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CORRELATION AND PREDICTION OF VAPOUR–LIQUID EQUILIBRIA IN TERNARY SYSTEMS FORMED BY HYDROCARBONS

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ABSTRACT

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

As a part of this work, the total pressure data for 4 ternary mixtures (*n*-hexane–cyclohexane–benzene, *n*-hexane–methylcyclopentane–benzene, 1-heptene–*n*-heptane–*n*-octane and cyclohexane–*n*-heptane–toluene) and 12 appropriate binary mixtures (*n*-hexane–cyclohexane, *n*-hexane–benzene, cyclohexane–benzene, *n*-hexane–methylcyclopentane, *n*-hexane–benzene, methylcyclopentane–benzene, 1-heptene–*n*-heptane, 1-heptene–*n*-octane, *n*-heptane–*n*-octane, cyclohexane–*n*-heptane, cyclohexane–toluene and *n*-heptane–toluene) have been selected and correlated by means of the NRTL, the UNIQUAC and the Wilson equations. Subsequently, the ternary VLE data have been predicted using the binary parameters of the equations calculated from appropriate binary VLE data.

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

INTRODUCTION

At present two fields of scientific activity constitute the most important task of the thermodynamics of phase equilibria: the first is the possibility of computation of phase equilibria in the entire range of concentration and over large temperature and pressure intervals, on the basis of the minimum amount of experimental data; the second is the possibility of prediction of

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thermodynamic properties of multicomponent mixtures using the data obtained from more simple systems and for pure substances.

The most essential step is to pass from binary to ternary systems and to determine the extent to which the phase equilibria in these systems can be predicted on the basis of binary data and to assess when the data reflecting ternary interactions are absolutely needed.

In spite of many years of effort and achievements in the field of correlation and prediction of phase equilibria, including statistical thermodynamic methods, various theoretical solution models and semiempirical equations, there is still no general method enabling the correlation and prediction of VLE within the accuracy achieved experimentally and, moreover, each method has its own area of application limited to particular kinds of systems. These difficulties continue to grow with increasing numbers of components.

To approach a reasonable practical solution of this problem, we have undertaken a systematic comparative investigation of the applicability of various methods for the prediction and correlation of ternary VLE data as a part of an international effort undertaken by the CODATA Task Group on Critically Evaluated Phase Equilibrium Data (CEPED).

The first step was the elaboration of the general assumptions of such investigations and selection of the experimental ternary data sets which could serve as test systems. This has been done and presented as a CODATA report [1] in 1987 and published in Zeitschrift für Physikalische Chemie (Leipzig) in 1988 [2].

The purpose of this work is to perform the investigations for the first selected group of systems [2] (systems with physical intermolecular interactions), i.e. hydrocarbons.

SELECTION OF THE SYSTEMS

The availability of reliable data for ternary systems is very limited. In total, VLE ternary data have been reported for about 500 systems but most reports contain only fragmentary data of a dubious, inconsistent quality. After checking the thermodynamic consistency, more of the existing data have to be rejected. Moreover, only data covering complete ranges of compositions, for which corresponding binary VLE data are available, can be taken into consideration.

Selection of the systems was based on two conditions: the first was the wide representation of various classes of hydrocarbons; and the second was the good thermodynamic consistency of the VLE data.

Looking for suitable ternary VLE systems, we searched the data given in the literature and also in the Budapest Data Bank and we could find only about 30 appropriate ternary data systems of which most were isobaric.

Any methods used to accurately describe (within the accuracy which can be achieved experimentally) VLE data in multicomponent systems have to be based on parameters which can only be adjusted from the results of measurements. The pressure dependence of parameters can be neglected at pressures up to 200 kPa but there is a problem with the temperature dependence. In some cases, it can be neglected but in others, it cannot. To check the influence of the parameter-temperature dependence on the results

TABLE 1

Results of correlation of the ternary VLE data by means of the NRTL and the UNIQUAC equations

System	Deviations (kPa) (Correlation of ternary data)			
	NRTL		UNIQUAC	
	D(P) [a]	A(P) [b]	D(P)	A(P)
Benzene–cyclohexane–methylcyclopentane				
$P=101.3250$ kPa	0.604	1.17	0.974	2.57
Benzene–n-hexane–cyclohexane				
$T=283.1500$ K	0.156	3.57	0.191	3.68
$T=288.1500$ K	0.050	1.02	0.118	3.14
$T=298.1500$ K	0.065	0.65	0.133	2.08
$T=343.1500$ K	0.524	1.16	0.794	1.54
$P=101.3250$ kPa	0.593	1.46	0.977	2.59
Cyclohexane–n-heptane–toluene				
$T=298.1500$ K	0.159	3.43	0.132	3.05
i-Pentane–n-hexane–toluene				
$P=101.3250$ kPa	3.542	7.12	2.795	6.12
n-Heptane–methylcyclohexane–toluene				
$P=101.3250$ kPa	4.394	11.03	5.234	13.75
Benzene–n-hexane–methylcyclopentane				
$P=101.3250$ kPa	0.797	2.01	0.604	1.21
n-Hexane–benzene–toluene				
$P=101.3250$ kPa	2.068	4.92	3.391	8.55
n-Hexane–methylcyclopentane–benzene				
$T=333.1500$ K	0.346	1.01	0.353	1.17
Toluene–n-octane–ethylbenzene				
$P=101.3250$ kPa	1.440	2.77	1.562	4.99
Benzene–cyclohexane–toluene				
$P=101.3250$ kPa	5.282	11.52	5.762	10.78

[a] D(P) is the root mean square deviation of P (kPa).

[b] A(P) is the maximum absolute deviation of P (kPa).

of correlation in the case of ternary data, we have performed calculations for some hydrocarbons. The results obtained are given in Table 1.

It can be seen, by comparing the results of correlation using both the NRTL [3] and the UNIQUAC [4] equations, that the results of correlation for isobaric data are much poorer than for isothermal data (sometimes even by a factor of 10–12). This is probably caused by the parameter-temperature dependence of the equations used.

For this reason, in order to avoid the problems with the temperature dependence of parameters we limited our interests to isothermal data. We finally selected the following 4 isothermal ternary VLE data:
(1) benzene–*n*-hexane–cyclohexane at $T = 343.15$ K [5];
(2) *n*-hexane–methylcyclopentane–benzene at $T = 333.15$ K [6];
(3) 1-heptene–*n*-heptane–*n*-octane at $T = 328.15$ K [7]; and
(4) cyclohexane–*n*-heptane–toluene at $T = 298.15$ K [8],
and 12 corresponding isothermal binary VLE data:
(1) benzene–*n*-hexane at $T = 343.15$ K [5];
(2) benzene–cyclohexane at $T = 343.15$ K [5];
(3) *n*-hexane–cyclohexane at $T = 343.15$ K [5];
(4) *n*-hexane–methylcyclopentane at $T = 333.15$ K [6];
(5) *n*-hexane–benzene at $T = 333.15$ K [6];
(6) methylcyclopentane–benzene at $T = 333.15$ K [6];
(7) 1-heptene–*n*-heptane at $T = 328.15$ K [9];
(8) 1-heptene–*n*-octane at $T = 328.15$ K [9];
(9) *n*-heptane–*n*-octane at $T = 328. 15$ K [9];
(10) cyclohexane–*n*-heptane at $T = 298.15$ K [8];
(11) cyclohexane–toluene at $T = 298.15$ K [8]; and
(12) *n*-heptane–toluene at $T = 298.15$ K [8].

Data for the correlation have been chosen from only a few laboratories which are the most reliable possible, and fulfilled an additional important condition that both binary and ternary data for each of the investigated systems were obtained from the same laboratory at the same temperature and using the same experimental procedure.

METHOD

Methods for correlation and prediction of phase equilibria, as has been mentioned [2], can be divided into three groups.

1. Methods for description of the activity coefficient:
(a) polynomial equations (Redlich–Kister [10], SSF [11], etc.);
(b) equations based on the local composition concept (Wilson [12], NRTL [9], UNIQUAC [4];
(c) equations based on some theories (Mecke–Kempter model [13], etc.); and

(d) equations that are a combination of two kinds of the above equations (e.g. NRTL equation for description of physical interactions and Mecke–Kempter model for association [14]).

2. Methods for description of excess thermodynamic functions:

(a) dependent on an equation for the activity coefficient; and

(b) independent of an equation for the activity coefficient.

3. Methods using equation of state.

All these methods can be used for correlation and prediction of phase equilibria for binary, ternary and multicomponent systems and the calculations can be carried out for one or more kinds of phase equilibrium data (e.g. simultaneous correlation of vapour–liquid and liquid–liquid equilibrium data).

In choosing the methods, one should take into account the accuracy of correlation of the binary VLE data which can be achieved by the methods and the possibility of description of ternary data with no further ternary terms than is absolutely necessary for prediction of the ternary VLE data from the binary data.

The second group of methods has been used recently for calculation of ternary data [15] but did not give good results. The third group, a recent rapidly developing application, describes the VLE data in ternary mixtures in an even less satisfactory manner [16]. Therefore, we selected methods belonging to group 1.

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

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

where G^{E} is the molar excess Gibbs energy for a multicomponent system and G^{E}_{ij} is the molar excess Gibbs energy for the binary system i–j.

For the NRTL equation

$$\frac{G^{\mathrm{E}}_{ij}}{RT} = \sum_{i=1}^{N} x_i \left(\frac{\sum_{j=1}^{N} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{N} G_{ki} x_k} \right) \tag{2}$$

where $\ln G_{ij} = -\alpha_{ij}\tau_{ij}$, $gt_{ij} = (g_{ij} - g_{ji})/RT$, and α_{ij}, τ_{ij} and τ_{ji} are adjustable parameters.

For the UNIQUAC equation

$$\frac{G^{\mathrm{E}}_{ij}}{RT} = \sum_{i=1}^{N} x_i \ln\frac{\Phi_i}{x_i} + \frac{z}{2} \sum_{i=1}^{N} q_i x_i \ln\frac{\theta_i}{\Phi_i} - \sum_{i=1}^{N} q_i x_i \ln\left(\sum_{j=1}^{N} \theta_j \tau_{ji} \right) \tag{3}$$

where $\Phi_i = r_i x_i / \sum_{k=1}^{N} r_k x_k$, $\theta_i = q_i x_i / \sum_{k=1}^{N} q_k x_k$, r_i and q_i are pure component parameters, z is a coordination number (equal to 10), $\ln \tau_{ij} = -(u_{ij} -$

$u_{jj})/RT$, and τ_{ij} and τ_{ji} are adjustable parameters. For the Wilson equation

$$\frac{G^{\mathrm{E}}_{ij}}{RT} = -\sum_{i=1}^{N} x_i \ln\left(\sum_{j=1}^{N} x_j \Lambda_{ij}\right) \tag{4}$$

where Λ_{ij} are adjustable parameters.

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

RESULTS

All selected VLE data have been correlated by means of the NRTL (with a constant value of $\alpha = 0.2$), the UNIQUAC and the Wilson equations. The computed values of root mean square deviations of pressure D(P) for all the investigated systems are given in Table 2 (binary VLE data) and Table 3 (ternary VLE data) where

$$\mathrm{D}(P) = \left(\frac{\sum_{i=1}^{n}\left(P_i^{\exp} - P_i^{\mathrm{cal}}\right)^2}{n-m-1}\right)^{\frac{1}{2}} \tag{5}$$

where $P_i^{\exp}$, 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.

Table 4 gives values of the adjustable parameters for all equations used for both binary and ternary VLE data.

Tables 2 and 3 also show the prediction (D(P)) of the binary VLE data from the ternary VLE data and the ternary VLE data from the binary VLE data, respectively. The first prediction (Table 2) was made using binary parameters of the equations obtained from correlation of appropriate ternary systems and the second prediction (Table 3) was 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 the binary parameters in the case of the correlation of the ternary systems were obtained by the same mathematical procedure to avoid the divergence in the description of multicomponent solutions due to former binary data regression.

The analysis of the D(P) shows that all investigated ternary VLE data were good, with an accuracy close to that obtained experimentally being achieved with all the equations used; moreover, it is impossible to distinguish which of the equations were used. All of them can be recommended

TABLE 2

Results of correlation and prediction (D(P)) for all investigated binary systems

	System	Ref.	Temp. (K)	D(P) for correlation (kPa)			D(P) for prediction on the basis of ternary system (kPa)		
				NRTL $\alpha = 0.2$	UNIQUAC	Wilson	NRTL $\alpha = 0.2$	UNIQUAC	Wilson
(1)	Benzene–cyclohexane	[5]	343.15	0.257	0.260	0.262	2.251	2.228	2.246
(2)	*n*-Hexane–cyclohexane	[5]	343.15	0.364	0.359	0.357	4.087	4.095	4.102
(3)	*n*-Hexane–benzene	[5]	343.15	0.203	0.201	0.201	3.390	3.400	3.402
(4)	Benzene–Methylcyclopentane	[6]	333.15	0.344	0.344	0.344	1.857	1.856	1.858
(5)	Benzene–*n*-hexane	[6]	333.15	0.631	0.633	0.634	1.642	1.642	1.642
(6)	Methylcyclopentane–*n*-hexane	[6]	333.15	0.009	0.009	0.009	2.420	2.426	2.430
(7)	*n*-Heptane–*n*-octane	[9]	328.15	0.019	0.020	0.020	0.965	0.921	0.744
(8)	1-Heptene–*n*-octane	[9]	328.15	0.092	0.076	0.070	0.874	0.869	0.927
(9)	1-Heptene–*n*-heptane	[9]	328.15	0.009	0.009	0.014	0.393	0.386	0.335
(10)	Cyclohexane–toluene	[8]	298.15	0.113	0.113	0.114	0.260	0.307	0.281
(11)	Cyclohexane–*n*-heptane	[8]	298.15	0.061	0.061	0.061	0.079	0.071	0.096
(12)	Toluene–*n*-heptane	[8]	298.15	0.124	0.124	0.124	0.308	0.264	0.293

TABLE 3

Results of correlation and prediction (D(P)) for all investigated ternary systems

	System	Ref.	Temp. (K)	D(P) for correlation (kPa)			D(P) for prediction on the basis of binary system (kPa)		
				NRTL $\alpha = 0.2$	UNIQUAC	Wilson	NRTL $\alpha = 0.2$	UNIQUAC	Wilson
(1)	*n*-Hexane–cyclohexane–benzene	[5]	343.15	0.190	0.190	0.190	2.593	2.799	2.837
(2)	*n*-Hexane–methylcyclopentane–benzene	[6]	333.15	0.106	0.107	0.107	2.583	2.466	2.491
(3)	1-Heptene–*n*-heptane–*n*-octane	[7]	328.15	0.275	0.273	0.267	0.469	0.457	0.452
(4)	Cyclohexane–*n*-heptane–toluene	[8]	298.15	0.078	0.077	0.083	0.215	0.215	0.215

for the correlation of ternary systems formed by hydrocarbons. The analysis also shows that the poorest prediction results (those for systems (1) and (2), see table 3) were obtained for those ternary systems for which the correlation of the corresponding binary data was poor (Table 2, (1), (2), (3), (4), (5) and 6). For ternary systems (Table 3, (3) and (4)) where the corresponding binary data were well correlated (Table 2, (7), (8), (9), (10), (11) and (12)), results of the prediction are very good (Table 3, (3) and (4)).

It is interesting to point out that for well correlated ternary systems (Table 3, (3) and (4)) and binary systems (Table 2, (7), (8), (9), (10), (11) and (12)), prediction of the VLE for binary systems from correlation of the ternary systems gives reasonable results which are only slightly worse than the opposite prediction. Such a prediction has no practical application, because the transfer from simple to more complicated systems is more important, but it serves to confirm the accuracy of the calculations.

CONCLUSIONS

The results obtained lead us to conclude that ternary VLE data for systems formed by hydrocarbons, i.e. systems where only physical intermolecular interactions are considered, are well correlated (with an accuracy close to that achieved experimentally) by equations based on the local composition concept (the NRTL, the UNIQUAC and the Wilson equations). This means that, irrespective of the kind and shape (benzene, cyclohexane, *n*-hexane, 1-heptene) of hydrocarbons, ternary VLE of these systems can be described taking into account only binary interactions; no ternary term is necessary for this purpose.

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 these equations can only be recommended when the binary data are well correlated by the equations. 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 if a good prediction of the ternary VLE data from the binary VLE data by an equation based on the local composition concept is required, the corresponding binary VLE data should be selected very carefully. They should be measured in the same laboratory using the same experimental procedure and at the same temperature as the ternary data 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.

It is advantageous to consider the obtained values of the adjustable parameters (Table 4). It can be seen that there is no systematic behaviour of the parameters of the correlation equations used with respect to the kind of

TABLE 4

Adjustable parameters for all equations used for calculations of binary and ternary VLE data

Equation:	NRTL $\alpha = 0.2$			UNIQUAC			Wilson		
Component:	1	2	3	1	2	3	1	2	3
Binary systems Benzene(1)–*n*-hexane(2)–cyclohexane(3) $T = 343.15$ K									
1	0.00	565.53	2271.12	0.00	−1000.46	12.69	0.00	1779.75	365.71
2	656.10	0.00	168.22	1637.26	0.00	106.11	−514.82	0.00	223.54
3	−1114.74	−32.26	0.00	335.99	−94.02	0.00	708.92	−2.29	0.00
Ternary system Benzene(1)–*n*-hexane(2)–cyclohexane(3) $T = 343.15$ K									
1	0.00	1303.76	702.00	0.00	−824.87	−589.49	0.00	1464.42	1045.27
2	−57.23	0.00	−54.13	1365.90	0.00	−141.92	−193.41	0.00	−1.22
3	300.71	−46.25	0.00	1073.41	86.15	0.00	−13.72	−42.23	0.00
Binary systems *n*-Hexane(1)–methylcyclopentane(2)–benzene(3) $T = 333.15$ K									
1	0.00	−363.75	−2051.61	0.00	−574.91	−13.51	0.00	−364.19	1346.13
2	406.16	0.00	723.48	619.83	0.00	1105.44	400.66	0.00	−58.37
3	4077.49	361.24	0.00	400.28	−586.33	0.00	480.40	1176.35	0.00
Ternary system *n*-Hexane(1)–methylcyclopentane(2)–benzene(3) $T = 333.15$ K									
1	0.00	−776.88	−1133.94	0.00	255.87	767.11	0.00	−38.91	589.59
2	900.13	0.00	−916.98	−252.62	0.00	400.11	145.44	0.00	666.00
3	2784.06	2077.65	0.00	−327.82	−31.01	0.00	985.44	439.96	0.00

Binary systems 1-Heptene(1)–*n*-heptane(2)–*n*-octane(3) $T = 328.15$ K

1	0.00	1256.15	4830.00	0.00	373.66	1649.84	0.00	216.67	−1019.93
2	−934.57	0.00	3974.61	−298.05	0.00	1348.26	21.68	0.00	−1089.65
3	−3070.97	−2775.27	0.00	−1146.52	−1010.53	0.00	2642.95	2105.07	0.00

Ternary system 1-Heptene(1)–*n*-heptane(2)–*n*-octane(3) $T = 328.15$ K

1	0.00	382.28	347.48	0.00	168.56	160.49	0.00	−897.34	3807.98
2	163.36	0.00	−192.77	−39.47	0.00	55.39	1978.99	0.00	2018.90
3	33.40	−42.79	0.00	−68.50	−89.92	0.00	−2153.32	−1573.99	0.00

Binary systems Cyclohexane(1)–*n*-heptane(2)–toluene(3) $T = 298.15$ K

1	0.00	−358.97	997.15	0.00	−664.11	571.25	0.00	1094.51	450.56
2	647.72	0.00	466.05	848.84	0.00	1098.95	−814.00	0.00	−121.25
3	247.41	641.40	0.00	−168.15	−691.78	0.00	839.12	1272.40	0.00

Ternary system Cyclohexane(1)–*n*-heptane(2)–toluene(3) $T = 298.15$K

1	0.00	2616.74	5906.58	0.00	1050.01	2562.67	0.00	795.10	−1053.20
2	−1870.98	0.00	−2380.03	−783.61	0.00	−697.73	−459.52	0.00	3031.75
3	−2873.34	5567.93	0.00	−1323.44	1343.79	0.00	3869.25	47.75	0.00

hydrocarbon, and it is impossible to attribute a physical meaning to them. They can be treated only as adjustable parameters which can be used only for these systems at the calculated temperature. Any extrapolation of their values with temperature or within the homologous series can lead to great errors in calculations of VLE. One can also see that although there is a difference between the binary parameters of the equations obtained from ternary VLE data and corresponding binary VLE data (Table 4), both sets of binary parameters adequately described the ternary VLE data. This is because of the form of the equations based on the local composition concept which cause local minima in the objective function which are very close to the global minimum and thus, similar results can be obtained for different sets of parameters.

As mentioned above, this work is part of a systematic investigation of the description of VLE in ternary and multicomponent systems and has concerned only the simplest group of systems, the hydrocarbons.

Even for this group of systems, it was difficult to find good, reliable and accurate ternary and binary VLE data which are absolutely essential in order to check the methods of correlation and prediction of ternary systems.

During collection of the data, it became evident that the substantial limitation in the description of the VLE in multicomponent systems is the scantiness of the experimental data.

For this reason, the recommendations resulting from the investigation in this field should include the encouragement to increase the effort to generate new experimental data, primarily for ternary systems.

The increasing range of the data needed for the full description of multicomponent systems makes the acquisition of the knowledge of the properties of these systems on the exclusive basis of experimental investigation unattainable [17]. Therefore, a comparative study of the prediction methods of VLE should help to answer the question as to what kind of experimental data is most appropriate for the prediction of the ternary interactions in solution.

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