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*Dedicated to Professor Ionel Haiduc*
*on the occasion of his 65th birthday*

# CHLORHIDRIC ACID REMOVAL FROM REACTION EFFLUENT IN MAKING ACETOCHLOR

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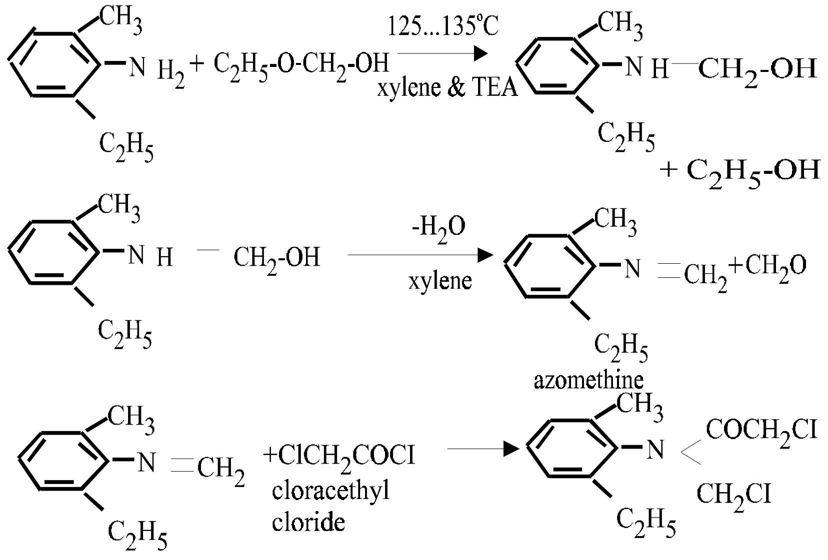
**ABSTRACT.** The paper present an experimental study of HCl extraction with water from the mixtures: HCl -ethanol-benzene-water, HCl-ethanol-xilene-water, HCl-ethanol-acetochlor-benzene-water. In this study repartition coeficcients of HCl between aqueous phase and organic phase were determinated. Also, base on experimental data it was established that the named systems obey the Nernst-Silov law.

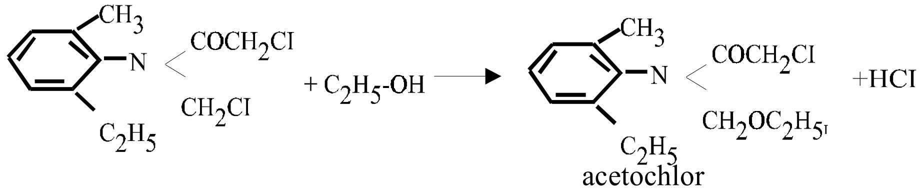
## 1. General considerations

In the last few years, in herbicides production was appeared new products which depend on acetochlor, as active substance for compounding.

In order, to obtain this chemical compound ther are used ethanol, formaldehyde, 2-methyl 6-ethyl aniline, the succession of reactions, which takes place in the xylene or benzene medium are next [1, 2]:

$$C_2H_5\text{-}OH + CH_2O \longrightarrow C_2H_5O\text{-}CH_2\text{-}OH$$





Finally, it was obtained an ethanol, benzene (or xylene), acetochlor and HCl mixture prezented in table1.

**Table 1**

The final composition of reaction mixture

| Component | Concentation, % weight |
|---|---|
| Acetochlor | 27.12 |
| Ethanol | 41.56 |
| Benzene (xylene) | 26.7 |
| HCl | 4.62 |
| Total | 100 |

In nowadays, in order to HCl removal from this mixture ther are uses two processes, based on two patents [1, 2]: first, a process based on the HCl neutralizating with $NH_3$, the $NH_4Cl$ formed is removed from the system by filtration [1] and second process is based on HCl extracting with water [2].

The filtration presents some troubles because the danger of frecvently clog of filtrant medium. For eliminated this inconvenient, a Romanian chemical company adopts an ICECHIM prosess for a acetochlor synthesis and for HCl removal it is proposed extraction with water.

In the literature [3] there are the liquid-liquid equilibrium data in the system HCl -water-benzene (xylene or toluene), presented graphicaly in figure 1.

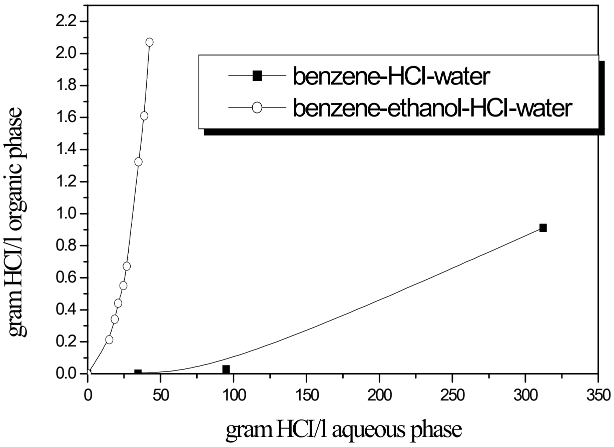


Figure 1. Comparative equilibrium liquid-liquid curves for systems: benzene-HCl -water and benzene-ethanol-HCl -water

The final mixture contains also benzene, acetochlor and ethanol, which significantlly changes the HCl repartition coefficient, especially because, simultaneous with HCl extraction from the organical phase the ethanol is extracted also.

Because the technological design of the HCl extraction with water requires to knowledges liquid-liquid equilibrium data, respectively the HCl repartition coefficients between the aqueous phase and the organic phase in this paper was proposed the experimental determination of these coefficients for this mixture.

## 2. Experimental determinations

The experimental determinations of HCl repartition coefficients was effectueted with a equilibrium cells at $20^0$C, for a synthetic mixture with composition presented in table 1, in two ways: first, it were determinated the repartition coefficients between the aqueous phase and the organic phase which contains only benzene (or xylene) and ethanol, in order to observe the influence of the ethanol presence on repartition coefficients and second, it were determinated the repartition coefficients between the aqueous phase and the organical phase which contains benzene, acetochlor and ethanol conform the synthesis reaction. The experimental results obtained in these two ways are presented graphical in figures 1, 2, 3, 4 and 5.

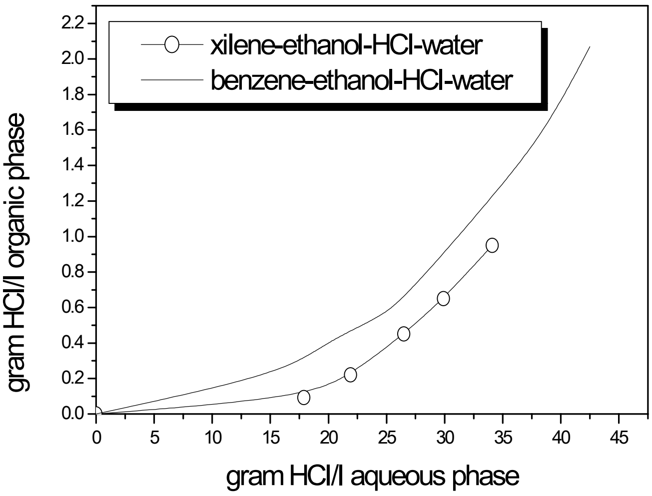


Figure 2. Comparative equilibrium liquid-liquid curves for systems: xylene-ethanol-HCl –water and benzene-ethanol-HCl –water

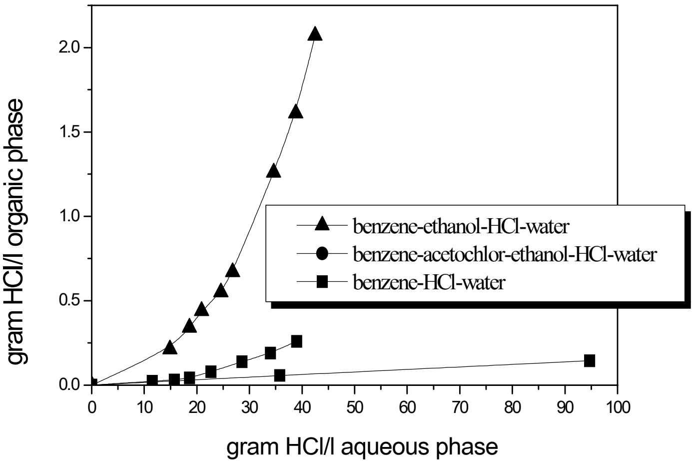


Figure 3. Comparative equilibrium liquid-liquid curves for systems: benzene-ethanol-HCl –water, benzene-acetochlor-ethanol-HCl -water and benzene-HCl -water

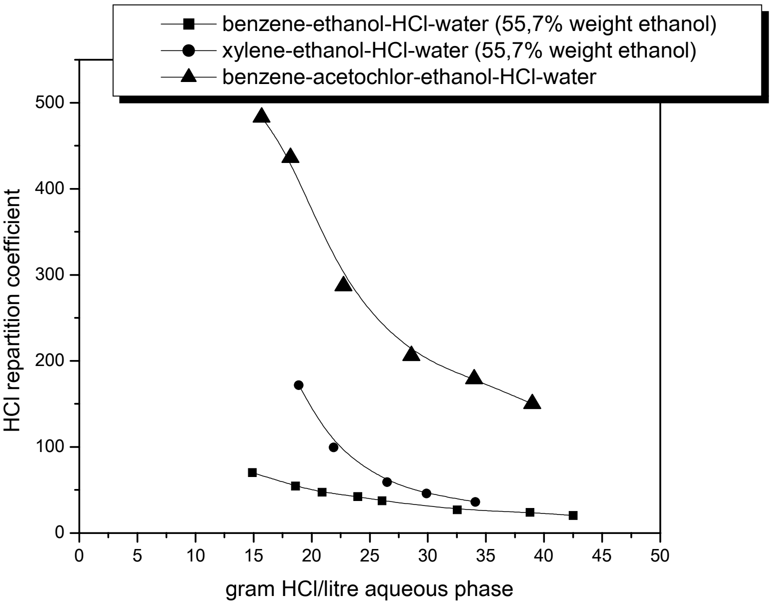


Figure 4. Comparative HCl repartition coefficient curves at 20˚C function by HCl concentration in aqueous phase for systems: benzene-ethanol-HCl –water, xylene-ethanol-HCl water and benzene-acetochlor-ethanol-HCl -water

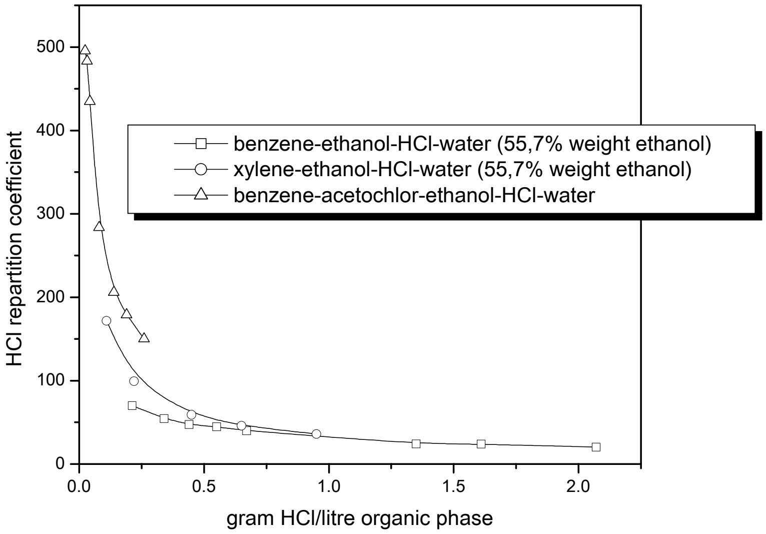


Figure 5. Comparative HCl repartition coefficient curves at 20ˇC function by HCl concentration in organic phase for systems: benzene-ethanol-HCl –water, xylene-ethanol-HCl water and benzene-acetochlor-ethanol-HCl -water

For all the cases, including the literature case, the HCl repartition coefficients decrease with the increasing its concetration in the aqueous phase (view figure 4).

The presence of ethanol in the aqueous phase substantial change the HCl repartition coefficients in sense of their decreasing. For example, in case of the mixture in which the ethanol by in organic phase is in a proportion of 55,7% against benzene, respectively xylene, the repartition coefficients decrease from 70,3 to 20,5 in benzene case, respectively from 171,8 to 35,9 in xylene case (view figure 4, 5). This thing is the result of two cumulative effects, namely: first, the high solubility of the ethanol in water, simultaneous with the HCl extraction, take place the extraction of a high quantity of ethanol from organic phase in aqueous phase. The quantity of this phase raise and, in consequently, for a quantity of HCl extract, the concetration in the aqueous phase will be lower and the second, in the organic phase still remains unextract ethanol which favorises the water solubility in the organic phase and, consequently, the HCl solubility, raising in this way the HCl concentration in organic phase.

The HCl repartition coefficients in the benzene-ethanol-HCl -water mixture are lower than the xylene-ethanol-HCl -water mixture case (view figure 4 and 5), because the way in which the ethanol and the water between the hydrocarbon phase and the aqueous phase are distributed.The liquid-

liquid equilibrium data in the benzene-ethanol-HCl -water and xylene-ethanol-HCl -water systems, show that the solubilities of ethanol and water in organic phase are higher in the benzene case than in the xylene case (view figure 2).

### 3. The mathematical processing of experimental data

In the liquid-liquid extraction with imiscible solvents [4, 5], in the equilibrium data can be exprimate either through Nernst's liniar relation (equation 1), or through Nernst-Silov's nonliniar relation (equation 2), or through a certain curve:

$$K=C_1/C_2 \qquad (1)$$

$$K = {C_1}\Big/{C_2^n} \qquad (2)$$

where:

K represent the HCl repartition coefficient ;

$C_1$-concentration of HCl in the aqueous phase;

$C_2$ -concentration of HCl in the organic phase;

n-specific constant of the system.

A simple looking through the liquid-liquid equilibrium data graphically represented in figures 1, 2 and 3 show that this data can be described either by the Nernst-Silov's rule or by a certain curve. In order to find this we appeal to the second equation which after logarithmation, becomes:

$$\ln C_1 = \ln K + n \ln C_2 \qquad (3)$$

So, in logaritmic coordinates the (3) equation represented the equation of a straight line with the slope equal to *n* and the intercept equal to *lnK*.

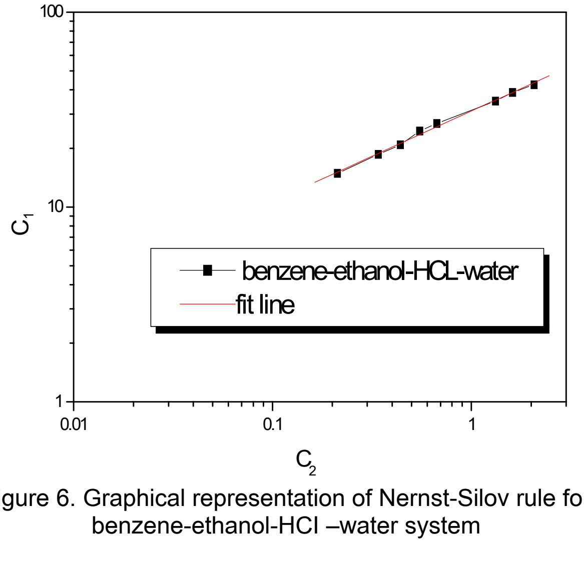


Figure 6. Graphical representation of Nernst-Silov rule for benzene-ethanol-HCl –water system

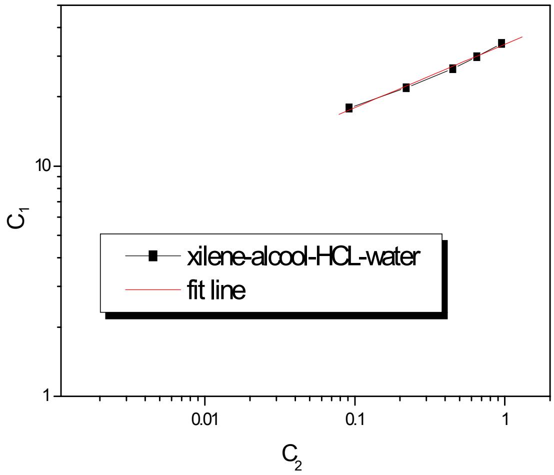


Figure 7. Graphical representation of Nernst-Silov rule for xylene-ethanol-HCl –water system

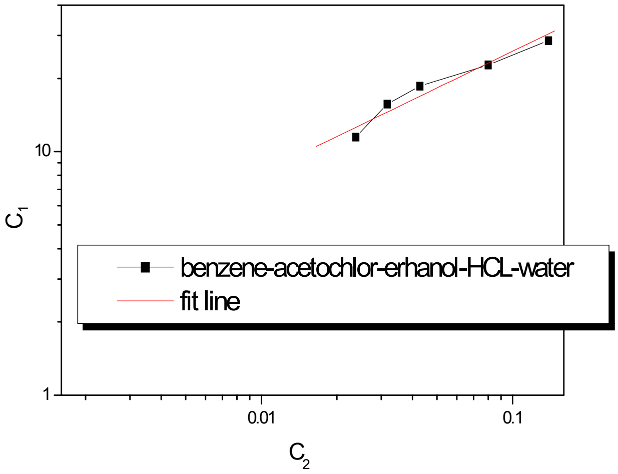


Figure 8. Graphical representation of Nernst-Silov rule for benzene-acetochlor-ethanol-HCl –water system

Grafical representions of these corelation in logarithmic graphics (view figure 6, 7, 8), show that: benzene-ethanol-HCl -water and xylene-ethanol-HCl-water systems obey very well the Nernst-Silov’s rule (staight line), while the third system the points spread is a litlle higher.

## Conclusions

An experimental study about HCl extraction with water from several systems, namely: benzene-ethanol-HCl-water, xylene-ethanol-HCl-water and benzene-ethanol-acetochlor-HCl-water at $20^0$C, was done. In the future will be elaborate a HCl removal technology using washing with water of the reaction effluent based on this experimental study.

The experimental data show that the present of the ethanol in organical phase decreases the HCl solubility in this phase; in this way the value of repartition coefficients between the aqueous phase and the organic phase become lower.

Finally, the mathematical processing of experimental data shows that these above-mentioned systems obey to the Nernst-Silov’s rule.

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