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CORRELATION AND PREDICTION OF VLE IN TERNARY SYSTEMS FORMED BY HYDROCARBONS AND ALCOHOLS

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ABSTRACT

The problem of the prediction and correlation of vapour–liquid equilibria (VLE) in ternary systems has been discussed and the limited applicability of the known methods for this purpose pointed out. A comparison of the efficiency of the various methods for ternary systems of different classes of mixtures has been undertaken.

As a part of this work, total pressure data for 6 ternary mixtures (cyclohexane–ethanol–toluene, cyclohexane–ethanol–benzene, *n*-hexane–ethanol–benzene, cyclohexane–2-propanol–benzene, *n*-hexane–1-propanol–benzene, cyclohexane–methanol–benzene) and 18 appropriate binary mixtures (cyclohexane–ethanol, cyclohexane–toluene, ethanol–toluene, cyclohexane–ethanol, benzene–cyclohexane, benzene–ethanol, ethanol–benzene, *n*-hexane–benzene, *n*-hexane–ethanol, benzene–2-propanol, benzene–cyclohexane, cyclohexane–2-propanol, benzene–1-propanol, benzene–*n*-hexane, *n*-hexane–1-propanol, cyclohexane–methanol, benzene–cyclohexane, benzene–methanol) were selected and correlated by means of the NRTL, UNIQUAC, Wilson and NRTLMK equations. The ternary VLE data were then predicted using the binary parameters of the equations calculated from appropriate binary VLE data.

The correlation and prediction results are fully discussed from the point of view of intermolecular interactions, and a number of recommendations on the use of the equations investigated for such calculations are made.

INTRODUCTION

The present work is a continuation of a systematic comparative investigation of the applicability of various methods for the prediction and correlation of ternary vapour–liquid equilibrium (VLE) data [1,2,3].

The first step was to elaborate on the general assumptions of such investigations, and select experimental ternary data sets which could serve as test systems [1,2]. The second step involved investigating the first group of systems selected: systems with physical interactions, i.e. hydrocarbons [3].

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The aim of the present work was to perform the same investigations for systems belonging to group b2 of our classification [1,2]: systems with physical and strong chemical interactions, i.e. hydrocarbons and alcohols.

The most essential step seems to be to pass from binary to ternary systems, and to answer the question to what extent we can predict the phase equilibria in these systems on the basis of binary data, and to what extent data reflecting the ternary interactions are absolutely necessary.

SELECTION OF THE SYSTEMS

The availability of reliable data for ternary systems is very limited. VLE ternary data have been reported for about 500 systems in total, but most of these reports contain only fragmentary data, and in many the data is inconsistent and of low quality. After checking for thermodynamic consistency, more of the existing data had to be rejected. Moreover, only those data which cover the full range of compositions and for which there are corresponding binary VLE data could be taken into consideration.

Selection of the systems was performed in the same way as for the hydrocarbons study [3], i.e. the systems were selected to fulfil two conditions. The first condition was that we achieve a wide representation of various kinds of hydrocarbons interacting with strong associating alcohols, and the second was that we select good consistent VLE data.

We based our search for appropriate ternary VLE systems on data given in the literature and in two data banks: the Dortmund Data Bank and the Budapest Data Bank. As previously [3], to avoid problems with temperature dependence of parameters, about which there has been some debate, we limited our interests to isothermal data only.

In the end, 6 sets of isothermal ternary VLE data were selected.

(1) cyclohexane–ethanol–toluene, at $T = 323.15$ K [4]
(2) cyclohexane–ethanol–benzene, at $T = 323.15$ K [5]
(3) *n*-hexane–ethanol–benzene, at $T = 328.15$ K [6]
(4) cyclohexane–2-propanol–benzene, at $T = 313.15$ K, 328.15 K [7]
(5) *n*-hexane–1-propanol–benzene, at $T = 348.15$ K [8]
(6) cyclohexane–methanol–benzene, at $T = 328.15$ K [9]

together with a corresponding 18 sets of isothermal binary VLE data

(1) cyclohexane–ethanol, at $T = 323.15$ K [5]
(2) cyclohexane–toluene, at $T = 323.15$ K [4]
(3) ethanol–toluene, at $T = 323.15$ K [4]
(4) cyclohexane–ethanol, at $T = 323.15$ K [5]
(5) benzene–cyclohexane, at $T = 323.15$ K [5]
(6) benzene–ethanol, at $T = 323.15$ K [5]
(7) ethanol–benzene, at $T = 328.15$ K [6]
(8) *n*-hexane–benzene, at $T = 328.15$ K [6]

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

Data chosen for correlation were from only a few of the most reliable laboratories possible, and in most cases fulfilled an important additional condition, in that both the binary and ternary data for each of the systems investigated had been obtained in the same laboratory, by the same experimental procedure.

METHOD

In choosing the methods we took into account the accuracy of correlation of binary VLE data which can be achieved by these methods, and whether or not they can be used to describe ternary data without any additional ternary terms, which is absolutely necessary if ternary VLE data are to be predicted from binary VLE data.

Additionally, we wanted to check the possibility of using equations which worked well for ternary mixtures of hydrocarbons [3].

For these reasons, we decided to carry out our calculations using the NRTL, the UNIQUAC and the Wilson equations, i.e. equations based on the concept of local composition (group 1b) which have the following forms of excess Gibbs energy for multicomponent systems

$$G^{\mathrm{E}} = \sum_i \sum_j G_{ij}^{\mathrm{E}} \tag{1}$$

This group was selected as a simple group of methods for the description of activity coefficients which can be used for the calculation of multicomponent VLE data based only on the corresponding binary parameters (without any extra ternary terms). Moreover, the equations selected are very popular and the most reliable and accurate equations for correlation of binary VLE data.

RESULTS

First, all the selected VLE data were correlated by means of the NRTL (with constant value of $\alpha = 0.2$), UNIQUAC and Wilson equations. The

TABLE 1

Results of correlation of binary VLE data for all systems investigated

No.	System	Ref.	T (K)	$D(P)$ for correlation (kPa)					
				NRTL $\alpha = 0.2$	NRTLMK $\alpha = 0.2$ $r = \text{const.}$ [a]	NRTLMK $\alpha = 0.2$ $K = \text{const.}$ [b] $r = \text{const.}$ [a]	NRTLMK $\alpha = 0.2$ $K = \text{const.}$ [b]	UNIQUAC	Wilson
1	Cyclohexane–ethanol	5	323.15	0.305	0.120	0.161	0.145	0.259	0.158
2	Cyclohexane–toluene	4	323.15	0.079	–	–	–	0.073	0.068
3	Ethanol–toluene	4	323.15	0.244	0.026	0.123	0.014	0.195	0.042
4	Cyclohexane–ethanol	5	323.15	0.304	0.124	0.176	0.139	0.245	0.153
5	Benzene–cyclohexane	5	323.15	0.166	–	–	–	0.163	0.152
6	Benzene–ethanol	5	323.15	0.164	0.113	0.121	0.081	0.126	0.112
7	Ethanol–benzene	6	328.15	0.738	0.252	0.372	0.268	0.545	0.270
8	*n*-Hexane–benzene	6	328.15	0.196	–	–	–	0.186	0.178
9	*n*-Hexane–ethanol	6	328.15	2.414	0.643	0.828	0.668	2.211	0.725
10	Benzene–2-propanol	7	313.15	0.021	0.003	0.097	0.097	0.067	0.131
11	Benzene–cyclohexane	10	313.15	0.046	–	–	–	0.045	0.046
12	Cyclohexane–2-propanol	7	313.15	0.279	0.025	0.203	0.084	0.248	0.121
13	Cyclohexane–2-propanol	7	328.15	0.205	0.182	0.117	0.082	0.182	0.096
14	Benzene–cyclohexane	8	328.15	0.144	–	–	–	0.145	0.147
15	Benzene–2-propanol	7	328.15	0.046	0.022	0.093	0.086	0.024	0.063
16	Benzene–1-propanol	11	348.15	0.456	0.385	0.798	0.510	0.392	0.403
17	Benzene–*n*-heptane	11	348.15	0.294	–	–	–	0.294	0.295
18	*n*-Heptane–1-propanol	11	348.15	1.524	1.488	1.330	1.128	1.523	1.553
19	Methanol–cyclohexane	9	328.15	2.490	0.472	0.584	0.453	1.426	2.315
20	Benzene–cyclohexane	9	328.15	0.144	–	–	–	0.145	0.147
21	Methanol–benzene	9	328.15	0.756	0.040	0.271	0.438	0.477	0.089

[a] The r value is assumed to be equal to the ratio of the molar volumes of the pure components.

[b] The K value is taken from the work of Nath and Bender [12].

TABLE 2

Results of prediction of binary VLE data for all systems investigated

No.	System	Ref.	T (K)	$D(P)$ for prediction on the basis of ternary systems (kPa)				
				NRTL $\alpha = 0.2$	NRTLMK $\alpha = 0.2$ r = const. [a]	NRTLMK $\alpha = 0.2$ K = const. [b] r = const. [a]	UNIQUAC	Wilson
1	Cyclohexane–ethanol	5	323.15	1.651	0.668	0.504	1.571	1.527
2	Cyclohexane–toluene	4	323.15	0.845	–	–	0.750	0.687
3	Ethanol–toluene	4	323.15	2.196	0.898	0.476	2.046	1.023
4	Cyclohexane–ethanol	5	323.15	1.161	2.170	2.234	1.839	2.387
5	Benzene–cyclohexane	5	323.15	4.040	–	–	6.917	1.406
6	Benzene–ethanol	5	323.15	0.902	1.822	1.219	3.282	0.540
7	Ethanol–benzene	6	328.15	2.482	1.712	2.051	2.580	5.424
8	*n*-Hexane–benzene	6	328.15	1.889	–	–	1.497	2.021
9	*n*-Hexane–ethanol	6	328.15	6.136	1.585	1.450	6.026	5.241
10	Benzene–2-propanol	7	313.15	2.200	1.730	2.029	2.214	2.120
11	Benzene–cyclohexane	10	313.15	2.184	–	–	2.125	2.808
12	Cyclohexane–2-propanol	7	313.15	0.931	0.847	0.839	0.973	0.861
13	Cyclohexane–2-propanol	7	328.15	2.086	1.853	1.037	1.724	1.850
14	Benzene–cyclohexane	8	328.15	2.303	–	–	3.077	3.886
15	Benzene–2-propanol	7	328.15	5.045	4.364	4.146	6.068	7.015
16	Benzene–1-propanol	11	348.15	3.637	0.937	2.169	3.536	3.934
17	Benzene–*n*-heptane	11	348.15	1.792	–	–	2.041	2.326
18	*n*-Heptane–1-propanol	11	348.15	2.625	2.013	2.625	2.757	2.436
19	Methanol–cyclohexane	9	328.15	11.406	6.808	0.663	8.460	16.107
20	Benzene–cyclohexane	9	328.15	15.944	–	–	8.873	21.403
21	Methanol–benzene	9	328.15	11.378	5.039	2.673	6.502	19.043

[a] The r value is assumed to be equal to the ratio of the molar volumes of the pure components.

[b] The K value is taken from the work of Nath and Bender [12].

TABLE 3

Results of correlation of ternary VLE data for all systems investigated

No.	System	Ref.	I (K)	$D(P)$ for correlation (kPa)					
				NRTL $\alpha = 0.2$	NRTLMK $\alpha = 0.2$ r = const. [a]	NRTLMK $\alpha = 0.2$ K = const. [b] r = const. [a]	NRTLMK $\alpha = 0.2$ K = const. [b]	UNIQUAC	Wilson
1	Toluene–cyclohexane–ethanol	4	323.15	0.474	0.376	0.310	0.238	0.417	0.319
2	Benzene–cyclohexane–ethanol	5	323.15	0.540	0.515	0.553	0.518	0.562	0.617
3	*n*-Hexane–ethanol–benzene	6	328.15	1.022	0.620	0.631	0.629	0.971	0.634
4	Benzene–cyclohexane–2-propanol	7	313.15	0.015	0.016	0.036	0.000	0.017	0.016
5	Benzene–cyclohexane–2-propanol	7	328.15	0.102	0.100	0.183	0.135	0.099	0.128
6	Benzene–*n*-heptane–1-propanol	8	348.15	0.669	0.666	0.637	0.620	0.669	0.664
7	Methanol–benzene–cyclohexane	9	328.15	0.147	0.016	0.369	0.244	0.193	0.547

[a] The r value is assumed to be equal to the ratio of the molar volumes of the pure components.

[b] The K value is taken from the work of Nath and Bender [12].

TABLE 4

Results of prediction of ternary VLE data for all systems investigated

No.	System	Ref.	T (K)	$D(P)$ for prediction on the basis of binary systems (kPa)					
				NRTL $\alpha = 0.2$	NRTLMK $\alpha = 0.2$ r = const. [a]	NRTLMK $\alpha = 0.2$ K = const. [b] r = const. [a]	NRTLMK $\alpha = 0.2$ K = const. [b]	UNIQUAC	Wilson
1	Toluene–cyclohexane–ethanol	4	323.15	1.837	1.045	0.892	0.409	1.948	1.013
2	Benzene–cyclohexane–ethanol	5	323.15	3.089	1.100	1.036	1.375	3.030	2.120
3	*n*-Hexane–ethanol–benzene	6	328.15	3.727	1.587	1.677	1.311	3.444	2.853
4	Benzene–cyclohexane–2-propanol	7	313.15	0.420	0.401	0.167	0.472	0.417	0.240
5	Benzene–cyclohexane–2-propanol	7	328.15	1.837	0.951	1.148	1.258	1.815	1.359
6	Benzene–*n*-heptane–1-propanol	8	348.15	4.569	2.987	2.356	2.700	4.443	4.000
7	Methanol–benzene–cyclohexane	9	328.15	5.884	2.185	1.284	2.433	5.400	4.377

[a] The r value is assumed to be equal to the ratio of the molar volumes of the pure components.

[b] The K value is taken from the work of Nath and Bender [12].

root mean square deviations of pressure $D(P)$ were calculated using

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

where $P_{i,\,\mathrm{exp}}$ and $P_{i,\,\mathrm{cal}}$ are the experimental and calculated total vapour pressures, respectively, n is the number of experimental data points, and m is the number of adjustable parameters. The values of $D(P)$ obtained for all the systems investigated are given in Tables 1 and 2 (binary VLE data) and Tables 3 and 4 (ternary VLE data).

Tables 2 and 4 also show the values of $D(P)$ predicted for the binary VLE data from the ternary VLE data, and for the ternary VLE data from the binary VLE data, respectively. The first set of predictions (Table 2) were made using binary parameters of the equations obtained from correlation of appropriate ternary systems. The second set (Table 4) were made using the binary parameters calculated from appropriate binary VLE data (three sets at the same temperature for one ternary system).

It should be pointed out that in the case of the correlation of the ternary systems, the binary parameters were obtained by the same mathematical procedure to avoid divergence in the description of multicomponent solutions owing to former binary data regression.

Analysis of the $D(P)$ data shows that all the ternary VLE data sets investigated were poorly predicted (i.e. predicted with accuracy much less than that achieved experimentally) by all the equations used; and that really it is impossible to distinguish between any of the equations. None of them can be recommended for the prediction of ternary systems formed by hydrocarbons with alcohols. Analysis also shows that the poorest prediction results (Table 4) were obtained for those ternary systems for which the correlation of the corresponding binary data was poor (Table 1). For ternary systems (Table 4) for which the corresponding binary data were well correlated (Table 1), the results of the predictions were better, though still far from experimental accuracy.

A separate problem is that of correlation of ternary data for systems formed by hydrocarbons and alcohols. The results obtained lead us to the conclusion that ternary VLE data for systems formed by hydrocarbons and alcohols, i.e. systems involving physical and strong chemical intermolecular interactions, are poorly correlated (i.e. correlated with accuracy much less than that achieved experimentally) by equations based on the local composition concept (the NRTL, UNIQUAC and Wilson equations). This means that irrespective of the kind and shape (benzene, cyclohexane, *n*-hexane, 1-heptene) of the hydrocarbons, the ternary VLE of these systems cannot be described if only binary physical interactions are taken into account.

For this reason, we decided to carry out further calculations using the modified NRTL equation (NRTLMK equation) [13], which enables description of the association of alcohols. This equation has given better results [14] for strongly associating systems than Nagata's similar modification of the UNIQUAC equation [15,16]. It was derived for binary systems [13], and for multicomponent systems with one associating compound it assumes the following form for the activity coefficient of the associating component (in this case, alcohol) ln τ_A

$$\ln \tau_A = (\ln \tau_A)_{NRTL} + \frac{1+K}{K}\ln\left[\frac{1+K}{1+Kz_A}\right] - \sum_i z_i \tag{3}$$

and the following form for the activity coefficient of the non-associating component (in this case, hydrocarbon) ln τ_i

$$\ln \tau_i = (\ln \tau_i)_{NRTL} - \frac{r_{iA}}{K}\ln(1+Kz_A) - r_{iA}z_i \tag{4}$$

where

$$r_{iA} \approx V_i/V_A$$

$$z_A = x_A/(x_A + \Sigma r_{iA}x_i)$$

$$z_i = r_{iA}x_i/(x_A + \Sigma r_{iA}x_i)$$

V_i and V_A being the molar volumes of the pure liquids, z_A and z_i being the volume fractions, and $(\ln \tau_A)_{NRTL}$ and $(\ln \tau_i)_{NRTL}$ having the same form as in the NRTL equation.

The NRTLMK equation in this form can have one or two adjustable parameters (K or r_{iA}, K and r_{iA}) more than the NRTL equation, or it can be used with the same number of parameters as the NRTL equation, assuming values of K and r_{iA} from the literature.

This equation was used to correlate all the data investigated. The values of $D(P)$ obtained are given in Tables 1–4.

The results of correlation of the binary data (Table 1) obtained by means of the NRTLMK equation are significantly better than those obtained using the NRTL, UNIQUAC and Wilson equations, which is in agreement with previous results [14] for such systems, but the results for ternary systems (Table 3) are only slightly better. This is because the K parameter is treated as an association constant and assumes only one value for ternary mixtures. This means that for correlation of binary mixtures we use two energetic parameters, one α NRTL parameter and a K parameter (four parameters), while for ternary mixtures we use six energetic parameters, one α NRTL parameter and only one K parameter (eight parameters). We could get better correlation results if we treated K as an adjustable parameter and for ternary systems adjusted to use two K parameters (making nine parameters altogether), but we would then lose the simple application of this equation to the prediction of multicomponent systems.

The NRTLMK equation was also used to predict VLE data for ternary systems. The results, which are given in Table 4, show that in all cases the prediction was much better (two to four times better) than with the NRTL, UNIQUAC and Wilson equations, and the $D(P)$ value obtained was not more than two times worse than the $D(P)$ value for correlation of the system in question.

The better predictions obtained in the case of the NRTLMK equation can be explained by the fact that this equation contains more physical information (association term) than the other equations used.

It is interesting to note that for well correlated ternary (Tables 3 and 4) and binary (Table 1) systems, predicting binary systems from the correlation of ternary systems gives reasonable results, only slightly worse than predictions in the opposite direction. Such predictions have no practical sense, given that the most important objective is to pass from simple to more complicated systems, but they confirm that the method of calculation is appropriate.

CONCLUSIONS

The results obtained lead us to the conclusion that ternary VLE data for systems formed by hydrocarbons with alcohols, i.e. systems involving physical and strong chemical intermolecular interactions, are not well correlated (i.e. correlated with accuracy close to that achieved experimentally) by equations based on the local composition concept (the NRTL, UNIQUAC and Wilson equations). This means that ternary VLE data for these systems cannot be described by taking into account binary physical interactions only. Introducing a chemical term into these equations improves the correlation results, but the accuracy obtained is still worse than that achieved experimentally. To obtain results of experimental accuracy it seems to be necessary to use an equation with an extra term, taking into account ternary interactions.

The situation is more complicated in the case of prediction of ternary VLE data from corresponding binary VLE data. Prediction of VLE data for ternary systems from binary VLE data using the NRTL, UNIQUAC and Wilson equations cannot be recommended because their adjustable binary parameters have no physical meaning and prediction of ternary data can sometimes be meaningless. Use of the NRTLMK equation (or similar equations with an association term) can be recommended for such predictions, but it should be remembered that the prediction results will not be better than the correlation results for the system, which are of worse than experimental accuracy.

It is worth pointing out that these equations can be recommended for use only when the binary data are well correlated by the equation in question. If the correlation results for the binary data are poor, then it is to be suspected that the prediction results for the ternary data will be very poor.

This means that if we want to achieve a good prediction of ternary VLE data from binary VLE data, the binary VLE data in question must be selected very carefully. Ideally, they should have been measured in the same laboratory using the same experimental procedure and at the same temperature as the ternary data to be predicted. Moreover, they must be well correlated by the equation, using the same mathematical procedure in all cases.

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