ON THE APPLICABILITY OF THE UNIQUAC METHOD TO TERNARY LIQUID - LIQUID EQUILIBRIA

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Abstract

The use of the UNIQUAC method for correlating experimental data in ternary liquid-liquid equilibria and its predictive capability is considered. It is concluded that parameters obtained by direct correlating techniques have large uncertainties. Hence, for predictive purposes the original approach should be used.

Resumen

Se analiza el uso y la capacidad predictiva del método UNIQUAC para correlacionar datos experimentales de equilibrios ternarios en sistemas líquido-líquido. Se concluye que la aplicación de técnicas de correlación numérica directa implica márgenes de error altos. Por lo tanto, en la predicción de propiedades se debe mantener el tratamiento original

Introduction

Predicting physico – chemical properties of liquid mixtures continues to be an important issue for chemical engineering. In fact, since industrial operations involve chemical and physical operations that are carried out in increasingly complex solutions, a large number of papers devoted to the study of phase equilibria in mixtures of three and four components are yearly published. In most of this work correlation parameters, that are supposed to be used for predicting properties beyond the experimental range explored, are obtained through the use of methods that, employing some degree of heuristic thinking, were proposed some thirty years before, when the presently available calculation power was almost unthinkable.

However, the dramatic increase of speed and capacity of computers makes more necessary than ever before to make a caveat on the way that those methods are applied to specific cases. In particular, it must always be reminded that obtaining a set of parameters that minimize the difference between experimental data and the values produced by a correlating equation is not a goal in itself. As a matter of fact, if those parameters cannot predict properties for other systems or, at least, for the same mixture under different conditions, the obtention of such a set of numbers is only an idle exercise.

In view of these arguments we began, some time ago, discussing the consequence of the naïve use of correlations in predicting the behaviour of ternary mixtures[1-2] and,

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recently, we have shown that one of these techniques, namely the non-random two-liquid (NRTL) method leads to inconsistencies if naively applied[3]. In this paper we consider in some detail the results obtained when the other most commonly used approach, the universal quasi-chemical (UNIQUAC) method[4], is used for correlating phase equilibria.

The UNIQUAC method

This method, introduced by the mid 70's by Abrams and Prausnitz[4], is one of the most frequently employed tools in correlating experimental data of phase equilibria. The basic equation of the method stems out from an essentially heuristic approach based on an extension of the quasi-chemical theory of Guggenheim[5] which includes the introduction of the local area fraction as the primary concentration variable and the use of a combinatorial factor proposed by Staverman[6].

Within this approach a liquid is considered as a three - dimensional lattice of equi - spaced sites in which the immediate vicinity of a site is called a *cell*. Each molecule in the liquid is divided into attached segments such that each segment occupies one cell and it is assumed that the total number of cells is equal to the total number of segments. Thus, for a binary solution of components **1** and **2**, it is considered that there are, respectively, r_1 and r_2 segments for molecule of each component. Also, it is assumed that all segments have the same size but different external contact area. Hence, for any component **i** the number of nearest neighbours is zq_i where **z** is the coordination number of the lattice and q_i is a parameter proportional to the molecule´s external surface area. Assuming that only nearest neighbours can be considered, the following equation is obtained for the activity coefficient of component **i** in a multicomponent mixture with molar fraction x_i:

$$\ln\gamma_i = \ln(\phi_i/x_i) + (z/2)\, q_i \ln(\theta_i/\phi_i) + \varepsilon_i - (\phi_i/x_i)\sum_j x_j\lambda_j - q_i \ln(\sum_j \theta_j\tau_{ij}) +$$
$$q_i - q_i \sum_j(\theta_j\pi_{ij}/\sum_k\theta_k x_{kj}) \tag{1}$$

where θ_i is the average area fraction, defined by:

$$\theta_i = q_i x_i / \sum_j(q_j x_j) \tag{2}$$

ϕ_i is the average segment fraction:

$$\phi_i = r_i x_i / \sum_j(r_j x_j) \tag{3}$$

λ_j is given by:

$$\lambda_j = (z/2)(r_j - q_j) - (r_j - 1) \tag{4}$$

and τ_{ij} is defined by:

$$\tau_{ij} = \exp\{-[u_{ij} - u_{jj}]/RT\} \tag{5}$$

where u_{ij} is the interaction energy.

The structural parameters **r** and **q** are defined, respectively, as the van der Waals volume and area of the molecule relative to those of a standard segment which, in turn is, as the authors state, "somewhat arbitrarily" chosen through an approximation[4].

With these equations, and assuming a certain value for **z** it is possible to calculate activity coefficients for liquid - liquid (LL) equilibria of multicomponent systems employing only two adjustable parameters per binary mixture and, hence, the composition of coexisting phases could be predicted.

Application of the UNIQUAC method

It is clear, from the preceding section, that the authors aim when devising this method was to develop a tool that could predict the behaviour of a multi - component system employing data for all the the possible binaries in the mixture. Thus, in a typical case, the liquid - liquid equilibria of a given ternary (A-B-C) mixture is predicted employing the τ_{ij} parameters obtained from the A-B, B-C and C-A binaries.

Under this approach, if good experimental data for vapour - liquid or liquid - liquid binary equilibria are available, it should be possible to calculate the τ_{ij} parameters to be used for the ternary system. In this case, since only two adjustable parameters are obtained per binary, 15 or 20 experimental points could be enough for attaining reasonable accuracy in each case.

However, the evolution of performance and availability of computers allowed that every laboratory measuring ternary liquid - liquid equilibria could easily employ the UNIQUAC equations to directly correlate experimental data by directly finding a convenient set of **six** energy parameters. Thus, the idea of applying the UNIQUAC method employing binary energy parameters obtained from independent experimental measurements was generally disregarded in favour of the direct correlation approach.

This procedure is obviously risky due both to the method itself as well as to experimental limitations. The following observations underline the most significant uncertainties involved:

a) Direct application of the UNIQUAC method to ternary systems involves six τ_{ij} energy parameters and the assumption that a single **z** value is applicable to all binaries.
b) Direct correlation methods obtain seven adjustable parameters from data sets consisting of no more than 10, and most times in the literarure 7 or 8, experimental measurements of conjugated phases.

Therefore, and as pointed out in our analysis of the NRTL method[3], in order to assess on the reliability of the parameters obtained by direct correlation of experimental data it is necessary to verify two essential points:

1. Whether there is **coherence** regarding parameter evolution when chemical properties of the components are varied
2. Whether the obtained parameters allow to **predict** the behaviour of other systems or, at least, of the same system under different experimental conditions.

Analysis of published results

In order to look for the answers to the points made above, it is necessary to have data on ternary systems of the type A – B – C, where C runs along a homologue series and on ternary systems for which UNIQUAC calculations were performed for data at different temperatures. Now, although there is a large number of published studies on ternary systems that apply the UNIQUAC method, most of this work has been performed at a single temperature and on systems that have been chosen for particular reasons. Hence, there are few papers dealing with a given system at varying temperature and, still less, with ternary systems in which one component is varied over a homologue series. From this reduced set we have selected some recent papers that are representative of the obtention of UNIQUAC parameters by correlation techniques. In doing so we have looked for data that can yield information on the two mentioned points. Thus, we have selected data that are taken on:

i.   Ternary systems in which one of the components varies along an homologue series
ii. Ternary systems measured at different temperatures

Regarding the first case it is difficult to find studies in which liquid-liquid equilibria were studied in systems in which the third component runs at least over three members of a homologue series. Thus, the work of Letcher and Naicker[7] in which mixtures of water (W) nitriles and alcohols was chosen. The employed nitriles were 1,4 dicyanobutane (DCB); butanenitrile (BTN) and benzonitrile (BZN) while the alcohols were methanol (MOH); 1-ethanol (EOH) and 1-propanol (POH). Table 1 shows the energy parameters obtained by these authors with z = 10.

Table 1. u_{ij}-u_{jj} values in J/mol for Water (1) - Alkanol (2) - Nitrile (3) systems obtained with z = 10. Ref. [7]

	W-DCB-MOH	W-DCB-EOH	W-DCB-POH	W-BTN-MOH	W-BTN-EOH	W-BTN-POH	W-BZN-MOH	W-BZN-EOH	W-BZN-POH
u_{12}-u_{22}	-327	32	5	88	8	336	117	-638	332
u_{21}-u_{11}	-325	-6	4	-424	-231	-187	-373	225	-218
u_{13}-u_{33}	25	-30	-75	151	76	62	52	4	57
u_{31}-u_{11}	450	525	664	553	710	640	672	4540	800
u_{23}-u_{33}	69	-264	-360	15	-493	-58	-30	-17	-45
u_{32}-u_{22}	266	1906	1675	-84	621	-442	338	-283	-351

Regarding case ii. we have taken the results obtained when the systems isooctane + o-xylene + methanol[8], limonene + linalool + diethylenglycol[9], water + propanoic acid + methyl ethyl ketone[10], water + propanoic acid + methyl propyl ketone[10], water + methanol + *tert*-amyl ethyl ether[11], water + ethanol + *tert*-amyl ethyl ether[12], water + 2-propanol + ethyl acetate[13], water + 2-propanol + isopropyl acetate[13], water + 2-propanol + ethyl caproate[13] and water + tetradecane + 2-butyloxyethanol[14] were studied at different temperatures. Table 2 shows the energy parameters obtained in these papers.

Table 2. u_{ij}-u_{jj} *values in J/mol for several ternary systems at different temperatures*

System	T/K	Δu_{12}	Δu_{21}	Δu_{13}	Δu_{31}	Δu_{23}	Δu_{32}
Isooctane + o-xylene + methanol	283.15	1814.1	*-1698.5*	5510.4	*-28.7*	*2914.4*	*-412.6*
	308.15	-230.1	*-2457.7*	5180.2	*-76.7*	*5980.6*	*-3244.3*
	318.15	-1683.1	*-1942.5*	4643.7	*31.58*	*2749.5*	*-3923.1*
Limonene + linalool + diethylenglycol	298.15	*-846.9*	*-367.2*	*3830.3*	*369.5*	*-1662.8*	*1312.7*
	308.15	*-1608.8*	*421.4*	*3825.2*	*346.9*	*-1322.5*	*796.8*
	318.15	*-1427.0*	*209.7*	*4324.3*	*396.1*	*-1554.7*	*1297.8*
water + propanoic acid + methyl ethyl ketone	298.15	998.9	-1183.5	12.3	2732.4	*764.4*	*-1206.8*
	308.15	1738.9	-1292.4	172.1	2572.1	*1600.0*	*-2073.5*
	318.15	1868.0	-1727.6	291.8	2462.3	*727.1*	*-2073.5*
water + propanoic acid + methyl propyl ketone	298.15	*119.1*	*-687.0*	*953.1*	*2506.5*	*6201.8*	*-4064.4*
	308.15	*2896.1*	*-1747.2*	*774.2*	*3170.4*	*262.1*	*-921.7*
	318.15	*1675.3*	*-1408.1*	*1098.8*	*2573.4*	*3125.4*	*-921.7*
water + methanol + *tert*-amyl ethyl ether	298.15	4232.9	-1268.7	4297.9	4330.4	1857.1	-2966.5
	308.15	3215.8	-1525.3	5809.0	5441.1	4269.4	-5124.4
	318.15	3054.4	-1627.6	6436.9	5742.6	8470.3	-6200.4
water + ethanol + *tert*-amyl ethyl ether	298.15	*3829.9*	*-1810.4*	5281.0	*1924.1*	*-122.6*	-601.6
	308.15	*3859.2*	*-1701.4*	5563.9	*1447.2*	*2378.5*	-1870.8
	318.15	*3754.3*	*-1930.1*	5794.0	*1968.4*	*1721.7*	-1989.3
water + 2-propanol + ethyl acetate	283.15	2389.8	*-1018.8*	*541.7*	*3711.9*	*1812.5*	-305.8
	308.15	2445.9	*-1156.3*	*1094.0*	*2789.9*	*6627.0*	-2029.5
	323.15	2586.5	*-1099.6*	*1078.6*	*2809.9*	*6513.1*	-2064.1
water + 2-propanol + isopropyl acetate	283.15	*2654.2*	*-1264.4*	*1204.9*	*4336.0*	3345.3	*-1501.5*
	308.15	*3124.9*	*-1153.0*	*820.5*	*4674.9*	3216.8	*-653.1*
	323.15	*2300.4*	*-1292.9*	*1160.4*	*3355.4*	1607.7	*-1651.7*
water + 2-propanol + ethyl caproate	283.15	*3527.6*	-1544.1	*2085.2*	*7238.4*	*157.0*	-578.3
	308.15	*3728.6*	-1647.9	*1630.3*	*7684.8*	*158.0*	-745.3
	323.15	*3627.8*	-2087.4	*3026.2*	*5464.9*	*1758.7*	-3058.8
water + tetradecane + 2-butyloxyethanol	298.15	*1906.5*	*-883.0*	1085.9	*13319.7*	*-296.6*	*1277.1*
	308.15	*1621.3*	*-571.9*	2155.1	*15930.4*	*-930.4*	*2121.8*
	318.15	*2960.7*	*-1291.2*	3081.3	*14483.7*	*-767.0*	*1803.4*

The results shown here are quite representative of what can be found in most of the published material on liquid - liquid equilibria in ternary systems and, as it is readily seen, UNIQUAC parameters obtained by correlation with experimental data yield values that do not show coherent behaviour with respect to what should be expected.

A first point to be made in this sense is that the energy parameters in the UNIQUAC method are not independent[15]. In fact, since:

$$u_{ij} = u_{ji} \tag{5}$$

it is readily seen that the method implies:

$$\Delta u_{12} + \Delta u_{13} + \Delta u_{23} - \Delta u_{32} - \Delta u_{31} - \Delta u_{21} = \Xi = 0 \qquad (6)$$

In all considered cases Ξ is not only different from zero but in average, and as shown in Table 3, more than doubles the mean value of the obtained Δu_{ij}.

Table 3. *Internal consistency of Δu_{ij} parameters obtained by direct correlation of experimental data in several systems*

System	Ref.	$\Xi / \Delta u^{\#}_{ij}|$
Water + methanol + DCB (298.15 K)	7	0.65
Water + methanol + BN (298.15 K)	7	1.36
Water + methanol + BZN (298.15 K)	7	2.94
Water + ethanol + DCB (298.15 K)	7	4.70
Water + ethanol + BN (298.15 K)	7	1.94
Water + ethanol + BZN (298.15 K)	7	4.03
Water + 1-propanol + DCB (298.15 K)	7	4.12
Water + 1-propanol + BN (298.15 K)	7	1.22
Water + 1-propanol + BZN (298.15 K)	7	1.91
Isooctane + o-xylene + methanol (283.15 K)	8	3.94
Isooctane + o-xylene + methanol (308.15 K)	8	1.82
Isooctane + o-xylene + methanol (318.15 K)	8	0.05
Limonene + linalool + diethylenglycol (298.15 K)	9	1.88
Limonene + linalool + diethylenglycol (308.15 K)	9	1.77
Limonene + linalool + diethylenglycol (318.15 K)	9	3.94
water + propanoic acid + methyl ethyl ketone (298.15 K)	10	1.84
water + propanoic acid + methyl ethyl ketone (308.15 K)	10	1.73
water + propanoic acid + methyl ethyl ketone (318.15 K)	10	1.02
water + propanoic acid + methyl propyl ketone (298.15 K)	10	2.08
water + propanoic acid + methyl propyl ketone (308.15 K)	10	2.72
water + propanoic acid + methyl propyl ketone (318.15 K)	10	3.41
water + methanol + *tert*-amyl ethyl ether (298.15 K)	11	3.40
water + methanol + *tert*-amyl ethyl ether (308.15 K)	11	2.86
water + methanol + *tert*-amyl ethyl ether (318.15 K)	11	2.61
water + ethanol + *tert*-amyl ethyl ether (298.15 K)	12	3.84
water + ethanol + *tert*-amyl ethyl ether (308.15 K)	12	3.45
water + ethanol + *tert*-amyl ethyl ether (318.15 K)	12	3.26
water + 2-propanol + ethyl acetate (283.15 K)	13	4.37
water + 2-propanol + ethyl acetate (308.15 K)	13	3.63
water + 2-propanol + ethyl acetate (323.15 K)	13	3.65
water + 2-propanol + isopropyl acetate (283.15 K)	13	4.25
water + 2-propanol + isopropyl acetate (308.15 K)	13	4.41
water + 2-propanol + isopropyl acetate (323.15 K)	13	2.89
water + 2-propanol + ethyl caproate (283.15 K)	13	4.32
water + 2-propanol + ethyl caproate (308.15 K)	13	4.16
water + 2-propanol + ethyl caproate (323.15 K)	13	2.75
water + tetradecane + 2-butyloxyethanol (298.15 K)	14	5.25
water + tetradecane + 2-butyloxyethanol (308.15 K)	14	5.23
water + tetradecane + 2-butyloxyethanol (318.15 K)	14	4.99

Taking now the case of compounds of a same homologue series, if data in Table 1 are considered, it is apparent that there is no rationale behind the change in the resulting values for Δu_{ij} as it is clear when, for example, the obtained Δu_{12} parameter is considered.

By the other hand, the values in Table 2 demonstrate that trying to estimate equilibrium compositions for a given system at other temperatures would yield a very uncertain result since, in most cases, indicated with bold italics, the change of Δu_{ij} with temperature is not monotonous and, hence, extrapolation, or interpolation, of these parameters will have serious limitations.

In order to have some further insight on the limitations of the UNIQUAC direct correlation method, we have performed some calculations on published data. With this purpose we have taken one of the ternary systems studied in Ref. [9], namely, the limonene (1) + linalool (2) + diethylenglycol (3) mixture and employing the experimental data shown in Table 4, obtained the u_{ij} - u_{jj} parameters.

Table 4. *Experimental tie-lines of the limonene (1) + linalool (2) + diethylenglycol (3) system from Ref. [8]*

Tie-line	x_{11}	x_{21}	x_{13}	x_{23}
N°	-----	-----	-----	-----
T = 298.15 K				
1	0.9868	0.0000	0.0118	0.0000
2	0.9597	0.0290	0.0145	0.0195
3	0.8756	0.0947	0.0237	0.0582
4	0.8078	0.1341	0.0360	0.0782
5	0.7428	0.1673	0.0496	0.0987
6	0.6125	0.2130	0.0813	0.1330
T = 308.15 K				
1	0.9897	0.0000	0.0119	0.0000
2	0.9511	0.0316	0.0155	0.0185
3	0.9266	0.0559	0.0200	0.0321
4	0.8898	0.0820	0.0221	0.0446
5	0.8491	0.1138	0.0278	0.0613
6	0.7726	0.1558	0.0405	0.0854
7	0.6199	0.2209	0.0740	0.1267
8	0.5674	0.2336	0.0913	0.1398
T = 318.5 K				
1	0.9892	0.0000	0.0100	0.0000
2	0.9004	0.0784	0.0152	0.0375
3	0.8152	0.1340	0.0262	0.0641
4	0.7069	0.1984	0.0492	0.1008
5	0.6061	0.2294	0.0689	0.1227
6	0.5060	0.2451	0.0947	0.1493

In doing this, we have taken z = 10 and the energy parameters were obtained by minimizing the objective function:

$$\Omega = \sum_{k=1,n} \sum_{j=1,2} \sum_{i=1,3} (x_{ijk} - x^*_{ijk})^2 \qquad (7)$$

where x_{ijk} is the experimental mole fraction of component **i** in the **j** phase, for the **kth** tie line and x^*_{ijk} is the calculated value.

These calculations were carried out in four different conditions:

I.   Employing all data in Ref. [9] using the steepest descent method.
II. Employing all data in Ref. [9] using the Newton Raphson method.
III. Employing all data in Ref. [9] with different z values.
IV. Taking out one of the experimental values and working with the N-1 remaining data.

The obtained u_{ij} - u_{jj} differences indicate that there is no significant difference in the results obtained with either of the employed numerical methods and that changing the z value affects the energy parameteyrs in less than 1%. However, if the number of experimental points employed is diminished in one datum, significant differences arise as shown in Tables 5 - 7.

Table 5. *u_{ij}-u_{jj} values in J/mol obtained at 298.15 K for the system limonene (1) - linalool (2) - diethylenglycol (3) deleting one of the tie-lines in Ref. [8].*

	All data included	Tie line 1 deleted	Tie line 2 deleted	Tie line 3 deleted	Tie line 4 deleted	Tie line 5 deleted	Tie line 6 deleted
u_{12}-u_{22}	3533.3	5717.2	3497.1	3691.3	3536.7	3459.4	3390.5
u_{21}-u_{11}	3446.1	4666.0	3285.6	3419.7	3438.6	3433.9	3424.2
u_{13}-u_{33}	-2117.9	-2957.4	-2003.9	-2209.0	-2112.3	-2052.5	-1995.2
u_{31}-u_{11}	-1023.9	-1957.4	-963.47	-1160.2	-1021.5	.942.16	-867.85
u_{23}-u_{33}	355.20	323.80	376.67	362.20	360.82	358.70	354.83
u_{32}-u_{22}	1536.4	2375.0	1628.5	1682.6	1549.6	1494.6	1448.5
Ω	0.292059	0.008566	0.131679	0.238367	0.291960	0.277116	0.251939

Table 6. u_{ij}-u_{jj} *values in J/mol obtained at 308.15 K for the system limonene (1) - linalool (2) - diethylenglycol (3) deleting one of the tie-lines in Ref. [8].*

	All data	Tie line 1 deleted	Tie line 2 deleted	Tie line 3 deleted	Tie line 4 deleted	Tie line 5 deleted	Tie line 6 deleted	Tie line 7 deleted	Tie line 8 deleted
u_{12}-u_{22}	3896.2	3709.8	3900.8	3910.6	3940.2	4037.6	3957.8	3809.3	3790.5
u_{21}-u_{11}	3658.6	3774.2	3707.3	3593.6	3647.5	3645.9	3654.5	3640.9	3641.0
u_{13}-u_{33}	-2257.1	-2312.0	-2244.5	-2250.5	-2283.3	-2326.2	-2259.3	-2191.1	-2190.2
u_{31}-u_{11}	-1087.2	-1066.4	-1054.3	-1116.1	-1123.3	-1191.7	-1095.8	-1004.6	-1002.1
u_{23}-u_{33}	325.9	292.17	306.48	345.68	327.45	334.95	329.61	327.62	327.62
u_{32}-u_{22}	1733.4	1473.5	1690.1	1797.0	1776.3	1861.2	1796.5	1682.5	1665.1
Ω	0.1926	0.1153	0.1576	0.1360	0.1818	0.1608	0.1803	0.1740	0.1670

Table 7. u_{ij}-u_{jj} *values in J/mol obtained at 318.15 K for the system limonene (1) - linalool (2) - diethylenglycol (3) deleting one of the tie-lines in Ref. [8].*

	All data included	Tie line 1 deleted	Tie line 2 deleted	Tie line 3 deleted	Tie line 4 deleted	Tie line 5 deleted	Tie line 6 deleted
u_{12}-u_{22}	4243.4	6403.8	4287.8	4391.8	4239.3	4127.9	4125.5
u_{21}-u_{11}	3664.9	4696.3	3557.1	3645.3	3643.2	3645.5	3649.3
u_{13}-u_{33}	-2322.1	-2703.2	-2337.0	-2377.6	-2318.9	-2246.6	-2236.7
u_{31}-u_{11}	-1223.7	-1819.1	-1291.8	-1310.4	-1223.7	-1133.3	-1116.8
u_{23}-u_{33}	450.21	323.12	453.36	464.08	466.94	457.92	450.50
u_{32}-u_{22}	2127.1	3199.0	2229.1	2277.8	2148.4	2053.8	2046.8
Ω	0.22718	0.06558	0.08266	0.21364	0.20733	0.19455	0.19048

Discussion

As it has been said, the UNIQUAC method was originally developed as a means to calculate equilibria in multicomponent systems employing u_{ij} - u_{jj} data obtained from measurements in binary systems. The use of direct correlation techniques for calculating energy parameters from experimental measurements in ternary systems leads to inconsistencies with respect to u_{ij} - u_{jj} dependence on chemical nature of the third component and on temperature.

These inconsistencies appear in all cases, independently of the mathematical method employed for determining the u_{ij} - u_{jj} set of values. In fact, the cases shown here use three different methods: an objective function similar to the one employed in this paper in the case of Ref. [7]; an algorithm developed by García Sánchez et al.[16] employed in Ref. [8] and the correlation method proposed by Sørensen[17] applied in Ref. [9].

Our recalculation of energy parameters from the data in Ref. [9] shows that the existence of local minima makes the result dependent of the employed method: application of the objective function approach gives different results from those of the Sørensen program. However, a most significant result stems from the fact that, as shown in Tables 5 - 7, the resulting u_{ij} - u_{jj} set of values depends on the number of experimental points available and the differences in them can be of more than 50% as seen in the case of the data at 298.15 if the first tie line is not included in the calculation. Anyway, and as it is shown in Table 6, where up to 8 experimental points were available, differences between the u_{ij} - u_{jj} values when a tie line is deleted do not allow to write these results with more than two significant figures. This should not be an unexpected result since a set of six parameters is correlated with 10 or less experimental points.

It is thus concluded that u_{ij} - u_{jj} parameters obtained by direct correlation of experimental data with the UNIQUAC equations can be in serious error and that if the method is to be applied with the aim of predicting physical properties of mixtures, the original approach involving the use of experimental data for binaries should be employed with due caution.

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