Liquid−Liquid−Solid Equilibria for the Quaternary System Water + Acetone + 1-Butanol + Sodium Chloride at 25 °C

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The liquid−liquid−solid equilibria for the quaternary system water + acetone + 1-butanol + sodium chloride at 25 °C have been determined. Tie-line and tie-triangle data for this system have been correlated using a modification of the Eisen−Joffe equation.

Introduction

Butanol can be obtained through fermentation of grain and molasses, acting as self-inhibitor, and acetone can be present in the fermentation broth (Malinowski and Daugulis, 1994). The salting-out effect can be used to improve the extraction of some solutes by modifying the solute distribution between two liquid phases. Therefore, the study of the equilibria in the liquid−liquid−solid quaternary system water + acetone + 1-butanol + sodium chloride can have an application in the extractive fermentation yield.

As shown in a previous paper (Ruiz and Marcilla, 1993), the methodology used to study the water−solute−solvent−inorganic salt systems has not always been adequate nor systematic, and it could lead to doubtful conclusions. These authors suggested a methodology for the determination of the equilibrium data of these types of systems, and they applied it to the water + ethanol + 1-butanol + sodium chloride system (Marcilla et al., 1995a) and the water + ethanol + acetone + sodium chloride system (Marcilla et al., 1995b). In the first system, water and 1-butanol are partially miscible, whereas in the second, water, ethanol, and acetone are miscible in all proportions, the two-liquid region appearing only when the salt is present. The methodology described had to be adapted to the different behavior of these systems.

In the present paper this method has been applied to the water + acetone + 1-butanol + sodium chloride system at 25 °C, where the quaternary two-liquid region is the result of two contributions: the partial miscibility of water 1-butanol and the partial miscibility of water and acetone when the salt is present.

The objective of the present work is to determine the solubility surface which separates one-liquid and two-liquid regions, tie-lines in two-liquid region, tie-triangles in the two-liquid−one-solid region, and the solubility surface which separates the one-liquid and one-liquid−one-solid regions. A modification of the Eisen−Joffe equation (Marcilla et al., 1995a,b) has been applied for the correlation of the tie-line and tie-triangle data.

Experimental Section

Chemicals. The chemicals used in this study were water, acetone, 1-butanol, sodium chloride, and 1-propanol (used as internal standard in the chromatographic analysis). The water used was bidistilled, acetone (Merck) was dried reagent grade, and 1-butanol and 1-propanol were analytical reagent grade (Merck). The contents of possible volatile impurities were examined by gas−liquid chromatography. The purity of all compounds was minimum 99.5%.

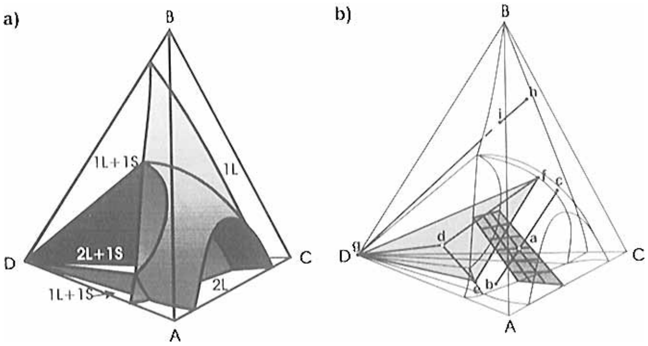

Figure 1. (a) Qualitative representation of the liquid−liquid−solid equilibrium in water + acetone + 1-butanol + sodium chloride at 25 °C. (b) Representation of the initial mixture network to determine the quaternary regions.

Analytical Methods. Equilibrium measurements were made by preparing mixtures of known overall composition, stirring intermittently for 48 h, and allowing the mixtures to settle for 24 h at a constant temperature of (25 ± 0.1) °C. At the end of each experiment, samples were taken from the liquid phases and analyzed. Water, acetone, and 1-butanol were determined by gas chromatography using a Shimadzu gas chromatograph GC-14A with an AOC-14 auto injector and an electronic integrator C-R64 Chromatopac. The column used was a 2 m × $^1/_8$ in. Porapack Q 80/100, and the column temperature was 180 °C. The helium flow rate was 15 $cm^3 \cdot min^{-1}$. The internal standard method was applied for the quantitative analysis, using 1-propanol as the standard. For the analysis of water, acetone, and 1-butanol in organic phases the detection was carried out by a thermal conductivity detector (TCD). When 1-propanol was added to the aqueous phases, sodium chloride precipitated. These samples were diluted with water until transparency, acetone and 1-butanol contents were determined using a flame ionization detector (FID), and the water content was calculated by mass balance.

Salt was determined by two different methods depending on its concentration. In samples with concentrations higher than 0.5% (mass) it was gravimetrically determined by evaporating the solution at 105 °C, until constant mass. Samples with lower concentrations were titrated with $AgNO_3$. At low salt concentrations the error involved with the gravimetrical method is large.

Duplicates of each heterogeneous mixture were prepared and analyzed. The relative accuracy of the mass fraction

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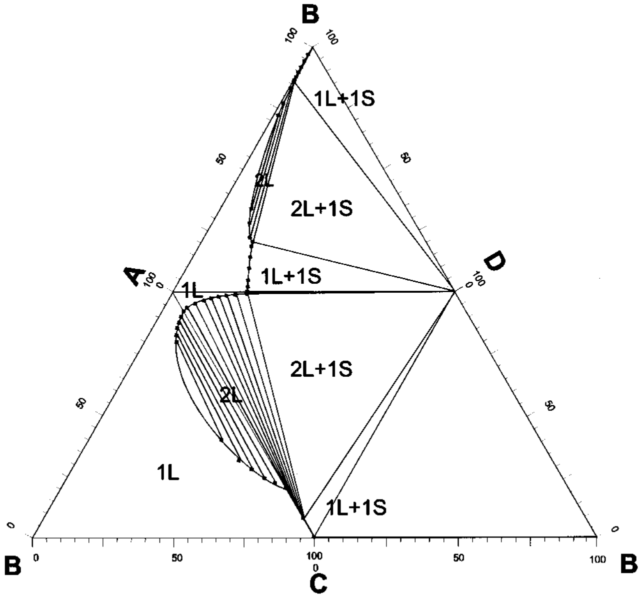

Figure 2. Representation of the four ternary systems: water + acetone + 1-butanol, water + acetone + sodium chloride, water + 1-butanol + sodium chloride, and acetone + 1-butanol + sodium chloride at 25 °C.

measurements of each of the components was approximately 1%.

In order to test the validity of the results obtained, the following mass balances were considered:

$$(w_A)_o = (A'/M')(w_A)_{aq} + (O'/M')(w_A)_{or}$$

$$(w_B)_o = (A'/M')(w_B)_{aq} + (O'/M')(w_B)_{or}$$

$$(w_C)_o = (A'/M')(w_C)_{aq} + (O'/M')(w_C)_{or}$$

$$(w_D)_o = (A'/M')(w_D)_{aq} + (O'/M')(w_D)_{or} + (S'/M') \quad (1)$$

where M' is the mass of the initial mixture, A', O', and S' are the masses of the aqueous phase, organic phase, and solid phase, respectively, $(w_i)_o$ is the mass fraction of component i (A = water, B = acetone, C = 1-butanol, and sodium chloride) in the initial mixture, and $(w_i)_p$ is the mass fraction of component i in phase p (aq = aqueous phase, or = organic phase). Obviously, $S' = 0$, in the two-liquid region.

With these four equations, it is possible to calculate the values of (A'/M'), (O'/M'), and (S'/M') from the experimental values $(w_i)_p$ by a least-squares fitting: if **M** is the matrix formed by the values of $(w_i)_o$, **K** is the transformation matrix (formed by the values of $(w_i)_p$), and **P** is the matrix formed by the relative masses of each phase ((A'/M'), $(O'/$), and (S'/M')), the previous system can be written as

$$\mathbf{M} = \mathbf{K}\cdot\mathbf{P} \quad (2)$$

Mathematical calculations lead to the expression

$$\mathbf{P} = (\mathbf{K}^t\cdot\mathbf{K})^{-1}\cdot\mathbf{K}^t\cdot\mathbf{M} \quad (3)$$

where $\mathbf{K}^t$ is the transpose matrix of **K** and $(\mathbf{K}^t\cdot\mathbf{K})^{-1}$ is the inverse matrix of $(\mathbf{K}^t\cdot\mathbf{K})$.

Thus, the values of (A'/M'), (O'/M'), and (S'/M') (matrix **P**), which minimize the errors of the previous system, have been calculated. The absolute value of the difference of the sum $((A'/M') + (O'/M') + (S'/M'))$ to 1 was always lower than 0.5%.

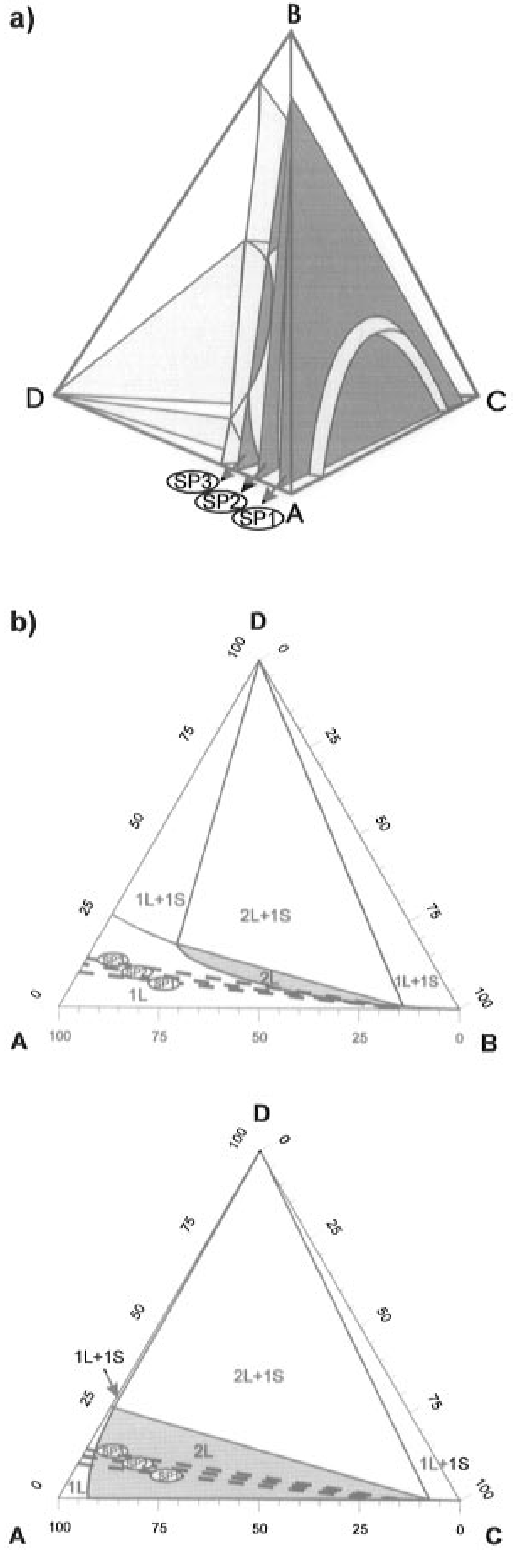

Figure 3. Representation of the sectional planes studied: (a) qualitative positions in the tetrahedron; (b) quantitative intersections with the ternaries water + acetone + sodium chloride and water + 1-butanol + sodium chloride.

Table 1. Cloud Points as Mass Fraction (w_i) for the Water (A) + Acetone (B) + 1-Butanol (C) + Sodium Chloride (D) System at 25 °C, Calculated in Sectional Plane 1 (SP1) [(90% A + 10% D) + (85% B + 15% A) + (80% C + 20% A)], Sectional Plane 2 (SP2) [(87.8% A + 12.2% D) + (85% B + 15% A) + (82.2% C + 17.8% A)], and Sectional Plane 3 (SP3) [(86% A + 14% D) + (85% B − 15% A) + (84% C + 16% A)]

SP1				SP2				SP3			
$100w_A$	$100w_B$	$100w_C$	$100w_D$	$100w_A$	$100w_B$	$100w_C$	$100w_D$	$100w_A$	$100w_B$	$100w_C$	$100w_D$
87.2	0	3.26	9.59	85.6	0	2.61	11.8	84.1	0	2.33	13.6
83.0	4.28	3.68	9.04	77.0	9.10	3.58	10.4	74.4	10.6	3.22	11.7
75.2	11.7	5.04	7.99	69.8	16.1	4.90	9.16	65.5	19.5	4.99	9.96
68.0	17.4	7.57	7.01	62.7	21.9	7.45	7.95	64.4	20.6	5.24	9.73
60.6	22.2	11.2	5.98	55.2	27.5	10.5	6.68	58.8	26.0	6.59	8.63
53.4	26.1	15.5	4.99	48.3	32.9	13.3	5.50	54.0	30.6	7.82	7.66
46.1	31.0	18.9	3.99	40.9	40.2	14.7	4.25	46.3*	39.1*	8.40*	6.16*
38.9	35.6	22.5	3.00	37.3*	45.1*	14.0*	3.66*	41.0*	46.8*	7.14*	5.11*
33.5	38.0	26.3	2.25	33.7*	49.7*	13.6*	3.05*	38.6*	50.9*	5.87*	4.64*
29.4	38.5	30.5	1.66	30.0*	54.0*	13.6*	2.44*	35.9*	60.0*	0*	4.12*
26.9	35.6	36.2	1.29	25.8*	56.1*	16.4*	1.71*	22.3*	55.3*	21.0*	1.40*
24.7	30.5	44.0	0.92	24.6*	49.3*	24.7*	1.46*	21.6*	51.0*	26.1*	1.25*
23.0	22.9	53.5	0.62	23.1	42.7	33.0	1.17	21.1	64.6	13.1	1.18
21.6	14.8	63.3	0.35	21.9	36.1	41.1	0.93	20.9	71.2	6.75	1.14
20.7	8.25	70.9	0.17	20.9	29.0	49.4	0.71	20.5	44.9	33.5	1.01
20.2	0	79.8	0.030	20.1	21.9	57.5	0.52	19.8	79.3	0	0.94
				19.3	15.1	65.3	0.35	19.7	37.4	42.2	0.82
				18.6	7.30	74.0	0.17	18.6	26.4	54.4	0.58
				17.8	0	82.2	<0.06	17.5	15.2	67.0	0.33
								16.9	7.23	75.6	0.20

Values with asterisks refer to iso-optical mixtures.

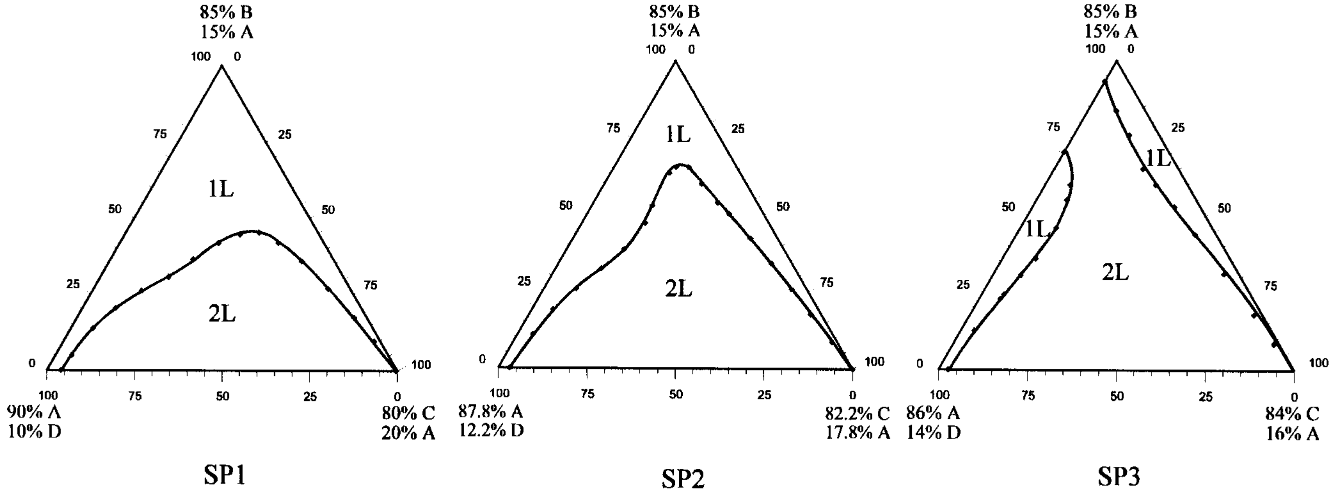

Figure 4. Representation of the solubility curves obtained in the three sectional planes studied.

To calculate equilibrium points, the cloud-point method (Ruiz and Prats, 1983a) was applied. Mixtures prepared close to the solubility surface in the heterogeneous region were titrated with mixtures close to the binodal curve, but in the homogeneous region. The transition from cloudiness to transparency indicates the end point of the titration. The system was contained in a thermostatic bath at (25.0 ± 0.1) °C and was continuously stirred by means of a magnetic stirrer.

Experimental Methodology. In a previous paper (Marcilla et al., 1995a) a method for determining the liquid−liquid−solid equilibrium in water + solute + solvent + inorganic salt was suggested and discussed, showing possible sources of error in other methodologies which consider these types of systems as pseudoternary systems. In the present paper this systematic method is applied to the system water + acetone + 1-butanol + sodium chloride.

Figure 1a shows a qualitative representation of the above system or similar systems, in which the following equilibrium regions can be distinguished: the two-liquid region, zone (2L); the two-liquid−one-solid region, zone (2L + 1S); the one-liquid region, zone (1L); and the one-liquid−one-solid region, zone (1L + 1S).

In order to study this equilibrium extensively, all surfaces, tie-lines, and tie-triangles in the different equilibrium regions have to be determined. Figure 1b shows a schematic representation of the methodology used, where the initial mixtures (a, d, h) and the compositions of the equilibrium phases (b−c, e−f−g, i−g) have been indicated.

In the 2L zone, an initial mixture, represented by point a, splits into two liquid phases (b and c).

In the 2L + 1S zone, an initial mixture, represented by point d, splits into two liquid phases (e and f) and one solid phase (g).

In order to study the 1L + 1S region only the determination of the solubility surface which separates the 1L and 1L + 1S region is required. When a ternary mixture such as h is oversaturated with salt, two phases in equilibrium appear: one liquid phase (i) and one solid phase (g).

Then, preparing initial mixtures such as a, d, and h and analyzing the compositions of the b−c, e−f−g, and i phases, one can determine all equilibrium data. In addition, the solubility surface which separates 2L and 1L regions has been determined by applying the cloud-point method to selected sectional planes which intercept this surface. The initial mixture points (as *a* in Figure 1b) to obtain the tie-

Table 2. Initial Mixtures Prepared in Sectional Plane 1 (SP1), (90% A + 10% D) + (85% B + 15% A) + (80% C + 20% A); Sectional Plane 2 (SP2), (87.8% A + 12.2% D) + (85% B + 15% A) + (82.2% C + 17.8% A); and Sectional Plane 3 (SP3), (86% A + 14% D) + (85% B + 15% A) + (84% C + 16% A) and Tie-Line Data Obtained as Mass Fraction (w_i) for the Water (A) + Acetone (B) + 1-Butanol (C) + Sodium Chloride (D) System at 25 °C

Initial Mixtures

$100w_A$	$100w_B$	$100w_C$	$100w_D$
	SP1		
55.03	0	39.96	5.01
50.95	8.51	36.05	4.49
47.02	17.00	31.98	4.00
46.51	25.48	24.01	4.00
46.24	29.74	20.02	4.00
	SP2		
52.84	0	41.06	6.11
49.00	8.57	36.94	5.49
48.35	29.74	16.42	5.49
46.63	16.99	31.26	5.12
44.96	25.55	24.61	4.88
	SP3		
51.03	0	41.96	7.01
47.35	12.77	33.58	6.30
43.69	25.46	25.25	5.60
43.62	33.99	16.78	5.60
40.00	42.48	12.62	4.90
36.40	50.89	8.51	4.20
32.88	59.42	4.19	3.51
32.74	63.76	0	3.50

Tie-Line Data

aqueous phase				organic phase			
w_A	$100w_B$	$100w_C$	$100w_D$	$100w_A$	$100w_B$	$100w_C$	$100w_D$
			SP1				
87.8	0	3.43	8.72	14.0	0	85.9	0.13
82.5	5.28	3.73	8.54	18.3	11.4	70.0	0.29
78.9	8.65	4.01	8.44	23.6	22.3	53.4	0.62
70.7	15.4	6.08	7.78	31.5	31.1	35.9	1.50
			SP2				
86.3	0	2.64	11.1	12.6	0	87.2	0.14
81.7	4.90	2.77	10.6	16.7	13.0	70.0	0.30
64.9	20.1	6.10	8.87	33.4	37.6	26.9	2.20
77.2	9.13	3.35	10.3	21.5	23.5	54.4	0.58
72.0	13.8	4.25	9.90	26.7	33.5	38.6	1.16
			SP3				
84.7	0	2.33	13.0	11.2	0	88.7	0.15
78.1	6.88	2.72	12.3	17.5	18.5	63.6	0.42
71.7	13.0	3.38	11.9	23.0	34.3	41.8	0.95
66.5	18.2	3.60	11.7	27.3	43.3	27.8	1.62
61.8	23.2	3.56	11.4	27.7	52.6	17.5	2.12
57.8	28.5	2.85	10.9	29.0	57.3	11.2	2.54
54.9	33.2	1.59	10.3	27.8	63.8	5.90	2.43
51.5	39.3	0	9.14	28.3	69.3	0	2.44
61.7	21.5	9.60	7.25	36.0	32.6	28.7	2.73

lines in the 2L region have been prepared in these sectional planes where the cloud-point method was applied. These mixture points, in different sectional planes, form a network similar to that shown in Figure 1b.

Heterogeneous samples splitting into two iso-optical liquid phases were detected in the 2L region. When this phenomenon occurred, the heterogeneous sample had a transparency similar to that of a homogeneous phase; therefore, the cloud-point method is not useful to define the solubility surface. In those cases, different samples close to the solubility surface were prepared and a dye which concentrates in one phase was added. If the initial sample was heterogeneous, it split into two phases with different colors. If the initial sample was homogeneous, no different colors were detected. This process was repeated until a homogeneous sample and a heterogeneous sample were found whose concentrations differed less than 1% in each component.

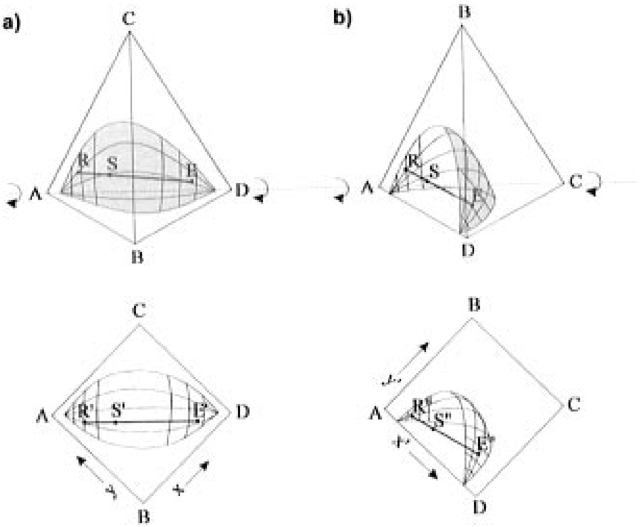

Figure 5. Equilibrium data representation for quaternary systems: (a) projection onto a plane parallel to edges A−C and B−D; (b) projection onto a plane parallel to edges A−C and B−D.

Results

Ternary Systems. Three of the four ternary systems included in the quaternary system studied in this paper have been published in previous papers: water + acetone + 1-butanol (Ruiz and Prats, 1983b); water + 1-butanol + sodium chloride (Marcilla et al., 1995a); water + acetone + sodium chloride (Marcilla et al., 1995b).

Acetone + 1-Butanol + Sodium Chloride. All tie-lines in this system pass through the sodium chloride vertex, and consequently, the data of the solubility surface are sufficient to represent this ternary. These data were obtained by titration with $AgNO_3$. The results obtained by this method are only approximate, due to the low solubility of sodium chloride in butanol (0.010%) and acetone (<10 ppm). So, when the percentage of 1-butanol in the sample is in the range 90−70%, the solubility of salt is around 0.008−0.009%. This value decreases when the percentage of acetone in the sample increases (around 0.005% in samples with 55% of 1-butanol, around 0.002% in samples with 40% of 1-butanol and <10 ppm in samples with less than 30% of 1-butanol). It has not been considered to determinate these values in a more precise way.

Figure 2 shows the four ternary systems. The solubility curve of the ternary system acetone + 1-butanol + sodium chloride is hardly distinguished in the figure. It appears very close to the axis 1-butanol + acetone as a consequence of the low solubility of sodium chloride in these solvents.

Quaternary System. Three sectional planes were selected to study the 2L region (A = water, B = acetone, C = 1-butanol, and D = sodium chloride):

SP1: (90% A + 10% D) + (85% B + 15% A) + (80% C + 20% A)

SP2: (87.8% A + 12.2% D) + (85% B + 15% A) + (82.2% C + 17.8% A)

SP3: (86% A + 14% D) + (85% B + 15% A) + (84% C + 16% A)

The position of these sectional planes in the tetrahedron is shown in Figure 3a,b.

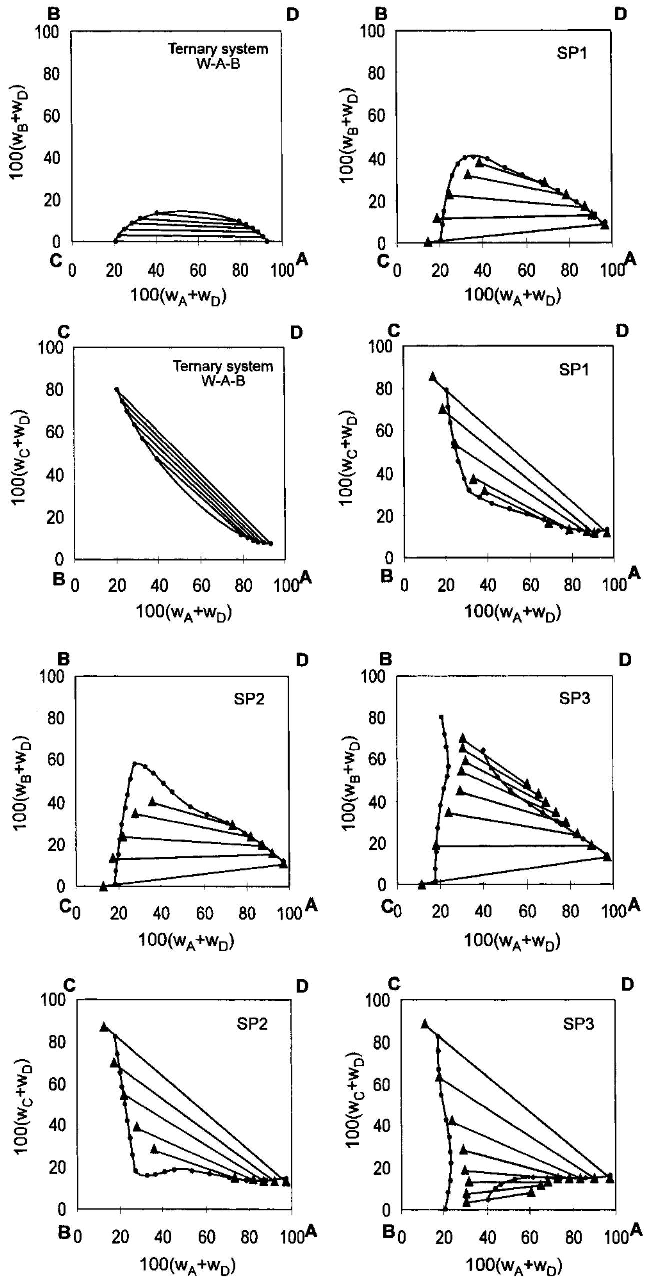

Figure 6. Solubility curves (●) and tie-lines (▲) in the ternary system water + acetone + 1-butanol and the sectional planes selected, in two Cruickshank projections.

Table 1 shows the compositions of the solubility curves obtained, by the cloud-point method, in these planes (those values marked by * were obtained using a dye, as explained in the Experimental Methodology section). These solubility curves are the intersection between the solubility surface which separates the 1L and 2L regions and the corresponding sectional planes. These results are represented in Figure 4. As can be seen, these sectional planes illustrate the evolution of the 2L region clearly.

Table 2 shows the initial mixtures prepared in the sectional planes SP1, SP2, and SP3 and the tie-lines obtained. The experimental results have been represented using Cruickshank projections (Cruickshank et al., 1950). In the Cruickshank projection the tetrahedron is projected onto a plane parallel to two nonintersecting edges. Figure 5a shows the immiscible region for the system A + B + C + D containing a partly miscible pair A−D. The tetrahedron is placed in such a way that the edge A−D lies in the plane of the paper; the projection is drawn in the paper plane after small rotation around the A−D axis until the edge B−C is parallel to the projection plane. A mixture of composition w_A, w_B, w_C, and w_D is located in this projection using the relations

$$x = w_D + w_C$$

$$y = w_A + w_C$$

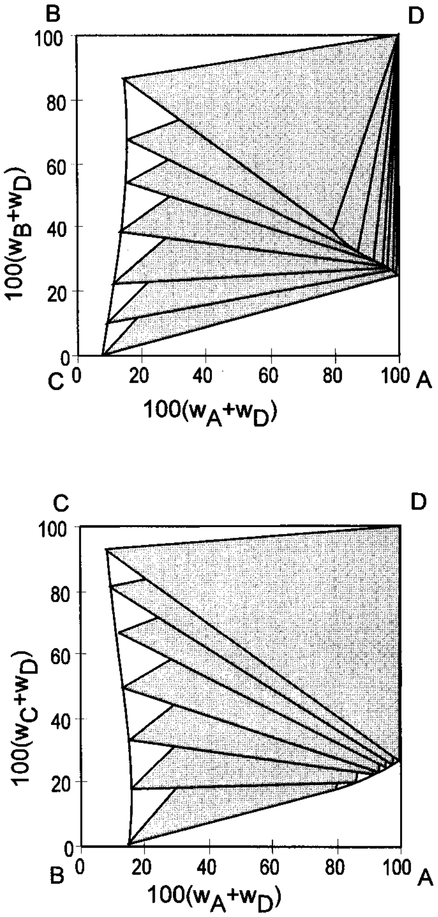

Figure 7. Tie-triangle in (2L + 1S) region in two Cruickshank projections. Both tie-triangles of the ternary systems water + acetone + sodium chloride and water + 1-butanol + sodium chloride have been included.

In the three-dimensional representation, a mixture S separates into two conjugated phases R and E. Obviously, the straight line in the space RSE is projected into another straight line R′S′E′ in the projected representation. Figure 5b shows in a similar way the projection onto a plane parallel to the edges A−C and B−D. Now the relationship between the coordinates of any point in the projected square and the corresponding composition is given by

$$x' = w_D + w_C$$

$$y' = w_B + w_C$$

The line RSE in the tetrahedron is projected into the straight line R″S″E″ in the resulting square. Thus the BACD and ABCD projections provide a graphical representation of the quaternary equilibrium data.

Figure 6 shows the solubility curves and the tie-lines obtained in the ternary system water + acetone + 1-butanol and in the quaternary sectional planes SP1, SP2, and SP3 in two Cruickshank projections. It is worth noting that the tie-line data do not lie on SP1, SP2, or SP3. Both projections must be combined to ascertain the three

Table 3. Initial Mixtures Prepared in the 2L + 1S Region and Tie-Triangle Data Obtained as Mass Fraction (w_i) for the Water (A) + Acetone (B) + 1-Butanol (C) + Sodium Chloride (D) System at 25 °C

Initial Mixtures

$100w_A$	$100w_B$	$100w_C$	$100w_D$
40.00	0	35.00	25.00
29.99	4.98	35.02	30.02
30.00	12.01	28.01	29.98
30.03	18.97	21.01	29.99
30.02	26.00	13.99	29.99
30.00	33.03	7.00	29.97
33.00	33.60	0	33.40

Tie-Line Data

aqueous phase				organic phase				solid phase
$100w_A$	$100w_B$	$100w_C$	$100w_D$	$100w_A$	$100w_B$	$100w_C$	$100w_D$	$100w_D$
73.1	0	0.72	26.1	7.53	0	92.3	0.19	100
72.1	1.80	0.74	25.3	8.82	9.76	81.1	0.29	100
71.1	4.24	0.77	23.9	11.1	22.3	66.2	0.42	100
70.2	6.36	0.79	22.6	12.8	38.4	48.2	0.54	100
70.0	7.50	0.77	21.8	14.7	51.9	32.8	0.63	100
67.0	13.0	0.61	19.4	15.4	67.0	16.9	0.63	100
61.4	20.4	0	18.2	13.8	85.7	0	0.48	100

Table 4. Quaternary Solubility Surface of Sodium Chloride for Water (A) + Acetone (B) + 1-Butanol (C) + Sodium Chloride (D) at 25 °C (Points on the Equilibrium Surface between One-Liquid and One-Liquid−One-Solid Regions); Results as Mass Fraction (w_i)

$100w_A$	$100w_B$	$100w_C$	$100w_D$
4.98	10.1	84.8	0.081
4.94	20.7	74.3	0.068
4.98	30.5	64.5	0.057
4.99	39.9	55.1	0.050
5.00	49.8	45.1	0.043
4.99	60.1	34.9	0.036
5.00	69.9	25.1	0.029
4.99	80.0	15.0	0.023
5.17	89.8	5.04	0.016
9.98	19.9	69.7	0.36
9.81	30.6	59.3	0.29
9.95	40.0	49.8	0.22
9.97	50.1	39.8	0.20
9.98	59.9	30.0	0.16
9.92	69.5	20.4	0.15
9.98	79.8	10.1	0.15
14.8	59.8	24.7	0.61
14.9	69.6	15.0	0.56
14.9	79.6	5.01	0.48

coordinates of each point (Ruiz and Prats, 1983c). Table 3 shows the initial mixtures prepared and the tie-triangles obtained in the study of the 2L + 1S region. Figure 7 shows these tie-triangles in two Cruickshank projections. Table 4 shows the solubility surface that separates the 1L and 1L + 1S regions.

Discussion

In order to analyze the salt effect, the distribution curves of acetone between water and 1-butanol (Figure 8a) and the selectivity curves of 1-butanol for the acetone extraction (Figure 8b) have been represented. The distribution (K_d) and the selectivity (m) coefficients are defined as

$$K_{d_i} = \frac{(w_i)_{or}}{(w_i)_{aq}} \tag{4}$$

$$m_i = \frac{\left(\dfrac{w_i}{(w_i + w_{water})}\right)_{or}}{\left(\dfrac{w_i}{(w_i + w_{water})}\right)_{aq}} \tag{5}$$

where $(w_i)_p$ is the mass fraction of component i (acetone in this case) in phase p (or = organic phase and aq = aqueous phase).

Table 5. Correlation Results

	eq 8	eq 9	eq 10
α	−1.005	−0.7121	0.4703
β	0.0820	−0.0676	−0.0186
γ	0.00905	0.0414	0.000573
δ	−1.237	−0.3185	3.4879
λ	0.0670	−0.0980	0.0124
η	0.0147	0.0352	−0.000619
φ	−0.731	−0.4973	0.7850
θ	0.0227	−0.0299	0.0198
ω	0.00977	0.0144	0.0134
OF	0.0148	0.0105	0.0125
σ	2.27		

In these figures, points corresponding to the tie-triangles, the tie-lines of SP1, SP2, and SP3, and the tie-lines of the ternary water + acetone + 1-butanol have been plotted. The ternary water + acetone + sodium chloride has not been included in the figures since this ternary has not any butanol, and therefore, the distribution of acetone in the organic phase (rich in butanol) and the selectivity of butanol for the acetone extraction cannot be studied. As can be observed, the distribution of acetone in the organic phase and the selectivity of butanol for the acetone extraction follow the sequence three-phase region > SP3 > SP2 > SP1 > no-salt ternary; consequently, these two coefficients are favored by increasing the amount of salt in the system.

The methods for correlating the equilibrium data can be classified into two broad general groups. The first group could be that including models with physical background, which use equations like NRTL, Margules, and Wilson to represent the interactions between the binary pairs. The second broad group corresponds to merely empirical models suitable for representing the behavior observed. The Eisen−Joffe equation (Eisen and Joffe, 1966) and the modified Eisen−Joffe equation (Marcilla et al., 1995a,b) belong to this latter group. This modified Eisen−Joffe equation was written as

$$\log\left(\frac{w_i}{w_j}\right)_{or} = (\alpha + \beta 100(w_{salt})_{aq}) + (\gamma + \delta 100(w_{salt})_{aq}) \times \log\left(\frac{w_{solute}}{w_{water}}\right)_{aq} + (\lambda + \eta 100(w_{salt})_{aq})\left(\log\left(\frac{w_{solute}}{w_{water}}\right)_{aq}\right)^2 \tag{6}$$

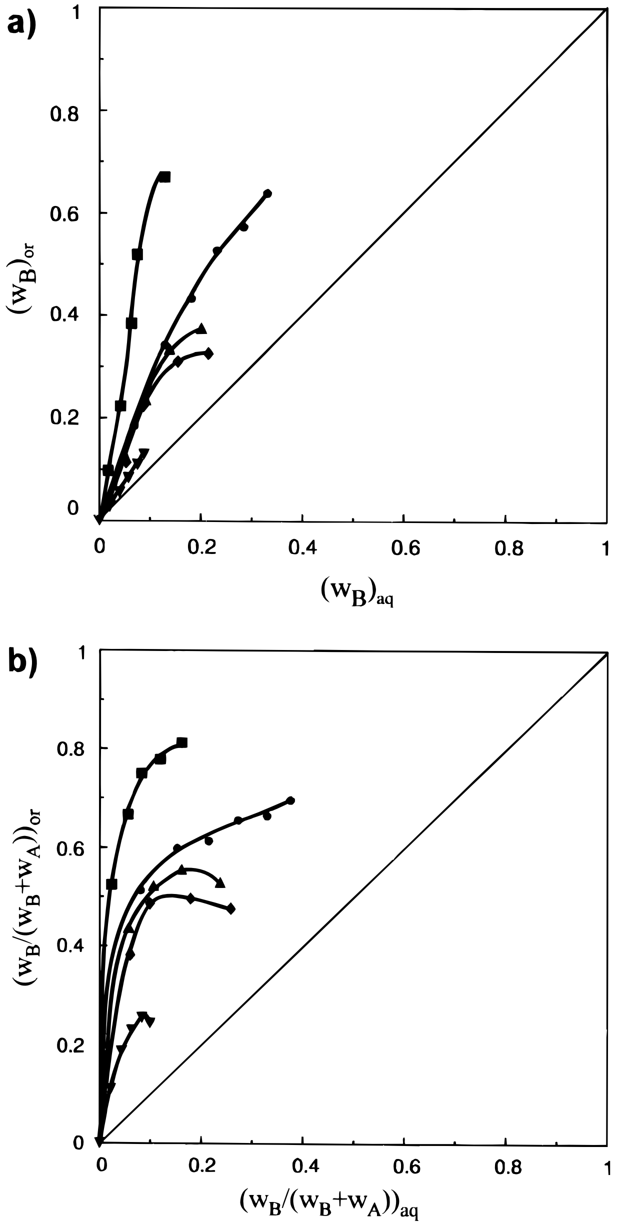

Figure 8. (a) Distribution curves of acetone. (b) Selectivity curves of 1-butanol for acetone extraction, obtained in the different regions studied at 25 °C: (▼) ternary system water (A) + acetone + 1-butanol (C); (♦) sectional plane 1 (SP1) in quaternary 2L region; (▲) sectional plane 2 (SP2) in quaternary 2L region; (●) sectional plane 3 (SP3) in quaternary 2L region; (■) 2L + 1S region.

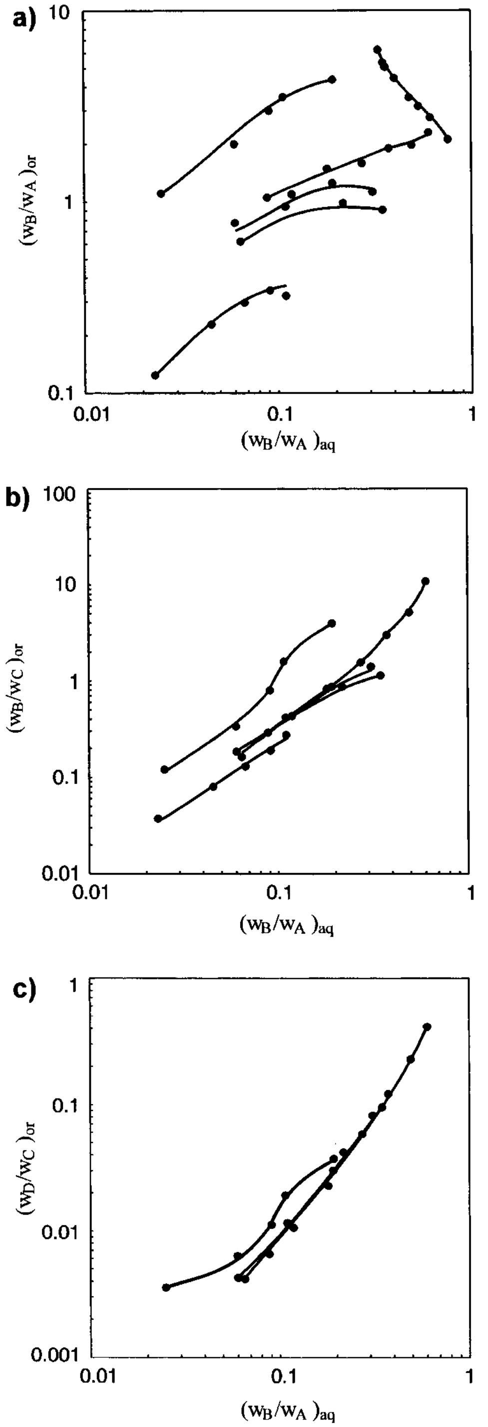

Figure 9. Correlation of results, using a modification of the Eisen−Joffe equation, for the water−acetone−1-butanol−sodium chloride system at 25 °C: (●) experimental; (—) calculated using (a) eq 8, (b) eq 9, and (c) eq 10.

and it was applied to the systems water + ethanol + 1-butanol + sodium chloride and water + ethanol + acetone + sodium chloride, very good agreements between experimental and calculated data being obtained ($(w_{\text{solute}}/w_{\text{water}})_{\text{aq}}$ was the ratio $(w_{\text{ethanol}}/w_{\text{water}})$ in the aqueous phase and the ratios $(w_i/w_j)_{\text{or}}$ selected were $(w_{\text{ethanol}}/w_{\text{water}})$, $(w_{\text{ethanol}}/w_{\text{solvent}})$, and $(w_{\text{sodium chloride}}/w_{\text{solvent}})$, in the organic phase).

However, this modified Eisen−Joffe equation does not lead to good results when it is used to correlate the tie-line and tie-triangle data of this system. According to the experimental data, the concentration of acetone in the organic phase is the value more affected by the amount of salt present. Thus, the concentration of acetone in the organic phase was included in the modified Eisen−Joffe equation, which was rewritten as

$$\log\left(\frac{w_i}{w_j}\right)_{\text{or}} = (\alpha + \beta 100(w_D)_{\text{aq}} + \gamma 100(w_B)_{\text{or}}) + (\delta + \lambda 100(w_D)_{\text{aq}} + \eta 100(w_B)_{\text{or}}) \log\left(\frac{w_B}{w_A}\right)_{\text{aq}} + (\varphi + \theta 100(w_D)_{\text{aq}} + \omega 100(w_B)_{\text{or}})\left(\log\left(\frac{w_B}{w_A}\right)_{\text{aq}}\right)^2 \quad (7)$$

where $(w_i)_p$ are the mass fraction of component i (A = water, B = acetone, C = 1-butanol, and D = sodium chloride) in phase p (or = organic phase and aq = aqueous phase) and α, *β*, *γ*, *δ*, *λ*, *η*, *φ*, *θ*, and *ω* are empirical parameters to be optimized.

In order to determine the organic phase in equilibrium with a given composition of the aqueous phase, three equations of this type are needed. The three equations selected have been

$$\log\left(\frac{w_{\mathrm{B}}}{w_{\mathrm{A}}}\right)_{\mathrm{or}} = (\alpha_1 + \beta_1 100(w_{\mathrm{D}})_{\mathrm{aq}} + \gamma_1 100(w_{\mathrm{B}})_{\mathrm{or}}) + (\delta_1 + \lambda_1 100(w_{\mathrm{D}})_{\mathrm{aq}} + \eta_1 100(w_{\mathrm{B}})_{\mathrm{or}}) \log\left(\frac{w_{\mathrm{B}}}{w_{\mathrm{A}}}\right)_{\mathrm{aq}} + (\varphi_1 + \theta_1 100(w_{\mathrm{D}})_{\mathrm{aq}} + \omega_1 100(w_{\mathrm{B}})_{\mathrm{or}})\left(\log\left(\frac{w_{\mathrm{B}}}{w_{\mathrm{A}}}\right)_{\mathrm{aq}}\right)^2 \quad (8)$$

$$\log\left(\frac{w_{\mathrm{B}}}{w_{\mathrm{C}}}\right)_{\mathrm{or}} = (\alpha_2 + \beta_2 100(w_{\mathrm{D}})_{\mathrm{aq}} + \gamma_2 100(w_{\mathrm{B}})_{\mathrm{or}}) + (\delta_2 + \lambda_2 100(w_{\mathrm{D}})_{\mathrm{aq}} + \eta_2 100(w_{\mathrm{B}})_{\mathrm{or}}) \log\left(\frac{w_{\mathrm{B}}}{w_{\mathrm{A}}}\right)_{\mathrm{aq}} + (\varphi_2 + \theta_2 100(w_{\mathrm{D}})_{\mathrm{aq}} + \omega_2 100(w_{\mathrm{B}})_{\mathrm{or}})\left(\log\left(\frac{w_{\mathrm{B}}}{w_{\mathrm{A}}}\right)_{\mathrm{aq}}\right)^2 \quad (9)$$

$$\left.\frac{w_{\mathrm{D}}}{w_{\mathrm{C}}}\right)_{\mathrm{or}} = (\alpha_3 + \beta_3 100(w_{\mathrm{D}})_{\mathrm{aq}} + \gamma_3 100(\omega_{\mathrm{B}})_{\mathrm{or}}) + (\delta_3 + \lambda_3 100(w_{\mathrm{D}})_{\mathrm{aq}} + \eta_3 100(w_{\mathrm{B}})_{\mathrm{or}}) \log\left(\frac{w_{\mathrm{B}}}{w_{\mathrm{A}}}\right)_{\mathrm{aq}} + (\varphi_3 + \theta_3 100(w_{\mathrm{D}})_{\mathrm{aq}} + \omega_3 100(w_{\mathrm{B}})_{\mathrm{or}})\left(\log\left(\frac{w_{\mathrm{B}}}{w_{\mathrm{A}}}\right)_{\mathrm{aq}}\right)^2 \quad (10)$$

where $(w_{\mathrm{i}})_{\mathrm{p}}$ are the mass fraction of component *i* (A = water, B = acetone, C = 1-butanol, and D = sodium chloride) in phase p (or = organic phase and aq = aqueous phase) and α, *β*, *γ*, *δ*, *λ*, *η*, *φ*, *θ*, and *ω* are empirical parameters to be optimized. The tie-triangle and tie-line data were fitted together. When the data were correlated using eq 8, the ternaries water + acetone + sodium chloride and water + acetone + 1-butanol were also included in the correlation (ternaries which contain acetone and water). When the equation used to correlate the data was eq 9, the ternary water + acetone + 1-butanol was included. No ternary could be included when eq 10 was used (in this equation all the components of the quaternary system are involved).

The simplex flexible method (Himmelblau, 1968) has been used as the optimization method to determine the parameters of the correlation. The objective function and the standard deviation used have been calculated using eqs 11 and 12, respectively, where i, j = water, acetone, 1-butanol, sodium chloride, i ≠ j, exp = experimental, cal = calculated, and *n* = number of tie-lines and tie-triangles.

$$\mathrm{OF} = \sum_{k=1}^{n}\left[\left(\log\left(\frac{w_{\mathrm{i}}}{w_{\mathrm{j}}}\right)_{k,\mathrm{or}}\right)_{\mathrm{exp}} - \left(\log\left(\frac{w_{\mathrm{i}}}{w_{\mathrm{j}}}\right)_{k,\mathrm{or}}\right)_{\mathrm{cal}}\right]^2 \quad (11)$$

$$\sigma = \sqrt{\frac{\sum_{k=1}^{n}((w_{\mathrm{i}})_{k,\mathrm{exp}} - (w_{\mathrm{i}})_{k,\mathrm{cal}})^2}{4n}} \quad (12)$$

Table 5 shows the results of the correlation (parameters calculated and objective function and standard deviation values). Figure 9 shows the experimental and calculated data for the three correlations carried out. A very good agreement can be observed for all the data.

Conclusions

The quaternary system water + acetone + 1-butanol + sodium chloride has been systematically studied at 25 °C.

The addition of sodium chloride to the ternary system water + acetone + 1-butanol has the following consequences:

The 2L quaternary region increases its size, very quickly, with the addition of salt, due to the partial miscibility of water−acetone when salt is in the system.

The addition of sodium chloride improves acetone extraction by 1-butanol. This improvement results from the salt effect which modifies the phase equilibria of the water + acetone + 1-butanol system, increasing the distribution coefficient for acetone and the selectivity of 1-butanol as the mass of salt increases.

A modification of the Eisen−Joffe equation has been used to correlate the tie-line and tie-triangle data for the 2L and 2L + 1S regions, yielding excellent results.

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