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THE PREDICTION OF ISOBARIC BINARY VAPOUR - LIQUID EQUILIBRIA FROM TWO ISOTHERMAL HEAT OF MIXING DATA

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ARSTRACT

The new modified forms of the Wilson and the NRTL equations of heat of mixing data were developed, whose application can be extended to isobaric binary VLE predictions. That was obtained assuming that the two Wilson and NRTL parameters are linear functions of temperature. Both equations give sufficient predictions for systems with max heats of mixing less then 130 cal / g. mol. However, the Wilson equation is incapable to describe the heat of mixing data for the system with large heats of mixing, the NRTL equation can overcome this problem, but the quality of the VLE predictions is still poor.

INTRODUCTION

Accurate isobaric binary VLE data are needed for the design of industrial distillation equipment. Although large amounts of such data are available in the literature, one often finds that the required VLE data are not presentable for the conditions at which the design is made. In such case, the designer must either measure VLE data at required conditions or predict the data by means of correlation methods. Because of the difficulties in design and operation of VLE apparatus, the experimental determination of VLE data for given binary systems become laborious and time consuming. Therefore the designer often tries to estimate VLE data using one of the prediction methods available.

Although VLE data for ideal systems can be easily calculated by applying Raoult's and Dalton's Law (1950), VLE data of non-ideal solutions which are subject to distillation can not be evaluated 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 (Wilson 1964, Orje 1965, Renon

1968). The usual approach to VLE data correlation or prediction is to measure the data (e.g. total pressure–composition or vapour–liquid composition data) from which liquid phase activity coefficients may be calculated.

THERMODYNAMICS OF VAPOUR–LIQUID EQUILIBRIA

In order to express the nonideality of a liquid mixture. Scatchard (1937) proposed the most useful thermodynamic concept called Gibbs excess energy, G^E. The G^E is expressed as a function of liquid phase activity coefficient at constant temperature and pressure.

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

If VLE data measured at some low temperature, say T_0, 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, Gibbs excess free energy at the temperature of interest by means of the integrated Gibbs–Helmholtz (1969) relation. G^E data are used to evaluate activity coefficients which in turn are used together with pure component vapour pressures to calculate VLE data.

$$G^E(T) = \frac{T}{T_0} G^E(T_0) - T \int_{T_0}^{T} \frac{H^E(T)}{T^2} dt \qquad (2)$$

where H^E (T) represents the heat of mixing of the system as a function of temperature and $G^E(T_0)$ is the low temperature reference set of data. Although Eq. 2 is tehermodynamically sound, H^E data covering the entire temperature range is required for the extrapolation. Since such H^E data is difficult to obtain, one prefers the use of semi–theoretical models to fit the existing VLE data. This sort of models involve one or more adjustable parameters, the values of which must be determined by curve fitting experimental data. The common method for achieving this is to curve fit either the avtivity coefficients or the $G^E(T_0)$ data. When this method is used, the representation of $H^E(T)$ is often not successful (Orje 1965, Wiehe 1965), although good correlation of the VLE data can be obtained.

In order to overcome this problem, Hanks et al (Hanks 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.

$$H^E = -T^2 \left[\frac{\partial (G^E/T)}{\partial T} \right]_{p,x} \tag{3}$$

Using the parameters thus obtained to calculate activity coefficients from G^E model together with pure component vapour pressures one may obtain the VLE data. Hanks et al (1971) showed that this method could be applied to isothermal binary systems, and they (Hanks 1979) also used the G^E model to predict high temperature VLE data from low temperature H^E data. Tan et al (1977, 1978) applied the same method to isobaric binary systems, isothermal and isobaric ternary systems. In these investigations hydrocarbon mixtures (Hanks, 1971, 1979 Tan, 1977, 1978), aromatic and aliphatic alcohols (Hanks 1979), and other organic subtances (Hanks 1971) were used.

H^E – VLE Relation

Eq.3 known as the Gibbs–Helmholtz relation represents a relation between H^E and G^E. If one integrates the Eq.3, Eq.2 results. If the $G^E(T_0)$ value at the reference temperature T_0 is available one may compute the value of G^E at any temperature, T. In other words, $G^E(T_0)$ data represents the initial condition of the integral form of the differential equation. It is possible to integrate the Eq.3 without taking into account the initial data, $G^E(T_0)$. Hanks at al (Hanks 1971) obtained this integration from semi–theoretical and empirical mathematical models of G^E data. These models all take the general form G^E (x_i, A_1, A_2, ... A_k) where x_i are the mole fractions of the $i=1, 2 \ldots N$ components in the mixture and the A_k are adjustable parameters which are determined by regression analysis of experimental G^E (x_i) data. For example one of the best known relation of these models is Wilson's equation (1964, 1965) given here in binary form

$$G^E = f\,(x_i, A_1, A_2 \ldots\ldots\ldots A_k) \tag{4}$$

$$\frac{G^E}{2.303\ RT} = -x_1 \log (x_1 + \Lambda_{12}x_2) - x_2 \log (x_2 + \Lambda_{21}x_1) \tag{5}$$

If the A_k are known, liquid phase activity coefficients, γ_i, can be calculated by applying the relation

$$\ln \gamma_i = \frac{\delta}{\delta x_i} (nTG^E)_{T,\, P,\, x_{k \neq i}} \tag{6}$$

to the algebraic function $G^E (x_i, A_1, A_2, \ldots A_k)$. For example, using Wilson's model, Eq.5. one obtains

$$\ln \gamma_1 = -\ln (x_1 + \Lambda_{12} x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right] \tag{7}$$

The A_k values, when introduced into the $G^E (x_i, A_1 A_2, \ldots A_k)$ function, permit the computation of G^E and also the *ln* x_i by means of Eq.6. Once the γ_i are known, one may calculate the required VLE data from the Eq.8.

$$y_i = \frac{x_i \gamma_i P_i^\circ}{z_i P} \tag{8}$$

If Eq.3 is applied to the function $G^E (x_i, A_1, A_2, \ldots A_k)$, another algebraic function $H^E (x_i, A_1, A_2, \ldots A_k)$ which contains the same set parameters A_k is obtained. For example, using Wilson's equation, applying the Gibbs–Helmholtz relation, Eq.3, to the Eq.5 one obtains

$$H^E = x_1 x_2 RT \left[\frac{\Lambda_{12} G_{12}}{x_1 + \Lambda_{12} x_2} + \frac{\Lambda_{21} G_{21}}{x_2 + \Lambda_{21} x_1} \right] \tag{9}$$

where, $G_{12} = (g_{12} - g_{11}) / RT$ and $\Lambda_{12} = \frac{V_2}{V_1} \exp(-G_{12})$ (10)

$$G_{21} = (g_{12} - g_{22}) / RT \text{ and } \Lambda_{21} = \frac{V_1}{V_2} \exp(-G_{21}) \tag{11}$$

If Eq.9 is curve–fitted to a set of experimental $H^E(x_i)$ data by regression analysis methods, the values of A_k may be determined from the experimental H^E data. γ_i values are then calculated by Eq.7 and the y_i are computed by Eq.8. Thus, one may, predict VLE data without ever measuring y_i–x_i data. This is equivalent to integrating Eq.3 without knowing G^E (T_0).

Since H^E data can easily be measured at moderate temperatures, this method simplifies the prediction of VL E data. It is not necessary to make the experimental determination of H^E data over the entire range of temperature. In many cases, it is more convenient to determine the H^E data than the $G^E(T_0)$ data.

Another well-known G^E model is called NRTL (Non-Random-Two Liquid) Equation which was first proposed by Renon and Prausnitz (1968). The NRTL equation for a binary mixture is given in the Eq.12.

$$\frac{G^E}{RT} = x_1 x_2 \left[\frac{\tau_{21}\ G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12}\ G_{12}}{x_2 + G_{12} x_1} \right]$$

$$\text{where,}\quad \tau_{12} = (G_{12} - G_{22}) / RT \qquad \tau_{21} = (G_{21} - G_{11}) / RT \qquad (12)$$

$$G_{12} = -\exp(-\alpha\tau_{12}) \qquad G_{21} = -\exp(-\alpha\tau_{21})$$

By substituting the Eq.12 into the Eq.2 and the Eq.6, the following relations are obtained

$$H^E = \frac{x_1 x_2 (g_{21} - g_{11})\ G_{21}}{(x_1 + x_2\ G_{21})} \left[1 - \frac{\alpha\tau_{21}\ x_1}{(x_1 + x_2 G_{21})} \right]$$

$$+ x_1 x_2 \frac{(g_{12} - g_{22}) G_{12}}{x_2 + x_1 G_{12}} \left[1 - \frac{\alpha\ \tau_{12}\ x_2}{x_2 + x_1 G_{12}} \right] \qquad (13)$$

and

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{(x_1 + x_2 G_{21})} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \qquad (14)$$

α, $(g_{21}-g_{11})$ and $(g_{12}-g_{22})$ parameters of H^E relation given by Eq.13 are determined from the experimental H^E data by regression analysis methods. Thus obtained parameters are used to calculate $\ln \gamma_i$ from Eq. 14 and then VLE data are evaluated by the Eq.8.

Applying the Wilson and the NRTL equations both, Hanks et al (Hanks 1971, 1979, Tan 1977, 1978) and Nagata et al (Nagata 1972, 1976) made successful predictions of isothermal VLE data from isothermal heat of mixing data.

Since the most separation processes in the chemical and petroleum industries are carried out under isobaric conditions, the prediction possibility of isobaric VLE data by means of the isothermal Wilson and NRTL equations is investigated in this work.

SELECTION OF BINARY MIXTURES FOR THIS WORK

The following requirements are kept in mind in choosing the binary mixtures for this work:

1. These systems should be non–hydrogen bonding type of hydrocarbon / hydrocarbon mixtures.

2. Two or more sets of H^E data each measured at a different temperature for each of the binary pairs of interest must be available in the literature.

3. Max. heat of mixing of each binary mixture must differ from each other. For example, such as 10 cal / mol, 230 cal / mol.

4. The experimental vapour–liquid equilibrium data of the binary pairs of interest must be available in the literature (Gardner 1955, Bromiley 1933, Rose 1955, Sieg 1950).

5. The vapour–liguid equilibrium data of the binary systems must be thermodynamically consistent when the experimental points are tested by means of the Herington Area Test (1951, 1959, 1982).

With these considerations M.C.H. / N–Heptane, N–Heptane / Toluen and Benzene / N–Heptane have been chosen to study the predictions of isobaric binary vapcur–linugid equilibria from two isothermal low tempereratu re heat of mixing data.

Correlation of Isothermal Binary Heat of Mixing Data by The Wilson Equation.

Two sets of isothermal heat of mixing data measured at two different low temperatures for each of the three binaries were fitted into the Eq.9. A. computer program was prepared for fitting the data and the normal objective function to be minimised was the sum of the square of the error (Jenson 1963, Prausnitz, 1969) $[\Sigma(H_{cal}-H_{exp})^2]$ The values of $(g_{12}-g_{22})$ and $(g_{21}-g_{11})$ parameters thus obtained were used to predict the isothermal heat of mixing data. The error between the calculated and the experimental values of H^E for a given system composition, x_1, is expressed in two different ways and their values are given in Fig. 1.

1. The Root Men Square Deviation (R.M.S.D.): $\sqrt{\dfrac{(H_{cal}-H_{exp})^2}{N}}$

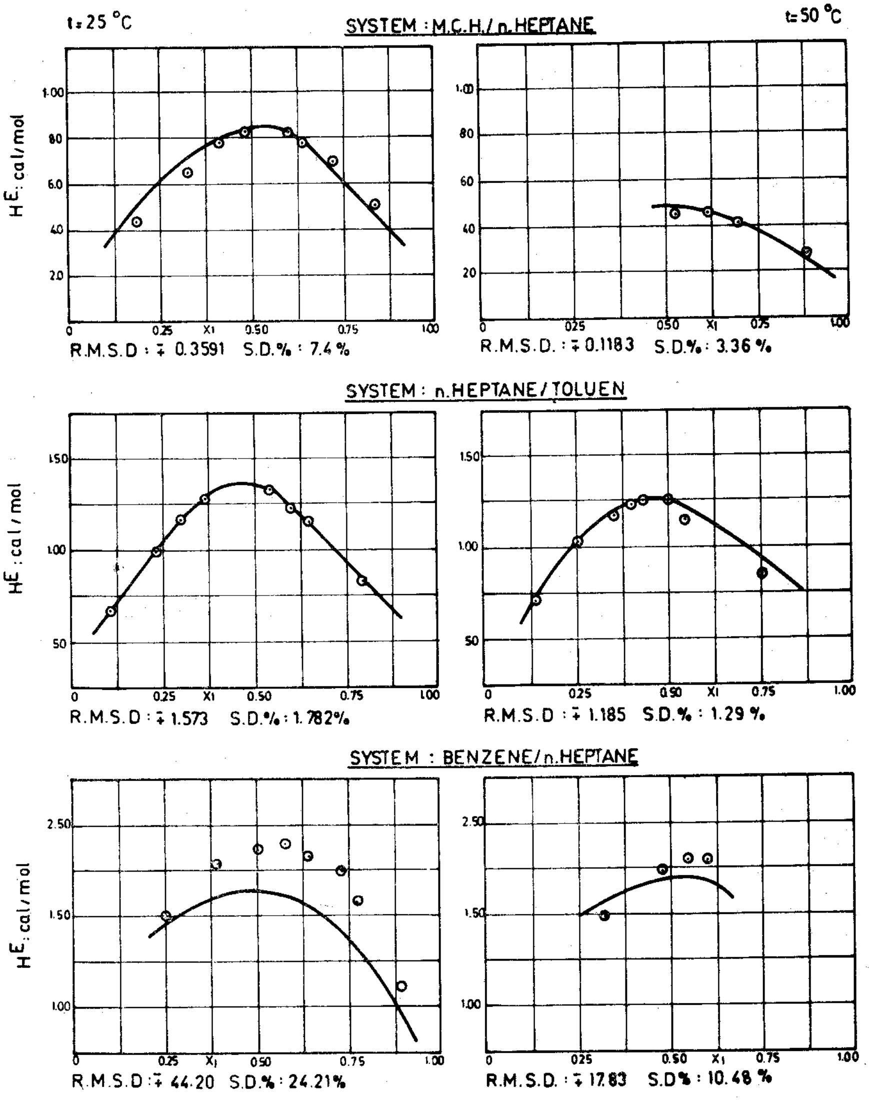
2. Percent Standard Deviation (S.D. %): $\sigma_H =$

$$\left\{ \frac{1}{N-1} \sum_i \left[(H_{cal}-H_{exp}) / H_{exp}\right]^2 \right\}^{1/2} \times 100$$

FIGURE 1. HEAT OF MIXING DATA

- EXPERIMENTAL POINTS

— PREDICTED FROM THE WILSON EQUATION



When the Fig. 1 is examined, one obtains that the Wilson Equation only gives satisfactory fits to the heat of mixing data for systems Where the max heat of mixing is less than 130 cal / mol. However, for benzene / N–heptane system, where the heats of mixing is quite higher, the Wilson equation is incapable of fitting the data. The R.M.S.D. of the experimental and calculated H^E values is as high as 44.20 cal / mol.

Correlation of Isothermal Binary Heat of Mixing Data By the NRTL Equation.

The Eq. 13 was fitted to the experimental heat of mixing data for the three binary systems to determine the $(g_{12}-g_{22})$ and $(g_{21}-g_{11})$ parameters of NRTL equation. In calculations was assumed constant and was fixed according to Renon's rules (1968) as $\alpha = 0.3$. It was also assumed that the α was not a function of temperature. Heat of mixing data measured and predicted by using the NRTL equation parameters for the three binary systems are given in fig. 2. For systems with low heats of mixing the NRTL equation gives similar results to the Wilson equation. The NRTL equation also fits heat of mixing data for the system with large heats of mixing. In the Benzene / N–Heptane example in Fig. 2 the R.M.S.D. of the experimental and calculated heats of mixing is 3.267 cal / mol.

PREDICTION OF ISOBARIC BINARY VLE DATA FROM ISOTHERMAL HEAT OF MIXING DATA

When the VLE data are isothermal and correspond in temperature to the H^E data, one needn't worry about the possibility of temperature dependence of the $(g_{12}-g_{22})$ and $(g_{21}-g_{11})$ parameters in the function H^E, although Asselineau and Renon (1970) showed that these parameters are often functions of temperature. Isobaric binary VLE data used in this work were measured at the solution boiling temperature range at atmospheric pressure. This temperature range differs significantly from the temperature used in measuring isothermal H^E data. Therefore, in the prediction of isobaric VLE data from isothermal H^E data determined at a different lower temperature, one must account for the temperature variability of the Wilson and the NRTL equation's parameters.

In this work, the values of $(g_{12}-g_{22})$ and $(g_{21}-g_{11})$ parameters of the Wilson and the NRTL equations obtained from two sets of H^E data each at a different temperature (25°C and 50°C) were extrapo-

FIGURE 2. HEAT OF MIXING DATA

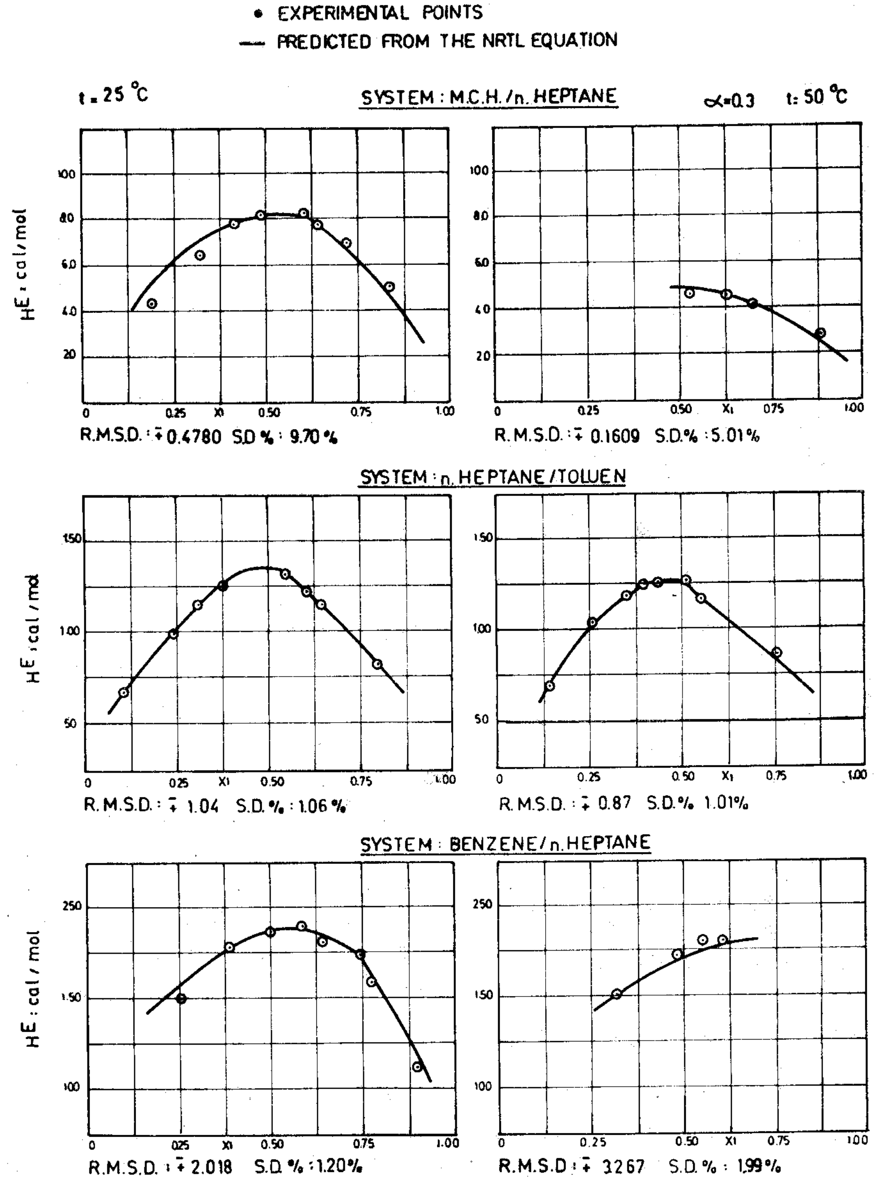


Table 1. Isobaric (760 mm Hg) VLE Predictions From the Modified Wilson and the Modified NRTL Equation for M.C.H. (1) / N– Heptane (2) System. The Experimental Data Is From Garner and Hall (1955).

Temp. B.P. °C t	Liquid Mole Fraction x_1	Exp Vapour Mole Fraction y_{exp}	Vapour Mole Fraction y_1			
			Calculated Modified Wilson y_{cal}	Deviation Δy	Calculated Modified NRTL y_{cal}	Deviation Δy
98.50	0.0675	0.0635	0.0621	–0.0014	0.0627	–0.0008
98.60	0.1520	0.1435	0.1406	–0.0029	0.1417	–0.0018
98.65	0.2195	0.2090	0.2037	–0.0053	0.2051	–0.0039
98.85	0.3250	0.3110	0.3041	–0.0069	0.3058	–0.0052
99.15	0.4435	0.4270	0.4196	–0.0074	0.4213	–0.0057
99.35	0.5095	0.4925	0.4854	–0.0071	0.4874	–0.0050
99.60	0.5980	0.5805	0.5746	–0.0059	0.5758	–0.0047
99.60	0.6075	0.5920	0.5838	–0.0082	0.5850	–0.0070
99.90	0.6930	0.6780	0.6723	–0.0057	0.6731	–0.0049
100.20	0.7850	0.7735	0.7686	–0.0049	0.7690	–0.0045
100.50	0.8820	0.8745	0.8712	–0.0033	0.8713	–0.0032
100.70	0.9485	0.9445	0.9421	–0.0024	0.9423	–0.0022
			R.M.S.D.: ± 0.0055 S.D. % : 1.641 % $g_{21}-g_{11} = 24.7308-0.3020t$ $g_{12}-g_{22} = 22.9521-0.2664\,t$		R.M.S.D.: ± 0.0044 S.D. % : 1.18 % $g_{21}-g_{11} = 9.116-0.0376t$ $g_{12}-g_{22} = 37.778-0.5111t$	

lated as a linear function of temeperature to the boiling point of the solution at which the VLE data were to be calculated, by applying the Least Square Method (1963). These functions are given in Tables 1, 2, 3, 4. The values of $(g_{12}-g_{22})$ and $(g_{21}-g_{11})$ determined by this extrapolation technique were used in equations (7) and (4) to compute the activity coefficient γ_1. The calculated γ_1 in turn was used, together with pure component vapour pressure, P°_1 computed by means of Antoine Equation (1953) to calculated the VLE data from Eq.8.

RESULTS AND DISCUSSION

Results Obtained By Means of The Wilson Equation

Assuming the $(g_{21}-g_{11})$ and $(g_{12}-g_{22})$ parameters of the Wilson equation to be linear functions of temperature, substituion into Eq. 7 gives a new function which is called "The Modified Wilson Equation".

$$g_{21}-g_{11} = C_1 + D_1 t \quad \text{and} \quad g_{22}-g_{12} = C_2 + D_2 t$$

Table 2. Isobaric (760 mm Hg) VLE Predictions From The Modified Wilson and The Modified NRTL Equation For M.C.H. (1)/ N. Heptane (2) System. The Experimental Data Is From BROMILET - QUIGGLE (1933).

Temp. B.P. °C t	Liquid Mole Fraction x_1	Exp. Vapour Mole Fraction y_{exp}	Vapour Mole Fraction y_1			
			Calculated Modified Wilson y_{cal}	Deviation Δy	Calculated Modified NRTL y_{cal}	Deviation Δy
98.43	0.0200	0.0140	0.0183	+0.0043	0.0185	+0.0045
98.48	0.0460	0.0375	0.0423	+0.0048	0.0427	+0.0052
98.54	0.0690	0.0600	0.0635	+0.0035	0.0641	+..0041
98.59	0.0940	0.0870	0.0868	—0.0002	0.0875	+0.0005
98.64	0.1210	0.1100	0.1119	+0.0019	0.1120	+0.0020
98.71	0.1570	0.1465	0.1457	—0.0008	0.1468	+0.0003
98.88	0.2440	0.2290	0.2280	—0.0010	0.2295	+0.0005
99.00	0.2910	0.2720	0.2732	+0.0012	0.2747	+0.0027
99.13	0.3530	0.3340	0.3331	—0.0009	0.3347	+0.0007
99.24	0.4010	0.3820	0.3800	—0.0020	0.3816	—0.0004
99.34	0.4410	0.4220	0.4194	—0.0026	0.4210	—0.0010
99.48	0.4990	0.4790	0.4769	—0.0021	0.4784	—0.0006
99.59	0.5440	0.5250	0.5220	—0.0030	0.5234	—0.0016
99.73	0.5990	0.5800	0.5776	—0.0024	0.5788	—0.0012
99.83	0.6370	0.6190	0.6162	—0.0028	0.6169	—0.0021
99.95	0.6830	0.6670	0.6634	—0.0036	0.6643	—0.0027
100.07	0.7285	0.7110	0.7103	—0.0007	0.7110	0.0000
100.22	0.7840	0.7710	0.7680	—0.0030	0.7685	—0.0025
100.30	0.8200	0.8080	0.8053	—0.0027	0.8053	—0.0027
100.45	0.8670	0.8570	0.8551	—0.0019	0.8552	—0.0018
100.52	0.9050	0.8970	0.8946	—0.0024	0.8947	—0.0023
100.62	0.9420	0.9380	0.9337	—0.0043	0.9338	—0.0042
100.71	0.9690	0.9650	0.9629	—0.0021	0.9629	—0.0021
			R.M.S.D. : ± 0.0026 S.D. % : 7.22 % $g_{21}-g_{11}=$ 24.7308–0.3020t $g_{12}-g_{22}=$ 22.9521–0.2664t		R.M.S.D. : ± 0.0024 S.D. % : 7.62 % $g_{21}-g_{11}=$ 9.116–0.0376t $g_{12}-g_{22}=$ 37.778–0.5111t	

$$\ln \gamma_1 = -\ln \left[x_1 + x_2 \frac{V_2}{V_1} \exp \left(- \frac{C_1 + D_1 t}{R\ (273.16 + t)}\right)\right]$$

$$+ x_2 \left[\frac{\frac{V_2}{V_1} \exp \left(-\frac{C_1 + D_1 t}{R(273.16 + t)}\right)}{x_1 + x_2 \frac{V_2}{V_1} \exp \left(-\frac{C_1 + D_1 t}{R(273.16 + t)}\right)} - \frac{\frac{V_1}{V_2} \exp \left(- \frac{C_2 + D_2 t)}{R(273.16 + t)}\right)}{x_2 + x_1 \frac{V_1}{V_2} \exp \left(- \frac{C_2 + D_2 t}{R(273.16+t)}\right)} \right] \quad (15)$$

VLE data predicted by the Modified Wilson Equation for M.C.H. (1) / N–Heptane (2) and N–Heptane (1) / Toluen (2) systems are given in Tables 1,2 and 3. The R.M.S.D. of the Bromiley–Quiggle's (1933) experimental and the modified Wilson Equations calculated vapour mol fractions for M.C.H. (1) / N–Heptane (2) is 0.0026 and the max. error is 0.0048 at $x_1 = 0{,}046$ and the S.D. % is 7.22 % in the prediction of the VLE data of Garner and Hall (1955) for the same system is 1.641 % . The difference between the two S.D. % values can be explained by taking into account the experimental error made in analyzing the liquid compositions by means of refractive index measurements and the error made due to the close values of x–y for this ideal system at both end points of the x–y diagram. The maximum errors correspond to the end points of x–y diagram. The R.M.S.D. of the Bromiley–Quiggle's experimental and calculated by applying the Raoult's (Özalp 1982). Law is 0.0027 and the max. error is 0.0054 at $x_1 = 0.046$ and S.D. % is 7.87 %. That is to say VLE data predictions of the modified Wilson Equation are in good agreement with the results of the Raoult's Law. The correlation of the Bromiley–Quiggles (1933) experimental VLE data with the three–suffix Margules equation (Özalp 1982) is less successful than the predictions made by the Modified Wilson equation. For example, the R.M.S.D. of the experimental and calculated by means of the margules equation is 0.0038 and the max. error is 0.0064 at $x_1 = 0.046$.

The R.M.S.D. and the S.D. % of the experimental data and the calculated vapour mol fractions by means of the Modified Wilson equa ation for the N–Heptane (1) / Toluen (2) system are 0.0389 and 12.40 % respectively. The VLE data predictions for this system is found in reasonable limits from industrial design point of view. The correlation of the experimental VLE data with the three–suffix Margules equation (Özalp 1982) is more succesful than the predictions made by the Modified Wilson equation.

The Wilson equation is incapable of fitting the data for the Benzene (1) / N–Heptane (2) system where the max. heat of mixing is more than 130 cal / mol, actually the max. value of H^E is 231 cal / mol. This is explained when the Wilson equation is examined carefuly,

Putting $G_{12} = (g_{12} - g_{22}) / RT \qquad G_{21} = (g_{21} - g_{22}) / RT$

and differentiating the Eq.9 with respect to G_{12} and G_{21}, for a maximum, providing that x_1, x_2, T and $V_2 / V_1 \neq 0$, $G_{12} \neq$ and $G_{12} \neq \infty$ one may obtain

$$\frac{\partial H^E}{\partial G_{12}} = 0 \quad \text{and} \quad \frac{\partial H^E}{\partial G_{21}} = 0$$

and consequently,

$$H^E\,(\text{max.}) = RT\,[x_1\,(G_{12}-1) + x_2\,(G_{21}-1)] \tag{16}$$

From Eq. 16, the maximum value that can be predicted for this system is 177.45 cal / mol at x_1 0.56, whilst the experimental value is 231 cal / mol. But the H^E value at $x_1 = 0.56$ predicted by the Wilson equation is 170.229 cal /mol. In other words, the Wilson equation is not capable of evaluating the experimental max. H^E value of 231 cal / mol. Since the Wilson equation is unable to predict the isothermal heat of mixing data for the Benzene (1) / N–Heptane (2) system, no attempt was made to predict the VLE data for this system with the Modified Wilson equation.

Results Obtained By Means of the NRTL Equation.

The NRTL equations parameters which are expressed as the linear function of temperature, in turn are used in Eq. 14 to calculate "*ln* γ_1". The new function is called "The Modified NRTL Equation".

$$g_{21}-g_{11} = C_3 + D_3t \quad \text{and} \quad g_{12}-g_{22} = C_4 + D_4t$$

$$ln\,\gamma_1 = x_2^2 \left[\frac{C_3 + D_3t}{R(273.16 + t)} \left(\frac{\exp\left(-\alpha\,\dfrac{C_3 + D_3t}{R(273.16 + t)}\right)}{x_1 + x_2 \exp\left(-\alpha\,\dfrac{C_3 + D_3t}{R(273.16 + t)}\right)} \right)^2 + \frac{\dfrac{C_4 + D_4t}{R(273.16 + t)} \exp\left(-\alpha\,\dfrac{C_4 + D_4t}{R(273.16 + t)}\right)}{\left((x_2 + x_1) \exp\left(-\alpha\,\dfrac{C_4 + D_4t}{R(273.16 + t)}\right)\right)^2} \right] \tag{17}$$

The isobaric VLE prediction results obtained from the Eq.17 are compared with the Modified Wilson equation results in Tables 1, 2 and 3. For systems with low heats of mixing the NRTL equation gives better results than the modified Wilson equation. In the Garner and Halls (1955) M.C.H. (1) / N–Heptane (2) example in Table 1, the R.M. S.D. of the experimental and calculated vapour mol fraction is 0.0044 and the S.D. % is 1.18 %. These are very small figures from industrial design point of view. The results obtained from the modified NRTL equation are in good agreement with the values predicted by the Raoult's Law (Özalp 1982) and Margules equations (Özalp 1982).

Table 3. shows that the R.M.S.D. of the experimental and calculated vapour mol fractions for the N–Heptane (1) / Toluen (2) system is 0.0434 and S.D. % is 15.68 %. When the values determined by the Modified NRTL equation are complared with the values of the Modified Wilson equation, one may obtain that the Modified Wilson equation has superiority over the modified NRTL equation for this system.

Table 3. Isobaric (760 mm Hg) VLE Predictions From the Modified Wilson and the Modified NRTL Equation for N- Heptane (1) / Toluen (2) System.

Temp. B.P. °C t	Liquid Mole Fraction x_1	exp. Vapour Mole Fraction y_{exp}	Vapour Mole Fraction y_2			
			Calculated Calculated Wilson y_{cal}	Deviation Δy	Calculated Modified NRTL y_{cal}	Deviation Δy
107.88	0.094	0.156	0.1984	+0.0424	0.2062	+0.0503
106.09	0.176	0.265	0.3203	+0.0553	0.3336	+0.0686
104.47	0.265	0.365	0.4209	+0.0559	0.4376	+0.0726
102.43	0.417	0.510	0.5541	+0.0441	0.5707	+0.0607
101.52	0.503	0.585	0.6188	+0.0338	0.6334	+0.0484
100.77	0.584	0.651	0.6767	+0.0257	0.6885	+0.0375
100.17	0.657	0.710	0.7282	+0.0182	0.7370	+0.0270
99.29	0.800	0.827	0.8341	+0.0071	0.8377	+0.0107
98.81	0.893	0.906	0.9073	+0.0013	0.9085	+0.0025
98.48	0.971	0.974	0.9732	—0.0008	0.9737	—0.0003
98.46	0.984	0.986	0.9855	—0.0005	0.9855	—0.0005
			R.M.S.D. : 0.0332 S.D. % : 12.38 % $g_{21}-g_{11}=$ 452.55–1.9876t $g_{12}-g_{22}=$ 395.30–1.3564t		R.M.S.D. : 0.0434 S.D. % : 15.68 % $g_{21}-g_{11}=$ 524.57–0.6028t $g_{12}-g_{22}=$ 192.33–1.3424t	

The quality of isobaric VLE predictions with the Modified NRTL equation for the Benzene (1) / N–Heptane (2) system is rather poor although the NRTL equation fits heat of mixing quite well for this system. This is shown in Table 4. where the R.M.S.D. of experimental and calculated vapour mol fraction is 0.0999 and S.D. % is 27.62 %.

In this work, the NRTL parameters are derived only from the heat of mixing data and the quality of the fits is reasonably good, if not better that those of Nagata (1972, 1976) which were obtained by fitting the parameters to both VLE and heat of mixing data simultaneously.

Table 4. Isobaric (760 mm Hg) VLE Predictions From the Modified NRTL Equation For Benzene (1)/N- Heptane (2) System.

Temp. B.P. °C t	Liquid Mole Fraction x_1	exp. Vapour Mole Fraction $y_{(exp)}$	Vapour Mole Fraction y	
			Calculated Modified NRTL y_{cal}	Deviation Δy
95.43	0.0880	0.1680	0.2536	+0.0856
93.52	0.1440	0.2540	0.3762	+0.1222
93.35	0.1520	0.2680	0.3921	+0.1241
91.60	0.2030	0.3420	0.5018	+0.1598
89.82	0.2770	0.4270	0.5780	+0.1510
89.10	0.2990	0.4550	0.5997	+0.1447
88.68	0.3180	0.4740	0.6189	+0.1449
87.88	0.3530	0.5210	0.6499	+0.1289
86.90	0.4030	0.5540	0.6883	+0.1343
85.73	0.4570	0.6040	0.7192	+0.1152
84.75	0.5240	0.6570	0.7558	+0.0988
83.92	0.5760	0.6980	0.7776	+0.0796
83.46	0.6080	0.7190	0.7903	+0.0713
82.29	0.6980	0.7790	0.8243	+0.0453
81.60	0.7710	0.8300	0.8562	+0.0262
80.75	0.8310	0.8700	0.8765	+0.0065
80.25	0.9350	0.9470	0.9439	−0.0031
80.23	0.9360	0.9450	0.9442	−0.0008
80.21	0.9360	0.9470	0.9436	−0.0034
80.12	0.9800	0.9820	0.9808	−0.0012
			R.M.S.D. : ± 0.0999 S.D. % : 27.62 % $g_{21}-g_{11}=$ 619.89 − 4.7976 t $g_{12}-g_{22}=$ 1110.30 − 6.8080 t	

CONCLUSIONS

General results obtained from the three binaries each having different isothermal heats of mixing value are summarized in the following.

1. The isobaric VLE data of the binary systems having max. H^E value less than 130 cal / mol, can be predicted with the S.D. % 7–15 from the vapour pressure of the pure component and two isothermal binary H^E data each meacsured at different lower temperatures.

2. Isobaric VLE data can be predicted as accurate as isothermal VLE data using isothermal heats of mixing.

3. In the prediction of isobaric binary VLE data for systems having max. H^E less than 130 cal / mol, the Modified Wilson Equation is more capable than the Modified NRTL Equation.

4. The Modified Wilson Equation is incapable for estimating the isobaric VLE data for Benzene (1) / N–Heptane (2) system where the max. H^E is 231 cal / mol. The R.M.S.D. in the predictions with the Modified NRTL Equation for the same system is as large as $+ 0.0999$.

5. When the α–parameter of the NRTL Equation is fixed, the other two $(g_{12}-g_{22})$ and $(g_{21}-g_{11})$ parameters become linear function of temperature.

SYMBOLS

A_k	Parameter
G^E	Gibb's Excess Free Energy
$g_{12}-g_{22}$	Wilson or NRTL Equation parameter
H^E	Heat of Mixing (cal / g mol)
P	Total Pressure (mm Hg)
P°_i	Vapour pressure of pure component i at the system boiling point. (mm Hg)
R	Ideal Gas Constant (cal / g mol °K)
T	Absolute Temperature (°K)
t	Temperature (°C)
V_1, V_2	Molar Volumes of Pure Components
x_i	Mol fraction of component i in liquid phase
y_i	Mol fraction of component i in vapour phase in equilibrium with x_i
z_i	The vapour phase fugacity coefficient

GREEK LETTERS

α	NRTL Equation parameter
γ_i	Activity coefficient of component i
Λ_{12}	Wilson Equation paremeter
τ_{12}	NRTL Equation parameter

ABBREVIATIONS

B.P.	Boiling Point
G_{12}	exp $(-\alpha\ \tau_{12})$, NRTL Equation parameter
Λ_{12}	V_2 / V_1 exp $(-G_{12})$, Wilson Equation parameter
T_{12}	$(g_{12}-g_{22}) / RT$, NRTL Equation parameter
max.	Maximum
M.C.H.	Methylcyclo hexane
NRTL	Non–Random Two–Liquid Equation
VLE	Vapour–Liquid Equilibria
R.M.S.D.	Root Mean Square Deviation
S.D. %	Percent Standard Deviation

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