



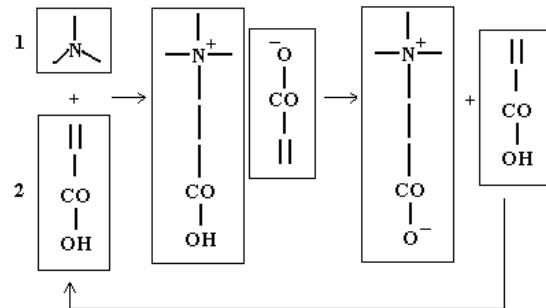
## A $^1\text{H}$ -NMR STUDY OF MECHANISM AND KINETICS ON REACTIONS OF ACRYLIC ACID WITH PYRIDINE AND IMIDAZOLE COMPOUNDS

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Received December 12, 2013

In order to clarify the mechanism of carboxybetaine formation in the reaction between tertiary aromatic amines and  $\alpha,\beta$ -unsaturated carboxylic acids, the reaction was monitored *in situ* using  $^1\text{H}$ -NMR. Based on the products identified and the kinetic data measured, we found a stable ion pair intermediary that is in equilibrium with the corresponding betaine. In the case of poly(carboxy-betaines), the intermediary is a cationic polyelectrolyte linked to carboxylate anions. We established that the addition rate constant can be determined with acceptable precision for oligomeric betaines, while this can only be estimated for polymeric betaines.



### INTRODUCTION

It is known that reactions between some tertiary amines and acids lead to betaine products. The main interest focuses on polymeric betaines for both scientific studies and applications in different fields, such as catalysts or surfactants used in the oil industry, hydrometallurgy and medicine. Of the main types of polybetaines, polycarboxybetaines, polysulfobetaines and polyphosphobetaines, the present article refers to the first ones. Such products can be synthesized by two main pathways: (i) alkylation with halogenated carboxylic acids or their esters, where the esters are then being finally hydrolyzed,<sup>1-3</sup> and (ii) via Michael addition<sup>4</sup> to  $\alpha,\beta$ -unsaturated acids.<sup>5a-5d</sup> In the case of macromolecular betaines, the amine group is usually part of the side chains, and rarely along the backbone. A comprehensive review about the synthesis and applications of carboxy and sulfobetaines was recently published.<sup>6</sup>

Since the first polycarboxybetaine reported by Ladenheim and Morawetz in 1957,<sup>1</sup> various structures and applications have been studied. For example, two recent applications refer to improved contacts between medical devices and biotissues<sup>7</sup> and as molecular imprinting polymers for selective detection and recognition of chemicals.<sup>8</sup> On the other hand, the formation of betaine has been less investigated. One exception was the study of the influence of the reactant's chemical structure on the reaction of  $\alpha,\beta$ -unsaturated carboxylic acids with pyridinic and imidazole polymers where it was found that the balancing between the reactions of neutralization and addition depends strongly on the reactant strength and structure.<sup>5a-5d</sup> For example, it was found that the most reactive acid is acrylic acid, and that while poly(2-vinylpyridine) provides mostly neutralization, poly(4-vinylpyridine) gives mainly addition products. The conclusion was that the addition reaction is more probable for unsubstituted acids and 4-alkylated pyridines.<sup>5a, 5d</sup>

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Several hypotheses on the reaction mechanism and kinetics were published<sup>9</sup> and it is the aim of the present paper to clarify how the betaine products are formed, and to formulate and prove related kinetics.

## RESULTS AND DISCUSSION

### Reaction mechanism of betaine formation

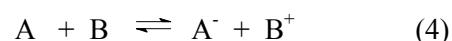
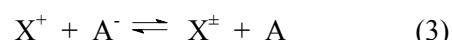
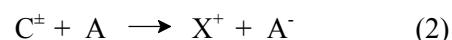
It is generally accepted that the addition between a tertiary amine and an  $\alpha,\beta$ -unsaturated carboxylic acid takes place by a nucleophilic attack of the nitrogen atom at the  $\beta$ -carbon atom of the carbon-carbon double bond of the acid, when an unstable carbanion,  $C^\pm$ , results (reaction 1).<sup>10</sup> The data obtained in our study confirmed this assumption by monitoring the  $\alpha$ -carbon atom deuteration which happens in a protic deuterated solvent like methanol-D<sub>4</sub>. The  $\alpha$ -carbon proton signal of the product of 4-methyl pyridine (4MP) and acrylic acid (AA) (peak **a** in Fig. 1A) is not a simple triplet but a complex signal, the intensity of which is about half the intensity of the peak at about 4.8 ppm that corresponds to the protons on the  $\beta$ -carbon atom (peak **b** in Fig. 1A). The position and relative intensity of these two signals confirm also the presence of a  $N^+-CH_2-CHD-COO^-$  bridge between the carbonyl carbon and nitrogen atoms.

A plausible hypothesis advanced for polymeric amines, poly(4-vinylpyridine) (P4VP) and poly(*N*-vinylimidazole) (PNVI), was that the evolution of the carbanion  $C^\pm$  to the betaine form  $X^\pm$  occurs via an intermediary  $X^+A^-$ , a cation-anion pair structure (See Scheme 1 for  $C^\pm$ ,  $X^\pm$  and  $X^+A^-$  structures).<sup>9</sup> This intermediary seems to be a fairly stable species because it can be isolated and stored under some conditions. So, the spectrum in Fig. 1A is of the product resulting after vacuum evaporation of volatile components (solvent and unmodified reactants) of the reaction medium. The peaks between 5.7 and 6.3 ppm in this spectrum are assigned to the carboxylate anion  $H_2C=CH-COO^- (A^-)$  of the ion pair  $X^+A^-$  and not to the salt  $A^-B^+$ , as these signals are perfectly correlated in intensity with both the signals of the pyridinium ring (7.89 and 8.85 ppm) and  $OOC-CHD-CH_2-N^+$  bridge (4.78 ppm for  $CH_2N^+$  protons). Consequently, this observation confirms the presence of reaction 2.

The presence of reaction 3 was suggested by the observation that the ion pair product generates the

betaine product  $X^\pm$  with the spectrum in Fig. 1B, when its solution in a protic solvent (methanol or water) is precipitated using a nonsolvent, such as acetone. This means that, in a protic solvent, the ion pair  $X^+A^-$  is in equilibrium with the betaine  $X^\pm$ .

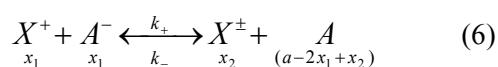
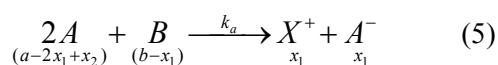
Finally, the neutralization reaction 4 is usually present when an amine reacts with an acid. Therefore, the complete proposed mechanism is comprised of reactions 1–4, where A and B are the  $\alpha,\beta$ -unsaturated carboxylic acid and tertiary amine, respectively,  $C^\pm$  is the carbanion,  $X^+$  and  $A^-$  are the cation and anion in the ion pair  $X^+A^-$ , and  $X^\pm$  is the betaine.



An important observation was that the neutralization reaction 4 is practically absent in methanol and methanol-water ( $\geq 1$ ) mixtures. This fact is supported by the equality of the molar concentrations of pyridinium rings (signals at 8.83 and 7.27 ppm) and  $CH_2N^+$  groups (signal at 4.78 ppm), which means that all pyridinium rings belong to the ion pair and/or betaine molecules, not to salt species. An illustration is presented in Fig. 2 where the spectrum recorded after a short time from the reaction mixture was prepared shows equal intensities for the mentioned signals. As it will be further on, the absence of salt products simplifies the problem of reaction kinetics.

### Description of reaction kinetics

Because carbanions are unstable species<sup>10</sup> (e.g., much more unstable than normal ions and zwitterions), reactions 1 and 2 can be combined into reaction 5, which is characterized by the addition rate constant  $k_a$ . Reaction 6 results by introducing the rate constants  $k_e$  and  $k_{-e}$  for the equilibrium reaction 3 between the species of ions pair and betaine. Finally, taking into account that the neutralization is absent in methanol, the reactions of acrylic acid with pyridine and imidazole reactants are:



which are mathematically described by the following equations:

$$dx_1/dt = k_a(a - 2x_1 + x_2)^2(b - x_1) \quad (7)$$

$$Kx_1^2 = x_2(a - 2x_1 + x_2) \quad (8)$$

where  $K = k_+/k_-$  and other parameters, such as concentrations, are given in Table 1.

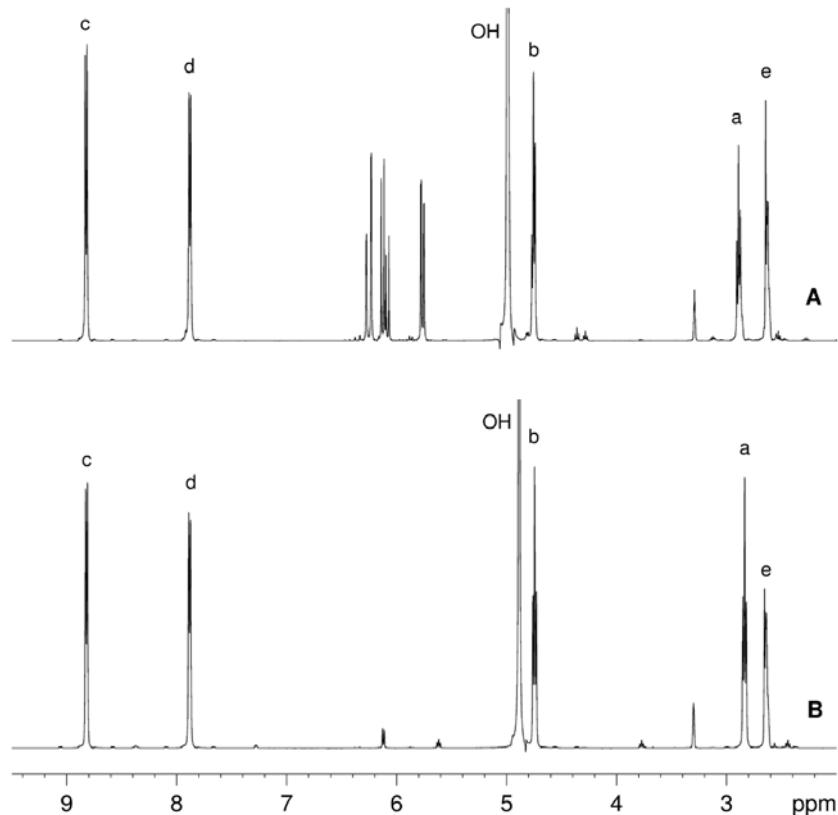
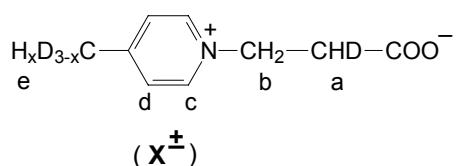
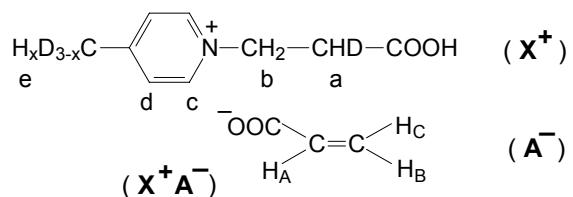
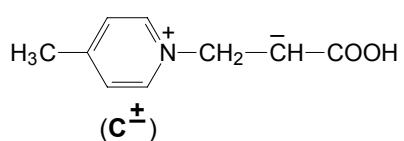


Fig. 1 –  $^1\text{H}$ -NMR spectra and peak assignment for the products which results from the reaction of 4MP and AA in  $\text{CD}_3\text{OD}$ : A – ion pair, and B – betaine. Recording conditions: 400 MHz,  $\text{CD}_3\text{OD}$  and 300 K. Reaction details for products: ion pair ( $r = 2.4$ ,  $\text{CD}_3\text{OD}$ , 50 °C, 24 h, final reaction mixture dried by vacuum), and betaine ( $r = 0.7$ ,  $\text{CH}_3\text{OH}$ , 50 °C, 24 h, final reaction mixture precipitated with acetone).  $r$  is the molar ratio acid to amine (Table 1).



Scheme 1 – Chemical structures of intermediaries and products for the reaction of 4MP and AA carried out in methanol-D<sub>4</sub>. The hydrogen notation of the products  $X^+A^-$  and  $X^\pm$  corresponds to the NMR signal assignment in Fig. 1 and Experimental Section.

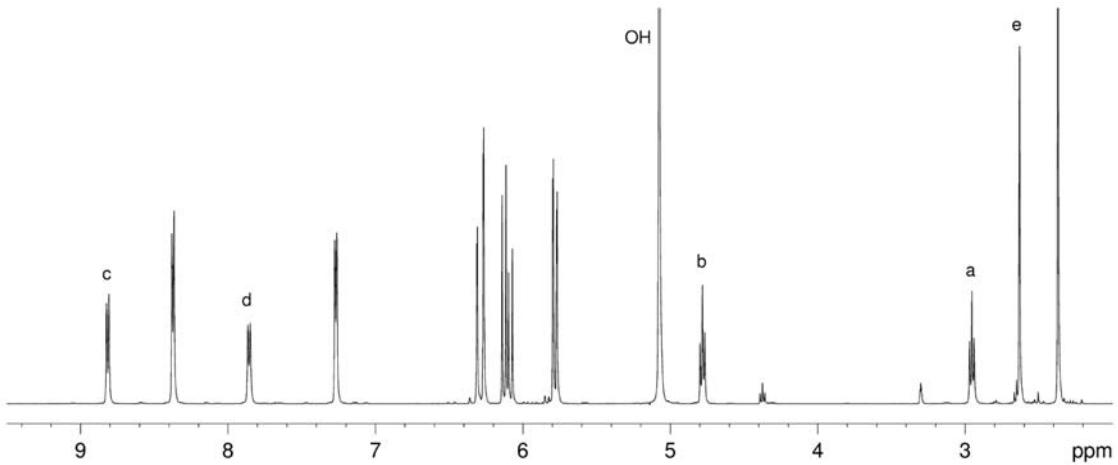


Fig. 2 –  $^1\text{H}$ -NMR spectrum recorded at the beginning of the reaction of AA and 4MP in  $\text{CD}_3\text{OD}$  at  $50^\circ\text{C}$  for an acid/amine ratio of 2.4.

Table 1

Notations for molar concentrations of reactants and products

	Absolute concentration	Normalized concentration
Initially	$a = [A]_0, b = [B]_0$	$r = a/b$
Instantaneously	$x_1 = [X^+ A^-] = [X^+] = [A^-]$ $x_2 = [X^\pm]$	$y_1 = x_1/b$ $y_2 = x_2/b$

Equations 7 and 8 are coupled and could be analytically solved but the expressions for  $x_1$  and  $x_2$  will be mathematically intractable. Therefore, in order to establish which product arises first,  $X^+ A^-$  or  $X^\pm$ , we preferred to solve the kinetic problem for two limit situations, when the products would be either  $X^+ A^-$  or  $X^\pm$ .

#### Case with ion pair ( $X^+ A^-$ ) as final product

This case is described by reaction 5 and the corresponding equation results from equation 7 by considering  $x_2 = 0$ , namely:

$$\frac{1}{(r-2)^2} \left[ \ln \frac{(r-2y_1)(1-y_{10})}{(r-2y_{10})(1-y_1)} - \frac{2(r-2)(y_1 - y_{10})}{(r-2y_1)(r-2y_{10})} \right] = k_a b^2 t \quad (11a)$$

for  $r \neq 2$ , and

$$\frac{1}{8} \left[ \frac{1}{(1-y_1)^2} - \frac{1}{(1-y_{10})^2} \right] = k_a b^2 t \quad \text{for } r = 2 \quad (11b)$$

where  $y_{10}$  is the amine conversion measured in the first recorded spectrum since the reaction medium

$$dx_1/dt = k_a (a - 2x_1)^2 (b - x_1) \quad (9)$$

or

$$dy_1/dt = k_a b^2 (r - 2y_1)^2 (1 - y_1) \quad (10)$$

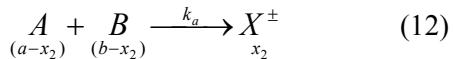
where the normalized concentration  $y_1 = x_1/b$  is used.

The integration of equation 10 let to the following solution:

was monitored by NMR. Normally, equation (11a) is valid when  $y_1 < r/2$ .

### Case with betaine ( $X^\pm$ ) as final product

It is assumed in this case that the only product is the betaine  $X^\pm$  at any reaction time. This means that the equilibrium of reaction 6 is completely shifted to right, i.e.  $K \gg 1$ . Under this assumption, reactions 5 and 6 can be merged, resulting that:



the equation of which:

$$dx_2/dt = k_a(a - x_2)(b - x_2) \quad (13)$$

or

$$dy_2/dt = k_a b(r - y_2)(1 - y_2) \quad (14)$$

has the solution:

$$\frac{1}{(r-1)} \ln \frac{(r-y_2)(1-y_{20})}{(r-y_{20})(1-y_2)} = k_a b t \quad (15a)$$

for  $r \neq 1$ , and

$$\frac{1}{(1-y_2)} - \frac{1}{(1-y_{20})} = k_a b t \quad \text{for } r = 1 \quad (15b)$$

where  $y_{20}$  is the amine conversion fraction since the NMR monitoring of the reaction medium was started.

### Proposed reaction mechanism

By analyzing the kinetic data, one should determine if reactions 5 and 12 are parallel or successive ones. To this aim, Fig. 3 shows the time dependence of the left parts of equations 11 and 15 ( $Y$  noted) for amine conversion versus time, for two acid/amine molar ratios, 1.3 and 2.4. It is noteworthy that the maximum conversion values were 0.361 for  $r = 1.3$  and 0.753 for  $r = 2.4$ , hence both values being lower than  $r/2$ .

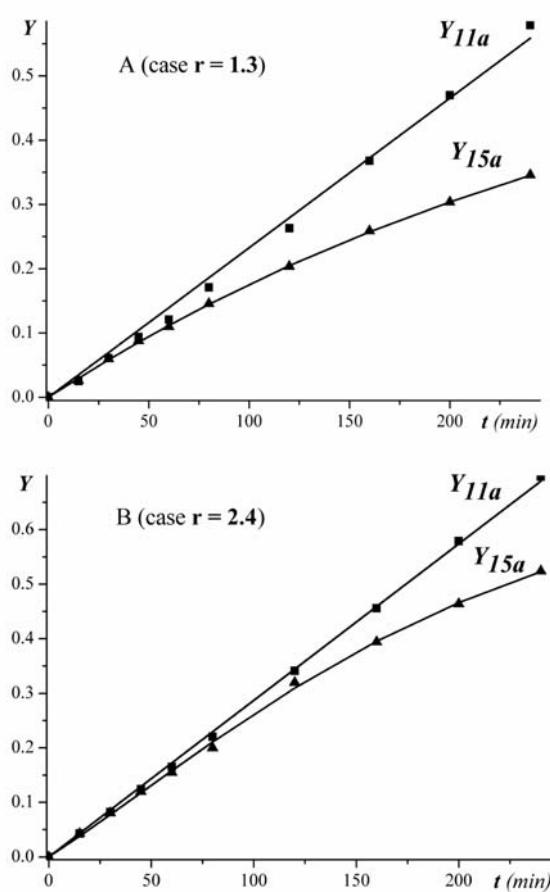


Fig. 3 – Plots of the amine conversion data processed according to equations 11a and 15a. The notation  $Y$  is for the left part of these equations. The conversion data were collected from the reaction of 4MP and AA carried out for two values of the ratio  $r$ . The corresponding fitting functions are plotted by continuous lines. Fitting equations for the time dependence of the points  $Y_{11a}$  are  $0.0023 t$  for  $r = 1.3$  and  $0.0029 t$  for  $r = 2.4$ .

As observed in the both cases, the dependence obtained with equation 11 is rather linear, unlike that calculated with equation 15. Taking into account the assumptions used to derive the two equations, one can conclude that the reaction 5 of ion pair formation is in fact the first stage of betaine formation. The appearance of betaine happens due to the reversible reaction 6, and its equilibrium shifts to right as the concentration of acid becomes too low to ensure reaction 5, namely when the conversion becomes higher than  $r/2$ .

Taking into account the slope of the fitting straight lines and the amine concentration,  $b = 1 \text{ mol L}^{-1}$ , the following values resulted for the addition rate constant,  $k_a$ :  $0.0023 \text{ mol}^2 \text{ L}^2 \text{ min}^{-1}$  for  $r = 1.3$  and  $0.0029 \text{ mol}^2 \text{ L}^2 \text{ min}^{-1}$  for  $r = 2.4$ . The fact that the two values of  $k_a$  are rather closed between them indicates the validity of the methodology based on NMR signals as well as the reaction mechanism and kinetics proposed.

It was observed that the reaction of AA and N-methyl imidazole (NMI) is similar to that of 4MP, but the conversion measurements were too imprecise due to the overlapping of NMR signals. However, the ion pair structure of the final product when  $r > 2$  and at the beginning of reaction for any acid/amine ratio indicates that the formation of ion pairs is also the first step on betaine formation.

### About the reaction of AA and polymers containing pyridine and imidazole groups

As in the case of NMI, kinetic studies on P4VP and PNVI were difficult due to the errors of conversion measurements. However, the presence of ion pair units in the modified polymers at both low and high conversions indicates a similar mechanism as that proposed before.

Fig. 4 shows the spectrum of P4VP as resulted from the reaction performed with  $r = 1.3$  in methanol at  $50\text{--}52^\circ\text{C}$  for 24 hours. According to the relative signal intensities, the product contains 70% betaine units, 25% ion pair units and 5% unmodified units. Similarly, Fig. 5 corresponds to the product from PNVI obtained under similar conditions as those for P4VP. Its composition consists of 84% betaine units, 12% ion pair units and 4% unmodified units. The total conversion is similar for the two polymers but the amount of ion pairs is lower in the product from PNVI, what means that the equilibrium  $\text{ion pair} \rightleftharpoons \text{betaine}$  is shifted more to the right for the reaction of this polymer.

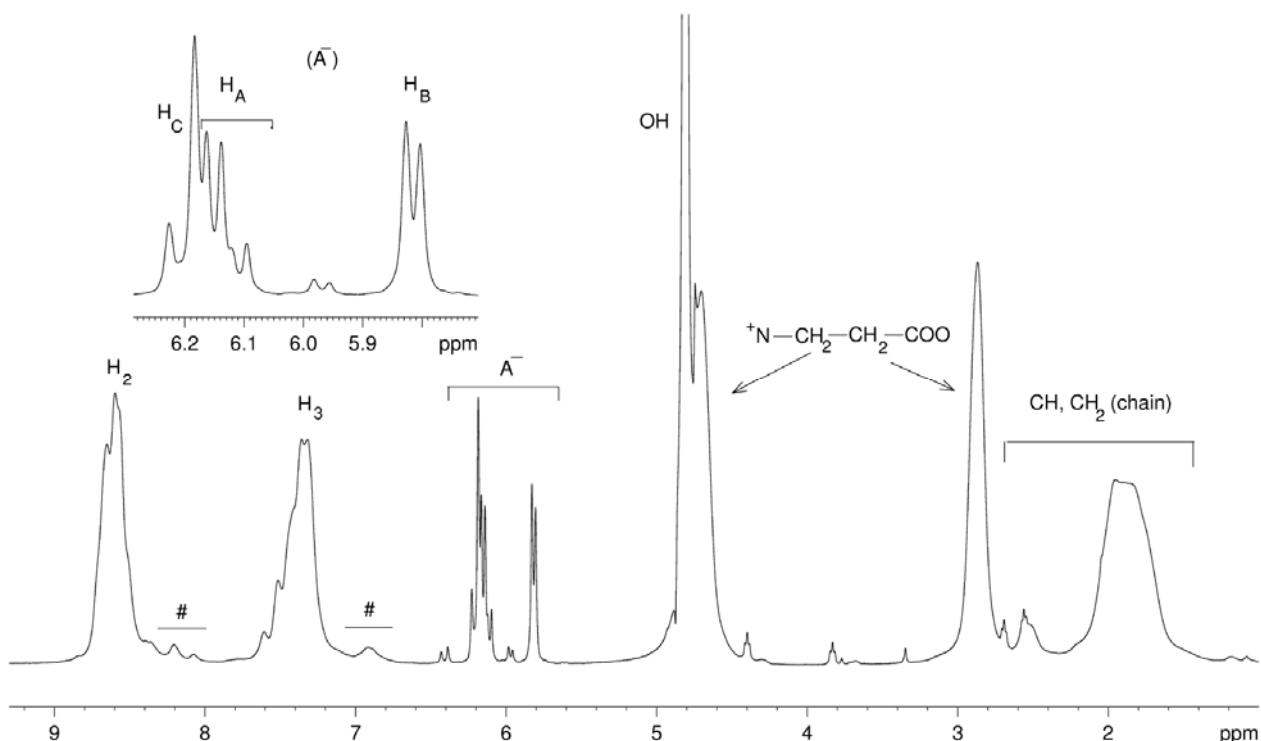


Fig. 4 –  $^1\text{H}$ -NMR spectrum and signal assignment of the crude reaction product of P4VP and AA ( $r = 1.3$ ) resulting in methanol at  $50^\circ\text{C}$  after about 24 hours. Recording conditions:  $\text{D}_2\text{O}$ , 300 K, TSP signal reference.

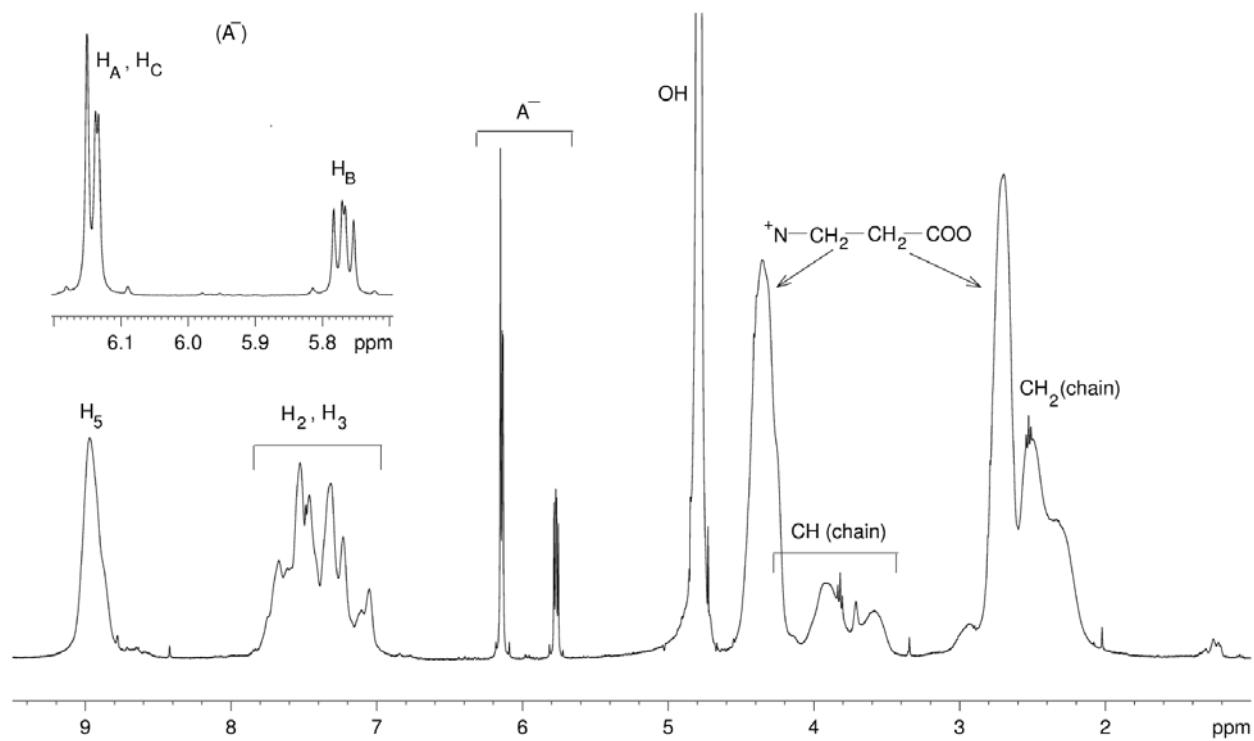
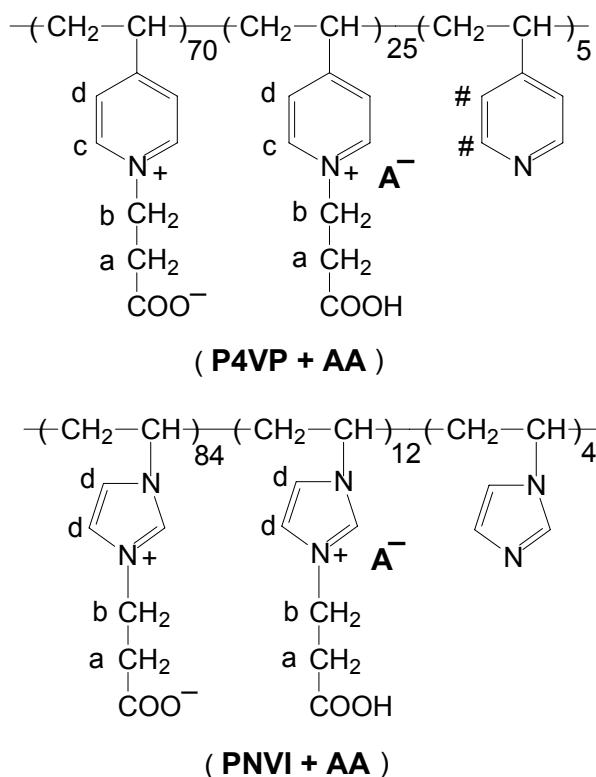


Fig. 5 –  $^1\text{H}$ -NMR spectrum and signal assignment of the crude reaction product of PNVI and AA ( $r = 1.3$ ) resulting in methanol at  $50^\circ\text{C}$  after about 24 hours. Recording conditions:  $\text{D}_2\text{O}$ , 300 K, TSP signal reference.



Scheme 2 – Chemical structures of products resulting from the reaction of AA with P4VP and PNVI ( $r = 1.3$ ) carried out in methanol at  $50^\circ\text{C}$ . The structure of anion  $A^-$  is presented in Scheme 1.

Table 2

Chemical shifts (in ppm relative to the TMS signal) and coupling constants (in Hz) of olefin protons in three compounds, in methanol<sup>a</sup>

Compound	$\delta_A$	$\delta_B$	$\delta_C$	$J_{AB} (cis)$	$J_{AC} (trans)$	$J_{BC} (vicinal)$
Pure AA	6.10	5.86	6.34	10.4	17.2	1.5
$A^-$ in P4VP product	6.13	5.81	6.20	9.6	17.2	< 0.5
$A^-$ in PNVI product	6.13	5.77	6.145	8.6	16.5	3.8

<sup>a</sup> Parameter values obtained by an iterative spectra simulation using a program from literature <sup>11</sup> with starting values approximated from normal and spin decoupled spectra.

The composition of the modified polymers is qualitatively supported by the stretching bands C=O and C-O that are characteristic to the groups COOH and COO<sup>-</sup> of ion pair and betaine units (See the IR product characterization in Experimental Section).

An approximate estimation of the addition rate constant  $k_a$  for the reaction of P4VP with  $r = 1.3$  in methanol at 50 °C was made measuring the conversion after 8 hours and applying equation 11 where the initial conversion,  $y_0$ , was neglected. So, for the measured conversion fraction of 0.33 ± 10%, the value found for  $k_a$  was 0.00105±19% mol<sup>-2</sup> L<sup>2</sup> min<sup>-1</sup>, therefore smaller than that found for 4MP. The value is lack of precision because the polymer signals are rather broad, what causes partial superposition of the signals of modified and unmodified units. In the case of PNVI the signal overlapping was even more pronounced than that for P4VP, what excluded conversion measurements performed in situ.

It is interesting to note that the signals of olefin protons show chemical shifts and coupling constants which differ from normal AA to the ion pair anions from P4VP and PNVI (Table 2). In fact, it was observed for 4MP that these parameters depend on the ion pair/betaine ratio. This confirms the presence of  $AA^-$  anions in the modified polymers, the corresponding NMR signals not coming from impurities of acid molecules.

## EXPERIMENTAL

### Materials, reaction conditions, spectra and instrumentation

4-Methyl pyridine (4MP), N-methyl imidazole (NMI) and acrylic acid (AA) from Aldrich were purified by vacuum distillation before use. Poly(4-vinylpyridine) (P4VP) with an average Mw of 160000 Da was obtained from Aldrich and

used as such. Poly(*n*-vinylimidazole) (PNVI) with an average Mw of 46000 Da was obtained by the radical polymerization of distilled monomer (Aldrich) in methanol at 50 °C.

Reactions of amines and AA were performed in methanol at 50 °C, usually for 24 h. Amine concentration was 1 mol L<sup>-1</sup>. The crude reaction products were obtained by removing the volatile components (unmodified reactants and solvent) by vacuum evaporation at about 70 °C. Such products were generally mixtures of betaine and ion pair compounds. Complete ion pair-betaine transformations were performed by dissolving in water and precipitation with anhydrous acetone.

Reaction products were identified from <sup>1</sup>H-NMR spectra and confirmed by IR spectra. The NMR spectra were recorded at 400 MHz with a Bruker Avance DRX 400 spectrometer in deuterated methanol (CD<sub>3</sub>OD) or deuterium oxide at 300 K. The chemical shifts are referred to the TMS signal. The IR spectra were obtained from KBr pastille with a Bruker Vertex 80 spectrophotometer. Because the products are highly hygroscopic, the IR spectra show some water absorptions which affect the form of some absorption bands. The characteristic stretching bands C=O, C=C, C=N and C-O are bellow mentioned.

Detailed kinetic analyses were performed for the reaction of 4MP and AA. In this case, the reaction was conducted in deuterated methanol and monitored *in situ* using <sup>1</sup>H NMR. Usually, the data were collected for up to 30% conversion of the acid.

### Product characterization

Ion pair from 4MP and AA ( $X^+ A^-$  in Scheme 1). <sup>1</sup>H-NMR: CD<sub>3</sub>OD, 300 K: 8.82 ppm, d, 2 p, H<sub>c</sub>; 7.72 ppm, d, 2 p, H<sub>d</sub>; 4.76 ppm, m, 2 p, H<sub>b</sub> of CH<sub>2</sub>N<sup>+</sup>; 2.90 ppm, m, approx. 1 p, H<sub>a</sub> of CHDCOO; 2.64 ppm, m, H<sub>a</sub> of CH<sub>x</sub>D<sub>3-x</sub>; 6.257 ppm, 1 p, H<sub>c</sub> in  $AA^-$ ; 6.108 ppm, 1 p, H<sub>A</sub> in  $AA^-$ , and 5.768 ppm, 1 p, H<sub>B</sub> in  $AA^-$ . IR: KBr tablet, cm<sup>-1</sup>: 1730, C=O in COOH; 1641, C=N<sup>+</sup>; 1590, C=O in COO<sup>-</sup>; 1395, C-O in COO<sup>-</sup>; 1181 C-O in COOH.

Betaine from 4MP and AA ( $X^\pm$  in Scheme 1). <sup>1</sup>H-NMR: CD<sub>3</sub>OD, 300 K: 8.65 ppm, d, 2 p, H<sub>c</sub>; 7.83 ppm, d, 2 p, H<sub>d</sub>; 4.72 ppm, m, 2 p, H<sub>b</sub> of CH<sub>2</sub>N<sup>+</sup>; 2.89 ppm, m, approx. 1 p, H<sub>a</sub> of CHDCOO; 2.62 ppm, m, H<sub>a</sub> of CH<sub>x</sub>D<sub>3-x</sub>. IR: KBr tablet, cm<sup>-1</sup>: 1643, C=N<sup>+</sup>; 1589, C=O in COO<sup>-</sup>; 1395, C-O in COO<sup>-</sup>.

P4VP reacted with AA,  $r = 1.3$  (P4VP + AA in Scheme 2). <sup>1</sup>H-NMR: D<sub>2</sub>O, 300 K: 9.62 ppm, 2 p, H<sub>c</sub> in Py<sup>+</sup>; 7.34 ppm, 2 p, H<sub>d</sub> in Py<sup>+</sup>; 4.70 ppm, 2 p, H<sub>b</sub> in CH<sub>2</sub>N<sup>+</sup>; 2.87 ppm, 2 p, H<sub>a</sub> in CH<sub>2</sub>COO; 1.5 – 2.7 ppm, 3 p, CH-CH<sub>2</sub> (chain); 5.7 – 6.3 ppm, approx. 0.8 p, H<sub>A</sub>, H<sub>B</sub> and H<sub>C</sub> of  $AA^-$  (A<sup>-</sup> anion). IR: KBr tablet,

$\text{cm}^{-1}$ : 1639, C=N<sup>+</sup>; 1581, C=O in COO<sup>-</sup>; 1388, C-O in COO<sup>-</sup>; 1716 (shoulder), C=O in COOH; 1166, C-O in COOH.

PNVI reacted with AA,  $r = 1.3$  (PNVI + AA in Scheme 2). <sup>1</sup>H-NMR: D<sub>2</sub>O, 300 K: 8.97 ppm, 1 p, H<sub>c</sub> in I<sup>+</sup>; 7.1–7.8 ppm, 2.1 p, H<sub>d</sub> in I<sup>+</sup>; 4.35 ppm, 2 p, H<sub>b</sub> of CH<sub>2</sub>N<sup>+</sup>; 2.70 ppm, H<sub>a</sub> of CH<sub>2</sub>COO<sup>-</sup>; 3.5 – 4.2 ppm, 1 p, CH (chain); 2.2 – 2.6 ppm, 2 p, CH<sub>2</sub> (chain); 5.7 – 6.15 ppm, approx. 0.36 p, H<sub>A</sub>, H<sub>B</sub> and H<sub>C</sub> of AA<sup>-</sup> ( $A^-$  anion). IR: KBr tablet,  $\text{cm}^{-1}$ : 1569, C=N<sup>+</sup>; 1555, C=O in COO<sup>-</sup>; 1392, C-O in COO<sup>-</sup>; 1710 (small shoulder), C=O in COOH; 1158, C-O in COOH.

## CONCLUSIONS

Proton NMR spectroscopy was proved to be the best method for both the identification of reaction products and the measurement of reaction mechanism and kinetics.

The main conclusion from kinetic data analysis is that the addition reaction of tertiary amines and  $\alpha,\beta$ -unsaturated carboxylic acids, if it occurs, consists of a first reaction to form an ion pair, followed by the transformation of the ion pair into a betaine zwitterion.

The synthesis of betaines is a case where the NMR methodology is the only method allowing to solve problems of chemical mechanism and kinetics.

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