Salt Effect in the Quaternary System Water + Ethanol + 1-Butanol + Potassium Chloride at 25 °C

M. M. Olaya, J. A. Conesa, and A. Marcilla*

Departamento de Ingeniería Química, Universidad de Alicante, Apartado 99, Alicante, Spain

The liquid−liquid−solid equilibria in the two-liquid and two-liquid + one-solid quaternary regions for the quaternary system water + ethanol + 1-butanol + potassium chloride at 25 °C have been determined. Distribution and selectivity curves are represented for this system, and they are compared with those previously obtained for the water + ethanol + 1-butanol + sodium chloride system at 25 °C; the different salt effects of both salts have been discussed. Tie-line and tie-triangle data have been correlated using a modification of the Eisen−Joffe equation.

Introduction

As it was shown in a previous paper (Ruiz Bevia and Marcilla Gomis, 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), the water + ethanol + acetone + sodium chloride system (Marcilla et al., 1995b), and the water + acetone + 1-butanol + sodium chloride system (Olaya et al., 1996). In the first system, water and 1-butanol are partially miscible; in the second, water, ethanol, and acetone are miscible in all proportions, the two-liquid region appearing only when the salt is present. Then, in the last system, the two-liquid quaternary 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.

In the present paper the methodology suggested for these authors is applied to the quaternary system water + ethanol + 1-butanol + potassium chloride. In this case only the equilibrium regions relevant to the discussion of the salt effect of potassium chloride for the aqueous ethanol extraction with 1-butanol are studied (2L and 2L + 1S quaternary regions), and the distribution and selectivity coefficients are compared with those obtained without salt and with those obtained when the salt is sodium chloride. 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. Water used was bidistilled, and ethanol, 1-butanol, and 2-propanol were analytical reagent grade (Merck). The contents of possible volatile impurities were examined by gas−liquid chromatography. The purity of all compounds determined by chromatography was minimum 99.5% (mass).

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, ethanol, 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 30 $cm^3 \cdot min^{-1}$. The internal standard method was applied for the quantitative analysis, using 2-propanol as the standard. For the analysis of water, ethanol, and 1-butanol in the organic phases, the detection was carried out by a thermal conductivity detector (TCD). Nevertheless, when 2-propanol was added to the aqueous phases, potassium chloride precipitated. Consequently, these samples were diluted with water until transparency, ethanol and 1-butanol contents were determined using a flame ionization detector (FID), and water was calculated by mass balance.

Potassium chloride 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 heterogeneus mixture were prepared and analyzed. The relative accuracy of the mass fraction measurements of each of the components was approximately 1%.

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

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

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

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

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

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 = ethanol, C = 1-butanol, and D = potassium 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.

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* To whom correspondence should be addressed.

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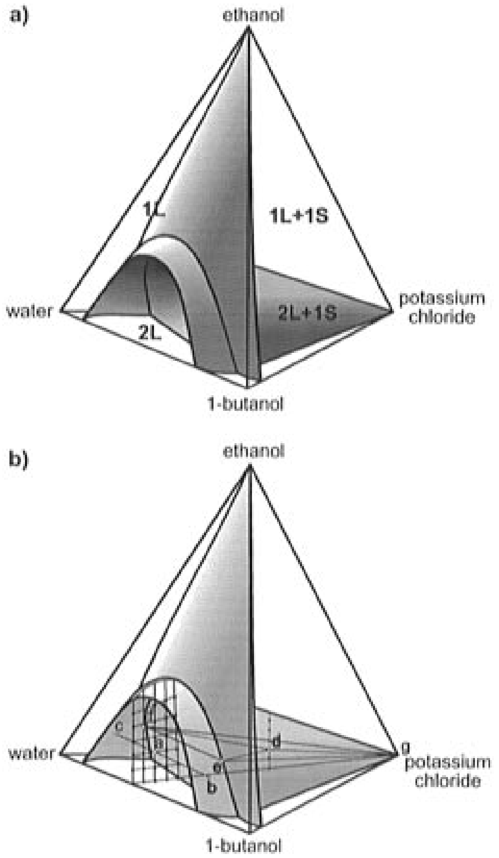

Figure 1. (a) Qualitative representation of the liquid−liquid−solid equilibrium in the water + ethanol + 1-butanol + potassium chloride system at 25 °C. (b) Representation of the initial mixture network to determine the quaternary regions.

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'/M'), and (S'/M')), the previous system can be written as

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

Mathematic calculations lead to the expression

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

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%.

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 that consider these types of systems as pseudoternary systems. In the present paper this systematic method is applied to calculate equilibrium data in the two-liquid and two-liquid + one-solid quaternary regions in the system water + ethanol + 1-butanol + potassium chloride.

Generally it is possible to deduce the approximate equilibrium diagram of a quaternary system if the behavior of the ternaries involved is known. The system water + ethanol + 1-butanol + sodium chloride was previously studied (Marcilla et al., 1995a), and the behavior of the ternaries is very close to that involving KCl instead of NaCl. Consequently a similar qualitative behavior is to be expected for this system. Figure 1a shows a qualitative representation of a quaternary system including one inorganic salt and with only one partially miscible liquid pair, the two other liquid pairs being totally miscible, as those commented on previously. For these systems 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)
the one-liquid + one-solid region, zone (1L + 1S)

In order to discuss the salt effect of the salt for the solute extraction, is necessary to determine the equilibrium data in the system without salt and in the 2L and 2L + 1S quaternary equilibrium regions. Figure 1b shows a schematic representation of the methodology used, where the initial mixtures (a and d) and the compositions of the equilibrium phases (b−c and e−f−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).

Then, when initial mixtures are prepared as a and d and the compositions of the b−c and e−f−g phases are analyzed, all equilibrium data can be determined. The initial mixture points (as a in Figure 1b) to obtain the tie-lines in the 2L region have been prepared in sectional planes. These mixture points, in different sectional planes, form a network similar to that shown in Figure 1b.

Results

Ternary Systems. Only one of the four ternary systems included in the quaternary system studied in this paper is of interest in knowing the salt effect of potassium chloride for the ethanol extraction with 1-butanol; this is the system without salt: water + ethanol + 1-butanol. The results for this system have been previously determined (Marcilla et al., 1995a).

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

$$\text{SP1: } B + (93\%\ A + 7\%\ D) + (81\%\ C + 19\%\ A)$$

$$\text{SP2: } B + (86\%\ A + 14\%\ D) + (85\%\ C + 15\%\ A)$$

The position of these sectional planes in the tetrahedron is shown in Figure 2.

Table 1 shows the initial mixtures prepared in the sectional planes SP1 and SP2 and the tie-lines obtained. The experimental results have been represented using Cruickshank type projections (Cruickshank et al., 1950). In the Cruickshank projection, the tetrahedron is projected onto a plane parallel to two nonintersecting edges. Figure 3a 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

$$x = w_D + w_C$$

$$y = w_A + \omega_C$$

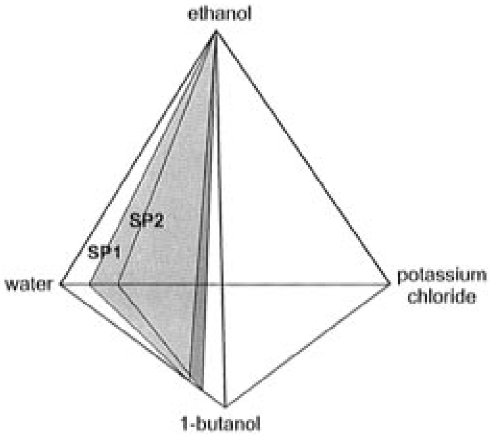

Figure 2. Qualitative position in the tetrahedron of the sectional planes studied.

Table 1. Initial Mixtures Prepared in Sectional Plane 1 (SP1), B + (93% A + 7% D) + (81% C + 19% A) and Sectional Plane 2 (SP2), B + (86% A + 14% D) + (85% C + 15% A) and Tie-Line Data Obtained as Mass Fraction (w_i) for the Water (A) + Ethanol (B) + 1-Butanol (C) + Potassium Chloride (D) System at 25 °C

Initial Mixtures

$100w_A$	$100w_B$	$100w_C$	$100w_D$
	SP1		
56.0	0	40.5	3.50
53.2	5.01	38.5	3.33
50.4	9.98	36.4	3.15
47.6	15.0	34.4	2.98
44.8	20.0	32.4	2.80
	SP2		
50.5	0	42.5	7.00
47.9	5.03	40.4	6.64
45.4	10.0	38.2	6.30
42.9	15.0	36.1	5.95
40.4	20.0	34.0	5.60
37.9	25.0	31.9	5.25

Tie-Line Data

aqueous phase				organic phase			
$100w_A$	$100w_B$	$100w_C$	$100w_D$	$100w_A$	$100w_B$	$100w_C$	$100w_D$
			SP1				
89.1	0	4.69	6.25	15.9	0	84.0	0.108
85.3	3.62	4.70	6.35	18.6	6.39	74.8	0.207
81.3	7.15	5.08	6.44	23.2	12.4	63.9	0.422
77.2	10.4	5.87	6.53	29.0	17.7	52.4	0.870
68.9	14.4	10.0	6.64	40.5	21.5	35.9	2.15
			SP2				
84.0	0	2.89	13.1	13.4	0	86.4	0.157
81.0	2.96	2.88	13.2	16.1	7.01	76.6	0.326
77.9	5.75	3.14	13.2	18.4	13.6	67.5	0.510
75.0	8.23	3.25	13.5	21.7	19.6	57.8	0.903
72.0	10.4	3.39	14.2	25.8	25.3	47.4	1.52
69.2	12.2	3.54	15.0	29.5	29.4	38.6	2.46

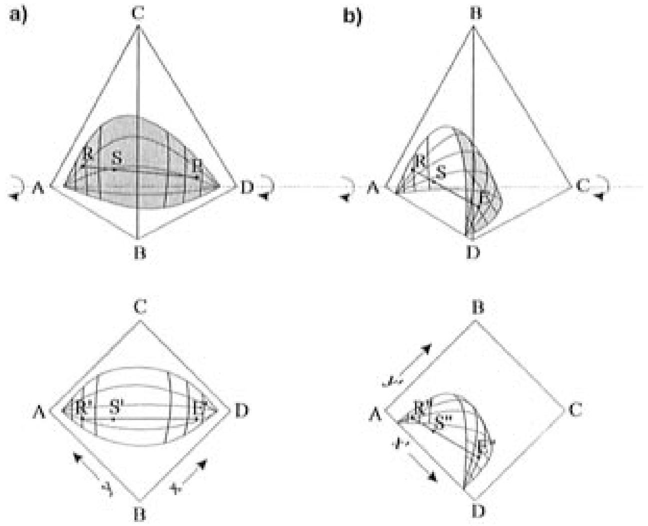

Figure 3. Equilibrium data representation for quaternary systems: (a) projection onto a plane parallel to edges A−D and B−C; (b) projection onto a plane parallel to edges A−C and B−D.

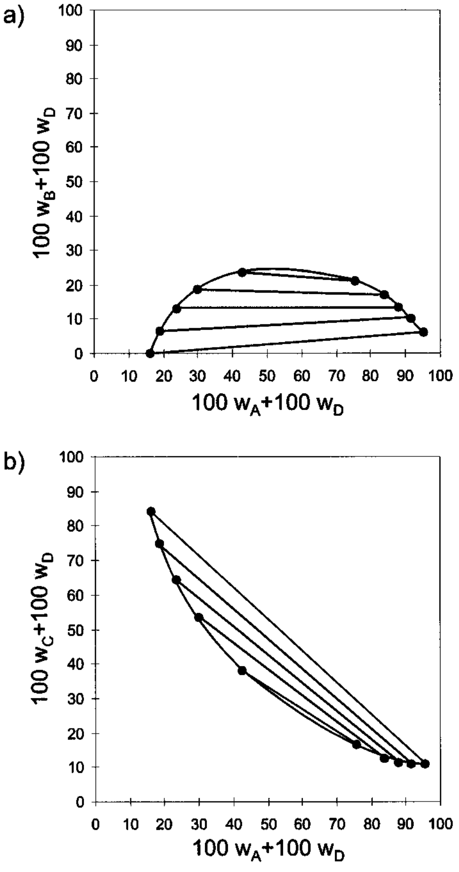

Figure 4. Tie-lines obtained preparing mixtures in the sectional plane 1 (SP1), in two Cruickshank projections: (a) projection onto a plane parallel to edges water + ethanol and 1-butanol + potassium chloride; (b) projection onto a plane parallel to edges water + 1-butanol and ethanol + potassium chloride.

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 3b 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.

Figures 4 and 5 show the tie-lines obtained in the quaternary sectional planes SP1 and SP2 in two Cruickshank projections, respectively. Both projections must be combined to ascertain the three coordinates of each point (Ruiz and Prats, 1983). Table 2 shows the initial mixtures

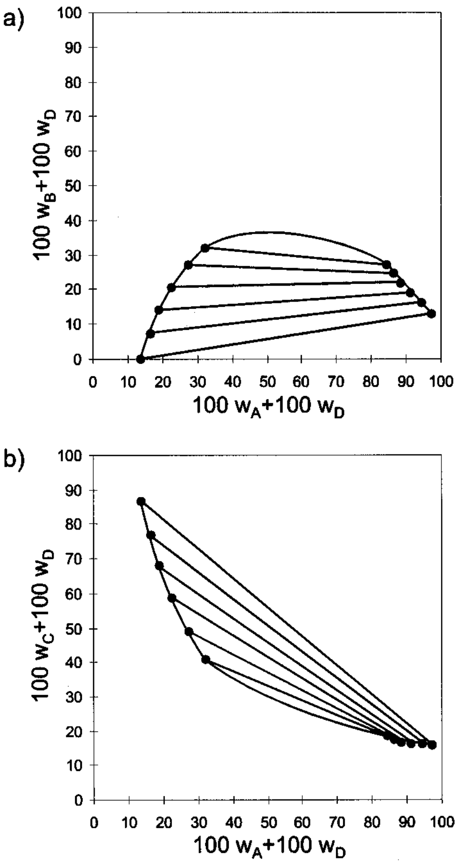

Figure 5. Tie-lines obtained preparing mixtures in the sectional plane 2 (SP2), in two Cruickshank projections: (a) projection onto a plane parallel to edges water + ethanol and 1-butanol + potassium chloride; (b) projection onto a plane parallel to edges water + 1-butanol and ethanol + potassium chloride.

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

Initial Mixtures

$100w_A$	$100w_B$	$100w_C$	$100w_D$
42.0	0	31.7	16.3
39.1	2.49	34.1	24.3
38.0	5.03	33.2	23.7
37.0	7.48	32.4	23.1
36.1	10.0	31.4	22.5
37.5	12.5	28.1	21.9
38.1	14.3	22.6	25.0
42.4	17.5	19.4	20.6
45.1	19.9	15.0	20.0

Tie-Line Data

aqueous phase				organic phase				solid phase
$100w_A$	$100w_B$	$100w_C$	$100w_D$	$100w_A$	$100w_B$	$100w_C$	$100w_D$	$100w_D$
73.3	0	1.01	25.7	9.52	0	90.3	0.178	100
73.0	1.10	1.07	24.8	10.5	4.57	84.7	0.228	100
72.6	2.30	1.16	24.0	11.7	9.33	78.6	0.322	100
72.2	3.52	1.20	23.1	13.6	13.6	72.4	0.432	100
71.8	4.66	1.24	22.3	14.8	17.6	67.0	0.603	100
70.9	5.91	1.43	21.8	17.0	21.6	60.6	0.807	100
70.1	7.97	1.74	20.2	19.4	26.2	53.2	1.25	100
68.0	11.0	2.35	18.7	24.2	30.0	43.9	1.91	100
65.5	14.1	3.87	16.5	31.7	33.0	31.7	3.64	100

prepared and the tie-triangles obtained in the study of the 2L + 1S region. Figure 6 shows these tie-triangles in two Cruickshank projections.

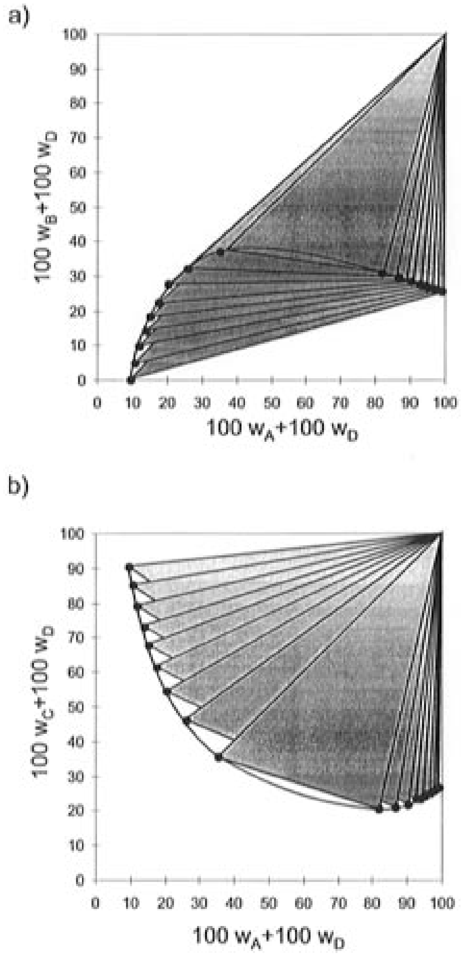

Figure 6. Tie-triangles in (2L + 1S) region in two Cruickshank projections: (a) projection onto a plane parallel to edges water + ethanol and 1-butanol + potassium chloride; (b) projection onto a plane parallel to edges water + 1-butanol and ethanol + potassium chloride.

Table 3. Correlation Results

	eq 7	eq 8	eq 9
α	0.518 56	−0.699 29	2.410 8
β	0.029 475	0.0312 28	−0.030 447
γ	1.279 9	−0.755 70	7.316 6
δ	0.020 796	0.004 746 9	−0.114 36
λ	0.054 957	−0.527 94	2.679 2
η	0.007 000 2	0.001 675 54	−0.060 099
OF	0.011 61	0.011 841	0.021 962
σ	1.074		

Discussion

In order to analyze the salt effect, the distribution curves of ethanol between water and 1-butanol (Figure 7a) and the selectivity curves of 1-butanol for the ethanol extraction (Figure 7b) 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 (ethanol in

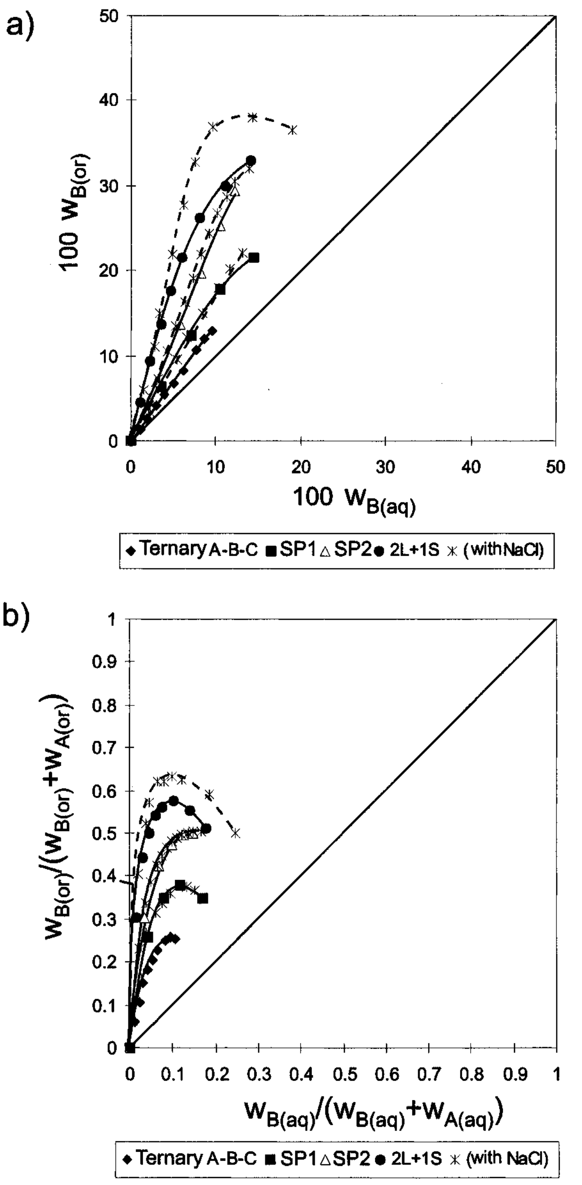

Figure 7. (a) Distribution curves of ethanol. (b) Selectivity curves of 1-butanol for ehanol extraction, obtained in the different regions studied for the quaternary system water + ethanol + 1-butanol + potassium chloride at 25 °C (corresponding results when the salt is sodium chloride instead of potassium chloride).

this case) in phase *p* (or = organic phase and aq = aqueous phase).

In these figures, points corresponding to the tie-triangles, the tie-lines of SP1 and SP2 for the quaternary system water + ethanol + 1-butanol + potassium chloride, and the tie-lines of the ternary water + ethanol + 1-butanol have been plotted. Besides, the corresponding results with sodium chloride have been simultaneously represented. As can be observed, for both salts, the distribution of ethanol in the organic phase and the selectivity of 1-butanol for the ethanol extraction follow the sequence: three-phase region > SP2 > SP1 > no-salt ternary. Consequently, these coefficients are favored by increasing the amount of salt in the system. It can also be observed that at low salt concentrations potassium chloride and sodium chloride have a similar effect. Nevertheless, at concentrations near saturation the salting-out effect produced by sodium chloride is much higher than that produced by potassium chloride.

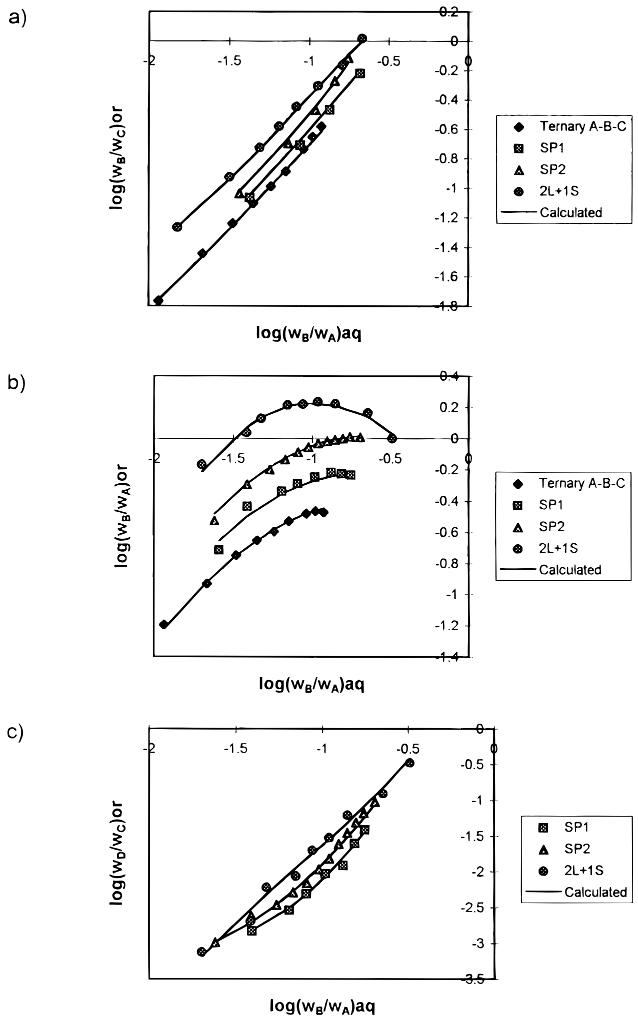

Figure 8. Correlation of results, using a modification of the Eisen–Joffe equation, for the water + ethanol + 1-butanol + potassium chloride system at 25 °C. Calculated data using (a) eq 7, (b) eq 8, and (c) eq 9.

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, UNIQUAC, ... to represent the interactions between the binary pairs. The second broad group corresponds to merely empirical models suitable of 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 later group. This modified Eisen–Joffe equation was written as

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

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

Table 4. Experimental and Calculated Data for Compositions in the Organic Phases

$100w_A$			$100w_B$			$100w_C$			$100w_D$		
exp	cal	exp−cal	exp	cal	exp−cal	exp	cal	exp−cal	exp	cal	exp−cal
21.0	22.2	1.2	1.34	1.35	0.01	77.7	76.5	1.2			
22.7	21.2	1.5	2.68	2.63	0.05	74.6	76.2	1.6			
23.4	22.3	1.1	4.18	4.08	0.10	72.4	73.6	1.2			
24.6	24.0	0.6	5.49	5.47	0.02	69.9	70.5	0.6			
26.8	26.0	0.8	6.83	6.94	0.11	66.4	67.0	0.6			
27.9	28.3	0.4	8.29	8.40	0.11	63.8	63.3	0.5			
31.9	31.6	0.3	10.6	10.4	0.2	57.5	58.0	0.5			
34.6	33.5	1.1	11.9	11.5	0.4	53.5	55.0	1.5			
38.1	35.5	2.6	12.9	12.5	0.4	49.0	52.0	3.0			
18.6	19.9	1.3	6.39	6.61	0.22	74.8	73.2	1.6	0.207	0.232	0.025
23.2	26.2	3.0	12.4	12.9	0.5	63.9	60.5	3.4	0.422	0.402	0.020
29.0	32.0	3.0	17.7	17.7	0.0	52.4	49.4	3.0	0.870	0.831	0.039
40.5	39.1	1.4	21.5	22.6	1.1	35.9	36.0	0.1	2.15	2.30	0.15
16.1	15.8	0.3	7.01	7.29	0.28	76.6	76.6	0.0	0.326	0.277	0.049
18.4	20.1	1.7	13.6	14.2	0.6	67.5	65.3	2.2	0.510	0.464	0.046
21.7	23.9	2.2	19.6	19.9	0.3	57.8	55.3	2.5	0.903	0.838	0.065
25.8	26.8	1.0	25.3	24.8	0.5	47.4	47.0	0.4	1.52	1.43	0.09
29.5	28.7	0.8	29.4	28.7	0.7	38.6	40.4	1.8	2.46	2.23	0.23
10.5	10.9	0.4	4.57	4.59	0.02	84.7	84.2	0.5	0.228	0.231	0.003
11.7	11.1	0.6	9.33	9.13	0.20	78.6	79.5	0.9	0.322	0.321	0.001
13.6	12.6	1.0	13.6	13.5	0.1	72.4	73.5	1.1	0.432	0.459	0.027
14.8	14.4	0.4	17.6	17.1	0.5	67.0	67.9	0.9	0.603	0.618	0.015
17.0	16.2	0.8	21.6	21.1	0.5	60.6	61.8	1.2	0.807	0.846	0.039
19.4	19.8	0.4	26.2	25.7	0.5	53.2	53.3	0.1	1.25	1.26	0.01
24.2	24.5	0.3	30.0	31.0	1.0	43.9	42.2	1.7	1.91	2.21	0.30
31.7	29.9	1.8	33.0	33.2	0.2	31.7	33.3	1.6	3.64	3.63	0.01

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 used to correlate the equilibrium quaternary data of the system water + ethanol + 1-butanol + potassium chloride have been

$$\log\left(\frac{w_B}{w_C}\right)_{or} = (\alpha + \beta\cdot 100(w_D)_{aq}) + (\gamma + \delta\cdot 100(w_D)_{aq})\cdot\log\left(\frac{w_B}{w_A}\right)_{aq} + (\lambda + \eta\cdot 100(w_D)_{aq})\cdot\left(\log\left(\frac{w_B}{w_A}\right)_{aq}\right)^2 \quad (7)$$

$$\log\left(\frac{w_B}{w_A}\right)_{or} = (\alpha' + \beta'\cdot 100(w_D)_{aq}) + (\gamma' + \delta'\cdot 100(w_D)_{aq})\cdot\log\left(\frac{w_B}{w_A}\right)_{aq} + (\lambda' + \eta'\cdot 100(w_D)_{aq})\cdot\left(\log\left(\frac{w_B}{w_A}\right)_{aq}\right)^2 \quad (8)$$

$$\log\left(\frac{w_D}{w_C}\right)_{or} = (\alpha'' + \beta''\cdot 100(w_D)_{aq}) + (\gamma'' + \delta''\cdot 100(w_D)_{aq})\cdot\log\left(\frac{w_B}{w_A}\right)_{aq} + (\lambda'' + \eta''\cdot 100(w_D)_{aq})\cdot\left(\log\left(\frac{w_B}{w_A}\right)_{aq}\right)^2 \quad (9)$$

where $(w_i)_p$ are the mass fractions of component i (A = water, B = ethanol, C = 1-butanol, and D = potassium chloride) in phase p (or = organic phase and aq = aqueous phase) and α, β, γ, δ, λ, and η are empirical parameters to be optimized. The tie-triangle and tie-line data were fitted together.

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 10 and 11, respectively

$$\mathrm{OF} = \sum_{k=1}^{n}\left[\left(\log\left(\frac{w_i}{w_j}\right)_{k,\,or}\right)_{exp} - \left(\log\left(\frac{w_i}{w_j}\right)_{k,\,or}\right)_{cal}\right]^2 \quad (10)$$

$$\sigma = \sqrt{\frac{\sum_{k=1}^{n}((w_i)_{k,exp} - (w_i)_{k,cal})^2}{4\cdot n}} \quad (11)$$

where i, j = water, ethanol, 1-butanol, potassium chloride, $i \neq j$, exp = experimental, cal = calculated, and n = number of tie-lines and tie-triangles.

Table 3 shows the results of the correlation (parameters calculated and objetive function and standard deviations values). Table 4 shows the experimental and calculated data for compositions in the organic phases. Figure 8 shows the representation of experimental and calculated data for the three correlations carried out. A very good agreement can be observed for all the data.

Conclusions

The two-liquid and two-liquid + one-solid quaternary regions of the system water + ethanol + 1-butanol + potassium chloride have been systematically studied at 25 °C.

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

At low salt concentrations potassium chloride and sodium chloride have a similar behavior, whereas at concentrations near saturation the salting out produced by sodium chloride is higher than that produced by potassium chloride for the extraction of ethanol with 1-butanol.

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 quaternary regions, yielding excellent results.

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