982)
		90	3.07 (Loblein and Prausnitz, 1982)
		99	2.97 (Loblein and Prausnitz, 1982)

	γ^{∞} of butanol	20	48.4 (Vrbka et al., 2005)
		25	51.37 (Islam et al., 2011)
		30	53.4 (Vrbka et al., 2005)
		35	57.2 (Vrbka et al., 2005)
		40	58.9 (Vrbka et al., 2005)
		45	60.2 (Vrbka et al., 2005)
		50	61.5 (Vrbka et al., 2005)
		55	62.8 (Vrbka et al., 2005)
		60	63.4 (Vrbka et al., 2005)
		70	63.8 (Vrbka et al., 2005)
	VLE	25	(Islam et al., 2011)
		35	(Gmehling et al., 1981)
		50	(Fischer and Gmehling, 1994)
		60	(Gmehling and Onken, 1977)
		70	(Gmehling and Onken, 1987)
		90	(Gmehling and Onken, 1987)
	H^E	30	(Christinsen et al., 1984)
		30	(Christinsen et al., 1984)
		30	(Goodwin and Newsham, 1971)
hexane-butanol	γ^{∞} of hexane	25	5.12 (Islam et al., 2011)
		50	5.6 (Dobrjakov et al., 2001)
		60	5.3 (Dobrjakov et al., 2001)
	γ^{∞} of butanol	25	38.6 (Islam et al., 2011)
		42	22.5 (Thomas et al., 1982)
		58	15.1 (Thomas et al., 1982)
		67	12.2 (Thomas et al., 1982)
	VLE	25	(Islam et al., 2011)
		30	(Gracia et al., 1992)
		35	(Gracia et al., 1992)
		40	(Gracia et al., 1992)
		45	(Gracia et al., 1992)
		50	(Gracia et al., 1992)
		59	(Gmehling and Onken, 2003)
		65	(Gmehling and Onken, 2003)
		75	(Gmehling and Onken, 2003)
	H^E	15	(Nguyen and Ratcliff, 1975)
		35	(Christinsen et al., 1984)
		45	(Christinsen et al., 1984)

APPENDIX B:
H^E EXPRESSION FOR NRTL WITH QUADRATIC TEMPERATURE-DEPENDENT INTERACTION PARAMETERS

For binary system,

$$\frac{g^E}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right) \tag{B1}$$

where

$$\tau_{12} = \frac{g_{12}-g_{22}}{RT} = \frac{a_{12}}{RT} = \frac{A_{12}+B_{12}T'+C_{12}T'^{2}}{RT}\ ;\ G_{12} = \exp\left(-\alpha\tau_{12}\right) \tag{B2}$$

and

$$\tau_{21} = \frac{g_{21}-g_{11}}{RT} = \frac{a_{21}}{RT} = \frac{A_{21}+B_{21}T'+C_{21}T'^{2}}{RT}\ ;\ G_{21} = \exp\left(-\alpha\tau_{21}\right) \tag{B3}$$

here $T' = T - 298.15$

The rate of change of excess Gibbs energy, and hence the activity coefficients, γ_i, with respect to temperature is proportional to the excess enthalpy and is given by the Gibbs-Helmotz equation

$$\frac{H^{E}}{T^{2}} = -\left[\frac{\partial\left(g^{E}/T\right)}{\partial T}\right]_{P,x} \tag{B4}$$

putting Eq. (B1) into Eq. (B4) and using relations (B2) and (B3),

$$H^{E} = x_1 x_2 \alpha\left[\frac{x_1\tau_{21}G_{21}\left(C_{21}T'^{2}-2C_{21}TT'-298.15B_{21}+A_{21}\right)}{\left(x_1+x_2G_{21}\right)^{2}} + \frac{x_2\tau_{12}G_{12}\left(C_{12}T'^{2}-2C_{12}TT'-298.15B_{12}+A_{12}\right)}{\left(x_2+x_1G_{12}\right)^{2}}\right] \tag{B5}$$

APPENDIX C:
BARKER'S NUMERICAL ACTIVITY COEFFICIENT METHOD

Barker's is a numerical method to calculate activity coefficient. This method is used to reduce experimental data that give the variation of total pressure with liquid composition at constant temperature. For analyzing P-x results the general expression can be put in the form (Marsh, 1977):

$$\frac{g^{E}}{RT(1\text{-}x)} = \frac{\sum_{m=0}^{m'} A_m z^{m}}{\sum_{n=0}^{n'} B_n z^{n}} = \frac{A}{B} \tag{C1}$$

where $z = (1-2x)$ and $B_0 = 1$

After differentiation of Eq. (C1) with respect to T,

$$\ln\gamma_1 = (1-z)^2\left\{AB + (1+z)(A'B - AB')\right\}/\,4B^2 \tag{C2}$$

$$\ln\gamma_2 = (1+z)^2\left\{AB - (1\text{-}z)(A'B - AB')\right\}/\,4B^2 \tag{C3}$$

here $A' = \sum_{m=0}^{n} mA_m z^{m-1}$; and $B' = \sum_{n=0}^{m} nA_n z^{n-1}$

Eqs (C2) and (C3) contain unknowns A_0, A_1, A_2, and B_1 (since B_0 is taken as one). These parameters are to be estimated by regressing the experimental P-x data.