

# Influence of partial neutralization on catalytic activity of ion exchange resin

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## Abstract

Concentration of acid centers in a commercial ion exchanger catalyst was controlled by partial neutralization of sulfonic groups with various primary, secondary and tertiary amines of different molecular size. The effect of the acid center concentration on catalytic activity of the ion exchangers was tested by measurements of initial reaction rate of re-esterification of ethyl acetate with 1-propanol in a CSTR-type reactor. There was found much higher than proportional dependence of the catalytic activity on the degree of the neutralization and the efficiency of various amines in the activity suppression decreased roughly in the order tertiary > secondary > primary.

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## 1. Introduction

Strongly acidic ion exchangers found important application as catalysts in various industrial processes where they have been replacing soluble mineral acids (see, e.g. [1] and references therein) and hence, they are the most significant representatives of heterogenized homogeneous catalysts. They are almost uniformly composed from monosulfonated styrene-co-divinylbenzene polymers and as catalysts, from the chemical point of view these resins are exceptionally well defined materials. However, due to the differences in the morphology of the polymer skeleton, various types of the resins of nominally identical chemical composition exhibit very different application properties. Attachment of the sulfonic groups to the polymer backbone fundamentally changes the character of the reaction environment in comparison with the environment of a free solution. Hodge [2] grouped the differences between reactions on polymer support and their low-molecular analogues into three main types: (i) effect resulting from the need for the soluble reactants to gain access to

the supported reactants, (ii) microenvironmental effects and (iii) site–site interactions. Due to the simplicity of the chemical composition, strongly acidic resins are suitable model system for studying of these effects.

Nature of the acidic site in the sulfonated resins is different in aqueous and non-aqueous media [3]. In water solutions, the resin-catalyzed reaction proceeds via mechanism of specific catalysis where the protonating agent is a hydrated proton existing in the liquid inside the gel space as a mobile counter-ion to the anion- $\text{SO}_3^-$ . This is the mechanism quite similar to that of the reactions catalyzed by soluble mineral acids. Hence, in the aqueous environment the major difference between resin and homogeneously catalyzed reactions are effects of the polymer chains influencing concentration of the reactants inside microreactor-like cavities of the three-dimensional polymer network. Part of these effects can be preferential absorption reactants poorly soluble in water, which may in some cases result in apparently better efficiency of a resin catalyst in comparison with an equimolar amount of soluble acid [4]. But anyhow, as the reaction proceeds within constrained space of the cavities between polymer chains, even in this case is very important the effect of steric exclusion. This effect diminishes the concentration

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of the reactants inside the polymer gel in dependence on their molecular size and the polymer chain density [5]. On the base of inverse steric exclusion chromatography, there is possible to obtain quantitative description of these effects in swollen resins and for situations not complicated by other effects, such description can be effectively used for explanation of the relations between morphology and catalytic activity. For sucrose hydrolysis on strongly acidic ion exchangers where preferential adsorption of the sugar does not occur, on the base of quantitative description of the steric effects there was possible to explain the differences in activities of a wide series of the resin catalysts and even the difference between them and the activity of soluble acid [6]. However, most of the industrial processes using ion exchanger catalysts proceed in the non-aqueous environment or in solutions with very low water concentrations. Reactants are there protonated by the undissociated sulfonic groups. It means that the polymer chains to which are functional groups bonded are no more a steric hindrance only. The reaction proceeds in direct contact with them after adsorption of the reactant on the chain by mechanism similar to conventional heterogeneous catalysis.

Simultaneous presence of enthalpic (adsorptive) and entropic effects makes quantitative description of relations between morphology and catalytic activity very difficult. In catalytic applications of ion exchangers in non-aqueous environment, the strong enthalpic interactions between polymer-bound sulfonic acid groups and reactant molecules quite significantly support penetration of the reactant into the dense domains [7]. At these conditions, the accessibility of the acidic centers is probably controlled more by the molecular sieve effect (molecules cannot enter spaces smaller than their dimensions) rather than by steric exclusion (lowering of the concentration of a substance inside of the pore in comparison with its concentration outside).

Information on swollen-state morphology of ion exchange resins obtainable using inverse steric exclusion chromatography (ISEC) is very valuable but for application of resin catalysts in non-aqueous solvents it has some limitations. ISEC based on the steric exclusion phenomenon “see” the swollen state morphology from the perspective not quite appropriate for correlation with processes governed by molecular sieve effect. Also, acidic resins cannot be investigated by ISEC in organic solvents but only in aqueous environment.

Kinetics of ion exchanger catalyzed reactions in non-aqueous environment is usually described using Langmuir–Hinshelwood equations constructed on the supposition of participation of more than one acidic center in the rate determining step, e.g. [8,9]. Interpretation of the participation of more than one center could be done in various ways, e.g. by assuming a multicentre adsorption of reacting molecules [10–17] or by the higher acidity of a certain grouping of sulfonic groups compared with an isolated acid center [18,19]. Regardless of the interpretation, important consequence of the catalysis by a multiplet of sulfonic groups is more-than-proportional dependence of the reaction rate on the concentration of the acidic centers. In studies of ion

exchanger catalyzed reaction in non-aqueous environment, where the concentration of the acidic centers was controlled by partial neutralization of the sulfonic groups with metal ions, a very steep dependence of the reaction rate on the degree of neutralization has been observed (e.g. [10,11,20]). The influence of partial neutralization on catalytic activity of ion exchange resins is important both from practical and theoretical point of view. In industrial condition, the poisoning with a base is one of the most important reasons for the catalyst deactivation. At the same time, the character of this effect is valuable source of information on mechanisms of processes within resin catalysts. Interpretation of the influence of the neutralization of sulfonic groups with metal ions is complicated by the fact that it influences not only the acid center concentration but also their accessibility. With the increase of the neutralization degree decreases the ability of the resin to swell in organic solvents. For example, in the mixture of ethylacetate and propanol the resin fully neutralized with alkali does not swell at all [20].

We decided to investigate the influence of partial neutralization on catalytic activity of strongly acidic resins by various amines supposing that the organic nature of these bases will help to diminish the detrimental effect of the neutralization on swelling ability of ion exchanger resins in organic solvents. We also hoped that variations in size and basicity of amines will allow detecting differences in accessibility or acid strength of the sulfonic groups.

## 2. Experimental

### 2.1. Chemicals

Gel-type strongly acidic resin Amberlyst 31 (Rohm and Haas Co., Philadelphia, USA) which swelling corresponds to the nominal content of divinylbenzene 4 mol%, was washed before use on column with diluted hydrochloric acid (10 wt.%) and then with deionized water till the eluate was free of chloride ions (negative test with silver chloride solution). Finally the resin was dried at 110 °C overnight. The exchange capacity of the dry resin as determined by titration was 5.35 mmol/g. Ethanolamine, decylamine, dipentylamine, tripropylamine, diethylenetriamine, triethanolamine and dibenzylamine (purum, Fluka, Switzerland) as well as 1-propanol and ethyl acetate (Lachema, Czech Republic) were used without preliminary purification.

### 2.2. Sorption of amines

Precisely weighed amount of dry resin (around 1 g) was pre-swollen in 5 cm<sup>3</sup> of methanol and to this suspension was added weighed amount of amine corresponding to neutralization of the desired fraction of the acidic groups of the resin. The solution was left in contact with the resin for 24 h with occasional stirring. Then the resin was quantitatively separated from the solution, washed with methanol and dried overnight

at 80 °C. Extent of the amine sorption was then determined both from the increase of the resin mass and from titration of aliquot of the resin with alkali.

### 2.3. Measurements of the catalytic activity

Catalytic activity of the resins was determined by measuring of the initial reaction rate of re-esterification of ethyl acetate with 1-propanol in a glass CSTR microreactor (volume 5 cm<sup>3</sup>) at steady-state conditions. This arrangement eliminates possible problems with changes in catalyst swelling during kinetic experiments, which are inevitable when the kinetic measurements with ion exchange resin catalysts are performed in batch arrangement. Measurements were done at 70 °C with reaction mixture of 1-propanol and ethyl acetate in molar ratio 1:1 with resin (0.05–5 g) of the particle size in the range 0.25–0.5 mm. For dosing of the reaction mixture (5–15 g/h) was used microprocessor controlled pump STEP-DOS 03 S (KNF Neuberger AG, Switzerland). Conversion of the reaction mixture was determined on the base of GC analyses using Series 600 GC (GOW-MAC, Inc., USA) and column 2 mm × 2 m filled with Porapak S (Alltech Associates, Inc., USA). It was verified that at these conditions the reaction kinetics on the full capacity resin (the most active one) was free of diffusion effects. For each catalyst, at least three values of the reaction were measured at different catalyst loads, when the conversion was not higher than 10%. The obtained reaction rates were practically independent of conversion and for further correlations there were used their average values.

### 2.4. Measurements of the absorption of the reaction mixture in the resin catalysts

Assessment of the swelling of the resin catalyst in the reaction environment at the true working condition is hardly possible and therefore the absorption of the reaction mixture was measured by determination of the liquid uptake at laboratory temperature. After equilibration of the sorbent with the reaction mixture, the surplus liquid was drained off, remaining occluded liquid was removed by centrifugation according to method described in the literature [21,22] and the amount of liquid imbibed into the sorbent was determined gravimetrically.

### 2.5. Measurements of amine/H<sup>+</sup> ion distribution coefficients

Assessment of strength of the bond between amine and the resin was performed by measurements of distribution coefficients of amines between resin phase and outer solution of hydrochloric acid. Five grams of dry resin in which 66% of sulfonic groups was neutralized with amine was contacted in a closed vessel with solution of hydrochloric acid (conc. 0.1098 mmol/g). Volume of the added solution was adjusted for to contain the same molar amount of the acid as was the molar content of amine in the resin sample (14.46–19.70 g, according to the amine molecular weight). The resin was left in contact with the solution with occasional stirring at laboratory temperature till reaching the equilibrium (at least 24 h). Equilibrium acid concentration in the solution above the resin was then determined by titration of an aliquot sample. The found equilibrium acid concentrations were in the range 0.0735–0.1092 mmol/g. Amount of liquid absorbed into the resin was determined gravimetrically, after removing the remaining occluded liquid by centrifugation (found values varied in the range 0.42–1.12 g liquid per g of the dry resin). From the material balance was then determined molar amounts of amine and H<sup>+</sup> ions in resin and outer solution, respectively, and finally the distribution coefficients.

## 3. Results and discussion

In Table 1 are listed exchange capacities of the resins resulting from contact with solutions containing selected amines with aliphatic alkyls – decylamine, dipentylamine, tripropylamine and polybasic diethylenetriamine, more hydrophilic ethanolamine, triethanolamine and aromatic dibenzylamine in molar amount corresponding to various fractions of the resin acidity.

The differences between the experimentally determined exchange capacities of resins neutralized by the same molar amount of different amines are quite significant. However, the values of the exchange capacities do not express correctly the changes in concentration of acidic groups in the resins as there have to be taken into account also the changes of the resin mass after absorption of amines. The effect of the partial neutralization should be properly characterized on the base

Table 1  
Exchange capacities of resins partially neutralized with various amines

Amine	Exchange capacity of the partially neutralized resin (mmol/g)			
	0.11 mmol/mmol	0.25 mmol/mmol	0.33 mmol/mmol	0.45 mmol/mmol
Tripropylamine	4.01	3.19	2.74	2.34
Triethanolamine	4.02	3.43	2.68	2.26
Dipentylamine	4.04	3.41	2.66	2.24
Dibenzylamine	4.09	3.03	2.41	1.92
Ethanolamine	4.21	3.67	3.07	2.48
Decylamine	4.29	3.32	2.83	2.17
Diethylenetriamine	2.81	0.84	0.32	–

of the acidity balance (Eq. (1)), which corrects also for possible differences in completeness of the drying of individual samples:

$$N = 100 \times \frac{C_p m_p}{C_s m_s} \quad (1)$$

In this equation,  $N$  is the degree of neutralization in % of the original content of the acidic groups in the resin,  $C_s$  and  $C_p$  are the exchange capacity of the starting and partially neutralized resins, respectively, while  $m_s$  is the weight of the starting resin before contact with the amine solution and  $m_p$  is the weight of the quantitatively collected partially neutralized resin just before the separation of the aliquot sample for the exchange capacity determination. In Fig. 1 are values of the neutralization degree  $N$  compared with the molar amounts of the added amine  $A$  expressed in % of the original content of the acidic groups in the resin (Eq. (2)). In this equation  $m_a$  is weight of the added amine and  $M_a$  is its molecular weight (for diethylenetriamine it was 1/3 of its molecular weight):

$$A = 100 \times \frac{m_a}{C_s m_s M_a} \quad (2)$$

From the comparison of the amounts of added amine  $A$  and the actually achieved degree of neutralization  $N$  shown in Fig. 1 is evident that with exception of minor deviations at very high neutralization degrees, the extent of the acidic groups neutralization corresponded to the amount of the added amine, regardless of the differences in amine molecular sizes or other properties. The interaction of acid groups with amines is too strong for to allow the much weaker steric effects to influence its equilibrium. Hence, our expectation that it this approach could be possible to use for deriving some information on differences in the sulfonic group accessibility were found to be unrealistic. As model reaction for testing the influence of the concentration of acid centers on catalytic activity in non-aqueous environment was selected re-esterification of ethyl acetate with 1-propanol. This reaction does not involve water

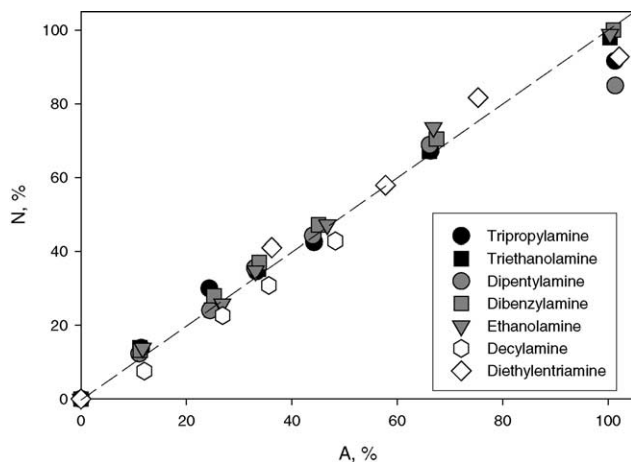


Fig. 1. Comparison of the amounts of added amine  $A$  and the actually achieved degree of neutralization  $N$ , both expressed in % of the original content of the acidic groups in the resin.

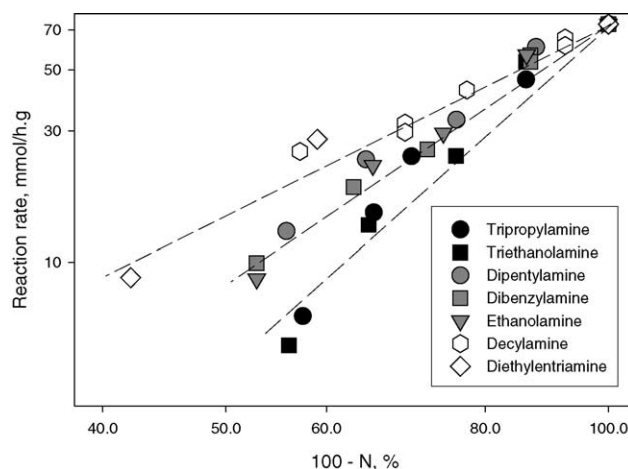


Fig. 2. Dependence of the catalytic reaction rate on the fraction (%) of the sulfonic groups unoccupied with amine.

even as a product and due to similarity of starting compounds and products it is possible to suppose that the ability of the reaction environment to swell the ion exchanger catalyst does not depend on the conversion of the reactant. For better comparison between resins modified with different amines, the measured initial rates of the test reaction were related to the unit mass of the resin from which was subtracted the weight of the absorbed amine, that is to the mass unit of that part of the catalyst formed by the original ion exchanger resin. Obtained results are shown in Fig. 2.

The decrease of the catalytic activities with the decrease of the fraction of the sulfonic groups unoccupied with amine was found to be very steep and most interestingly, the dependencies were possible to categorize into three groups. The strongest influence on the catalytic activity had the neutralization with tertiary amines (tripropylamine and triethanolamine). Intermediate effect was observed after neutralization with secondary amines (dipentylamine and dibenzylamine) and with ethanolamine. Relative mildest slope of the dependence of the activity on the fraction of the sulfonic groups remaining in the acidic form was observed after neutralization with decylamine and diethylenetriamine. If plotted on logarithmic scale (Fig. 2), the basic features of the results can be shown by drawing straight lines based on the least-square correlation through each of the above specified amine groups. The slopes of the lines are 4.45, 3.22 and 2.35, respectively, but the lines should be considered as visualization of the basic features of the experimental data and not as a formal correlation. Explanation of these findings is not easy or straightforward.

Beside the concentration of the acidic centers, the partial neutralization of the sulfonic groups diminishes also the ability of the resin to swell. Diminished swelling may restrict the accessibility of the acid centers for the reactants. Measurements of the resin swelling at the reaction condition could be difficult but it is easily possible to measure the absorption of the reaction mixture into the resin catalyst at the laboratory

Table 2

Absorption of the reaction mixture of ethyl acetate and 1-propanol (mol ratio 1:1) in the unmodified resin catalyst Amberlyst 31 and in the resins in which about 665 of acidic groups were neutralized with various amines

Resin	Equilibrium amount of the absorbed liquid (g/g dry resin)
Unmodified	0.958
Tripropylamine	0.320
Triethanolamine	0.204
Dipentylamine	0.298
Dibenzylamine	0.291
Ethanolamine	0.275
Decylamine	0.399
Diethylenetriamine	0.331

temperature. In re-esterification is the nature of the starting compounds and the products so similar that it is possible to suppose that the results of such measurements are not substantially influenced by changes of the composition of the reaction mixture during the experiment (Table 2).

It is obvious that the decrease of absorption of the reactants and hence the swelling of the resin catalyst due to partial neutralization with amine is a factor amplifying the decrease of the catalytic activity due to the diminishing of the acidic center concentration. It probably contribute to the higher than proportional decrease of the catalytic activity with the decrease of the acid center concentration, but the size of this effect for individual amines is quite similar and cannot explain the grouping of the amine effects on the catalytic activity depicted in Fig. 2. This grouping, roughly in the order tertiary > secondary > primary, suggests a connection with the strength of the bases. However, the tabled values of dissociation constants of organic bases in aqueous solutions (e.g. [23]) do not correlate with it. In spite of it, substantial differences in the strength of bonding of various amines to the sulfonated resin do exist. In Table 3 are shown equilibrium coefficients of the amine/H<sup>+</sup> exchange  $K$  (Eq. (3)) measured in 0.1 N HCl:

$$K = \frac{[\text{amine}_{\text{resin}}][\text{H}_{\text{liquid}}^+]}{[\text{amine}_{\text{liquid}}][\text{H}_{\text{resin}}^+]} \quad (3)$$

With one exception (ethanolamine) the strength of amine–resin bond characterized by the distribution coefficient  $K$  correlates well with the efficiency of the amine for diminishing of the catalytic activity: the stronger the affinity between amine and the resin, the lower is its effect on

Table 3

Equilibrium coefficients of the amine/H<sup>+</sup> exchange  $K$  measured in 0.1 N HCl

Amine	$K$
Tripropylamine	1.9
Triethanolamine	1.1
Dipentylamine	19.6
Dibenzylamine	23.7
Ethanolamine	1.0
Decylamine	39.6
Diethylenetriamine	48.2

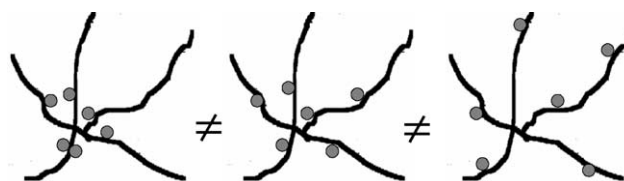


Fig. 3. Schematic depiction of differences in various distributions of functional groups in polymer matrix.

the catalytic activity. Reasons for the different findings for ethanolamine are open to speculations. Anyhow it shows that in such complicated systems as the resin catalysts are, an explanation based on a single factor may not be universally applicable.

Strongly acidic ion exchangers are practically the simplest resin supported catalysts. They can be considered as a model immobilized homogeneous catalysts and results of their investigation may be relevant for other polymer-supported catalysts. The study of the influence of partial neutralization of ion exchanger catalysts with various amines demonstrated a few generally applicable points: Working-state morphology of functional polymers is not determined solely by the support morphology but it depends also on the nature and distribution of the functional groups. Chemical modification of functional groups also changes the working state morphology of the all polymer.

Active groups or their modification need not be homogeneously distributed. In fact the homogeneous (statistical) distribution of reaction centers within polymer networks is probably exception rather than rule. Location of the active group within the polymer network may influence both the accessibility of the group and its intrinsic reactivity. In Fig. 3 are shown different distributions of the same number of active groups within the same polymer matrix. It is evident that in spite of the same overall concentration, the differently distributed groups will have also different condition for functioning and/or for mutual interaction. Hence, formally identical chemical content or overall concentration of the functional groups does not mean that the groups have also identical reactivity.

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