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CORRELATION AND PREDICTION OF VAPOUR–LIQUID EQUILIBRIA IN TERNARY SYSTEMS FORMED BY WEAK POLAR COMPONENTS

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ABSTRACT

The efficiencies of various methods for the correlation and prediction of vapour–liquid equilibria (VLE) in ternary systems of different classes of mixture have been compared.

The total pressure data for five ternary systems (acetonitrile–ethanol–water, acetone–ethanol–water, 1,4-dioxan–ethanol–water, benzene–2-butanone–ethanol, acetone–acetonitrile–methyl acetate) and VLE data for 15 corresponding isothermal binary systems (acetonitrile–ethanol, acetonitrile–water, ethanol–water, acetone–ethanol, acetone–water, ethanol–water, 1,4-dioxan–ethanol, 1,4-dioxan–water, ethanol–water, benzene–2-butanone, 2-butanone–ethanol, benzene–ethanol, acetone–acetonitrile, acetone–methylacetate and acetonitrile–methyl acetate) have been selected and correlated by means of the NRTL, UNIQUAC, Wilson and NRTLMK equations. The ternary VLE data have then been predicted by the use of the binary parameters of the equations calculated from the appropriate binary VLE data.

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

INTRODUCTION

This work is a continuation [1–4] 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 selection of the experimental ternary data sets which could serve as test systems [1,2] and elaboration of the general assumptions of such investigations. The second step concerned investigation of selected systems [3] (those with physical interactions only, i.e. hydrocarbons). In the third step, the most complicated systems [4] (with physical

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and strong chemical interactions, i.e. hydrocarbons and alcohols) were investigated.

The purpose of this work is to investigate systems which belong to groups b1 and b3 of the authors' classification [1], i.e. systems with physical and weak or intermediate chemical interactions. Systems in which the effects of intermolecular interactions can be compensated, and in which global deviation from ideality is not too great, also belong to this class of systems.

The essential problems are to pass from binary to ternary systems, to discover the extent to which the phase equilibria in ternary systems can be predicted on the basis of binary data, and to establish the conditions in which data reflecting the ternary interactions are necessary.

SELECTION OF THE SYSTEMS

The systems were selected in the same way as in the case of hydrocarbons [3,4], i.e. the selected system had to fulfil two conditions: (1) there should be a wide representation of different kinds of systems which contain more than one associating component, and (2) there should be good thermodynamic consistency of VLE data.

In the search for appropriate ternary VLE systems, data from the literature and from two data banks (the Dortmund Data Bank and the Budapest Data Bank) were used and, as before [3,4], to avoid problems of temperature dependence of the parameters, the study is limited to isothermal data only.

VLE data for the following five isothermal ternary systems were selected:
(1) acetonitrile–ethanol–water at $T = 323.15$ K [5];
(2) acetone–ethanol–water at $T = 323.15$ K [6];
(3) 1,4-dioxan–ethanol–water at $T = 323.15$ K [7];
(4) benzene–2-butanone–ethanol at $T = 328.15$ K [8];and
(5) acetone–acetonitrile–methyl acetate at $T = 323.15$ K [9], and VLE data for fifteen corresponding isothermal binary systems were selected:
(1) acetonitrile–ethanol at $T = 323.15$ K [5];
(2) acetonitrile–water at $T = 323.15$ K [5];
(3) ethanol–water at $T = 323.15$ K [5];
(4) acetone–ethanol at $T = 323.15$ K [6];
(5) acetone–water at $T = 323.15$ K [6];
(6) ethanol–water at $T = 323.15$ K [6];
(7) 1,4-dioxan–ethanol at $T = 323.15$ K [7];
(8) 1,4-dioxan–water at $T = 323.15$ K [7];
(9) ethanol–water at $T = 323.15$ K [7];
(10) benzene–2-butanone at $T = 328.15$ K [8];
(11) 2-butanone–ethanol at $T = 328.15$ K [8];
(12) benzene–ethanol at $T = 328.15$ K [8];
(13) acetone–acetonitrile at $T = 323.15$ K [9];

(14) acetone–methyl acetate at $T = 323.15$ K [9]; and
(15) acetonitrile–methyl acetate at 323.15 K [9].

The data for correlation were chosen from the most reliable laboratories and in most cases fulfilled an additional important condition that both the binary and the ternary data for each of the investigated systems were obtained in the same laboratory and with the same experimental procedure.

METHOD

In choosing the methods, account has been taken of the accuracy of the correlation of the binary VLE data and the possibility of description of the ternary data without any additional ternary terms. This means that the ternary VLE data have been predicted from the binary VLE data.

In addition, as it was wished to check the use of the equations which had worked well for ternary mixtures of hydrocarbons [3], it was decided to carry out the calculations using the NRTL [10], UNIQUAC [11] and Wilson [12] equations, i.e. equations based on the local composition concept (group b1). For these equations, the excess Gibbs energy has the following form for multicomponent systems:

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

These equations were selected as the simplest methods for the description of activity coefficients, which can be used for calculation of multicomponent VLE based only on the corresponding binary parameters (without any extra ternary terms). Moreover, the selected equations are very popular and can be considered to be the most reliable and accurate method for the correlation of binary VLE data.

RESULTS

First, all selected VLE data were correlated by means of the NRTL (with a constant value of $\alpha = 0.2$), UNIQUAC, Wilson and NRTLMK [13] equations. For computation of the vapour-phase nonideality, the Hayden–O'Connell [14] correlation was applied. The computed values of root mean square deviations of pressure (eqn. (2)) $D(P)$ for all investigated systems are given in Table 1 for the binary VLE data and in Table 2 for the ternary VLE data.

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

TABLE 1

Results of correlation of the VLE data for all selected binary systems

System	Temp. (K)	$D(P)$ (kPa)				Ref.
		NRTL	UNIQUAC	Wilson	NRTLMK	
Acetonitrile–ethanol	323.15	0.135	0.129	0.127	0.099	5
Acetonitrile–water	323.15	0.591	0.568	0.548	0.456	5
Ethanol–water	323.15	0.063	0.070	0.069	0.067	5
Acetone–ethanol	323.15	0.082	0.079	0.080	0.076	6
Acetone–water	323.15	0.501	0.306	0.430	0.287	6
Ethanol–water	323.15	0.041	0.071	0.051	0.042	6
1,4-Dioxan–ethanol	323.15	0.075	0.073	0.071	0.063	7
1,4-Dioxan–water	323.15	0.121	0.411	0.231	0.107	7
Ethanol–water	323.15	0.034	0.057	0.045	0.035	7
Benzene–2-butanone	328.15	0.161	0.190	0.174	0.112	8
2-Butanone–ethanol	328.15	0.230	0.230	0.225	0.128	8
Benzene–ethanol	328.15	0.117	0.071	0.109	0.068	8
Acetone–acetonitrile	323.15	0.110	0.112	0.102	0.087	9
Acetone–methyl acetate	323.15	0.036	0.036	0.036	0.035	9
Acetonitrile–methyl acetate	323.15	0.040	0.038	0.036	0.037	9

where P_i^{exp} and P_i^{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 prediction was made using the binary parameters calculated from the appropriate (three sets at the same temperature for one ternary system) binary VLE data. Table 3 shows the obtained accuracy of prediction $D(P)$ of the ternary VLE data from the corresponding binary VLE data.

It should be pointed out that the binary parameters for the correlation of the ternary systems were obtained by the same mathematical procedure to

TABLE 2

Results of correlation of the ternary VLE data for all selected systems

System	Temp. (K)	$D(P)$ (kPa)				Ref.
		NRTL	UNIQUAC	Wilson	NRTLMK	
Acetonitrile–ethanol–water	323.15	0.13	0.15	0.16	0.12	5
Acetone–ethanol–water	323.15	0.16	0.17	0.15	0.13	6
1,4-Dioxan–ethanol–water	323.15	0.05	0.08	0.07	0.05	7
Benzene-2-butanone–ethanol	328.15	0.42	0.47	0.47	0.37	8
Acetone–acetonitrile–methyl acetate	323.15	0.07	0.06	0.09	0.07	9

TABLE 3

Results of prediction of the ternary VLE data from the corresponding binary VLE data for all selected systems

System	Temp. (K)	$D(P)$ (kPa)				Ref.
		NRTL	UNIQUAC	Wilson	NRTLMK	
Acetonitrile–ethanol–water	323.15	0.41	0.28	0.30	0.24	5
Acetone–ethanol–water	323.15	0.71	0.31	0.41	0.23	6
1,4-Dioxan–ethanol–water	323.15	0.30	0.30	0.28	0.20	7
Benzene–2-butanone–ethanol	328.15	0.62	0.53	0.67	0.45	8
Acetone–acetonitrile–methylacetate	323.15	0.31	0.28	0.29	0.22	9

avoid divergence in the description of the multicomponent solutions as a result of regression of the binary data.

Analysis of $D(P)$ shows that all investigated ternary VLE data were predicted reasonably well (with accuracy close to that achieved experimentally) by the equations used. The best results were obtained with the NRTLMK equation, but the remaining equations also gave acceptable predictions. Therefore all of these equations can be recommended for the prediction of the type of ternary systems studied here. The analysis also shows that the poorest prediction results (Table 3) were obtained for those ternary systems for which the correlation of the corresponding binary data was poor (Table 1). For the ternary systems (Table 2) where the corresponding binary data were well correlated (Table 1) the results of the prediction were much better.

The correlation of the ternary data is a separate problem. The results obtained lead to the conclusion that the ternary VLE data for the systems with physical and weak or intermediate chemical intermolecular interaction are well 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 VLE in those systems can be described by taking into account only binary physical interactions.

CONCLUSIONS

It should be noted that the prediction of VLE data for the ternary systems from the binary VLE data by the use of local composition equations can be recommended only when all the binary data are well correlated by the equations applied. If the results of correlation of the binary data are poor, the prediction of the ternary data is suspected to be very poor.

This means that, to obtain a good prediction of the ternary VLE data from the binary VLE data by an equation based on the local composition concept, the corresponding binary VLE data should be selected very carefully. They should be measured in the same laboratory, and with the same experimental procedure. Moreover, they should be obtained at the same temperature as the ternary data which are to be predicted. Moreover, they have to be well correlated (with an accuracy close to that achieved experimentally) by the equation, using the same mathematical procedure in all cases.

The results of the correlation of the binary and ternary data (Tables 1 and 2) obtained by means of the NRTLMK equation are better than those with the NRTL, UNIQUAC and Wilson equations, which agrees with earlier [15] results for similar systems. However, as the difference is not too great, for systems where the effects of intermolecular interactions have been compensated for, deviation from ideality, for a good description of the VLE data it is sufficient to use equations based on the local composition concept.

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.

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