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Influence of Organic Phase Polarity on Interfacial Mechanism and Efficiency of Reactive Extraction of Acetic Acid with Tri-*n*-octylamine

Dan Caşcaval,*[,†] Lenuţa Kloetzer,[†] and Anca-Irina Galaction[‡]

[†]Faculty of Chemical Engineering and Environmental Protection, Department of Biochemical Engineering, "Gh. Asachi" Technical University, D. Mangeron 71, 700050 Iasi, Romania

[‡]Faculty of Medical Bioengineering, Department of Biotechnologies, "Gr.T. Popa" University of Medicine and Pharmacy, M. Kogalniceanu 9-13, 700454 Iasi, Romania

ABSTRACT: The reactive extractions of acetic acid, HAc, with tri-*n*-octylamine (TOA), Q, dissolved in three solvents with different dielectric constants (dichloromethane, butyl acetate, and *n*-heptane) without and with 1-octanol as phase modifier have been comparatively analyzed. The results indicated that the mechanism of the interfacial reaction between acid and extractant is controlled by the organic phase polarity. In absence of 1-octanol, the structures of the extracted complexes are HAc.Q for dichloromethane, $HAc.Q_2$ for butyl acetate, and $(HAc)_2Q_4$ for *n*-heptane. These structures are modified by adding 1-octanol and become HAc.Q for extraction in dichloromethane or butyl acetate and $(HAc)_2Q_2$ for extraction in *n*-heptane, respectively. Although the presence of 1-octanol improves the extraction efficiency, it leads to the reduction of extraction constants for lower-polar solvents, influence that is more significant for *n*-heptane.

INTRODUCTION

Acetic acid is one of the simplest carboxylic acids, being an important raw material or reagent for chemical, pharmaceutical, and food industries. The global demand of acetic acid is about 7×10^6 tonnes/year. This acid can be obtained by chemical synthesis, but the most applied method at industrial scale is the acetic fermentation on various substrates. Its separation from fermentation broths is achieved by distillation. However, due to the formation of water−acetic acid azeotrope, the separation method is rather difficult, needing important energy costs.

Acetic acid is also obtained by mixed acid fermentation. In this case, the final fermentation broths contain complex mixtures of formic, acetic, propionic, lactic, pyruvic, and succinic acids produced by *Escherichia coli*, *Clostridium formicoaceticum*, *Propionibacterium acidipropionici*, *Propionibacterium freudenreichii*, *Actinobacillus succinogenes*, *Actinobacillus succiniproducens*, and *Mannheimia succiniproducens*.[1−9] The selective separation of the acids from these mixtures occurs by precipitation as calcium salts, ionic exchange followed by elution and crystallization, but also with high energy and materials consumption.[10]

For many technologies, the liquid−liquid extraction constitutes a viable solution, due to its technical accessibility and high efficiency. However, its application is limited for the ionizable compounds, namely the carboxylic acids, due to their low solubility in usual organic solvents. In these cases, the performances of the extraction process can be enhanced by reactive extraction with an extractant added into the organic phase. Thus, the reactive extraction using extractants of organophosphoric or high molecular weight amines types has been successfully applied to the separation of some carboxylic acids obtained by fermentation.[10−16]

Due to the low solubility of acetic acid in organic solvents immiscible with water, its separation by physical extraction is not efficient (the maximum extraction yield is reached for aliphatic alcohols with over 4 carbon atoms, but this method is not viable because the acid reacts with the alcohols[12]). For this reason, the reactive extraction of acetic acid with different extractants has been previously investigated. Table 1 presents a brief survey on the literature dedicated to the reactive extraction of this acid with extractants of aminic type.[12,14,17−19] However, there have not been studies of the effect of variation of solvent polarity or established rigorous correlations between the solvent polarity and the number of aminic molecules participating to the interfacial reaction with acetic acid.

In this context, this paper presents the results of the comparative study on reactive extraction of acetic acid with tri-*n*-octylamine (TOA) dissolved in different solvents, with and without addition of 1-octanol as a phase modifier. Because the solvent polarity controls the extraction efficiency, the extraction mechanisms and influencing factors have been analyzed in direct correlation with the polarity of the considered solvents (dichloromethane, *n*-butyl acetate, and *n*-heptane).

MATERIALS AND METHOD

The experiments have been carried out using an extraction column with vibratory mixing, which offers high interfacial area and the possibility to reach rapidly the equilibrium state. The laboratory equipment has been described in detail in previous papers.[20] The phase mixing was made by means of a perforated disk with 45 mm diameter and 20 % free section. The vibrations had a frequency of 50 s^{-1} and 5 mm amplitude. The perforated disk position was maintained at the initial contact interface between the aqueous and organic phases. The extraction time

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Table 1. Previous Studies on Reactive Extraction of Acetic Acid with Aminic Extractants

extractant	solvent	ref
primary, secondary, tertiary amines	various	12
TOA	toluene, chloroform, methyl isobutyl ketone	14
diethylamine, triethylamine, TOA	methyl isobutyl ketone, chloroform	17
TOA	1-octanol	18
TOA	methyl isobutyl ketone	19

Table 2. Dielectric Constants of the Used Solvents at 293.15 K[21]

solvent	dielectric constant
dichloromethane (≥ 99.9 %, Fluka)	9.08
n-butyl acetate (≥ 99 %, Fluka)	5.01
n-heptane (≥ 99 %, Merck)	1.90

was 1 min at a constant temperature of 298.15 K. The resulted emulsion was broken in a centrifugal separator at 5000 rpm.

The initial concentration of acetic acid (≥ 99 %, Fluka) in aqueous solution was 5 $g \cdot L^{-1}$ (0.083 M). The reactive extraction was made with tri-n-octylamine (TOA) (≥ 99.9 %, Aldrich) solved in three solvents with different dielectric constants (Table 2).

1-Octanol (≥ 98 %, Merck) (dielectric constant of 10.3 at 298.15 K[21]) has been dissolved into the above-mentioned solvents, its volumetric fraction being 0.10 and 0.20. The extractant concentration in organic phase (solvent or solvent and 1-octanol) varied between 5 and 120 $g \cdot L^{-1}$ [(0.014 to 0.34) M]. The volumetric ratio of aqueous and organic phase was 1 (20 mL of each phase).

The pH value of initial aqueous solution was varied between 1 and 8. The pH adjustment was made with a solution of 3 % sulfuric acid or 3 % sodium hydroxide, function on the prescribed pH value. The pH values were determined using a digital pH meter of Consort C836 type and have been recorded throughout each experiment. Any pH change was recorded during the extraction experiments.

The extraction process was analyzed by means of the extraction degree, distribution coefficient and extraction constant. For calculating these parameters, the acetic acid concentration in the initial aqueous solution and in the raffinate have been measured. For determining the acid concentration into the solvent phase the mass balance has been used. The acid concentration has been determined by high performance liquid chromatography technique (HPLC, Star Varian Chromatography Workstation) with a PL Hi-Plex H column (7.7 mm diameter, 300 mm length, 8 μm porous particle), provided with UV Prostar 330 PDA detector.[22] The mobile phase was a solution of 0.1 % trifluoroacetic acid with a flow rate of 0.6 $mL \cdot min^{-1}$. The analysis has been carried out at 33.15 K.

Each experiment has been repeated for two or three times for identical conditions, the average value of the considered parameters being used. The maximum experimental error was of ± 4.77 %.

RESULTS AND DISCUSSION

The reactive extraction of monocarboxylic acids with an amine occurs by means of the interfacial interactions between the solute and the extractant. These interactions could be of hydrogen bonding type, for the undissociated acid, or of ionic type, if the acid dissociates in the aqueous solution.[11,12] Furthermore, in function of the structures and concentrations of system components, as well as of solvent polarity, the acidic or aminic adducts could be formed at the interface, the general mechanism of the interfacial reaction being as follows:

$$n\mathrm{R-COOH}_{(aq)} + p\mathrm{Q}_{(o)} \rightleftarrows \mathrm{R-COOH}_n\mathrm{Q}_{p(o)}$$

(Q symbolizes the aminic extractant).

In the case of reactive extraction of acetic acid with TOA, the previous studies indicated that the extractant reacts only with the undissociated molecules of acid.[14] Moreover, if low-polar solvents are used (for example, toluene), the dimers of acetic acid are formed in organic phase through the intermolecular hydrogen bonding.[14]

Because the polarities of the used solvents differ significantly, the mechanism of the reactive extraction of acetic acid, HAc, with TOA is verified by taking into consideration the following expressions of the interfacial reaction between solute and extractant (the number of acid molecules participating to the interfacial complex formation depends on the solvent polarity):

- dichloromethane, butyl acetate

$$\mathrm{HAc}_{(aq)} + p\mathrm{Q}_{(o)} \rightleftarrows \mathrm{HAc.Q}_{p(o)}$$

- *n*-heptane

$$2\mathrm{HAc}_{(aq)} + p\mathrm{Q}_{(o)} \rightleftarrows (\mathrm{HAc})_2\mathrm{Q}_{p(o)}$$

These mechanisms have been analyzed distinctly for each solvent. Therefore, for the solvents with higher polarity, the distribution coefficient, D, is calculated with the relationship:

$$D = \frac{[\mathrm{HAc.Q}_{p(o)}]}{[\overline{\mathrm{HAc}_{(aq)}}]} \quad (1)$$

where $[\overline{\mathrm{HAc}_{(aq)}}]$ and $[\mathrm{HAc.Q}_{p(o)}]$ symbolize the total concentrations of acetic acid and extracted compound at the equilibrium state in the related phases.

According to the interfacial equilibrium, the extraction constant, K_E, can be calculated with the following expression:

$$K_E = \frac{[\mathrm{HAc.Q}_{p(o)}]}{[\mathrm{HAc}_{(aq)}][\mathrm{Q}_{(o)}]^p} \quad (2)$$

The concentration of undissociated acid from aqueous phase, $[\mathrm{HAc}_{(aq)}]$, can be calculated by means of its overall concentration in aqueous phase, dissociated acid concentration and the dissociation constant, K_a. Thus, the concentration of undissociated acetic acid from the aqueous phase is

$$[\mathrm{HAc}_{(aq)}] = \frac{[\overline{\mathrm{HAc}_{(aq)}}]}{1 + \frac{K_a}{[\mathrm{H}^+]}} \quad (3)$$

Therefore, by combining the eqs 1 and 3, the following expression for the distribution coefficient, D, between aqueous phase and dichloromethane or butyl acetate is obtained

$$D = \frac{K_E[\mathrm{Q}_{(o)}]^p}{1 + \frac{K_a}{[\mathrm{H}^+]}} \quad (4)$$

The correlation 8 represents in logarithmic form the equation of a straight line

$$\ln D + \ln\left(1 + \frac{K_a}{[H^+]}\right) = \ln K_E + p \ln[Q_{(o)}] \quad (5)$$

Because the initial concentration of extractant is higher than the initial concentration of acetic acid, $[Q_{(o)}]$ could be assumed to be the initial concentration of TOA in organic phase. Consequently, from the slope of the straight line given by eq 5 it is possible to determine the number of extractant molecules, p, which participate to the formation of the interfacial compound, and from its intercept the value of extraction constant, K_E.

For reactive extraction in *n*-heptane, by means of the corresponding interfacial equilibrium, the distribution coefficient and the extraction constant become

$$D = \frac{2[(HAc)_2Q_{p(o)}]}{[HAc_{(aq)}]} \quad (6)$$

$$K_E = \frac{[(HAc)_2Q_{p(o)}]}{[HAc_{(aq)}]^2[Q_{(o)}]^p} \quad (7)$$

Respecting a similar algorithm, the logarithmic form of specific relationship for calculating the distribution coefficient becomes

$$\ln \frac{D}{2[HAc_{(aq)}]} + 2\ln\left(1 + \frac{K_a}{[H^+]}\right) = \ln K_E + p\ln[Q_{(o)}] \quad (8)$$

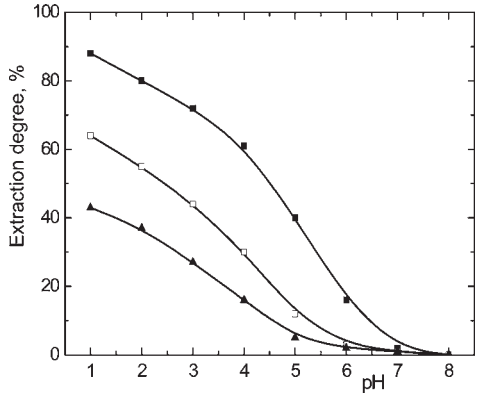

Figure 1. Influence of pH value of aqueous phase on reactive extraction degree of acetic acid (TOA initial concentration = 40 $g \cdot L^{-1}$; ■, dichloromethane; □, butyl acetate; ▲, *n*-heptane).

which can be used for calculating the number of extractant molecules, p, and the extraction constant, K_E.

Indifferent of the extraction mechanism and solvent type, the pH value of the aqueous solution controls the separation efficiency. From Figure 1 and Table 3, for extraction systems without 1-octanol, it can be observed that the reactive extraction degree is reduced by increasing the pH, due to the acetic acid dissociation, this effect becoming more pronounced for pH values higher than 4 ($pK_a = 4.76$[22]). For pH over 7 the extraction of acetic acid is not possible. Due to the superior ability of dichloromethane to solubilizing the dissociated molecules, the difference between the variations of extraction yield corresponding to the pH domains lower and higher than 4, respectively, is less important than in the case of other two solvents.

The highest extraction efficiency is reached for dichloromethane, due to its superior dielectric constant. Thus, at pH 1, in absence of 1-octanol, the extraction yield of acetic acid with TOA decreases from 88 % for dichloromethane to 64 % for butyl acetate and, finally, to 43 % for *n*-heptane.

The increase of extractant concentration in the solvent phase exhibits a favorable effect on the acid extraction, due to the increase of the interfacial amount of one of the reactants. Figure 2 indicates that the influence of TOA concentration is important only for its variation below a certain value, over this level the effect becoming insignificant. The value of amine concentration corresponding to the change of the magnitude of this effect increases with the solvent polarity, from about 30 $g \cdot L^{-1}$ (0.085 M) for dichloromethane to 60 $g \cdot L^{-1}$ (0..17 M) for butyl acetate and *n*-heptane. This variation can be attributed to the modification of the interfacial reaction mechanism, respectively to the modification of the number of TOA molecules participating to the formation or solvation of the extracted complex.

For establishing the structure of the interfacial complex, the straight lines described by eqs 5 and 8 were plotted in Figure 3, for solvent phases without 1-octanol. The values of the straight lines slope, implicitly the number of TOA molecules included in the chemical structure of this complex, depend on solvent polarity, being given in Table 4.

The obtained values suggest that in the case of dichloromethane and butyl acetate the interfacial complex structures are HAc.Q and $HAc.Q_2$, respectively. For extraction in *n*-heptane, the structure is modified, becoming $(HAc)_2Q_4$. These results confirm the important role of the solvent polarity on the extraction of ionizable solutes. The dielectric constant is considered a characteristic of extractant - solute local interactions, inducing the limitation of solute solvation by aminic extractant,

Table 3. Variation of Extraction Degree (%) of Acetic Acid with pH Value of Aqueous Phase, for 40 $g \cdot L^{-1}$ TOA Dissolved in Solvents without and with 1-Octanol (Volumetric Fraction 0.01)

	without 1-octanol			with 1-octanol		
pH value	*n*-heptane	butyl acetate	dichloromethane	*n*-heptane	butyl acetate	dichloromethane
1	43	64	88	50	65	86
2	37	55	80	44	58	80
3	27	44	72	34	48	71
4	16	30	61	18	30	51
5	5	12	40	5	10	20
6	2	3	16	1	2	3
7	1	1	2	0	0	0
8	0	0	0	50	65	86

due to the presence of ionizable groups in the solute chemical structure.[23] The modification of dielectric constant has a smaller effect on the solubility and extraction of nonelectrolytes or weak electrolytes, but it becomes an important factor for the extraction of dissociable solutes, as acetic acid.

The proposed structures of the interfacial complexes are also confirmed by the variation of reactive extraction yield with TOA concentration plotted in Figure 2. For the solvent with the highest polarity, namely dichloromethane, Figure 2 indicates that the extraction degree continuously increases with the increase of TOA concentration only for extractant concentration below 30 $g \cdot L^{-1}$ (0.084 M), value that corresponds to a molar ratio of 1:1 between the acid and the amine. This ratio is changed to 1:2 for butyl acetate and corresponds to 60 $g \cdot L^{-1}$ (0.167 M) TOA. Also for *n*-heptane, the variation of extraction yield becomes slower over 60 $g \cdot L^{-1}$ (0.167 M) extractant concentration, this level suggesting the molar ratio acetic acid: TOA of 2:4.

The efficiency of reactive extraction can be improved by adding of a higher-polar solvent in the organic phase. This solvent increases the organic phase polarity and, consequently, exhibits a favorable effect on the solubilization of polar molecules. Moreover, it possesses the ability to induce the breakage of the stable "third phase" emulsion which could appear in the systems using amines as extractants, being called "phase modifier".

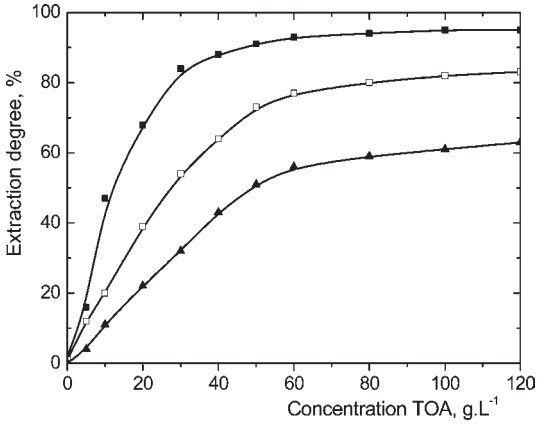

Figure 2. Influence of TOA concentration on reactive extraction degree of acetic acid (pH 1; ■, dichloromethane; □, butyl acetate; ▲, *n*-heptane).

Generally, this phase modifier is an alcohol with an aliphatic chain with at least 8 carbon atoms.[12] In this purpose, 1-octanol has been used in the presented experiments.

The addition of 1-octanol into the organic solvent does not change the general shape of the dependence between the extraction efficiency and pH of the aqueous phase. However, as it can be seen from Figure 4 and Table 3, it leads to the increase of acetic acid extraction degree, this effect being amplified for low-polar solvents. In the same time, for strong acidic domain of pH, the slow variations of extraction yield become more evident for butyl acetate and *n*-heptane with 1-octanol than for these solvents without 1-octanol, owing to the partial solubilization of dissociated molecules of acetic acid by increasing the solvent polarity in presence of alcohol.

For underlining the positive influence of 1-octanol on reactive extraction, the dependences between the amplification factor and the pH value of aqueous phase were plotted in Figure 5 for the studied extraction systems (the amplification factor was defined as the ratio between the acetic acid extraction degrees for the solvent with and, respectively, without 1-octanol). These variations indicate that the effect of 1-octanol addition is more important for butyl acetate and *n*-heptane. Thus, compared to the extraction systems without 1-octanol, for a volumetric fraction of this alcohol of 0.20, the maximum increase of extraction yield of acetic acid is of 1.7 times for dichloromethane, 2.28 times for butyl acetate and 4.13 times for *n*-heptane, respectively.

For all considered solvents, the maximum value of amplification factor is reached at pH 5, due to the higher concentration of dissociated acid molecules which cannot be extracted in absence of 1-octanol. The further increase of pH value induces the formation of sodium acetate and, implicitly, the reduction of acid extraction yield.

For establishing the mechanism of the interfacial reaction between acetic acid and TOA in presence of phase modifier, the

Table 4. Number of TOA Molecules Included in the Interfacial Compound Structure, *p*, for Solvents without 1-Octanol

solvent	*p*	error, %	R^2
dichloromethane	1.11	±8.03	0.969
butyl acetate	1.91	±5.20	0.984
n-heptane	4.07	±6.21	0.978

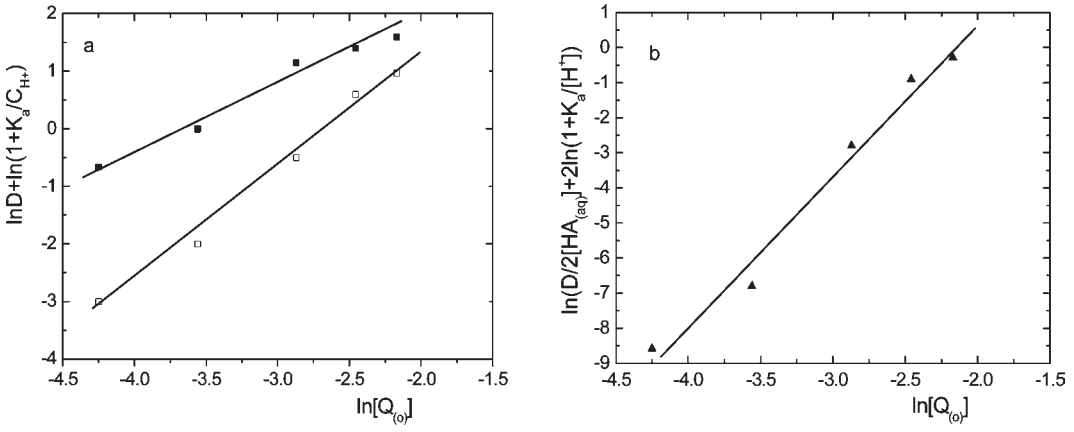

Figure 3. Graphical representation of the straight lines given by eqs 5 and 8 for solvents without 1-octanol (a: ■, dichloromethane; □, butyl acetate, b: ▲, *n*-heptane).

straight lines described by eqs 5 and 8 were plotted and analyzed for 20 % vol. 1-octanol added into solvent phase. According to Figure 6, the obtained values of the straight lines slopes are listed in Table 5.

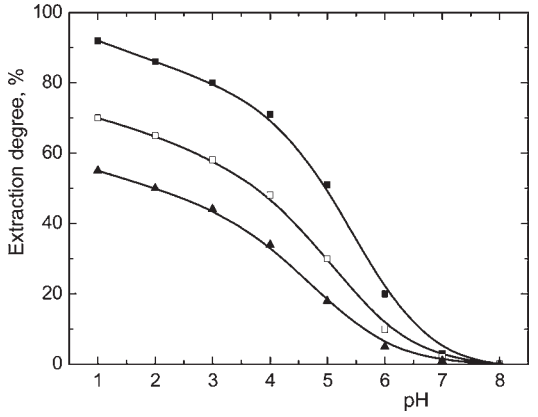

Figure 4. Influence of pH value of aqueous phase on reactive extraction degree of acetic acid in presence of 1-octanol (TOA initial concentration = 40 g·L^{-1}, 1-octanol volumetric fraction = 0.10; ■, dichloromethane; □, butyl acetate; ▲, *n*-heptane).

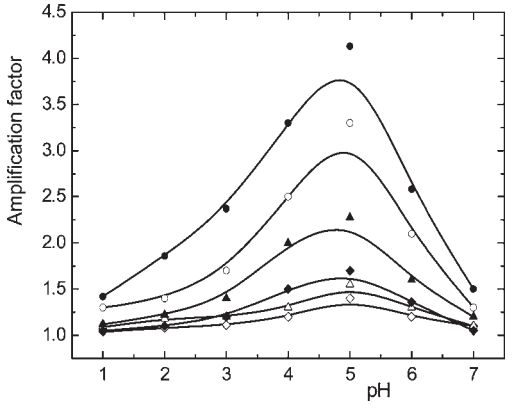

Figure 5. Influence of pH value of aqueous phase on amplification factor (TOA initial concentration = 40 g·L^{-1}; ●, *n*-heptane + 20 % vol. 1-octanol; ○, *n*-heptane + 10 % vol. 1-octanol; ▲, butyl acetate + 20 % vol. 1-octanol; ♦, dichloromethane + 20 % vol. 1-octanol; △, butyl acetate + 10 % vol. 1-octanol; ◇, dichloromethane + 10 % vol. 1-octanol).

Compared to the results recorded for the reactive extraction of acetic acid without 1-octanol, the addition of this alcohol reduces the number of extractant molecules included in the chemical structures of the extracted compounds. This effect is due to the hindrance of the aminic adducts formation in solvents with higher polarity. Therefore, the interfacial complexes structures become HAc.Q for butyl acetate, and $(HAc)_2Q_2$ for *n*-heptane, respectively. The extraction in dichloromethane constitutes the exception, the structure of the extracted compound remaining the same as in the absence of 1-octanol.

Being directly related to the extraction mechanism, the value of the extraction constant for a certain solvent is modified in presence of 1-octanol (Table 6). The obtained values underline the importance of the solvation of acetic acid by extractant molecules in the interfacial equilibrium stability. As can be observed in Table 6, the highest values of K_E corresponds to the formation of the complex $(HA)_2Q_4$, for extraction into *n*-heptane without alcohol. For the extraction in butyl acetate and *n*-heptane, in presence of 1-octanol the number of TOA molecules from the structure of interfacial complex is reduced, this leading to the significant decreasing of the extraction constant. The most important reduction is recorded for extraction in *n*-heptane and is the result of the most important diminution of the number of extractant molecules participating to the interfacial compound formation. Thus, it can be concluded that the increase of solvent polarity exhibits a negative effect on the interfacial equilibrium by hindering the solute solvation.

For the extraction systems based on the same interfacial mechanism of reaction between acetic acid and TOA (HAc.Q formation for extraction in dichloromethane without or with 1-octanol and in butyl acetate with 1-octanol), the increase of solvent dielectric constant exhibits a positive effect on K_E, owing

Table 5. Number of TOA Molecules Included in the Interfacial Compound Structure, *p*, for Solvents with 1-Octanol

solvent	*p*	error, %	R^2
dichloromethane	0.88	±4.54	0.994
butyl acetate	1.04	±4.45	0.997
n-heptane	1.89	±5.82	0.980

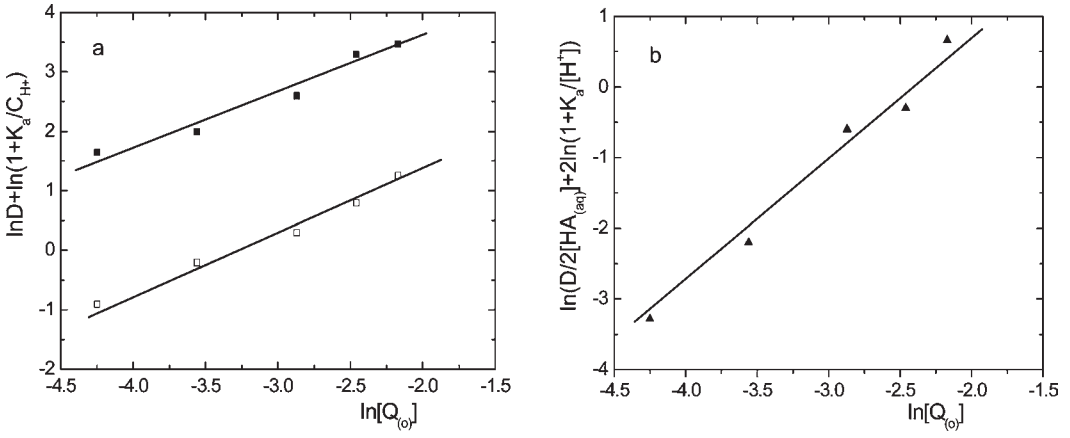

Figure 6. Graphical representation of the straight lines given by eqs 5 and 8 for solvents with 1-octanol (1-octanol volumetric fraction = 0.20; a, dichloromethan and butyl acetate; b, *n*-heptane).

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Table 6. Expressions and Values of Extraction Constants for the Studied Systems

organic phase	extraction constant	value	error, %	R^2
dichloromethane	$K_E = ([HAc.Q_{(o)}])/([HAc_{(aq)}][Q_{(o)}])$	55.15 (L/mol)	±7.43	0.973
dichloromethane + 20 % vol. 1-octanol	$K_E = ([HAc.Q_{(o)}])/([HAc_{(aq)}][Q_{(o)}])$	3.21×10^2 (L/mol)	±3.55	0.992
butyl acetate	$K_E = ([HAc.Q_{2(o)}])/([HAc_{(aq)}][Q_{(o)}]^2)$	2.21×10^2 (L^2/mol^2)	±4.06	0.989
butyl acetate + 20 % vol. 1-octanol	$K_E = ([HAc.Q_{(o)}])/([HAc_{(aq)}][Q_{(o)}])$	29.66 (L/mol)	±3.67	0.991
n-heptane	$K_E = ([(HAc)_2Q_{4(o)}])/([HAc_{(aq)}]^2[Q_{(o)}]^4)$	4.49×10^3 (L^5/mol^5)	±7.11	0.974
n-heptane + 20 % vol. 1-octanol	$K_E = ([(HAc)_2Q_{2(o)}])/([HAc_{(aq)}]^2[Q_{(o)}]^2)$	1.66×10^2 (L^3/mol^3)	±6.12	0.981

to the improvement of the solvent ability to solve the interfacial complex.

CONCLUSIONS

The solvent polarity controls the structure of the interfacial compounds formed by reaction between acetic acid and TOA. Thus, by changing the solvent in the following sequence: dichloromethane, butyl acetate and *n*-heptane, the following compounds are formed HAc.Q, $HAc.Q_2$, and $(HAc)_2Q_4$, respectively.

For all studied systems, the addition of 1-octanol into the solvent phase led to the increase of extraction efficiency and to the modification of extraction mechanism. The most inportant influences have been recorded for *n*-heptane. Thus, the maximum amplification factors obtained for a volumetric fraction of alcohol of 0.20 in *n*-heptane as solvent was for about 2.4 times higher than that corresponding to dichloromethane, and for about 1.8 times higher than that recorded for butyl acetate. Moreover, in presence of 1-octanol the number of TOA molecules included in the interfacial compound structure is reduced to one for butyl acetate, and for two for *n*-heptane.

The addition of 1-octanol exhibited a negative effect on the extraction constants, especially for the low-polar solvent, namely *n*-heptane.

AUTHOR INFORMATION

Corresponding Author

*Fax: +40.232.271.311. E-mail: dancasca@ch.tuiasi.ro.

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