

Aqueous phase diagrams containing oxalic acid at 303.15 K

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Abstract

Phase diagrams of ternary systems: water + oxalic acid + (1-pentanol or + isobutyl acetate or + methyl isobutyl ketone) were obtained at 303.15 K. The system containing 1-pentanol was revised [Faizal et al., J. Chem. Eng. Data 35 (1990) 352–354] in order to show the presence of the dihydrate of oxalic acid, by means of the analysis of the solid phase using FT–IR spectrum, melting point data, and acid–base titration. Experimental results show that all aqueous oxalic acid systems have one region where both acid forms are mixed, and three solid–liquid zones where the solid is the hydrated oxalic acid. The recovery of oxalic acid from aqueous solutions was evaluated analyzing their distribution coefficients, selectivities and distribution curves on a solvent-free basis. None of the three solvents studied here were found suitable for oxalic acid extraction processes, because distribution coefficients are always smaller than 1 and selectivities are not high enough. © 1997 Elsevier Science B.V.

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1. Introduction

Oxalic acid is widely used as a neutralizing and acidifying agent, in preference to more common mineral acids, when its properties justify its higher cost. It is also used in textile manufacture and processing, wood and metal treatment, and the manufacture of miscellaneous chemical derivatives. The acid and its salts are extensively used as reagents in chemical analysis. Oxalic acid readily forms the dihydrate, containing 71.42% anhydrous oxalic acid and 28.58% water, which is its commercial form [1]. Consequently, ternary aqueous phase diagrams containing oxalic acid must reflect this fact, since both acid forms: anhydrous and dihydrate, must be present in them. Faizal et al. [2], report three aqueous oxalic systems (the third component being 1-pentanol, or 2-methyl-1-propanol, or 3-methyl-1-butanol), in which the hydrate form does not appear. Consequently, their phase diagrams are

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incomplete. Whenever more than one component can be present in the solid phase in equilibrium with a saturated solution, the solid must be analyzed in order to determine its nature. Since IR spectra of each oxalic acid form show nine characteristic absorption bands, their melting points are very different, and acid–base titration is easy to perform, we employ all these methods to identify the nature of the solid present in the solid–liquid saturation zones.

In this work, we first repeat the study of one of the systems considered by Faizal et al. [2]: water + oxalic acid + 1-pentanol. We then obtain two additional phase diagrams using isobutyl acetate or methyl isobutyl ketone as a third component at 303.15 K. Finally, we determine the performance of these three solvents in the recovery of oxalic acid from aqueous solutions analyzing their distribution coefficients, selectivities and distribution curves on a solvent-free basis. All the selected solvents have an extracting ability with regard to the carboxylic acid resulting from the solvation character of the oxygen group attached to a carbon atom, which acts as a Lewis base.

Solid–liquid equilibrium and liquid–liquid equilibrium data of aqueous solutions containing oxalic acid with a third component, are not easy to find in the literature [2–5].

This paper is a continuation of our research on ternary systems containing solid phases [6,7].

2. Experimental

2.1. Materials

Water (W) was bidistilled. Isobutyl acetate (iBuAc) and 1-Pentanol (P) (Mallinckrodt, A.R.), were used without further purification. Methyl isobutyl ketone (MIK) (Mallinckrodt, A.R.), was dried over anhydrous K_2CO_3 and fractionally distilled under nitrogen atmosphere. The middle fractions were collected and stored over activated molecular sieves to prevent water absorption. Their purities were checked by comparing the measured densities of the components with those reported in the literature [8], shown in Table 1. Mutual binary solubilities and melting points of both oxalic acid forms are also included for comparison. As can be seen from Table 1, our experimental results are in agreement with literature values.

Hydrated oxalic acid (HOA) (Merck, pa), was used without further purification. The anhydrous oxalic acid (AOA) was obtained from the hydrated form heating it under appropriate conditions and storing in a desiccator to prevent water absorption. Standard sodium hydroxide (0.1 M) was used to check the purities of both acid forms, using phenolphthalein as indicator.

2.2. Apparatus and procedure

In order to determine the liquid–liquid and solid–liquid equilibria, anhydrous oxalic acid was always used.

Isothermal solubility curves and tie-lines were obtained simultaneously in the liquid–liquid region. Mixtures with compositions ranging within the heterogeneous zone were vigorously shaken for at least 1 h at constant temperature of 303.15 ± 0.1 K. After decantation, the oxalic acid present in the equilibrium phases was titrated with standard sodium hydroxide (0.1 M) and phenolphthalein as indicator. The error due to titration and weighting was less than 1%. The mass fraction of water in each liquid equilibrium phase, was determined by Karl Fischer titration using a Mettler DL18 Karl

Table 1

Densities (ρ) of pure components at 293.15 K, melting points and mutual binary solubilities at 303.15 K

| Compound | ρ (kg m^{-3}) | | Melting point (K) | |
|----------|-------------------------------|---------------------|-------------------|---------------------|
| | Exptl. | Lit. | Exptl. | Lit. |
| W | 998.2 | 998.23 ^a | – | – |
| P | 815.2 | 814.45 ^b | – | – |
| iBuAc | 873.1 | 872.8 ^b | – | – |
| MIK | 800.4 | 801.0 ^b | – | – |
| AOA | – | – | 460.4 | 462.65 ^c |
| HOA | – | – | 375.3 | 374.65 ^c |

| Binary systems | Water in solvents | | Solvents in water | |
|----------------|--------------------|-------------------|-------------------|-------------------|
| | Exptl. | Lit. | Exptl. | Lit. |
| W + P | 10.99 [*] | 10.5 ^d | 1.78 [*] | 2.04 ^d |
| W + MIK | 2.78 [*] | 2.5 ^e | 1.79 [*] | 1.7 ^e |
| W + iBuAc | 1.18 [*] | 1.12 ^f | 1.00 [*] | 0.61 ^f |

* Determined by a cloud-point method.

^a From Ref. [12].^b From Ref. [8].^c From Ref. [1].^d Interpolated from Ref. [13].^e Interpolated from Ref. [14].^f Interpolated from Ref. [15].

Fischer Titrator (using Hydra Point Titrant 5 and Hydra Point Solvent G, Baker Analyzed Reagent), and was generally accurate to within 0.5%. Taking into account that the calculation by difference of the minor components produce great errors, mutual solubilities of the binary partially miscible systems were obtained by the cloud-point method.

Solid–liquid saturation curves were obtained from saturated solutions using, for the liquid phase analysis, the same procedure indicated for liquid–liquid equilibrium. The nature of the solid in equilibrium with the liquid phase was determined by its melting point, infrared absorption spectrum, and acid–base titration. For the determination of the melting points, the samples were enclosed in sealed capillary tubes which were pasted on a bulb thermometer and immersed in a Thiele apparatus, which was slowly heated until fusion. The accuracy of the temperature reading was ± 0.5 K.

The infrared absorption spectra were recorded in the range 4000–400 cm^{-1} on a Perkin Elmer FTIR spectrophotometer, model 1600. Oxalic acid disks were prepared by carefully mixing it with KBr and pressing to 10 atm.

Densities of the pure components and their ternary mixtures were measured using a KEM, DA-300 Density Meter with an accuracy of ± 0.1 kg m^{-3} .

3. Results and discussion

Tables 2–4 present the experimental results of tie-line data and solid–liquid equilibrium compositions of water + oxalic acid ternary systems with the following solvents: 1-pentanol, isobutyl acetate,

Table 2

Ternary system: water (1) + oxalic acid (2) + 1-pentanol (3) at 303.15 K ^a*Liquid–liquid equilibrium tie line data, wt%*

| Aqueous phase (R) | | | Organic phase (E) | | | |
|-------------------|----------|--------|-------------------|----------|--------|-------|
| w_{11} | w_{21} | ρ | w_{13} | w_{23} | ρ | m |
| 98.22 | 0.00 | 992.5 | 10.99 | 0.00 | 826.1 | – |
| 93.23 | 3.02 | 1005.9 | 11.31 | 1.30 | 832.1 | 0.430 |
| 91.13 | 5.37 | 1016.8 | 11.37 | 2.41 | 838.3 | 0.448 |
| 88.43 | 7.84 | 1026.2 | 11.41 | 4.10 | 845.2 | 0.523 |
| 85.14 | 10.80 | 1042.4 | 11.48 | 5.13 | 851.2 | 0.475 |
| 83.63 | 13.31 | 1052.6 | 11.92 | 7.43 | 871.4 | 0.558 |

Solid–liquid equilibrium compositions, wt%

| Aqueous phase (R) | | | Organic phase (E) | | |
|-------------------|-------|--------|-------------------|-------|--------|
| w_1 | w_2 | ρ | w_1 | w_2 | ρ |
| 87.67 | 12.33 | 1053.9 | 7.67 | 6.35 | 846.9 |
| 85.69 | 13.48 | 1052.3 | 5.38 | 6.01 | 843.2 |
| 84.62 | 13.49 | 1051.2 | 4.07 | 6.62 | 844.0 |
| 83.25 | 13.32 | 1050.8 | 2.81 | 7.56 | 859.6 |
| 82.63 | 13.31 | 1052.6 | 0.87 | 10.17 | 866.2 |
| 11.92 | 7.43 | 871.4 | 0.71 | 12.02 | 871.3 |
| 9.89 | 6.13 | 853.2 | 0.00 | 15.94 | 897.7 |

^a ρ (kg m^{-3}), wt% (mass fraction %).

Table 3

Ternary system: water (1) + oxalic acid (2) + isobutyl acetate (3) at 303.15 K ^a*Liquid–liquid equilibrium tie line data, wt%*

| Aqueous phase (R) | | | Organic phase (E) | | | |
|-------------------|----------|--------|-------------------|----------|--------|-------|
| w_{11} | w_{21} | ρ | w_{13} | w_{23} | ρ | m |
| 99.00 | 0.00 | 995.4 | 1.18 | 0.00 | 988.2 | – |
| 96.29 | 1.63 | 1002.1 | 1.79 | 0.16 | 861.9 | 0.098 |
| 92.28 | 4.89 | 1019.5 | 1.66 | 0.44 | 864.0 | 0.089 |
| 88.63 | 8.25 | 1033.0 | 1.88 | 0.98 | 866.1 | 0.118 |
| 84.11 | 11.85 | 1054.9 | 1.80 | 1.35 | 867.0 | 0.114 |

Solid–liquid equilibrium compositions, wt%

| Aqueous phase (R) | | | Organic phase (E) | | |
|-------------------|-------|--------|-------------------|-------|--------|
| w_1 | w_2 | ρ | w_1 | w_2 | ρ |
| 87.67 | 12.33 | 1053.9 | 1.80 | 1.35 | 867.0 |
| 86.67 | 11.41 | 1055.1 | 1.28 | 1.15 | 866.3 |
| 86.34 | 11.40 | 1054.6 | 0.46 | 4.08 | 879.0 |
| 85.21 | 11.87 | 1052.8 | 0.41 | 5.42 | 884.8 |
| 84.11 | 11.85 | 1054.9 | | | |

^a ρ (kg m^{-3}), wt% (mass fraction %).

Table 4

Ternary system: Water (1) + oxalic acid (2) + methyl isobutyl ketone (3) at 303.15 K ^a

Liquid–liquid equilibrium tie line data, wt%

| Aqueous phase (R) | | | Organic phase (E) | | | |
|-------------------|----------|--------|-------------------|----------|--------|-------|
| w_{11} | w_{21} | ρ | w_{13} | w_{23} | ρ | m |
| 98.21 | 0.00 | 993.3 | 2.78 | 0.00 | 796.1 | – |
| 93.30 | 4.77 | 1014.5 | 2.89 | 0.91 | 800.3 | 0.190 |
| 88.40 | 9.55 | 1036.5 | 2.97 | 1.81 | 806.4 | 0.189 |
| 86.50 | 11.42 | 1047.0 | 2.99 | 2.57 | 809.3 | 0.225 |

Solid–liquid equilibrium compositions, wt%

| Aqueous phase (R) | | | Organic phase (E) | | |
|-------------------|-------|--------|-------------------|-------|--------|
| w_1 | w_2 | ρ | w_1 | w_2 | ρ |
| 87.67 | 12.33 | 1053.9 | 1.85 | 3.08 | 807.4 |
| 86.75 | 12.33 | 1052.1 | 0.32 | 3.92 | 805.7 |
| 86.50 | 11.42 | 1047.0 | 0.17 | 4.79 | 811.0 |
| 2.99 | 2.57 | 809.3 | 0.00 | 13.65 | 825.3 |

^a ρ (kg m^{-3}), wt% (mass fraction %).

and methyl isobutyl ketone, respectively. Concentration determinations were accurate to ± 0.001 mass fraction.

Figs. 1–3 show the experimental equilibrium diagrams at 303.15 K for these systems. The smoothed curves connecting the experimental data points on the binodal curves are hand-drawn, since no attempt was made to fit the data by means of an empirical equation. Ternary phase diagrams with solid phases might belong to the type IV of the classification proposed by Treybal [9]. As can be seen, each system shows a region where both acid forms coexist, in agreement with what was indicated above.

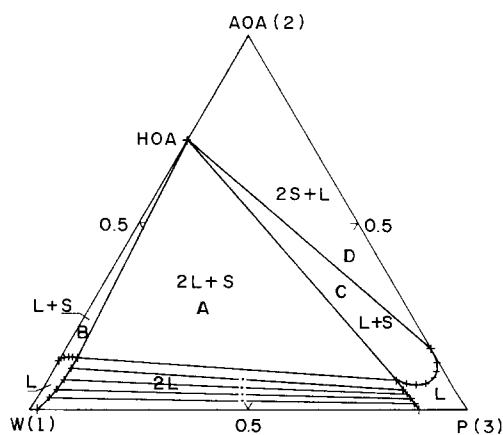


Fig. 1. Water (1) + oxalic acid (2) + 1-pentanol (3) phase diagram with tie lines at 303.15 K. S = solid. L = liquid. (●) Overall composition for tie-lines.

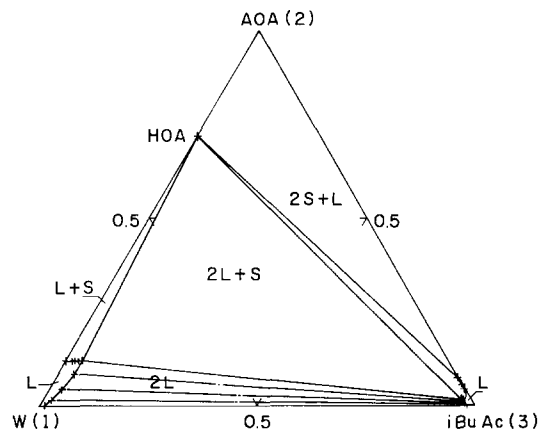


Fig. 2. Water (1) + oxalic acid (2) + isobutyl acetate (3) phase diagram with tie lines at 303.15 K. S = solid. L = liquid. (●) Overall composition for tie-lines.

The effect of the aqueous oxalic acid concentration on the oxalic acid distribution coefficient and on the solvent selectivity, are important factors in the selection of solvents. The oxalic acid distribution coefficient, m , is defined as the ratio of the acid mass fraction in the organic phase (w_{23}) to that in the aqueous phase (w_{21}). Its dependence on the acid mass fraction in the organic phase (w_{23}) is different for the three solvents. Oxalic acid distribution coefficients between water and 1-pentanol, isobutyl acetate, and methyl isobutyl ketone are given in Tables 2–4 for different acid concentrations. As can be seen, 1-pentanol presents the highest distribution coefficient among the solvents studied here ($0.430 \leq m^P \leq 0.558$), whereas isobutyl acetate presents the lowest ($0.089 \leq m^{iBuAc} \leq 0.118$). This is an important extractive property since it influences selectivity, and a more favorable coefficient ($m > 1$) will lead to a better selectivity. Since all distribution coefficients are smaller than unity, these solvents appear as inappropriate for the extraction of oxalic acid.

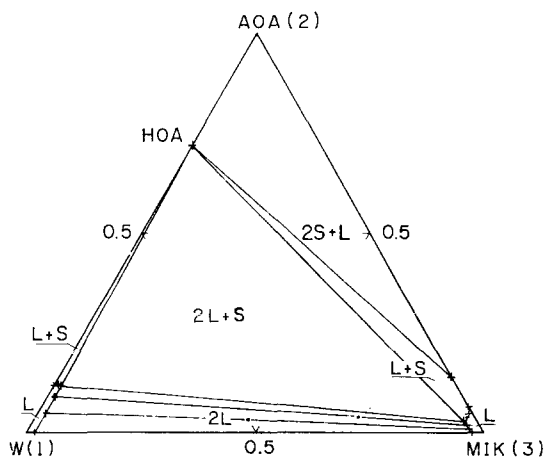


Fig. 3. Water (1) + oxalic acid (2) + methyl isobutyl ketone (3) phase diagram with tie lines at 303.15 K. S = solid. L = liquid. (●) Overall composition for tie-lines.

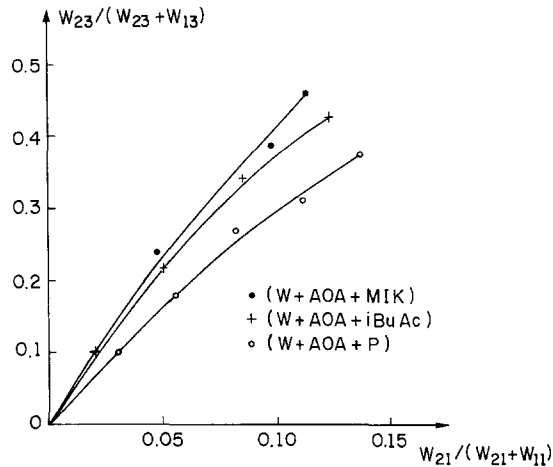


Fig. 4. Distribution curves on a solvent-free basis at 303.15 K.

Fig. 4 shows a distribution curve on a solvent-free basis, which makes it possible to analyze the feasibility of the extraction of oxalic acid from water solutions with these three solvents. This plot shows that methylisobutyl ketone and isobutyl acetate have similar behavior.

Fig. 5 shows a selectivity (β) diagram on a solvent-free basis [9], where the acid is the distributed substance. It shows that the highest selectivity corresponds to the system with methyl isobutyl ketone, and that the selectivity trend is as follows:

$$\beta^{MIK} > \beta^{iBuAc} > \beta^P$$

Selectivity is other important property in deciding the applicability of a solvent, and it refers its ability to extract one component of a solution in preference to another. Systems with an unfavorable distribution coefficient ($m < 1$, as in our case) will not give necessarily values of β lesser than unity

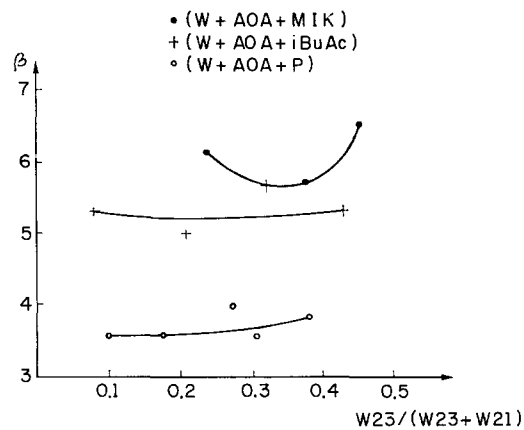


Fig. 5. Selectivity curves on a solvent-free basis at 303.15 K.

as can be seen in Fig. 5. However, their values are not high enough to outweigh the poor distribution coefficients.

3.1. Melting point study

The melting point values of the solid phase corresponding to the solid–liquid equilibria for the regions A, B, and C, Fig. 1, were lower (372.15–374.15 K) than those of pure hydrated oxalic acid reported in the literature, 374.65 K, Table 1, probably due to a little contamination of the other components. For the region D, Fig. 1, their values were between 408.15 and 444.15 K, increasing when the tested sample was nearest to the anhydrous oxalic acid vertex. From these experimental results we conclude that: (i) hydrated oxalic acid is in equilibrium with the corresponding saturated solutions in the regions A, B, and C, and (ii) mixtures of both oxalic acid forms are present in the region D. It is only possible to have pure anhydrous oxalic acid in the binary side of the diagram, between the solvents and the anhydrous oxalic acid vertex.

3.2. Infrared spectroscopy study

Table 5 shows the characteristic absorption maxima of anhydrous and hydrated oxalic acid taken from the literature [10] recorded in nujol together with the assignments of the different bands. The absorption bands obtained from Fig. 6 are also shown. Fig. 6 shows the spectrum of the solid phase in KBr for water + oxalic acid + 1-pentanol system which corresponds to the zone A (see Fig. 1). Similar spectra were obtained for the other zones of all the ternary systems studied here, which is the reason why they are not shown.

Table 5
Characteristic absorption maxima (cm^{-1}) of anhydrous (AOA) and hydrated (HOA) oxalic acid taken from literature and absorption bands of the solid phase for water + oxalic acid + 1-pentanol system

| Band assignment | AOA ^a | HOA ^a | Solid phase ^b |
|------------------|------------------|------------------|--------------------------|
| Stretching | | 3488.8 | 3422.2 |
| | | 3113.1 | 1922.1 |
| | | 1756.0 | 1868.0 |
| | | 1698.0 | 1252.8 |
| | | 1394.8 | 1129.0 |
| | | 1173.4 | 723.9 |
| | | 793.7 | 727.8 |
| | | 721.7 | |
| Bending | | 1688.2 | 1700.0 |
| | | 686.1 | |
| | 654.3 | | |
| Librational mode | | 599.0 | 661.1 |
| | | 572.8 | 477.8 |

^a From Ref. [10] (mull of nujol).

^b In KBr disks.

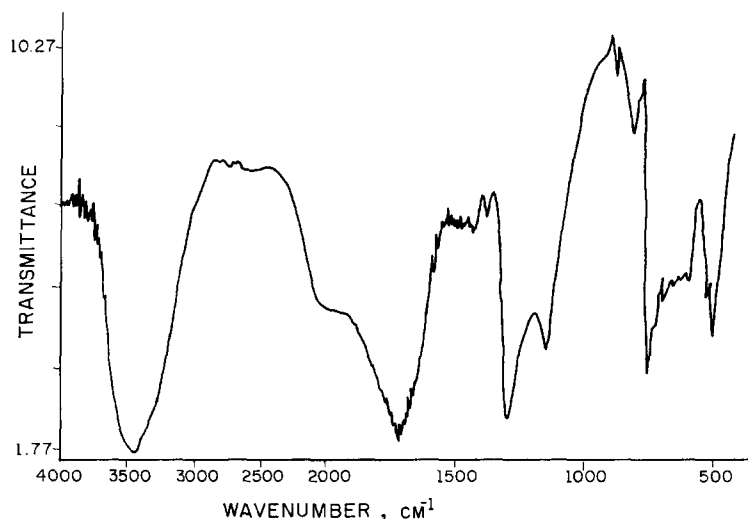


Fig. 6. IR spectrum of solid phase corresponding to zone A in Fig. 1 in KBr.

In general, lattice water absorbs at $3550\text{--}3200\text{ cm}^{-1}$ (OH stretching) and at $1630\text{--}1600\text{ cm}^{-1}$ (HOH bending). In the low frequency region, lattice water exhibits 'librational modes' due to rotational oscillations of the water molecule, restricted by interactions with neighboring atoms. These modes have been located by van der Elsken and Robinson in the $600\text{--}300\text{ cm}^{-1}$ region for the hydrated alkali and alkaline earth halides [11].

From the analysis of these spectra, we conclude that the nature of the solid in equilibrium with ternary saturated solutions corresponds to the hydrated form of oxalic acid for the regions A, B and C, because the IR spectrum (see Fig. 6) shows a stretching absorption band of OH (3422.2 cm^{-1}) a bending one of HOH (1700.0 cm^{-1}) and two librational modes (661.1 and 477.8 cm^{-1}) in agreement with the literature (see Table 5). The spectrum of both mixed oxalic acid forms (zone D, Fig. 1) was similar to that shown in Fig. 6, because the spectrum of the hydrated form is superposed with the anhydrous one, so that the spectrum of this last chemical can not be clearly seen. These conclusions are in agreement with those obtained from the melting point and acid–base titration data.

4. Conclusions

Equilibrium diagrams for the ternary mixtures (water + oxalic acid + 1-pentanol), (water + oxalic acid + isobutyl acetate), and (water + oxalic acid + methyl isobutyl ketone) were obtained at 303.15 K.

The diagram for water + oxalic acid + 1-pentanol is in disagreement with the one determined by Faizal et al. [2] due to the presence of the hydrated form of the acid. A new region where hydrated and anhydrous oxalic acid forms are mixed appears in the complete diagram. The other two ternary systems studied here have similar diagrams.

The capability of a solvent as an extractive agent can be determined by the evaluation of the distribution coefficient defined as $m = w_{23}/w_{21}$, the selectivity defined as $\beta = mw_{11}/w_{13}$, (where

w_{11} and w_{13} are the mass fractions of water in the raffinate and the extract phases, respectively), and the distribution curve on a solvent free basis.

From the experimental results, none of the three solvents studied here were found suitable for oxalic acid extraction processes: their distribution coefficients are always smaller than 1 and the selectivity values are not high enough to outweigh them. This would make a recovery cycle costly and yield a poor process economy. This conclusion is in agreement with Scott et al. [5] who shows that the extraction of oxalic acid with single solvents is not likely to be practical and that the addition of extractants to promote extraction is necessary.

5. List of symbols

| | |
|-------|--|
| AOA | Anhydrous oxalic acid. |
| E | Extract phase. |
| HOA | Hydrated oxalic acid. |
| iBuAc | Isobutyl acetate. |
| MIK | Methylisobutyl ketone. |
| m | Experimental oxalic acid distribution coefficient. |
| P | 1-Pentanol. |
| R | Raffinate phase. |
| W | Water. |
| w | Mass fraction of component i in phase j . |

5.1. Greek letters

| | |
|---------|---------------------------------|
| ρ | Density (kg m^{-3}). |
| β | Selectivity. |

5.2. Subscripts

| | |
|-----|---|
| i | Component (1, 2 and 3). |
| j | Phase (1, raffinate phase and 3 extract phase). |

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