Thermochimica Acta, 170 (1990) 269–276
Elsevier Science Publishers B.V., Amsterdam

APPLICABILITY OF THE UNIFAC METHOD FOR PREDICTION OF BINARY AND TERNARY VAPOUR–LIQUID EQUILIBRIUM DATA IN SYSTEMS FORMED BY HYDROCARBONS AND ALCOHOLS

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(Received 14 March 1990)

ABSTRACT

The problem of the prediction and correlation of vapour–liquid equilibria in binary and ternary systems has been discussed and the limitation in the applicability of the UNIFAC method for this purpose has been pointed out.

The total pressure data for six ternary systems (cyclohexane–2-propanol–benzene, cyclohexane–ethanol–benzene, *n*-heptane–1-propanol–benzene, *n*-hexane–ethanol–benzene, cyclohexane–methanol–benzene, cyclohexane–ethanol–toluene) and eighteen corresponding binary mixtures (benzene–2-propanol, benzene–cyclohexane, cyclohexane–2-propanol, cyclohexane–ethanol, cyclohexane–benzene, ethanol–benzene, ethanol–benzene, *n*-hexane–benzene, *n*-hexane–ethanol, benzene–1-propanol, benzene–*n*-hexane, *n*-heptane–1-propanol, cyclohexane–methanol, benzene–cyclohexane, benzene–methanol, cyclohexane–ethanol, benzene–cyclohexane, benzene–ethanol) have been selected and correlated by means of the Redlich–Kister equation and compared with the results predicted by the UNIFAC method.

The correlation and the prediction results have been fully discussed from the point of view of intermolecular interactions and some recommendations have been made on the use of the methods investigated for such calculations.

INTRODUCTION

This work is the continuation [1–5] of a systematic comparative investigation of the applicability of various methods for the prediction and correlation of ternary vapour–liquid equilibrium (VLE) data.

The first step was the elaboration of the general assumptions of such investigations and the selection of experimental ternary data sets which could serve as test systems [1,2]. The second step concerned investigations (correlation and prediction using different equations based on the local composition concept and combining various expressions for G^E [6]) of all selected classes of system [3–5], i.e. systems with physical interactions, physical and weak interactions, and intermediate and strong chemical interactions.

0040-6031/90/$03.50

The purpose of this work is to check the possibility of using the UNIFAC [7] method for prediction of VLE in binary and ternary systems formed by hydrocarbons (systems with physical interactions) and hydrocarbons and alcohols (systems with physical and strong chemical interactions). These two groups of systems have been selected as the most interesting from the point of view of the current investigations. The first class of systems (both binary and ternary systems) can be very well described (with accuracy very close to that achieved experimentally) by almost any correlating equations. To obtain a good description of the second group it is usually necessary to use a special type of equation. For binary systems it is necessary to use an equation which takes association into consideration; however, this will not describe ternary VLE data with experimental accuracy. It seems that, in this case, to obtain a good description of VLE data it is necessary to introduce an extra term which takes into consideration ternary molecular interactions.

SELECTION OF THE SYSTEMS

In the open literature, ternary VLE data have been reported for about 500 systems. In most cases the data are only fragmentary and are frequently inconsistent and of low quality. After checking for thermodynamic consistency, other existing data have had to be rejected. Moreover, only those data can be used which cover a full range of compositions and for which the corresponding binary VLE data are available.

The systems were selected in the same way as before [3–5], i.e. the systems had to fulfil two conditions: (1) there should be wide representation of various kinds of hydrocarbons interacting with strong associating alcohols, and (2) the data should have good consistency.

Selection of appropriate ternary VLE systems was based on data reported in the literature and also those available in two data banks (the Dortmund Data Bank and the Budapest Data Bank).

As before [3], to avoid problems of temperature dependence of parameters, isothermal data only were used. In addition, for possible comparison with earlier investigations, this study was based mostly on data selected for earlier studies [3,4].

The following six isothermal ternary systems were chosen:

(1) cyclohexane–2-propanol–benzene at $T = 313.15$ K, 328.15 K [8];
(2) cyclohexane–ethanol–benzene at $T = 323.15$ K [9];
(3) *n*-heptane–1-propanol–benzene at $T = 348.15$ K [10];
(4) *n*-hexane–ethanol–benzene at $T = 328.15$ K [11];
(5) cyclohexane–methanol–benzene at $T = 328.15$ K [12]; and
(6) cyclohexane–ethanol–toluene at $T = 323.15$ K [13], and eighteen corresponding isothermal binary VLE systems were chosen:

(1) benzene–2-propanol at $T = 313.15$ K, 328.15 K [8];

(2) benzene–cyclohexane at $T = 313.15$ K [8], 328.15 K [12];
(3) cyclohexane–2-propanol at $T = 313.15$ K, 328.15 K [8];
(4) cyclohexane–ethanol at $T = 323.15$ K [9];
(5) cyclohexane–benzene at $T = 323.15$ K [9];
(6) ethanol–benzene at $T = 323.15$ K [9];
(7) ethanol–benzene at $T = 328.15$ K [14];
(8) *n*-hexane–benzene at $T = 328.15$ K [14];
(9) *n*-hexane–ethanol at $T = 328.15$ K [14];
(10) benzene–1-propanol at $T = 348.15$ K [15];
(11) benzene–*n*-hexane at $T = 348.15$ K [15];
(12) *n*-heptane–1-propanol at $T = 348.15$ K [15];
(13) cyclohexane–methanol at $T = 328.15$ K [12];
(14) benzene–cyclohexane at $T = 328.15$ K [12];
(15) benzene–methanol at $T = 328.15$ K [12];
(16) cyclohexane–ethanol at $T = 323.15$ K [13];
(17) benzene–cyclohexane at $T = 323.15$ K [13];
(18) benzene–ethanol at $T = 323.15$ K [13].

Data for correlation were chosen from only a few laboratories which were considered to be the most reliable, and in most cases these data fulfilled an additional important condition that both the binary and ternary data for each of the systems investigated were obtained in the same laboratory and with the same experimental procedure.

RESULTS

In choosing the UNIFAC method, account has been taken of the possibility of description of binary and ternary VLE data without any adjustable parameters; it was also wished to check the accuracy of prediction given by this method.

In addition, for comparison with correlation results, it was decided to use the Redlich–Kister [16] (R–K) equation (the simplest polynomial equation) for correlation of the selected data.

For binary systems this equation has the following form:

$$G_{ij}^{\mathrm{E}} = RTx_i x_j \sum_{k=0}^{m} A_k (x_i - x_j)^k \tag{1}$$

where $m + 1$ is the number of adjustable constants A, R is the gas constant, T is the temperature (in K), G_{ij}^{E} is the excess Gibbs energy of 1 mole of mixture of i and j, and x_i and x_j are molar fractions of components i and j, respectively. For ternary systems, the equation is as follows:

$$\begin{aligned} G^{\mathrm{E}} = {} & RT\big(G_{12}^{\mathrm{E}} + G_{13}^{\mathrm{E}} + G_{23}^{\mathrm{E}}\big) \\ & + x_1 x_2 x_3 \big[B + B_1(3x_1 - 1) + B_2(3x_2 - 1)\big] \end{aligned} \tag{2}$$

TABLE 1

Results of prediction by means of the UNIFAC method and correlation by the Redlich–Kister (R–K) equation for all binary systems investigated

System	T (k)	R–K $D(P)$ (KPa)	UNIFAC $D(P)$ (KPa)	UNIFAC D(Y)	Ref.
Benzene–2-propanol	313.15	0.081	0.3165	0.0072	8
Cyclohexane–2-propanol	313.15	0.379	0.6719	0.0146	8
Benzene–cyclohexane	313.15	0.076	0.2717	0.0099	9
Benzene–2-propanol	328.15	0.096	0.4541	0.0082	8
Cyclohexane–2-propanol	328.15	0.306	2.1426	0.0165	8
Benzene–cyclohexane	328.15	0.244	0.2045	0.0030	12
Benzene–ethanol	323.15	0.163	0.3740	0.0112	9
Benzene–cyclohexane	323.15	0.268	0.8610	0.0042	9
Cyclohexane–ethanol	323.15	0.404	0.9315	0.0096	9
1-Propanol–benzene	348.15	0.546	2.3305	0.0113	15
1-Propanol–*n*-heptane	348.15	1.584	3.5491	0.0370	15
Benzene–*n*-heptane	348.15	0.354	1.4747	0.0087	15
n-Hexane–ethanol	328.15	2.715	2.2647	0.0364	14
Ethanol–benzene	328.15	0.828	0.9770	0.0175	14
n-Hexane–benzene	328.15	0.266	0.5539	0.0033	14
Benzene–cyclohexane	328.15	0.184	0.2045	0.0030	12
Methanol–cyclohexane	328.15	2.690	2.8564	0.0340	12
Methanol–benzene	328.15	0.896	3.0793	0.0270	12
Ethanol–toluene	323.15	0.244	0.1580	0.0049	13
Cyclohexane–toluene	323.15	0.149	0.2539	0.0027	13
Ethanol–cyclohexane	323.15	0.412	0.8352	0.0102	13

TABLE 2

Results of prediction by means of the UNIFAC method and correlation by the R–K equation for all ternary systems investigated

System	T (K)	R–K $D(P)$ (KPa)	UNIFAC $D(P)$ (KPa)	UNIFAC $D(Y)$	Ref.
2-Propanol–benzene–cyclohexane	313.15	0.036	0.2127	0.0080	8
Benzene–cyclohexane–2-propanol	328.15	0.195	0.6451	0.0431	8
Benzene–cyclohexane–ethanol	323.15	0.631	1.0149	0.0175	9
1-Propanol–*n*-heptane–benzene	348.15	0.724	2.0529	0.0146	19
n-Hexane–ethanol–benzene	328.15	1.101	1.4435	0.0235	11
Methanol–benzene–cyclohexane	328.15	1.320	1.6807	0.0110	12
Toluene–cyclohexane–ethanol	323.15	0.512	0.5685	0.0100	13

For computation of the vapour-phase nonideality the Hayden–O'Connell [17] correlation was applied. The computed values of root mean square deviations of the pressure $D(P)$ and the molar fraction of vapour phase $D(Y)$ (eqn. (3)) for all investigated systems are given in Table 1 for binary VLE data and in Table 2 for ternary VLE data.

$$D(Z)=\left[\frac{\sum_{i=1}^{n}\left(Z_i^{\exp}-Z_i^{\mathrm{cal}}\right)^2}{n-m-1}\right]^{1/2} \tag{3}$$

where $Z_i^{\exp}$ and Z_i^{cal} are the experimental and calculated total vapour pressures or molar fractions of vapour phase, respectively, n is the number of experimental data points and $m+1$ is the number of adjustable parameters.

The prediction $D(Z)$ of the binary and the ternary VLE data by the UNIFAC method is shown in Tables 1 and 2.

The comparison of results shows that in all cases (even for hydrocarbons) the UNIFAC method gives very poor prediction (accuracy is very far from that achieved experimentally) of binary and ternary VLE data, 2–10 times worse than the results of their correlation. It is impossible to find a trend in the behaviour of values of deviations with respect to type or configuration of hydrocarbons and alcohols.

The comparison of results shows also that in the case of binary and ternary systems formed by hydrocarbons and alcohols the UNIFAC method gives prediction on the same level of accuracy (but far from that achieved experimentally) as in the case of ternary systems formed by hydrocarbons.

CONCLUSIONS

The UNIFAC method cannot be recommended as a procedure for prediction of binary and ternary VLE data with an accuracy similar to that achieved experimentally. However, the results of prediction in binary (Table 1) and ternary (Table 2) systems show that the UNIFAC method, irrespective of type of systems (aliphatic, cyclic, aromatic hydrocarbons, hydrocarbons with alcohols), gives prediction of VLE on the same level of accuracy. The fact that the same accuracy of prediction is obtained for systems which belong to different classes and consist of different numbers of components means that the UNIFAC method can be useful for many purposes.

It is interesting to compare the results of prediction of ternary VLE data given by the UNIFAC method and by the use of equations based on the local composition concept [3–5]. The comparison shows that for ternary systems formed by hydrocarbons and alcohols the UNIFAC method gives prediction on the same level of accuracy (but far from that achieved experimentally) as the NRTL, UNIQUAC and Wilson equations (Table 3). For ternary systems formed by hydrocarbons the prediction given by the UNIFAC method is much poorer (two to four times worse than that obtained by the use of the equations based on the local composition concept). This agrees with results of correlation and prediction of ternary VLE data for such systems [3–5] where the local composition equations give results close to that achieved experimentally for systems formed by hydrocarbons and far from that for systems formed by hydrocarbons and alcohols.

The R–K equation (two to four parameters for each binary and up to twelve for ternary systems) describes all investigated systems (Tables 1 and 2) on the same level as the equations based on the local composition concept. Moreover, the R–K equation as a temperature-independent polynomial equation cannot be used directly for calculation of other thermodynamic functions. Therefore it is not recommended for correlation of VLE data in multicomponent systems.

TABLE 3

Results of correlation of ternary VLE data for systems formed by hydrocarbons and alcohols

System	T (K)	NRTL $\alpha = 0.2$	NRTLMK $\alpha = 0.2$ r = const.	NRTLMK $\alpha = 0.2$ K = const. r = const.	NRTLMK $\alpha = 0.2$ K = const.	UNI QUAC	Wilson
2-Propanol–benzene–cyclohexane	313.15	0.015	0.016	0.036	0.000	0.017	0.016
Benzene–cyclohexane–2-propanol	328.15	0.102	0.100	0.183	0.135	0.099	0.128
Benzene–cyclohexane–ethanol	323.15	0.474	0.376	0.310	0.238	0.417	0.319
1-Propanol–*n*-heptane–benzene	348.15	0.669	0.666	0.637	0.620	0.669	0.664
n-hexane–ethanol–benzene	328.15	1.022	0.620	0.631	0.629	0.971	0.634
Methanol–benzene–cyclohexane	328.15	0.147	0.016	0.369	0.244	0.193	0.547
Toluene–cyclohexane–ethanol	323.15	0.474	0.376	0.310	0.238	0.417	0.319

It should be also pointed out that the representation of VLE data by means of algebraic equations is always subject to error. Even if systematic errors in the experimental procedure are eliminated by carefully checking the "thermodynamic consistency", there remain, in addition to random experimental errors, systematic errors involved in the algebraic form of the equation used.

From the data collection available, it is evident that a substantial limitation in the description of the VLE in multicomponent systems is the scantiness of experimental data. This is why predictive methods which do not use adjustable parameters are very important and play a major role in the description of industrial processes.

As it was mentioned above, this work is part of a systematic investigation of the description of VLE in ternary and multi-component systems. To check, select and give a final recommendation on the methods of correlation and prediction in ternary systems it is necessary to have much more high-quality experimental VLE ternary and binary data.

ACKNOWLEDGEMENT

This work was carried out within the Polish Academy of Sciences Research Project CPBR 3.20.61.

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