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THE PREDICTION OF HIGH TEMPERATURE VAPOR–LIQUID EQUILIBRIA FROM LOWER TEMPERATURE HEAT OF MIXING DATA*

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SUMMARY

A method for predicting high temperature vapor–liquid equilibria using only lower temperature heat of mixing data and pure component vapor pressure data is presented. Ten binary hydrocarbon liquid mixtures were studied. The method consists of evaluating the parameters of the LEMF equation at different temperatures from isothermal heat of mixing data of the binary pair at the respective temperatures. The parameters obtained are extrapolated as a linear function of temperature to the temperature at which the VLE data are to be calculated. The parameters are used to compute actively coefficients which in turn are used together with pure component vapor pressures to calculate VLE data. Results were also obtained when heats of mixing data for a given system were available at only two temperatures.

For the systems studied, this method predicted the composition of the vapor phase with an average standard deviation of 4–5% for those systems where heat of mixing data is available at three or more temperatures and of 10–12% for those systems where only two sets of heat of mixing data are available.

INTRODUCTION

Designers of separation equipment for the chemical process and petroleum industries need accurate vapor–liquid equilibrium (VLE) data, often at a variety of conditions. Although large amounts of such data are available in the literature, one frequently finds that data are not available for the conditions at which a design must be made. In such a situation, the designer must either make new measurements of VLE data at appropriate conditions or estimate the required data by means of some data correlation or model in which he has confidence. Because of the difficulties associated with obtaining good VLE data experimentally, the designer often turns to estimation methods to get his data, especially for preliminary design work.

Reliable VLE data are relatively scarce for temperatures much in excess of 100°C and almost nonexistent for temperatures in excess of 200°C. If one has available

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a set of VLE data for the system of interest at some low reference temperature, say T_0, and several sets of heat of mixing data covering a range of temperatures, one may estimate the excess Gibbs energy (from which activity coefficients, and hence VLE data, may be derived) at the temperature of interest by means of the integrated Gibbs–Helmholtz relation

$$g^E = \frac{T}{T_0} g^E(T_0) - T \int_{T_0}^{T} \frac{h^E(T)}{T^2} \, dT \tag{1}$$

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.

In principle, this procedure is sufficient and thermodynamically sound. In practice, however, it requires $h^E(T)$ data covering the entire temperature range of interest. These data may be difficult to obtain. Thus, the use of semi-theoretical models to fit the existing VLE data and to extrapolate to other conditions is common[1,2]. Models of this type generally involve one or more adjustable parameters, the values of which must be determined by curve fitting experimental data. The usual method[2] for doing this is to curve fit either the activity coefficients or the $g^E(T_0)$ data. Frequently when this approach is used, the representation of $h^E(T)$ by a given model is not very good[3,4] although good correlation of the VLE data may be obtained.

An alternative approach[5] is to determine 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

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

to a set of experimental h^E data. These parameters are then used in the g^E model to calculate activity coefficients and hence VLE data. This method has been shown[5] to be valid for isothermal binary systems, isobaric binary systems[6], and isothermal and isobaric ternary systems[7]. In each of these previous studies, the h^E and VLE data used were fairly close to each other in temperature. The purpose of the present paper is to extend the earlier work to include the prediction of VLE data at temperatures significantly removed from those for which h^E data are available.

PREDICTION METHOD

Common to nearly all derivations of h^E expressions from g^E models is the assumption of temperature independence of the parameters. Although this is not strictly true, it does simplify the resulting equations which otherwise become very cumbersome[8]. In extending the Hanks et al. method[5] to isobaric systems, Tan et al. observed[7] that the parameters of Renon and Prausnitz' NRTL equation[9], when it was used as a three-parameter model, did not exhibit any systematic temperature dependence. However, when the NRTL model was used as a two-parameter model

(α was set to a constant value of 0.3 as recommended by Renon and Prausnitz[9]) the parameters exhibited a distinct temperature dependence. Hanks et al.[10] studied the parametric behavior of several currently used g^E models and found that the LEMF model[11] which is essentially the NRTL equation with $\alpha = -1$, behaved best under extreme conditions. This model will be used here.

The LEMF model is described by the following equations[10, 11]

$$\frac{g^E}{RT} = x_1x_2\left[\frac{G_1}{x_1 + x_2\tau_1} + \frac{G_2}{x_2 + x_1\tau_2}\right] \tag{3}$$

$$\frac{h^E}{RT} = \frac{g^E}{RT} + x_1x_2\left[\frac{x_1\tau_2G_2^2}{(x_2 + x_1\tau_2)^2} + \frac{x_2\tau_1G_1^2}{(x_1 + x_2\tau_1)^2}\right] \tag{4}$$

$$\ln\gamma_1 = x_2^2\left[\frac{G_2}{(x_2 + \tau_2x_1)^2} + \frac{G_1\tau_1}{(x_1 + x_2\tau_1)^2}\right] \tag{5}$$

$$\ln\gamma_2 = x_1^2\left[\frac{G_1}{(x_1 + x_2\tau_1)^2} + \frac{G_2\tau_2}{(x_2 + x_1\tau_2)^2}\right] \tag{6}$$

where $G_1 = (g_{12} - g_{22})/RT$, $G_2 = (g_{12} - g_{11})/RT$, $\tau_1 = \exp(-G_1)$ and $\tau_2 = \exp(-G_2)$. $(g_{12} - g_{22})$ and $(g_{12} - g_{11})$ are adjusted to fit the data.

The method used here consists of fitting eqn. (4) to a set of experimental h^E data at a given temperature by a numerical curve fitting technique[5]. Two or more sets of h^E data, each at a different temperature, are fitted in this manner and the values of $(g_{12} - g_{22})$ and $(g_{12} - g_{11})$ thus obtained are extrapolated as a linear function of temperature to the temperature at which the VLE data are to be calculated. The values of $(g_{12} - g_{22})$ and $(g_{12} - g_{11})$ determined by this extrapolation technique are used in eqns. (5) and (6) to compute the activity coefficients γ_1 and γ_2. These in turn are used, together with pure component vapor pressures, P_1 and P_2, to calculate the VLE data from

$$y_j = \frac{x_j\gamma_jP_j}{\sum_{k=1}^{2} x_k\gamma_kP_k} \tag{7}$$

which presumes ideal gas behavior in the vapor phase. For the temperatures and pressures encountered here, vapor phase nonideality corrections are minor[6]. In order to be strictly consistent thermodynamically with respect to eqn. (2), one should include the temperature-dependent functions for $(g_{12} - g_{22})$ and $(g_{12} - g_{11})$ in the expression for g^E as done by Asselineau and Renon[8]. This, however, renders the equations for h^E so complex as to be practically useless. The present method is thermodynamically correct for isothermal systems. In essence, what we are doing here is observing that a number of separate isothermal systems, each of which is itself thermodynamically consistent at its own temperature, can be empirically correlated by the scheme used when a particular model (the LEMF model) is used. This observation permits us to avoid the excessive complexity enforced by the more rigorous nonisothermal approach[5] while retaining thermodynamic consistency between h^E–g^E data at any given temperature.

RESULTS AND DISCUSSION

The purpose of the present study was to see if the above method of predicting VLE data could be used to estimate VLE data at temperatures rather substantially removed from those for which h^E data are available. A survey of VLE literature for nonassociating nonelectrolyte mixtures revealed some 75–80 binary systems with VLE data in the 90–200°C range. However, unavailability of h^E data at more than one temperature reduced the number of systems which could be studied to ten. Of these, only five had h^E data available at three or more temperatures. These five systems were (I) benzene (1)–cyclohexane (2); (II) benzene (1)–*n*-heptane (2); (III) benzene (1)–toluene (2); (IV) methylcyclohexane (1)–*n*-heptane (2); and (V) cyclohexane (1)–*n*-heptane (2). The most extensive h^E data were available for system I.

The h^E data for five different temperatures for system I were fitted with eqn. (4)

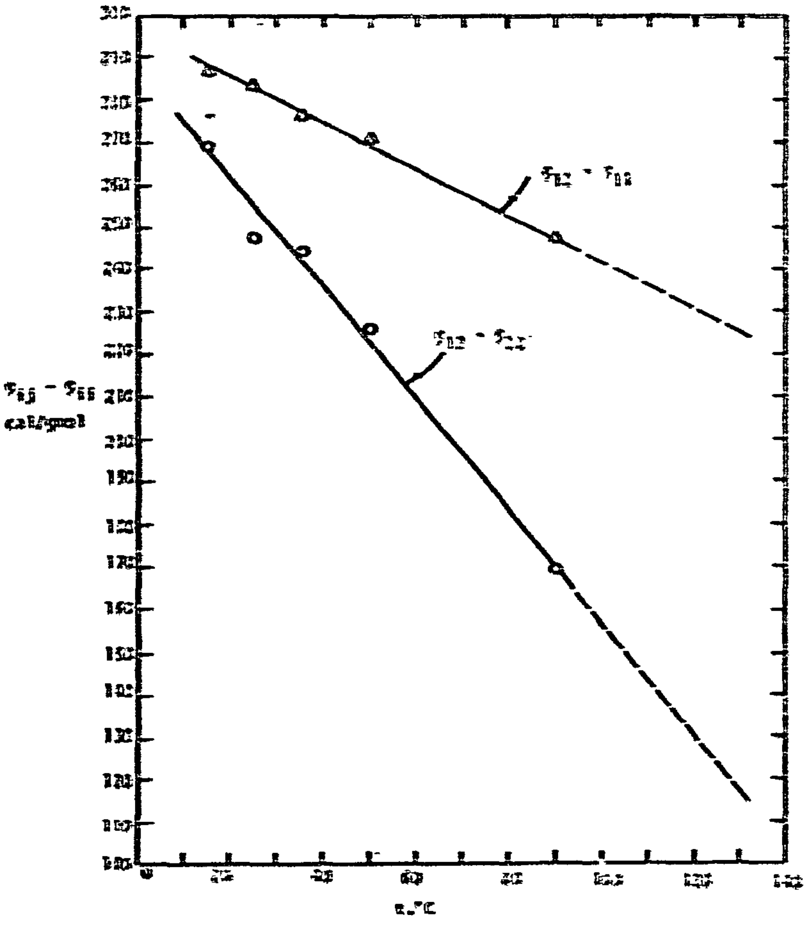

Fig. 1. LEMF parameters as a function of temperature for the system benzene (1)–cyclohexane (2).

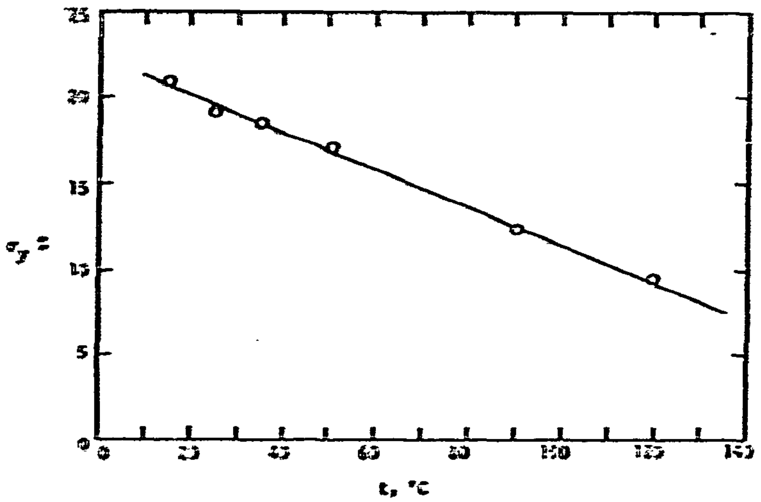

Fig. 2. Effect of temperature at which LEMF constants are evaluated on prediction of VLE data at 119 °C for system benzene (1)–cyclohexane (2).

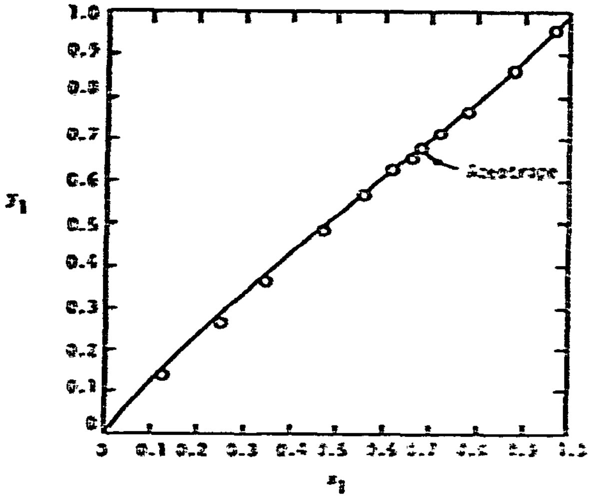

Fig. 3. Comparison of predicted (solid line) with experimental data (data points) at 18.3 atm for system benzene (1)–cyclohexane (2). (Data of Kumarkrishna Rao et al.[13].

and the respective parameters obtained are shown in Fig. 1 as a function of temperature. It is apparent from Fig. 1 that, for this system at least, both $(g_{12} - g_{11})$ and $(g_{12} - g_{22})$ are linear functions of temperature. Similar results were found for systems II–V although the data for them are not so extensive as for system I.

To examine for system I the influence of the temperature at which the h^E data were obtained upon the accuracy of prediction of VLE data at higher temperatures, the following procedure was used. The constants $(g_{12} - g_{11})$ and $(g_{12} - g_{22})$ obtained at each temperature for which h^E data were available (see Fig. 1) were used to estimate isothermal VLE data for system I at 119.3 °C. These estimated reults were then compared with the actual experimental data[12]. For each of these comparisons, a statistical standard deviation, σ_y, was computed where σ_y is the percent standard

TABLE I

SUMMARY OF VLE PREDICTIONS FROM h^E DATA USING LEMF EQUATION FOR FIVE SYSTEMS HAVING h^E DATA AT THREE OR MORE TEMPERATURES

System[a]	*Type of VLE data*[b]	*Deviation of predicted from experimental VLE data*[c] σ_y (%)	*References*	
			VLE data	*h^E data*[d]
I	Isothermal, 119.3 °C	9.4	12	17 (15 °C), 18 (25 °C, 35 °C), 19 (50 °C), 20 (90 °C)
I	Isobaric, 18.28 atm. (215.7–219.5 °C)	3.4	13	
II	Isothermal, 50 °C	0.66	21	22 (15 °C, 35 °C), 23 (20 °C), 24 (25 °C), 25 (45 °C)
II	Isobaric, 1 atm (50.07–95.5 °C)	2.93	26	
II	Isobaric, 1 atm (50.07–95.5 °C)	1.56	27	
II	Isobaric, 1 atm (50.07–95.5 °C)	1.77	28	
III	Isothermal, 79.7 °C	0.26	14	29 (20 °C), 30 (25 °C), 31 (35 °C)
III	Isobaric, 1 atm (81.18–108.75 °C)	2.11	15	
III	Isothermal, 120 °C	2.53	16	
	200 °C	12.48		
	250 °C	15.10		
IV	Isobaric, 1 atm (98.5–100.7 °C)	2.85	32	33 (20 °C), 19 (25 °C, 50 °C)
IV	Isobaric, 2.97 atm (140.8–145.3 °C)	3.59	34	
IV	Isobaric, 4.57 atm (164.1–167.7 °C)	5.59	34	
V	Isobaric, 1 atm (81.65–97.1 °C)	5.90	35	23 (20 °C), 36 (25 °C), 19 (50 °C)

[a] System I, benzene (1)–cyclohexane (2); system II, benzene (1)–*n*-heptane (2); system III, benzene (1)–toluene (2); system IV, methylcyclohexane (1)–*n*-heptane (2); system V, cyclohexane (1)–*n*-heptane (2).

[b] Boiling range for isobaric data is given in parentheses.

[c] $\sigma_y = 100\ \{\sum_j^N [(y_{j,\mathrm{calc.}} - y_{j,\mathrm{exp}})/y_{j,\mathrm{exp}}]^2/(N-2)\}^{1/2}$.

[d] Temperatures of h^E data are shown in parentheses.

deviation of the fitted VLE data from the experimental values. The values of σ_y thus obtained are shown in Fig. 2 as a function of the temperature of the h^E data used for the determination of the LEMF parameters. Also shown is a value of σ_y = 9.4% obtained with LEMF parameters extrapolated to 119 °C from Fig. 1.

Two observations may be made concerning the results in Fig. 2. First, it is evident that much better estimates of the VLE data (lower σ_y values) are obtained when the LEMF parameters are obtained from h^E data at temperatures closer to the temperature of the VLE data. Second, it appears that the linear extrapolation of the LEMF parameters to the higher temperature where no h^E data are available is feasible and produces the best estimates (lowest σ_y value) of the VLE data.

As a further test of the extrapolation method for system I, the isobaric data of Kumarkrishna Rao et al.[13] at 18.3 atm (215.7–219.5°C) were predicted and a value of $\sigma_y = 3.4\%$ was obtained. The results of this calculation are shown in Fig. 3. These results show that the extrapolation method can produce acceptable VLE data for isobaric as well as isothermal systems.

Table I contains a complete summary of the results obtained by the extrapolation method for all five systems. The VLE data were evaluated at temperatures ranging from 20°C to as much as 245°C higher than the highest temperature at which the h^E data were measured.

With the exception of the two sets of benzene (1)–toluene (2) data (system III) above 200°C, all predictions are quite acceptable. The larger σ_y values for the 200°C and 280°C data for system III are probably due to the extreme range of temperature

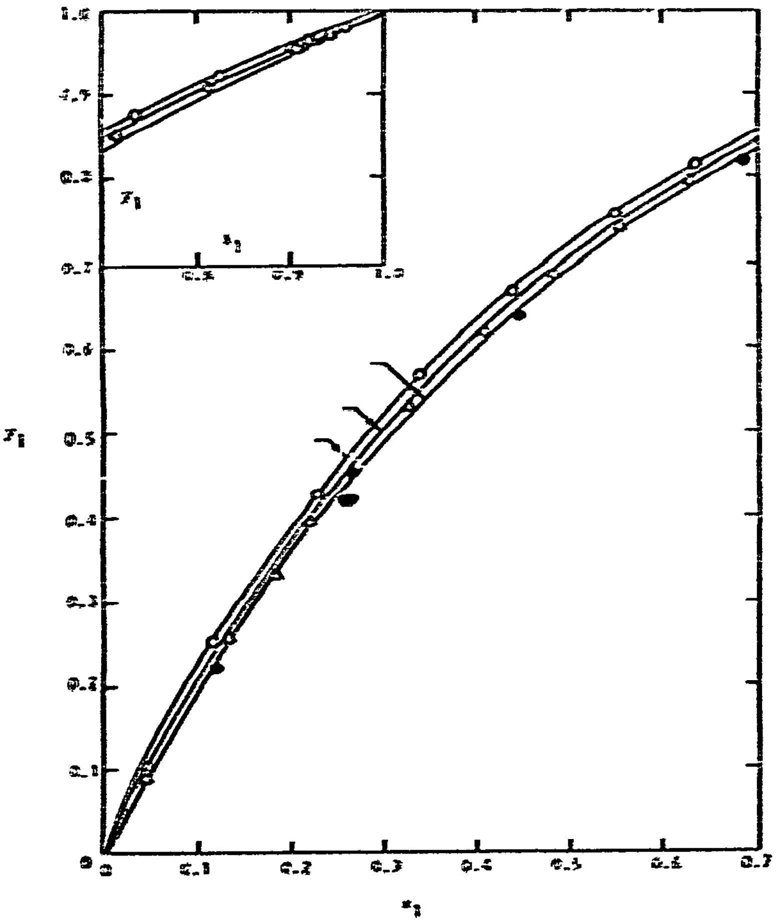

Fig. 4. Comparison of predicted values (——) with the isothermal data of Rosanoff et al.[14] at 79.7°C (○), the isobaric data of Heertjes[15] at 1 atm (81.2–108.8°C) (△), and the isothermal data of Griswold et al.[16] at 120°C (●) for the system benzene (1)–toluene (2).

extrapolation of the $(g_{12} - g_{11})$ and $(g_{12} - g_{22})$ values. Lower σ_y values would probably be obtained if higher temperature h^E data were available. Figure 4 shows the results for the three lower temperatures sets of data for this system.

Five other binary systems having only two sets of h^E data were also identified in the literature search. The five systems were (VI) benzene (1)–*n*-hexane (2); (VII) cyclohexane (1)–toluene (2); (VIII) benzene (1)-2,2,4-trimethylpentane (2); (IX) toluene (1)–*n*-heptane (2); and (X) octane (1)–2,2,4-trimethylpentane (2). These systems were subjected to the same analysis as the ones above using a linear extrapolation of the LEMF parameters based on two temperatures. The results of these calculations are summarized in Table 2. The VLE data were evaluated at temperatures ranging from 45°C to as much as 145°C higher than the highest temperatures at which the h^E data were measured.

Examination of the σ_y values listed in Table 2 shows them to be somewhat higher on average than those of Table 1 (9–10% compared with 4.7%). This is to be expected because only two temperature points were used in the extrapolation of the

TABLE 2

SUMMARY OF VLE PREDICTIONS FROM h^E DATA USING LEMF EQUATION FOR FIVE SYSTEMS HAVING h^E DATA AT ONLY TWO TEMPERATURES

System[a]	*Type of VLE data*[b]	*Deviation of predicted from experimental VLE data* σ_y *(%)*	*References*	
			VLE data	*h^E data*[c]
VI	Isobaric, 4 atm (119.9–129.1°C)	13.17	13	29 (20°C), 37 (25°C)
VI	Isobaric, 6.03 atm (139.8–150.1°C)	10.25	13	
VI	Isobaric, 8 atm (155–163.8°C)	10.93	13	
VI	Isobaric, 10 atm (167.2–179.4°C)	9.46	13	
VII	Isobaric, 1 atm (81.8–104.9°C)	7.36	38	29 (20°C), 36 (25°C)
VIII	Isobaric, 1 atm (80.12–95.6°C)	8.87	27	19 (25°C, 50°C)
IX	Isobaric, 1 atm (98.51–109.8°C)	13.53	39	
X	Isobaric, 1 atm (100.9–124.0°C)	4.61	40	

[a] System VI, benzene (1)–*n*-hexane (2); system VII, cyclohexane (1)–toluene (2); system VIII, benzene (1)–2,2,4-trimethylpentane (2); system IX, toluene (1)–*n*-heptane (2); system X, octane (1)–2,2,4-trimethylpentane (2).

[b] Boiling range for isobaric data is given in parentheses.

[c] Temperatures of h^E data are shown in parentheses.

LEMF parameters for systems VI–X whereas three or more were used for systems I–V. From Fig. 1, it can be seen that if only the 15 °C and 25 °C points had been used to make the extrapolation of $(g_{12} - g_{11})$ and $(g_{12} - g_{22})$ for system I, considerable error in the higher temperature predictions would have occurred. The very low σ_y value listed for system VII in Table 2 is therefore quite probably fortuitous.

Because of the requirement that h^E data be available at two or more temperatures, only ten binary systems were studied. Many of these systems were nearly ideal as indicated by the fact that for nearly half the systems Raoult's low gave a σ_y value which was equal to or less than the σ_y value reported in Tables 1 and 2. Work is now in progress to measure h^E data as a function of temperature to extend the method to systems that show large deviations from ideal solution behavior.

CONCLUSIONS

The results of this study suggest that if h^E data are available at three or more temperatures, one may reasonably expect to predict VLE data at higher temperatures to within 4–5% using the LEMF model and extrapolating its parameters linearly with temperature. If two sets of h^E data are available, one may reasonably expect 10–12% accuracy in predicting VLE data at higher temperatures. All these estimates apply to temperature extrapolation of the order from 20 to 150 °C. Further h^M data is needed as a function of temperature to extend the method to more non-ideal mixtures.

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