

## Kinetics of the Transfer of Protonated Triazines Across the water|1,2-dichloroethane Interface

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Kinetics of the transfer of protonated triazines across the water|1,2-dichloroethane interface by mean cyclic voltammetry and electrochemical impedance spectroscopy was studied. The transfer Gibbs energy ( $\Delta G_t^{o,w \rightarrow o}$ ) and the apparent rate constants ( $k_s$ ) across the liquid-liquid interface for atrazine, ametryn, terbutryn and prometryn were evaluated. The results showed that hydrophobicity and the molecular size of these herbicides play an important role in the kinetics values. Thus the atrazine (smaller molecular dimensions) have larger  $k_s$  value compared to the ametryn, terbutryn and prometryn (larger molecular dimensions). The explanation of this difference is in the structural ability of the molecule to protect the charged group which is the one responsible for transporting the current across the interface. The present study can be an important approach to help understand the permeation kinetics of molecules across biological membranes.

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**Keywords:** ITIES, Triazines, Kinetic process, ion transfer

### 1. INTRODUCTION

Investigations on the interface of two immiscible electrolyte solutions (ITIES) have been carried out by several research groups all over the world [1-7], since ITIES allows to understand the ionic transfer phenomena across the biphasic system (water|oil), such as heavy metal extraction, transfer of organic molecule of pharmacological importance [8], as well as the electron transfer reaction that could be similar to that happening in biological systems [9].

The ITIES can be polarized from an external power source; this is a great advantage, since the distribution of ionic equilibrium across the interface can be manipulated. Kinetics studies of the charge

transfer at liquid|liquid have been carried out for several cations, as an example, tetramethylammonium cation, small amines [9, 10] and highly hydrophobic long chain amines (octylaniline, hexadecylaniline and dodecylaniline [11]. Another study is the kinetics of facilitated proton transfer by 18-crown-6 [12] by means of the impedance electrochemistry spectroscopy where the ligand concentration has no effect on the rate transfer at the ITIES. In similar research, the kinetics of nickel extraction at the biphasic system [13] has also been studied. In this matter, important work was carried out on the facilitated ion transfer followed by organic complexation (TOC or EC mechanism) which took into account the kinetics of this complexation reaction, and which was discussed by solving an equation for the normal pulse voltammetric and chronoamperometric [14].

In previous studies dealing with the triazine herbicide transfer at the water|1,2-dichloroethane interface, it was demonstrated that the pH plays an important role in the transfer mechanism across the interface; at the  $\text{pH} < \text{pK}_a$ , the triazine is transferring as a whole protonated molecule, while at  $\text{pH} > \text{pK}_a$ , the triazine acts as a mobile proton carrier across the interface; in this case the herbicide molecule remains in the organic phase and the protonation takes place at the interface [15]. These results were shown through a partition ionic diagram (Galvani potential-pH) [9, 16]. In fact, a theoretical study of the partitioning process of amines transfer process at the water|1,2-dichloroethane interface has also been carried out [9, 17]. Other interesting applications of the ITIES are the studies of small interface to detect cadmium by square voltammetry techniques [18]. Recently, the ion-transfer voltammetric detection of the protonated  $\beta$ -blocker propranolol was carried out in nanoscale interface (nanoITIES) [19] and the detection of ractopamine at microITIES [20]. Triazines herbicides have also been studied at ITIES [21] from an electroanalytical point of view; also, the herbicide metamitron has been studied on a modified liquid-liquid interface with phosphatidylcholine [22].

The kinetics of the charge transfer at the ITIES can be dependent on the dissolution-resolvation process, since the transfer mechanism involves two solvents of different physicochemical properties. In a biological system, the permeation kinetics of antioxidants cations (the triphenylphosphonium cation) is an important step in mitochondria [23]. The kinetics process for the electron transfer reaction between two novel multicenter redox molecules (triferrocenylmethane and triferrocenylmethanol) has been studied in a thin film of nitrobenzene (NB) on a graphite electrode and an aqueous electrolyte process at the ITIES [24]. In fact, the studies discussed above show that the kinetics reaction process can be carried out in nontraditional electrochemical system, whereas the electrochemical techniques such as ac impedance can be applied to extract kinetics parameters of the charge transfer at the ITIES.

The aim of this work was to study the kinetics for a series of triazines herbicides transfer across the water|1,2-dichloroethane interface in order to find out the variables that may control this process.

## 2. EXPERIMENTAL SECTION

For electrochemical experiments, a two-electrode cell configuration was employed. Two Ag/AgCl electrodes with a large area of  $7.0 \text{ cm}^2$  and the planar interface were easily adjusted in the cell with a syringe.

Tetraphenylarsonium chloride (TPAsCl, Fluka), 1,2-dichloroethane (1,2-DCE, Gold Label, Aldrich) and potassium tetrakis(4-chlorophenyl)borate (KTPBCl, Fluka purum) were used as received. Tetraphenylarsonium tetrakis(4-chlorophenyl)borate (TPAsTPBCl) was precipitated from the corresponding chemicals and re-crystallized twice from acetone (BDH, AnalaR). The herbicides atrazine (ATR), ametryn (AME), terbutryn (TRB) and prometryn (PRM) (Riedel-de-Haen) were used as received. LiCl (sigma-Aldrich) was used as supporting electrolyte in the aqueous phase. The pH was adjusted with H<sub>2</sub>SO<sub>4</sub> (Sigma-Aldrich) in order to have a pH < pK<sub>a</sub>; this ensured a completely protonated molecule [15], thus the kinetics of the whole transferring molecule across the interface was monitored. The aqueous solutions were prepared in ultrapure water (Easypure UV, Barnstead). All the experiments were carried out at 25 ± 1 °C. During measurements, the electrochemical cell was placed inside a Faraday cage.

The potentials were reported on the Galvani potential scale and calculated according to [25]:

$$E_{CELL} = \Delta_o^w \phi - \Delta_o^w \phi_{TPAs^+} \quad (1)$$

where  $\Delta_o^w \phi$  was the Galvani interfacial potential and  $\Delta_o^w \phi_{TPAs^+}$  the organic reference liquid junction potential [26]. The standard transfer potential of TPAs<sup>+</sup>,  $\Delta_o^w \phi_{TPAs^+}^o$  for TPAs<sup>+</sup> was taken as -0.364 V [27].

The cyclic voltammetry and the electrochemical impedance spectroscopy (EIS) were carried out with a potentiostat/galvanostat PGSTAT30 (Autolab). The EIS was performed with a sinusoidal signal of 10 mV for different imposed potentials and no IR compensation was used. Finally, the spectra signal was recorded from a 1-1000 Hz of frequencies. The solution resistance was extrapolated at high frequency in the impedance plot.

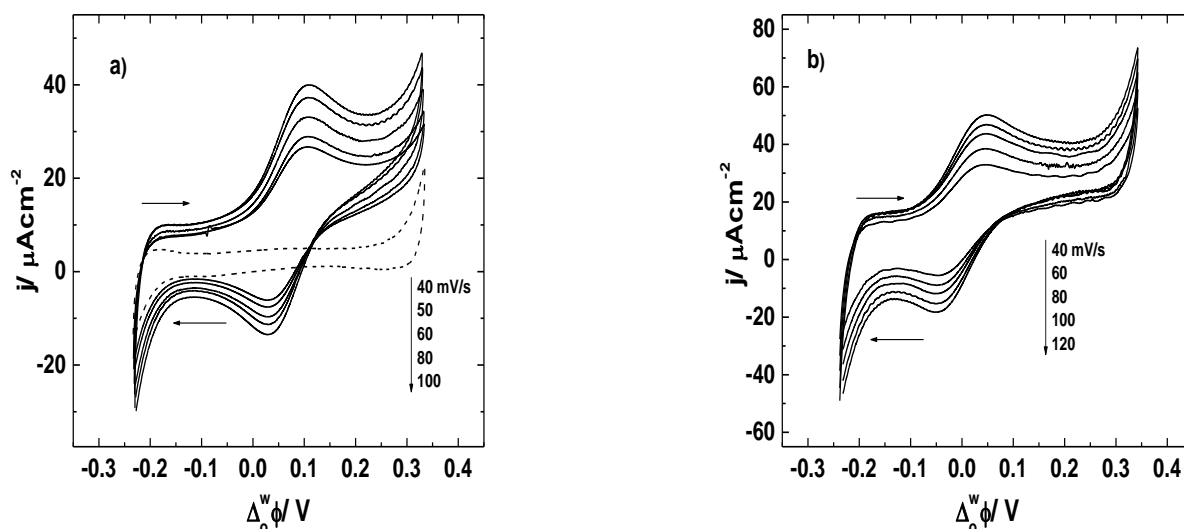
### 3. RESULTS AND DISCUSSION

#### 3.1 Cyclic voltammetry

In the present work, when polarization scan rate goes in the positive direction of electrical potential, the aqueous phase is considered to be more positive than the organic phase; in this way the negative species move from the organic phase to the aqueous phase and the positive species in the aqueous phase are transferred to the organic phase.

Figure 1a shows the CV for the AME transfer at the water|1,2-DCE interface. Firstly, the CV was carried out for the base line (dotted line) at a polarization scan rate of 50 mV/s, the pH of the aqueous phase was adjusted to 2.4. This value is below the pK<sub>a</sub> of AME, which is 4.2 [28.]. At this pH, the herbicide is completely protonated, as was demonstrated in previous work [15]. The AME was injected into the organic phase and after twenty minutes of equilibrium, the CV was performed. As can be seen in figure 1a (solid line), during the polarization in the positive direction, the CV shows a positive current peak; this means that the herbicide was transferred into the organic phase, since the

aqueous phase became more positive than the organic phase. When the direction of polarization was inverted, a negative current peak was observed; in such case the protonated ametryn returned to the aqueous phase. The transfer of the AME was a reversible process, and the current peak was dependent of the diffusion of the herbicide. The current peak remained in the same potential as a function of the polarization sweep rate. In the case of the TRB transfer, this shows a different behavior than AME, with current peak transfer at more negative potential (figure 1b). However, the process still been reversible for the TRB transfer.



**Figure 1.** Cyclic voltammetry for the transfer of ametryn (a) and terbutryn (b) (0.1mM) (solid line) at the water|1,2-DCE interface. Supporting electrolyte: TPAsTPBCl 0.2 mM in the organic phase and LiCl 0.1 M in the aqueous phase.

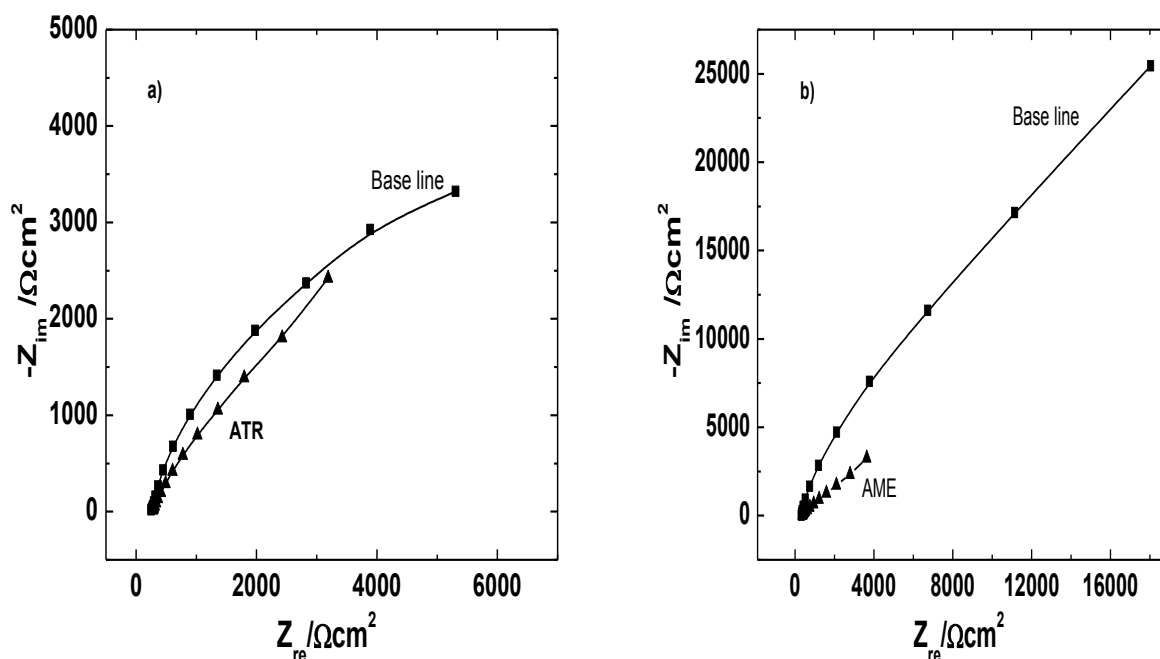
The same experimental procedure was carried out for the ATR and PRM. The result of the CV experiments for these two herbicides showed a similar behavior, and from a thermodynamic point of view, the transfer of these two herbicides at the water|1,2-DCE interface is a reversible process. The half-wave potential obtained with the two electrode configuration cell are close to the values with the traditional four electrode configuration cell [15]. Also, the experiment results follow the same behavior as that observed previously (table 1) [15]. In some way, these transfer potentials values are related to the Gibbs energy of transfer ( $\Delta G_{t,A}^{o,w \rightarrow o}$ ) for these herbicides across the water|1,2-DCE interface, and the ionic transfer coefficient partition can be written as [8]:

$$\log P_{AH^+}^{0'} = - \frac{\Delta G_{t,A}^{o',a \rightarrow o}}{2.3RT} \quad (2)$$

if the value of  $\log P_{AH^+}^{0'}$  is more negative, the molecule is considering more hydrophilic, meaning that the molecules require more energy to be transferred into the organic phase.

3.2 EIS studies

Figure 2, shows the electrochemical impedance spectra (Nyquist plot) for the base line and in the presence of the herbicide in the organic phase. The EIS signal for the supporting electrolyte was subtracted from the total impedance. Finally, the faradaic impedance that corresponds to the reaction in which the transfer of the herbicide takes place was estimated. The EIS was performed every 10 mV, considering a potential difference before and after the half-wave potentials. As it can be observed, the impedance for the base line always offered a high resistance solution. When the herbicide is present in the system ATR (fig. 2a) and AME (fig. 2b), the impedance values decrease significantly, and this is the result of the current transfer across the interface, which is attributable to the transfer of the protonated herbicide. A similar behavior was observed for the other herbicides that were studied. In fact, in all cases the typical semicircle was not observed, since the impedance is dominated by the high solution resistance.



**Figure 2.** Complex plane impedance plot in absence and in the presence of the herbicide AME (a) and AME (b) at the half-wave potential (water|1,2-DCE interface system).

The kinetics parameters were evaluated according to the Randles method. This allows to express the real and imaginary components of the impedance spectra for the herbicide transfer,  $r_s = Z' + 1/\omega c_s = Z''$  as a function of the  $\omega^{-1/2}$ , where  $\omega$  is the angular frequency ( $\omega=2\pi f$ ,  $f$  = frequency in Hz), and  $c_s$  is the related capacitance to the transfer process (Fig. 3), as reported previously in ref. [29]:

$$r_s = R_{CT} + \sigma \omega^{-1/2} \tag{3}$$

and

$$1/\omega c_s = \sigma / \sqrt{\omega} \tag{4}$$

where  $\sigma$  is the Warburg coefficient and depends on the diffusion of the herbicide and  $R_{ct}$  is the charge transfer resistance. The experimental data obtained for all triazines follow a linear relationship, as was predicted by the equations (3) and (4) shown in Figure 3. On the other hand,  $\sigma$  can be expressed as a function of the diffusion coefficient of the herbicide in both phases  $D_{TH^+}^o$  and  $D_{TH^+}^w$ , organic and aqueous, respectively, according to [29, 9]:

$$\sigma = \frac{RT}{\sqrt{2} z^2 F^2 A} \left( \frac{1}{\sqrt{D_{TH^+}^o c_{TH^+}^o}} + \frac{1}{\sqrt{D_{TH^+}^w c_{TH^+}^w}} \right) \tag{5}$$

while  $c_{TH^+}^w$  and  $c_{TH^+}^o$  are the concentrations of the herbicides in the aqueous and the organic phase, respectively. However, in acid conditions in which the concentration of the herbicides are considered,  $c_{TH^+}^w = c_{TH^+}^o$ . Thus, the dependence of the potential can be considered and this formalism has been discussed in previous references [9, 11, 29]:

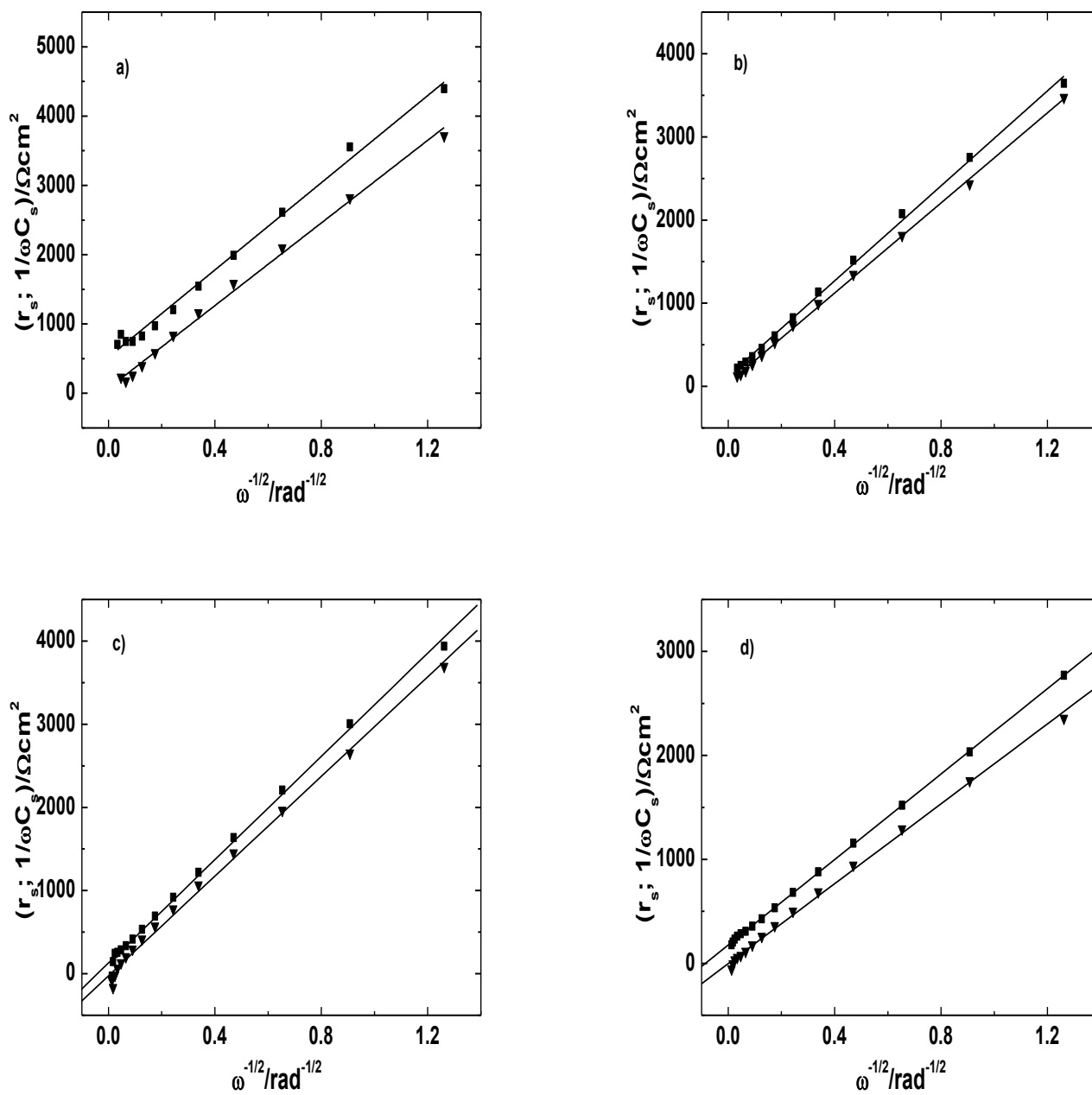
$$\ln \left( \frac{\delta}{1 + \exp(-b)} \right) = \ln \Lambda + \alpha b \tag{6}$$

where  $\delta = \frac{(2\omega)^{1/2}}{(\omega r_s c_s - 1)}$  and  $b = \frac{zF(\Delta_o^w \phi - \Delta_o^w \phi_{1/2})}{RT}$ . From the parallel line, taking a single frequency, the  $c_s$  can be measured, thus  $\delta$  can be estimated.

The apparent rate constant ( $k_s$ ) is estimated through  $\Lambda$ , which is described in the follow equation [9]:

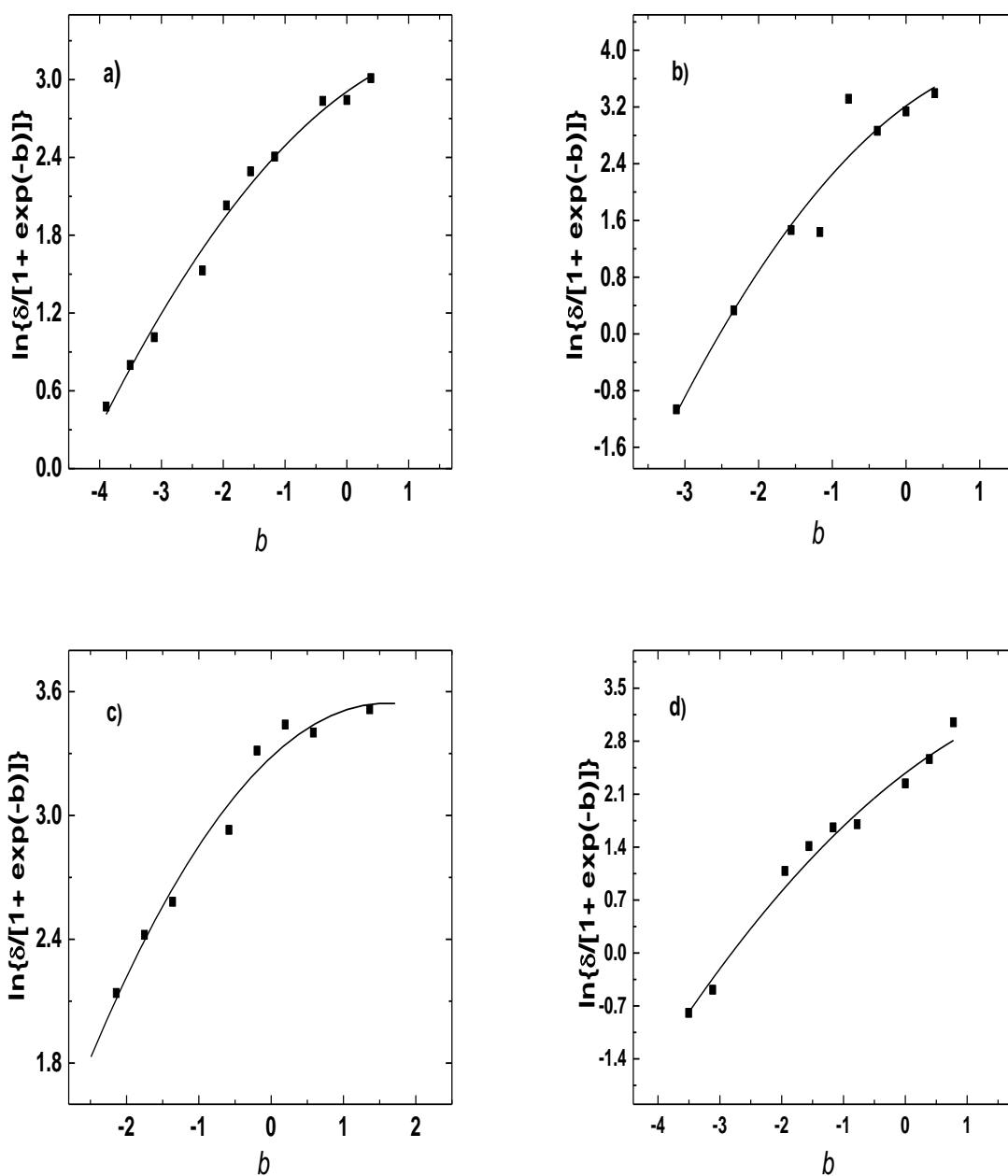
$$\Lambda = k_s \left( \frac{1}{\sqrt{D_{TH^+}^w}} \right)^\alpha \left( \frac{1}{\sqrt{D_{TH^+}^o}} \right)^\beta \tag{7}$$

where  $\alpha$  and  $\beta$  are the transfer coefficient for the species that cross the interface. From an experimental point of view, non-linear dependence between  $\ln\{\delta/[1+\exp(-b)]\}$  was observed and the applied potential ( $b$ ) (equation 6). This behavior was observed for all triazines herbicides studied, as is shown in figure 4. In addition, the kinetics parameters were evaluated from these kinds of plots; in fact, the results are adjusted to a quadratic equation for a non-linear regression; as mentioned,  $\alpha$  and  $k_s$  were calculated with equation (6), when  $b=0$ . The obtained data are summarized in table 1.



**Figure 3.** Dependence of real (■) and imaginary (◆) components of the triazines transfer on  $\omega^{-1/2}$  at half-wave potential for: (a) ATR; (b) TER, (c) AME and (d) PRM.

Since solvation and dissolution are involved in the transfer phenomena of these molecules, the dimensions and the hydrophobicity of the molecules must play an important role in these processes as show in figures 5 and 6. The results in Table 1 show that the rate constant increases when the herbicide is smaller.



**Figure 4.** Dependence of  $\ln\{\delta/[1+\exp(-b)]\}$  on applied potential for: (a) ATR; (b) TRB; (c) AME and (d) PRM.

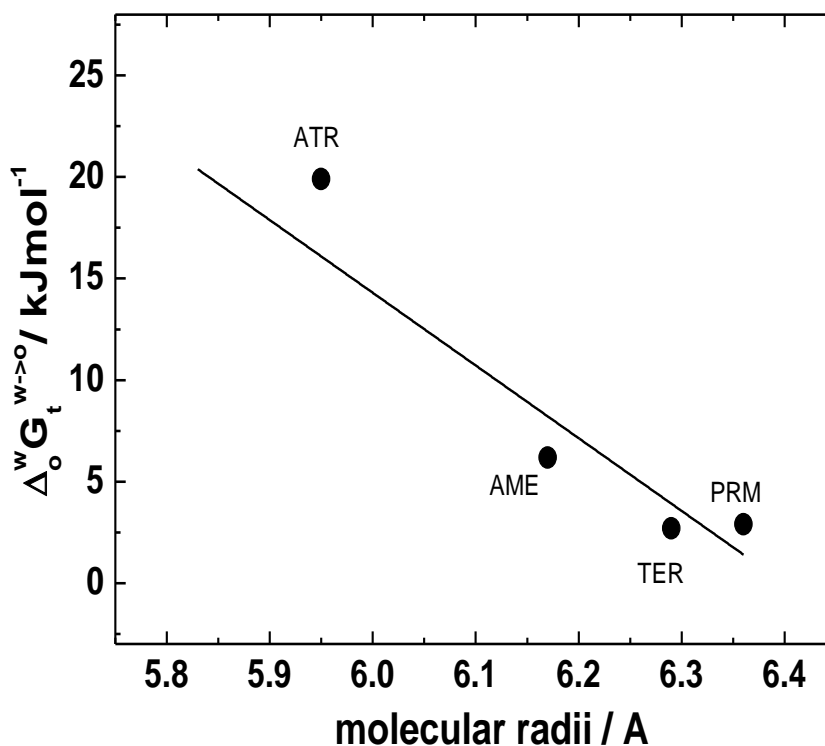
Moreover, for the more hydrophobic herbicides (thio-triazines), values of its kinetic constants are smaller to the chloro-triazine (atrazine). The less hydrophobic nature of atrazine is reflected at a very high rate to be transferred to the organic phase, which is probably related to its small molecular size (5.95 Å) compared to prometryn (6.36 Å), terbutryne (6.29 Å) and ametryn (6.17 Å) (figure 6) [15]. Another consideration is the position of the protonated amino group located at the center of the molecule, which makes it possible to hide the hydrophilic part of the molecule and to protect it from the hydrophobic environment. This makes the movement of the molecule in the aqueous phase



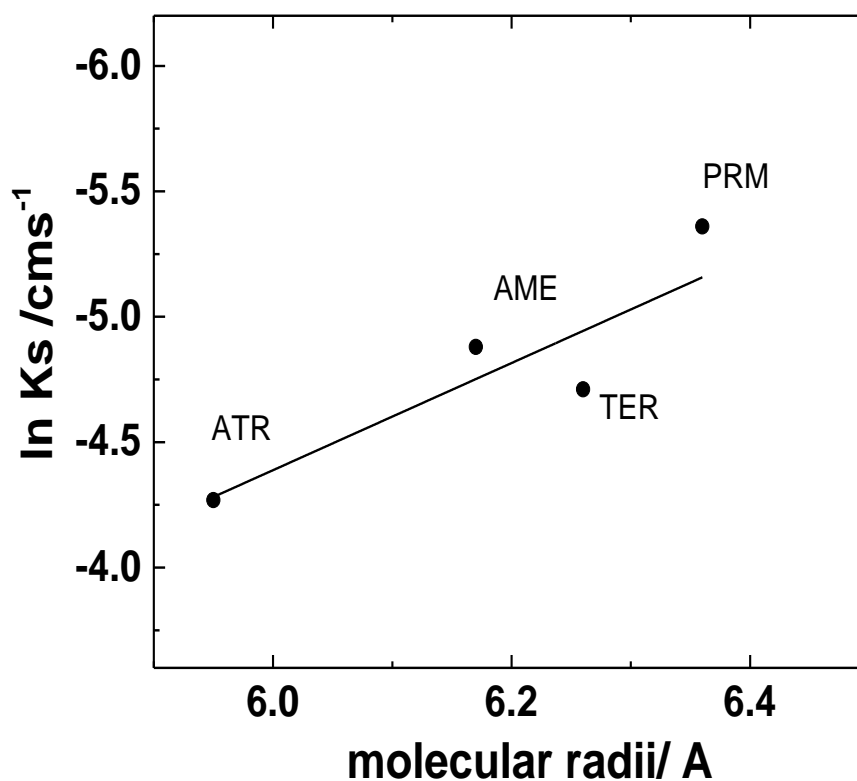
sluggish; as a consequence, the ionizable group is not able to interact with the solvent, which probably explains the values of their kinetic constants and lipophilicity. What we could say here is that the size and chemical nature of the molecule plays a role in the transfer kinetics through the water|1,2-dichloroethane interface.

**Table 1.** Physiochemical parameters for the transfer of the protonated triazines across the water|1,2-DCE interface.

Herbicide	$\Delta_o^a \phi_{TH^+}^{0'}$ / V	$\Delta G_{t,TH^+}^{o,a \rightarrow o}$	$\log P_{TH^+}$	$k_s / \text{cm s}^{-1}$	$\alpha$
ATR	0.206	19.87	-3.48	$1.4 \times 10^{-2}$	0.35
AME	0.064	6.17	-1.08	$6.6 \times 10^{-3}$	0.40
TRB	0.028	2.70	-0.47	$9.4 \times 10^{-3}$	0.53
PRM	0.030	2.89	-0.50	$5.5 \times 10^{-3}$	0.45



**Figure 5.** Dependence of the Gibbs transfer energy on the function of the molecular dimensions of the herbicides.



**Figure 6.** Dependence of the apparent rate constant on the function of the molecular dimensions of the herbicides.

#### 4. CONCLUSION

It was shown that the kinetics of transfer for a number of herbicides studied across the water|1,2-DCE interface depends on the chemical nature of the herbicide, where the hydrophobicity and the molecular dimensions play an important role in the kinetics transfer process at the biphasic system. The present results can help to understand the equilibrium partitioning of the chemical compounds that have environmental importance.

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