Thermochimica Acta, 60 (1983) 327–339
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

THE PREDICTION OF VAPOR–LIQUID EQUILIBRIUM DATA FROM HEAT OF MIXING DATA FOR THREE NON-IDEAL BINARY SYSTEMS

T.A. McFALL, R.W. HANKS and J.J. CHRISTENSEN

*Department of Chemical Engineering and The Thermochemical Institute *, Brigham Young University, Provo, UT 84602 (U.S.A.)*

(Received 30 June 1982)

ABSTRACT

The method of Hanks et al. was used with the heat of mixing data of McFall et al. for 1,3-butadiene + propylene, 1-butene + methyl *tert.*-butyl ether, and carbon disulfide + methanol to predict the vapor–liquid equilibrium behavior for these systems. The method involves curve-fitting an excess enthalpy model derived from an excess Gibbs energy model by means of the Gibbs–Helmholtz equation to the heat of mixing data, determining the adjustable parameters from this fit, and using the original excess Gibbs function equation to predict the vapor–liquid equilibrium behavior. The predicted vapor–liquid equilibrium values were compared with experimental values and good agreement was found.

INTRODUCTION

Accurate vapor–liquid equilibrium data are needed for the design of separation equipment for the chemical and petroleum industries. If vapor–liquid equilibrium data are not available in the literature, they must be measured or estimated. Since it is sometimes difficult to obtain good vapor–liquid equilibrium data experimentally, estimation methods are often used, especially for preliminary design work.

One useful method for estimating vapor–liquid equilibrium (VLE) data from heat of mixing data is the method described by Hanks et al. [1]. Their method involves deriving an algebraic h^E expression from an algebraic g^E model by application of the Gibbs–Helmholtz relation

$$h^E = -T^2 \left[\frac{\partial (g^E/T)}{\partial T} \right]_{p,x} \tag{1}$$

The parameters of the h^E model are determined by curve-fitting the expression for h^E to a set of experimental heat of mixing data. These parameters

---

* Contribution No. 285 of The Thermochemical Institute.

are then used in the original g^E model to calculate first activity coefficients and then vapor–liquid equilibrium data. This method has been successfully applied to numerous binary hydrocarbon + hydrocarbon (hydrocarbon being alkane, alkene, alicyclic, aromatic or arene), and hydrocarbon + alcohol mixtures and to one or more binary mixtures of hydrocarbon + ester, hydrocarbon + ketone, hydrocarbon + aliphatic nitrite, hydrocarbon + alkyl halide, and alkyl halide + ketone [2–6].

The systems presently studied are 1,3-butadiene + propylene (diene + alkene) at 273.15, 293.15, 313.15, and 333.15 K; 1-butene + methyl *tert.*-butyl ether (alkene + ether) at 293.15, 313.15, and 333.15 K; and carbon disulfide + methanol (CS_2 + alcohol) at 293.15 K. They represent types of binary mixtures not previously investigated with respect to the method of Hanks et al. These systems were chosen in conjunction with an American Institute of Chemical Engineers DIPPR project being conducted here in an associated laboratory involving the measurement of vapor–liquid equilibrium data for these systems. Independently, heat of mixing data were measured [7] and have been reported elsewhere [8]. This paper is concerned with using these data to further test and substantiate the method of Hanks et al. as a method of vapor–liquid equilibrium prediction.

PREDICTION METHOD

The method used here for predicting vapor–liquid equilibrium data has been described in detail elsewhere [1]. It involves curve-fitting an algebraic thermodynamic excess enthalpy model to heat of mixing data in order to evaluate the model's adjustable parameters. The h^E model is derived from a g^E model by use of the Gibbs–Helmholtz equation. Some g^E equations which might be used are the non-random, two-liquid (NRTL) equation, the Wiehe–Bagley equation and the continuous linear association model (CLAM) equation. The adjustable parameters determined in the above manner are used in the original g^E expression to calculate liquid phase activity coefficients from the relation

$$\ln \gamma_i = \frac{g_i^E}{RT} = \frac{1}{RT}\left(\frac{\partial G^E}{\partial n_i}\right)_{P,T,n_j} \qquad (i \neq j) \tag{2}$$

Vapor phase mole fractions are then calculated from

$$y_i = \frac{x_i \gamma_i P_{\pi i} \nu_i^0}{\pi_{calc} \nu_i} \tag{3}$$

where γ_i are the liquid phase activity coefficients calculated from eqn. (2), π_{calc} is the calculated total pressure, ν_i^0 and ν_i are the fugacity coefficients for pure component and mixture, respectively, and $P_{\pi i}$ is the pure component vapor pressure, P_i^0, multiplied by the Poynting correction

$$P_{\pi i} = P_i^0 \exp\left[\frac{\bar{v}_i}{RT}\left(\pi_{\text{calc}} - P_i^0\right)\right] \tag{4}$$

where $\bar{v}_i$ is the liquid molar volume.

Four g^{E} models were used in the present study: the NRTL model [9], the LEMF model [10], the Wiehe–Bagley model [11], and the CLAM model [12].

NRTL and LEMF model equations

The NRTL model is described by the equation [5]

$$\frac{g^{\text{E}}}{RT} = x_1 x_2 \left[\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right] \tag{5}$$

where $\tau_{12} = (g_{12} - g_{22})/RT$, $\tau_{21} = (g_{12} - g_{11})/RT$, $G_{12} = \exp(-\alpha\tau_{12})$, $G_{21} = \exp(-\alpha\tau_{21})$, and the adjustable parameters are α, $(g_{12} - g_{22})$, and $(g_{12} - g_{11})$. Equation (5) can be used to derive the following expressions for heat of mixing and the activity coefficients.

$$\frac{h^{\text{E}}}{RT} = \frac{g^{\text{E}}}{RT} - x_1 x_2 \alpha \left[\frac{x_1 \tau_{21}^2 G_{21}}{(x_1 + x_2 G_{21})^2} + \frac{x_2 \tau_{12}^2 G_{12}}{(x_2 + x_1 G_{12})^2} \right] \tag{6}$$

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{21})^2} \right] \tag{7}$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \tag{8}$$

The LEMF model is obtained from the above equations by setting $\alpha = -1$. The NRTL and LEMF models have been found to work well in the method of Hanks et al. for mixtures involving primarily hydrocarbon–hydrocarbon interactions, and also for mixtures involving hydrocarbon–ester, hydrocarbon–ketone, hydrocarbon–aliphatic nitrile, hydrocarbon–alkyl halide, and alkyl halide–ketone interactions.

Wiehe–Bagley model equations

The Wiehe–Bagley model, which was developed to describe alcohol–hydrocarbon systems, is described by the equation [11]

$$\frac{g^{\text{E}}}{RT} = x_{\text{A}} \ln\left[\frac{1 + K_{\text{A}}}{\rho x_{\text{B}} + (1 + K_{\text{A}}) x_{\text{A}}} \right] + x_{\text{B}} \ln\left[\frac{\rho}{\rho x_{\text{B}} + x_{\text{A}}} \right] + \frac{1}{K_{\text{A}}} \left[x_{\text{A}} \ln(1 + K_{\text{A}}) - (x_{\text{A}} + \rho x_{\text{B}}) \ln\left(1 + \frac{x_{\text{A}} K_{\text{A}}}{\rho x_{\text{B}} + x_{\text{A}}} \right) \right] \tag{9}$$

where component A is the alcohol, component B is the inert solvent, ρ is the ratio of molar volumes, V_A/V_B, and K_A is the equilibrium constant for alcohol complexing. From this model, one may derive the following expressions for the heat of mixing and the activity coefficients.

$$h^E = -\frac{h_A}{K_A}\left[(\rho x_B + x_A)\ln\left(1 - \frac{x_A K_A}{\rho x_B + x_A}\right) - x_A \ln(1 + K_A)\right] \tag{10}$$

$$\ln \gamma_A = \ln\left[\frac{1 + K_A}{\rho x_B + (1 + K_A)x_A}\right] + \frac{x_B}{\rho x_B + x_A} + \frac{1}{K_A}\ln\left[1 + \frac{\rho K_A x_B}{\rho x_B + (1 + K_A)x_A}\right] \tag{11}$$

$$\ln \gamma_B = \ln\left[\frac{\rho}{\rho x_B + x_A}\right] + \frac{x_A}{\rho x_B + x_A} + \frac{\rho}{K_A}\ln\left[\frac{\rho x_B + x_A}{\rho x_B(1 + K_A)x_A}\right] \tag{12}$$

where h_A is the standard enthalpy of hydrogen bonding defined as -24.7 kJ mole^{-1} [11].

CLAM model equations

The CLAM model is as follows [12].

$$\frac{g^E}{RT} = x_A \ln\left(\frac{\phi_A}{x_A}\right) + x_B \ln\left(\frac{\phi_{B1}}{\phi_{B1}^* x_B}\right) + K x_B(\phi_{B1} - \phi_{B1}^*) + \frac{\beta\phi_B\phi_B}{RT}(x_A V_A + x_B V_B) \tag{13}$$

where component A is the hydrocarbon, component B is the alcohol, ϕ_B is the overall volume fraction of alcohol, ϕ_A is the overall volume fraction of hydrocarbon, K is the association constant for hydrogen bonding and β is a physical interaction parameter.

$$\phi_{B1} = \frac{1 + 2K\phi_B - \sqrt{1 + 4K\phi_B}}{2K^2\phi_B} \tag{14}$$

$$\phi_{B1}^* = \frac{1 + 2K - \sqrt{1 + 4K}}{2K^2} \tag{15}$$

Equation (13) leads to the following expressions for the heat of mixing and the activity coefficients.

$$h^E = \frac{\Delta h^0 x_B}{2K\phi_B}\left\{1 - \phi_B - \sqrt{1 - 4K\phi_B} + \phi_B\sqrt{1 + 4K}\right\} + \beta\phi_A\phi_B(x_A V_A + x_B V_B) \tag{16}$$

$$\ln \gamma_A = \ln\left(\frac{\phi_A}{x_A}\right) + \phi_B\left(1 - \frac{V_B}{V_A}\right) + K\frac{V_A}{V_B}\phi_B\phi_{B1} + \frac{\beta}{RT}V_A\phi_B^2 \tag{17}$$

$$\ln \gamma_B = \ln\left(\frac{\phi_{B1}}{\phi_{B1}^* x_B}\right) + \phi_A\left(1 - \frac{V_B}{V_A}\right) + K(\phi_B\phi_{B1} - \phi_{B1}^*) + \frac{\beta}{RT}V_B\phi_A^2 \tag{18}$$

where h^0 is the enthalpy of hydrogen bond formation taken as -25.1 kJ mole^{-1} [8]. The CLAM model has been found to work well in the methods of Hanks et al. for mixtures involving hydrocarbon–alcohol interaction.

Computation procedure

The values of the activity coefficients to be used in the method of Hanks et al. can be obtained from either eqns. (7) and (8), (11) and (12), or (17) and (18). The thermodynamic models used in the approach described above were used to fit the heat of mixing data only. The parameters were allowed to vary freely in order to obtain the closest fit to the heat of mixing data. Therefore, no attempt has been made to assign a physical interpretation to the parameters which were obtained. A nonlinear least squares regression algorithm [13] was used for the curve-fitting.

RESULTS AND DISCUSSION

The heat of mixing data used were measured with an isothermal high-pressure flow calorimeter and have been reported elsewhere [8]. The temperatures and pressures at which the data were taken are given in Table 1. All three systems exhibited non-ideal behavior. The carbon disulfide + methanol system also exhibits an immiscible region.

The heat of mixing data for the system 1,3-butadiene + propylene were fit and the adjustable parameters determined using the NRTL and the LEMF equations. Only these two equations were used as this system is similar to other hydrocarbon–hydrocarbon systems for which these two equations have been successfully used to fit h^E data and predict VLE data [1–5].

TABLE 1

Temperature and pressures at which each system was studied

System	Temperature (K)	Pressure (kPa)
1,3-Butadiene + propylene	273.15	4,978
	293.15	4,978
	313.15	4,978
	333.15	4,978
1-Butene + MTBE	293.15	1,806
	313.15	1,806
	333.15	1,944
Carbon disulfide + methanol	273.15	531
	293.15	531

TABLE 2

Results of curve fits of h^E data to predict vapor–liquid equilibrium data

System	Temperature (K)	Model	σ_h	$\overline{\Delta y}$
1,3-Butadiene + propylene	273.15	NRTL	0.0439	0.0053
	273.15	LEMF	0.0470	0.0069
	293.15	NRTL	0.6342	0.0052
	293.15	LEMF	0.6391	0.0088
	313.15	NRTL	0.0718	0.0073
	313.15	LEMF	0.0385	0.0127
	333.15	NRTL	0.1500	0.0024
	333.15	LEMF	0.0864	0.0182
1-Butene + MTBE	293.15	NRTL	0.0294	0.0141
	293.15	LEMF	0.1171	0.0040
	293.15	Wiehe–Bagley	0.0117	0.0077
	293.15	CLAM	0.0197	0.0171
	313.15	NRTL	0.0709	0.0093
	313.15	LEMF	0.0711	0.0095
	313.15	Wiehe–Bagley	0.0714	0.0111
	313.15	CLAM	0.0723	0.0111
	333.15	NRTL	0.3849	0.0070
	333.15	LEMF	0.3117	0.0112
	333.15	Wiehe–Bagley	0.4154	0.0207
	333.15	CLAM	0.6076	0.0089
Carbon disulfide + methanol	293.15	NRTL	0.2166	0.0356
	293.15	LEMF	0.2471	0.1163
	293.15	Wiehe–Bagley	0.2575	0.1331
	293.15	CLAM	0.1925	0.0840

The heat of mixing data for the systems 1-butene + methyl *tert*-butyl ether (MTBE) and carbon disulfide + methanol were used with all four thermodynamic models described previously. All models were used since the types of system represented by these two systems (alkene + ether and CS_2 + alcohol) have not been examined previously with respect to the method of Hanks et al.

The method of Hanks et al. was used to predict vapor–liquid equilibrium data for the system 1,3-butadiene + propylene at 273.15, 293.15, 313.15, and 333.15 K and for the system 1-butene + MTBE at 293.15, 313.15, and 333.15 K and the results compared with the vapor–liquid equilibrium data of Lundell [14]. Predicted values of vapor–liquid equilibrium data for the system carbon disulfide + methanol at 293.15 K were compared with the measured values of Niini [15]. No experimental vapor–liquid equilibrium data could be found for the carbon disulfide + methanol system at 273.15 K, so no comparisons could be made.

Table 2 shows the results of the fit of each equation used with respect to both the heat of mixing data and the vapor–liquid equilibrium data for the three systems studied. The standard deviations for the heat of mixing, σ_h, and the mean deviation for the vapor–liquid equilibrium, $\overline{\Delta y}$, reported in Table 2 were calculated from

$$\sigma_h = \left[\frac{\sum_j^M \left[\frac{h^E(\mathrm{calc}) - h^E(\mathrm{expt})}{h^E(\mathrm{expt})} \right]_j^2}{n - nc} \right]^{1/2} \tag{19}$$

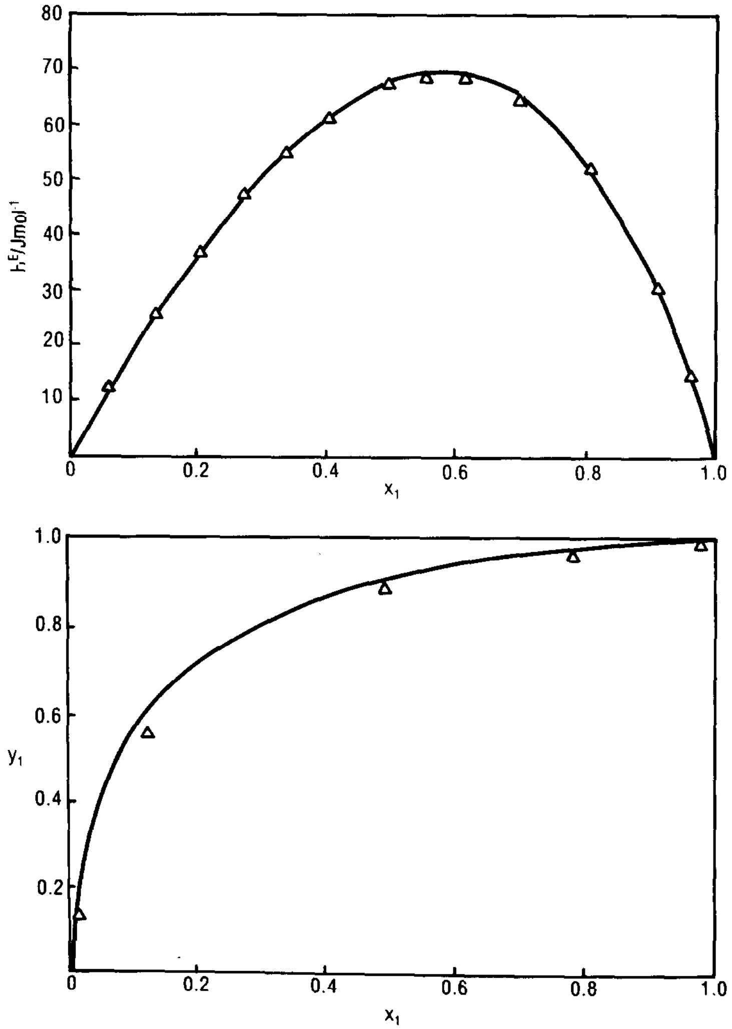

Fig. 1. Comparison of calculated and experimental data for the system 1-butene(1)+MTBE(2) at 293.15 K. Solid curves calculated from the NRTL equation.

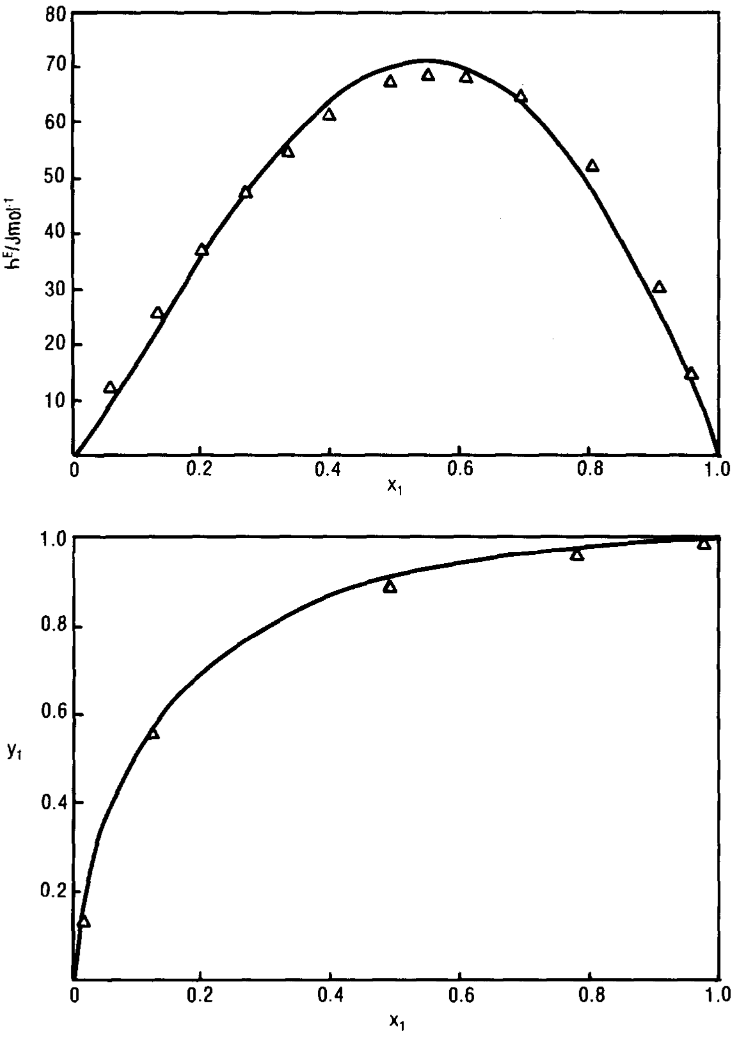

Fig. 2. Comparison of calculated and experimental data for the system 1-butene(1)+MTBE(2) at 293.15 K. Solid curves calculated from the LEMF equation.

and

$$\overline{\Delta y} = \frac{\sum_{j}^{n} |y(\text{calc}) - y(\text{expt})|_j}{n} \tag{20}$$

where n is the number of data points, nc is the number of constants in the fit, h^E is the heat of mixing, and y is the vapor mole fraction. In general, we have found that mean deviations calculated using eqn. (20) give the best indication of how well VLE data can be predicted from h^E data. Values of $\overline{\Delta y}$ less than 0.03 are comparable with fits obtained by curve-fitting experimental

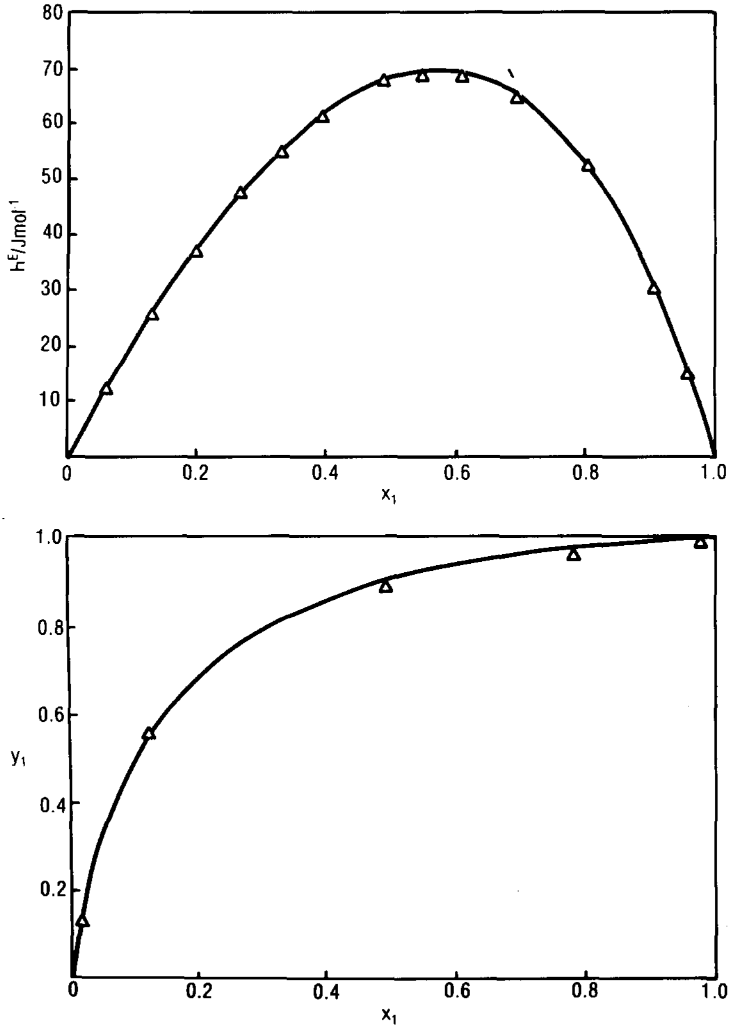

Fig. 3. Comparison of calculated and experimental data for the system 1-butene(1)+MTBE(2) at 293.15 K. Solid curves calculated from the Wiehe–Bagley equation.

VLE data directly with an expression for g^E such as the Wilson, NRTL, CLAM, etc. equations [16,17].

As indicated before, only the NRTL and LEMF equations were used for the system 1,3-butadiene + propylene since this is a hydrocarbon–hydrocarbon system. As shown in Table 2, the NRTL equation and the LEMF equation at all four temperatures gave similar fits of the heat of mixing data and the vapor–liquid equilibrium data as indicated by the values of σ_h and $\overline{\Delta y}$. The NRTL equation, however, always gave slightly better predictions of the vapor–liquid equilibrium data than the LEMF equation as indicated by the values of $\overline{\Delta y}$.

All four models (NRTL, LEMF, Wiehe–Bagley, and CLAM) were tried in

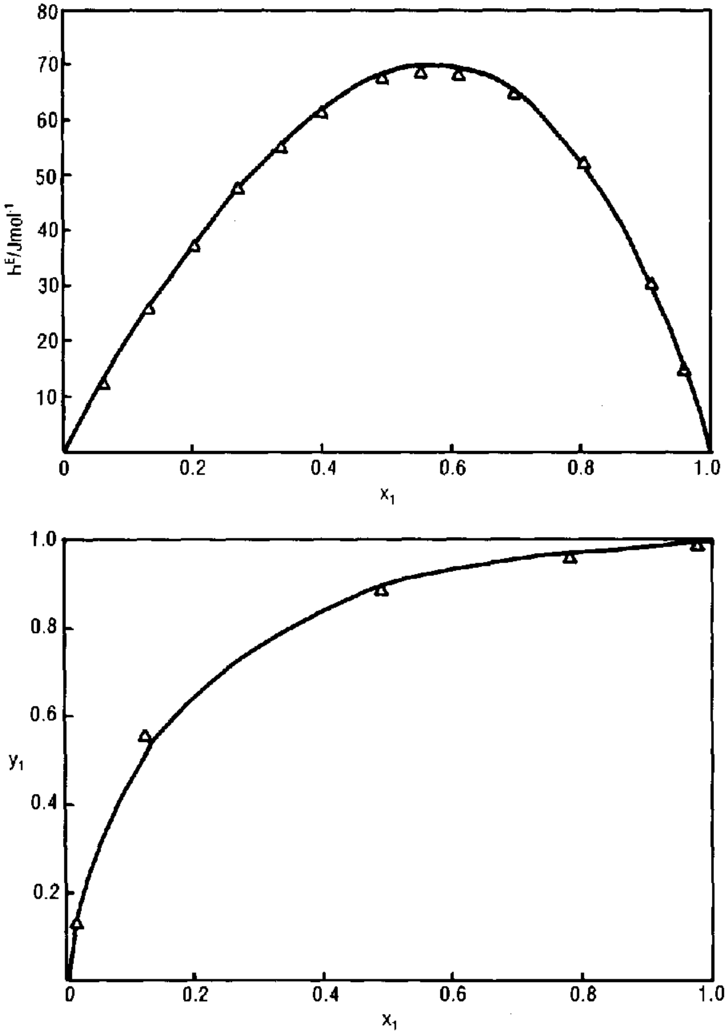

Fig. 4. Comparison of calculated and experimental data for the system 1-butene(1)+MTBE(2) at 293.15 K. Solid curves calculated from the CLAM equation.

an attempt to determine which one might best fit the data for the 1-butene + MTBE system. The values for σ_h and $\overline{\Delta y}$ in Table 2 indicate that there was no one model which consistently gave the best fit of both the heat of mixing and the vapor–liquid equilibrium data. At 293.15 K, the Wiehe–Bagley equation gave the best fit of both the heat of mixing data and the vapor–liquid equilibrium data. The LEMF equation did not give a very good fit of the heat of mixing data and the CLAM equation had the highest $\overline{\Delta y}$ value. Figures 1–4 show graphically the fits obtained at 293.15 K for the heat of mixing data and the vapor–liquid equilibrium data using the four models. Values of σ_h and $\overline{\Delta y}$ given in Table 2 can be compared with the data shown in Figs. 1–4 to obtain an indication of the relationship between the numerical values in Table 2 and the fits shown in Figs. 1–4. At 313.15 K, all four models gave good representations of both the heat of mixing data and the vapor–liquid equilibrium data. At 333.15 K, the best fit of the vapor–liquid equilibrium data was obtained using the NRTL equation. The Wiehe–Bagley and CLAM equations did not fit the heat of mixing data well, even though they predicted vapor–liquid equilibrium values which were close to the experimental values. Over the temperature range studied, the NRTL equation gave the best prediction of vapor–liquid equilibrium data with $\overline{\Delta y}$ values from 0.0040 to 0.0112. However, all four models at all three temperatures

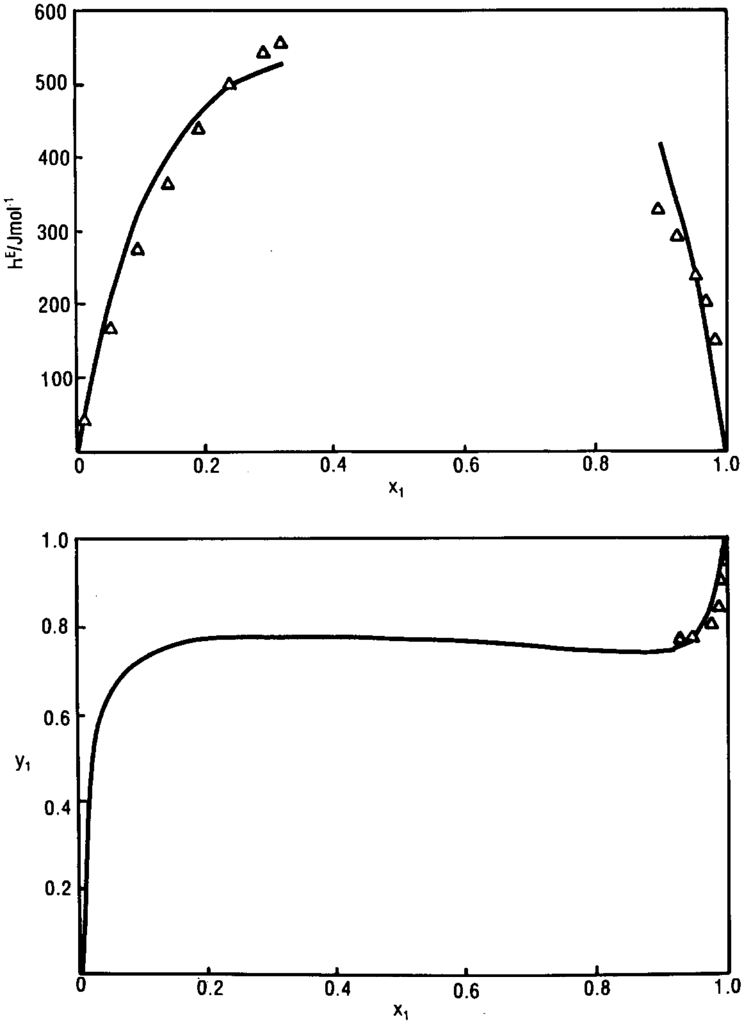

Fig. 5. Comparison of calculated and experimental data for the system carbon disulfide(1)+methanol(2) at 293.15 K. Solid curves calculated from the NRTL equation.

successively predicted vapor–liquid equilibrium data with $\overline{\Delta y}$ values ranging from 0.0040 to 0.0207, which is well within the range of $\overline{\Delta y}$ values observed for direct fits of VLE data.

All four models, NRTL, LEMF, Wiehe–Bagley, and CLAM, were used with the h^E data of the carbon disulfide + methanol system. The four models gave similar fits of the heat of mixing data. None of the models gave a close fit of the heat of mixing data, which may be due to the immiscible region in this system. The NRTL equation gave the best prediction of the vapor–liquid equilibrium data. Figure 5 shows the fit of the NRTL equation to this system. Calculated and experimental x–y data could only be compared at high mole fraction of carbon disulfide since no x–y data could be found in the literature at mole fractions of carbon disulfide less than 0.9.

Extensive tables showing the h^E data, the equation used to fit the h^E data and the parameters determined, the predicted x–y data, the literature x–y data, and graphs of the h^E and x–y data for each determination are given by McFall et al. [8].

CONCLUSIONS

The results of this study indicate that heat of mixing data can be used with success to predict vapor–liquid equilibrium data for the three general types of binary systems diene + alkene, alkene + ether, and CS_2 + alcohol. The NRTL equation predicted the vapor–liquid equilibrium data for 1,3-butadiene + propylene with $\overline{\Delta y}$ values from 0.0024 to 0.0182. Literature values are typically 0.01–0.03. These results are consistent with previous findings that the NRTL and LEMF equation can successfully predict VLE data from h^E data for a wide variety of hydrocarbon + hydrocarbon interactions. All four models tested were successful in predicting vapor–liquid equilibrium data for 1-butene + MTBE system giving $\overline{\Delta y}$ values ranging from 0.0040 to 0.0207 with the LEMF equation giving the lowest $\overline{\Delta y}$ values over the temperature range studied. The carbon disulfide + methanol system was best represented by the NRTL equation with a $\overline{\Delta y}$ value of 0.0356. These studies confirmed previous work in that good results are obtained in predicting VLE data from h^E data using the method of Hanks et al. by using the NRTL or LEMF equation for all systems we have studied except for hydrocarbon + alcohol mixtures for which the CLAM equation should be used.

REFERENCES

1 R.W. Hanks, A.C. Gupta and J.J. Christensen, Ind. Eng. Chem. Fundam., 10 (1971) 504.
2 R.L. Tan, R.W. Hanks and J.J. Christensen, Thermochim. Acta, 21 (1977) 157.

3 R.W. Hanks, R.L. Tan and J.J. Christensen, Thermochim. Acta, 23 (1978) 41.
4 R.L. Tan, R.W. Hanks and J.J. Christensen, Thermochim. Acta, 23 (1978) 29.
5 R.W. Hanks, R.L. Tan and J.J. Christensen, Thermochim. Acta, 27 (1978) 9.
6 R.W. Hanks, T.K. O'Neill and J.J. Christensen, Ind. Eng. Chem. Process Des. Dev., 18 (1979) 408.
7 T.A. McFall, M.S. Thesis, Brigham Young University, 1982.
8 T.A. McFall, M.E. Post, J.J. Christensen and R.M. Izatt, J. Chem. Thermodyn., 14 (1982) 509.
9 H. Renon and J.M. Prausnitz, AIChE J., 14 (1968) 135.
10 J.M. Marina and D.P. Tassios, Ind. Eng. Chem. Process Des. Dev., 12 (1973) 67.
11 I.A. Wiehe and E.B. Bagley, Ind. Eng. Chem. Fundam., 6 (1967) 209.
12 H. Renon and J.M. Prausnitz, Chem. Eng. Sci., 22 (1967) 299.
13 R.H. Pennington, Introductory Computer Methods and Numerical Analysis, Macmillan, New York, 2nd edn., 1970.
14 S.O. Lundell, M.S. Thesis, Brigham Young University, 1982.
15 A. Niini, Ann. Acad. Sci. Fenn. Ser. A, (1940) 53.
16 M. Hirata, S. Che and K. Nagahama, Computer Aided Data Book of Vapor–Liquid Equilibria, Kodansha, Tokyo, 1975.
17 J. Gmehling and V. Onken, Vapor–Liquid Equilibrium Data Collection, Chemistry Data Series, Vol. 1, Part 2a, Dechema, Frankfurt, 1977.