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Authors: Nikolay Tarabanko, Valery Evgenievich Tarabanko, and Oxana Pavlovna Taran

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Unidimensional Approximation of the Diffuse Electrical Layer in the Inner Volume of Solid Electrolyte Grains in Absence of Background Ions

Nikolay Tarabanko^{*[a]}, Valery E. Tarabanko^[a], Oxana P. Taran^[a,b]

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^aDr. N. Tarabanko, Prof. V. E. Tarabanko, Prof. O. P. Taran Institute of Chemistry and Chemical Technology SB RAS, Federal Research Center "Krasnoyarsk Science Center SB RAS"; Akademgorodok 50/24, Krasnoyarsk 660036, Russia

^bProf. O. P. Taran Boreskov Institute of Catalysis SB RAS, Lavrentiev Av. 5, Novosibirsk 630090, Russia

* tarabanko.nv@icct.krasn.ru

Abstract

In this paper we continue working on our theory of electrical double layers resulting exclusively from dissociation of a solid electrolyte, which we previously proposed as a medium for catalytic interaction between solid cellulose and solid acid catalysts of hydrolysis. Two theoretical unidimensional models of the inner grain volume are considered: an infinitely long cylindrical pore, and a gel electrolyte near a grain outer surface. Despite the model simplicity, the predictions for the cylindrical pore case are in semi-quantitative agreement with literature data on electroosmotic experiments, adequately explaining high proton selectivity of sulfonic membranes, and decline of such selectivity at high background acid concentration. The gel model predicts less concentrated diffuse layer in comparison to electrolytes with impenetrable skeleton (e.g., sulfonated carbons). This suggests limited suitability of gel electrolytes as catalysts if a substrate cannot diffuse into the gel bulk and the reaction is thereby spatially limited to the near-surface region, for example if a substrate is solid like aforementioned cellulose.

1 Introduction

Electrical double layers at solid-liquid interface (hereinafter, EDL) play an important role in numerous fields of science and engineering, e.g., electric energy storage,^[1] colloid science,^[2] rheology,^[3] ion-selective membranes,^[4–6] novel microelectronics and chemical sensors.^[7,8] EDLs are a relevant subject in catalysis too. While their role in electrocatalysis is quite obvious,^[9–13] there also exist EDL-related phenomena that can manifest in a catalytic process even without application of extraneous current—like electrocapillarity^[14] and high viscosity of the layer.^[15]

Discussion of EDLs in scientific literature almost exclusively focuses on their formation via interaction of the solid with the background electrolyte by adsorption of ions from the latter. While participation of the solid's surface electrolyte groups in generation of the surface charge is often accounted for, this phenomenon is still viewed in combination with the influence of the background electrolyte.^[16–19] The situation where the surface charge and the counter-ions in the diffuse layer are both generated exclusively by dissociation of the electrolyte species contained on the solid surface is pretty much ignored in scientific literature (to distinguish this type of double layers, we will hereinafter refer to it as "autodissociative EDL"). We proposed the concept of autodissociative EDL as a possible explanation of chemical interaction between solid cellulose and solid acid catalysts of hydrolysis.^[20] Using a simple unidimensional model that considers interaction of two flat surfaces, we analyzed the possibility of cellulose hydrolysis by protons of the diffuse layer, assisted by electrostatic attraction between the solid acid polyanion and the cellulose which is protonated by the same protons. Despite the model's simplicity, a number of experimental facts known from earlier literature were successfully explained.^[20] This suggests that the role of EDLs in catalysis may not be limited to just the aforementioned physical effects like electrocapillarity and viscosity; in fact, a diffuse layer may itself act as a thin layer of effectively homogeneous catalyst.

A catalytically active autodissociative diffuse layer would be particularly beneficial when acting on a solid substrate since it extends the action of a catalyst outside of the latter's surface, thus excluding problematic direct solid-to-solid contact as the prerequisite for the chemical reaction (an example of such solid-to-solid catalytic process is the aforementioned cellulose hydrolysis^[21–27]). However, it may also be helpful in reactions with dissolved substrates, particularly if the functional group upon which the catalyst acts is sterically hindered and its interfacing with a solid catalyst surface is thereby complicated.^[28,29] In short, formation of a catalytically active diffuse layer by the solid catalyst self-dissociation would allow combining the advantages of homogeneous catalysts (high activity) with those of heterogeneous catalysts (ease of isolation and reuse); however, this is true only if reaction substrate and products are non-electrolytes since otherwise the solid electrolyte catalyst would undergo ion exchange with the solution bulk. The potential area of importance of autodissociative EDLs is not limited by catalysis. For example, another possible application is ion-selective membranes whose ability to deny permeation by ions depends on electric charge of pore walls.^[4–6]

Presently, the theoretical basis for autodissociative EDLs in scientific literature appears to be limited to our aforementioned earlier work.^[20] We intend to further develop this theory, and at this time we would like to resolve a couple of questions that can be answered within the same unidimensional approximation as in our initial paper. These address the role of the inner volume of a solid electrolyte particle. Specifically, we perform theoretical modeling to analyze formation of a diffuse electrical layer in two systems: inside an infinitely long cylindrical pore, and near a flat surface of a gel electrolyte. The importance of analyzing the situation inside pores arises from the fact that high catalyst porosity and surface area are preferable for reactions with soluble substrates in order to maintain high reaction rate. Gel electrolytes are interesting because many ion exchange resins have gelular structure^[30] and they are frequently used as catalysts in aqueous media;^[31] gel electrolytes are also important in EDL transistors.^[8]

2 Theoretical

If a double layer formed by dissociation of a solid electrolyte surface can be represented or approximated as spatially unidimensional, then a previously reported method for calculation of double layer configurations can be employed.^[20] In short, the solution of any such problem must satisfy the mass balance (the amounts of ions in the diffuse layer and the counter-ions in the dissociated solid must be equal. Also, dissociation equilibrium must be maintained in every point of the system). Another law that must be obeyed is the Poisson-Boltzmann equation (a differential equation with boundary values) that defines the charge spatial distribution with the minimum of electrostatic potential energy. Although this concept is equally suitable for any kind of electrolyte (acid, base, salt) as long as it can be described with a dissociation equilibrium constant, in this text we will usually refer to a modeled solid electrolyte as acid to keep the terminology and mathematical symbols familiar and consistent with the previous work.^[20]

Here, a brief summary will be given for the two EDL models studied in this paper. Their detailed mathematical description and the numerical calculation procedure are available in the Electronic Supporting Information.

The first model that we consider is an infinitely long cylindrical pore whose surface is uniformly functionalized with acid groups of equal strength (Figure 1). Distribution of protons inside an infinitely long pore with unchanging cross-section is uniform in the lengthwise direction. Because this cross-section is cylindrical, the transverse distribution is circularly symmetric. So, there remains only one independent coordinate—distance from the pore axis (or the wall). The negative charge of the dissociated groups is considered to be uniformly "smeared" on the pore surface, and the corresponding protons are considered to create a spatially continuous charge density function inside the pore.

The second model is a gel electrolyte with flat surface (Figure 2). The space near an infinitely spanning flat surface obviously can be considered a unidimensional system (or as a reasonable approximation, a curved surface whose curvature radius is much greater than the distances away from the surface which are considered in our calculations). In fact, this is what was done in our previous work.^[20] The difference from said work is that we need to account for the possible dissociation of the acid groups that are located "beneath" the gel surface (inside of the gel), and that the corresponding protons can travel into the liquid medium outside of the gel, contributing to the outer proton concentration. The inner volume of the gel is regarded as a continuum in which the charge of the ions it contains is distributed uniformly in space, and every point in it can be characterized with finite local concentration of both the anions bound to the gel structure and the free-roaming protons. Understandably, in a real gel there exists a finite distance between the neighboring acid groups, and trying to model the space between these groups as containing continuous negative charge is far removed from reality. However, jumping a bit ahead in the narration, there is a good reason for choosing this model, and even such a model leads to interesting qualitative conclusions; more is explained in the ESI. Optionally, there may be a layer of acid groups located on the flat gel surface.

Another noteworthy difference from our previous work is that we consider the influence of local electric field on the dissociation constant of the functional groups—the phenomenon known as the second Wien effect; this effect is generally acknowledged to play important role in double layer formation.^[32] We account for this effect using Onsager's theory of field influence



Figure 1: Schematic of the infinite cylindrical pore model used in the calculations. HA and A^- denote undissociated acid groups and acid anions on the surface, respectively. Every point inside the pore can be characterized with finite local concentration of protons C_{H^+} and with the local electric potential



Figure 2: Schematic of the gelular acid model used in the calculations. The gel is regarded as a continuum in which the charge of the ions it contains is distributed uniformly in space, and every point in it can be characterized with finite local concentration of protons C_{H^+} and the acid anions C_{A^-} , and also with the local electric potential φ . The surface layer is permeable to protons and bears the same acid groups as inside the gel; HA and A⁻ denote undissociated acid groups and acid anions on the surface, respectively. The surface concentration of the acid groups is assigned arbitrarily. Acid dissociation equilibrium with the local proton concentration is maintained inside the gel and at the surface.

3 **Results and Discussion**

3.1 Results for the Infinitely Long Cylindrical Pore Model

Figure 3 shows the calculated cross-sectional distributions of proton concentration and electrostatic potential in infinitely long cylindrical pores for different pore radii and different acidity constants of the functional groups on the pore surface; Table 1 shows the percentage of the dissociated surface acid groups in each case. It can be seen that the second Wien effect (Equation S12) has the most pronounced effect on the moderately acidic surface (pK 1). In case of weaker acids, the dissociation extent is too low to create the surface charge density and electric field intensity necessary to considerably affect the dissociation constant. On the other hand, the strongly acidic surface is already mostly dissociated, and a further increase of the dissociation constant due to the Wien effect cannot significantly alter the dissociation extent. Wider pores result in greater dissociation percentage, while narrower pores result in higher proton concentrations. This fact can be utilized in catalysis for choosing the appropriate textural characteristics of a solid electrolyte catalyst. If the reaction order in protons is not higher than unity, then wider pores would be more beneficial since the reaction rate effectively depends on the number of available protons in the reaction volume rather than their concentration, and wider pores are conducive to fuller dissociation of the solid acid. On the other hand, if the reaction order in protons is higher than unity (a rare but possible situation^[35]), then the proton concentration becomes a more sensitive factor, and narrower pores become preferable. Of course, these kinetic considerations assume no reaction limitation by diffusion.

Pore radius [nm]	pK _{E=0}	α_{diss} (with Wien effect) [%]	α_{diss} (no Wien effect) [%]
1	-1	96	76
	1	25	18
	3	2.4	2.3
8	-1	98	84
	1	38	27
	3	5.3	5.0
64	-1	98	86
	1	44	31
	3	7.4	6.8

Table 1: Percentage of dissociated acid groups α_{diss} on the surface of infinitely long cylindrical pores according to the calculations presented in Figure 3.

In our opinion, practical evidence of autodissociative EDL formation in pores of a solid electrolyte can be easily observed in electroosmotic phenomena. In electroosmosis of sulfuric acid solutions through porous Nafion-120® and MRF-26 membranes bearing sulfonic groups, the proton transference number very close to unity can be observed, and this number begins decreasing rapidly when H_2SO_4 concentration in the solution exceeds 1.5–2 M.^[36] There are two facets to this phenomenon. First, the fact that the electroosmosis occurs indicates directly that there exists electrically charged liquid inside the pores (i.e., the existence of an EDL). Second,



Figure 3: The calculated proton concentrations C_{H^+} and electrostatic potentials φ inside infinitely long cylindrical pores as functions of the distance x from the pore wall. Pore radii r_p (**a**) 1 nm, (**b**) 8 nm, (**c**) 64 nm. Other parameters: temperature T 300 K, relative permittivity ε 77.3 (pure water^[34]), surface density of acid groups G_{AHA} 8.57·10⁻⁷ mol m⁻². pK_{E=0} values represent acidity constants at zero electric field, i.e., before considering the second Wien effect.^[33]

the near-perfect selectivity of the membrane towards protons indicates that the negative charge on the pore walls is significant enough to reliably repel the solution anions (pore radius in Nafion-120 is estimated at 1.3–2.4 nm^[37]). Within our autodissociative EDL theory, this negative charge arises from dissociation of the sulfonic groups at the pore surface. However, this selectivity deteriorates at higher H_2SO_4 concentration in the solution,^[36] and a possible explanation is that at high concentration this dissolved acid begins to suppress dissociation of the solid acid according to the Le Chatelier principle. The resulting decrease of the magnitude of negative charge at the pore surface leads to less likely electrostatic rejection of anions by the pores, and the proton transference number begins decreasing. On related note, significant ionization extent of Nafion's sulfonic groups in presence of water is evidenced by FTIR spectrometry.^[38,39]

Coincidentally, the predicted proton concentration at the strongly acidic pore wall in thin pores is 3–4 M (Fig. 3a, pore radius 1 nm, pK 1) is comparable to the concentration of H_2SO_4 in solution (2 M) at which this proton selectivity decrease occurs in Nafion,^[36] which is similarly narrow-pored.^[37] Proton selectivity in MRF-26 begins deteriorating at lower H_2SO_4 concentration (1.5 M). Little is known about this type of membrane, although it was described as having wider pores than Nafion while having similar content of sulfonic groups.^[40] Wider pores lead to lower predicted proton concentrations in the pores (Fig. 3), and this result is consistent with the fact that lower concentration of H_2SO_4 in solution is necessary to break the MRF membrane's perfect proton selectivity in comparison to the Nafion one. So, there appears to be semi-quantitative consistency between our model's prediction and the discussed electroosmotic phenomena.

The discussed model predicts that in case of strongly acidic pore surfaces (pK -1, for comparison toluenesulfonic acid has pK -1.34^{1}) they are almost completely dissociated (Table 1). Assuming that the prediction is valid, this implies that an acid-catalyzed reaction would occur almost exclusively in the diffuse layer rather than on the surface, since the latter has almost no acid groups that still have an associated proton. Direct probing of the dissociation extent in solid acids is technically possible, e.g., by the aforementioned IR spectroscopy; and as mentioned, adsorption of water indeed appears to result in complete dissociation of sulfonic groups in Nafion ionomers.^[38,39] We could not find any further similar data in literature, and conducting such experiments ourselves falls outside of the present paper's scope. Nonetheless, such subject as existence of non-dissociated acid groups in strong solid acids immersed in water poses an interesting scientific problem for future discussion.

3.2 **Results for the Gel Electrolyte Model**

Figure 4 shows the calculated distributions of proton concentration and electrostatic potential for the model of gelular acid with flat surface for different acidity constants of the functional groups in the system, and for different distances between the gel and the bounding cellulose surface. Perhaps the most important observation that needs to be pointed out is that the near-surface slice of the gel that participates in the double layer formation (i.e., where the local proton concentration deviates from the plateau) is very thin: This slice never exceeds 1 nm of thickness. In fact, the thickness of this slice is similar to the typical distance between neighboring acid groups in

¹Validity of assigning acidity of monomeric acids to the corresponding solid polyelectrolytes was discussed in our previous work^[20]



Figure 4: The calculated proton concentrations C_{H^+} and electrostatic potentials φ for the gelular acid model as functions of the distance x from the gel surface. Negative x represents the inner gel volume. Outside of the gel, the system is bounded by a flat cellulose surface that is parallel to the gel surface (see Section S1.2). Interplanar distances d_{ip} (a) 1 nm, (b) 8 nm, (c) 64 nm. Other parameters: concentration of acid groups in the gel ε_{AHA} 3.8 mol L⁻¹, temperature T 300 K, relative permittivity inside and outside of the gel ε , ε_g 77.3 (pure water^[34]). If a surface layer is present, density of acid groups Γ_{AHA} 8.57·10⁻⁷ mol m⁻² (for explanation of the surface layer, see Fig. 2). pK_{E=0} values represent acidity constants at zero electric field, i.e., before considering the second Wien effect.^[33] pK_{E=0} values are constant across the entire gel in each case. The "only surface layer" case accounts for the Wien effect.

actual gel acids. For example, in swollen Amberlyst-36®, whose approximate concentration of acid groups according to Equation S7 and data in^[30] is 3.4 mol L⁻¹, one acid group on average occupies a cube of space which is 0.79 nm wide. It should be reminded here that the theoretical model assumes that the acid groups at the gel-liquid interface are aligned on a perfectly flat smooth surface, but in practice surface irregularities are inevitable. Due to the presence of bumps and dents on the surface of a real solid acid, all acid groups are located at slightly different distance from any plane defined by the distance x in our model. Although addition of a hypothetical perfectly flat surface layer of exposed functional groups at the interface between the gel and the liquid almost completely negates the bulk gel's involvement in the diffuse layer formation (Fig. 4a, particularly noticeable at pK -1), such surface layer would be impossible in reality. We propose that if the surface irregularities like bumps and dents are comparable in size to the calculated depth of the bulk gel participating in the diffuse layer formation, then the EDL configuration predicted by the "gel, no surface layer" variant of the model is a reasonable approximation for such irregular solid electrolyte surface. The difference between proton concentrations generated by a perfect flat surface and a gel is not particularly large, differing by a factor of 1.5–2 near the interface itself. Moreover, at long distance (Fig. 4b,c) the concentration curves representing the "gel, no surface layer" and "only (perfectly flat) surface layer, no gel" become almost identical. Within the "gel model \approx rough surface" approximation, this makes sense because if observed from a long distance, irregularities of a rough surface will become indistinguishable and insignificant.

Speaking of the "gel model \approx rough surface" approximation, it may be worth pointing out that if the near-surface proton concentrations from the previously discussed pore model (Fig. 3) are adjusted by the factor 1.5–2 to account for pore surface irregularities within the accepted rough surface approximation, then almost exact coincidence can be observed between the predicted adjusted near-surface proton concentration and the concentration of background sulfuric acid required to break the perfect proton selectivity of a Nafion membrane in electroosmotic experiments. The possible meaning behind this coincidence was discussed in Subsection 3.1.

An understandable possible point of contention for the presented results (Fig. 4) is the numeric characteristics of the gel bulk: its relative permittivity ε_a and acidity constants pK. Concerning the former number, some experimental results rate ε_q at approximately 50,^[41,42] which is not a very large deviation from pure water (77.3^[34]). On the other hand, acidity of the bulk functional groups can can be affected drastically: For example, titration of methacrylic acid polymer gels provides pK \approx 6.5 within the Henderson-Hasselbalch approximation;^[43] for comparison: pK for monomeric methacrylic acid is 4.7.^[44] Figure 5 shows how the diffuse layer parameters change when we adjust ε_a and acidity constants pK. We assume that the acidity constant K_a cannot change immediately when crossing the gel surface. Therefore, for this calculation we assume that at the surface $K_a = 10$ (comparable to sulfonic acids^[44]), and K_a decreases linearly with x, until it stabilizes at the depth of -1 nm with $K_a = 0.1$ (a drop by two orders of magnitude corresponds to the herein above described difference in acidities of methacrylic acid and its polymer gel). It can be seen that with such configuration the proton concentrations outside the gel are close to those in case of the weakly acidic gel with uniform $K_a = 0.1$, despite the presence of more acidic species at the surface and near it. Apparently, the protons from the strongly acidic near-surface region of the gel are more prone to migrating deeper into the bulk rather than outside of the gel. This is understandable: Although initially

there is shortage of protons both outside of the gel (the diffuse layer is not yet formed) and deep in the bulk (due to lower acidity there), the latter is more favorable for the protons because the anions that are present there are diluting the cationic positive charge, resulting in lower potential inside the gel.



Figure 5: (magenta line) The calculated proton concentrations C_{H^+} and electrostatic potentials φ as functions of the distance x from the surface of a gelular acid with variable acidity constant K_a . K_a is 10 at the surface, and K_a decreases linearly with x, until it stabilizes at the depth x - 1 nm with K_a value 0.1. Outside of the gel, the system is bounded by a flat cellulose surface that is parallel to the gel surface (see Section S1.2). Interplanar distance d_{ip} 1 nm. Negative x represents the inner gel volume. Bulk gel relative permittivity ε_g 50. For other conditions, see Fig. 4. (red and blue lines) These are the copies of the curves from Fig. 4a for the "gel, no surface layer" case, presented here for easy comparison.

Based on what was said above, it appears that within the predictions of our model, from the standpoint of generating a more concentrated diffuse layer, there are no particular benefits in choosing a catalyst that is a gelular solid electrolyte (like weakly crosslinked Amberlyst® ionomers) instead of electrolytes with rigid impenetrable skeleton (e.g., sulfonated carbons, sulfated zirconia or silica). It would be interesting to test this hypothesis against experimental data, but there is a certain difficulty involved in this: Not every chemical reaction is suitable as a probe for the catalytically active diffuse layer. For example, in case of a low molecular weight soluble substrate (e.g., hydrolysis of sucrose), the reaction kinetics are considerably complicated by penetration of the substrate into the gel bulk where the reaction is catalyzed as well.^[45] High temperature is necessary to attain appreciable reaction rate with high molecular weight soluble substrates (hydrolysis of hemicelluloses^[46] or starch^[47]); however, such harsh conditions typically result in leaching of sulfuric acid from ionomer resins^[48,49] and sulfated oxide materials,^[50,51] which also complicates the analysis of reaction kinetics. Sulfonated carbons are more

stable,^[24] but kinetics of carbohydrate hydrolysis with such catalysts are complicated by direct interaction of the substrate with the organic functional groups at the surface.^[52,53] Based on the listed complications, a very peculiar model reaction will be necessary for probing the catalytically active diffuse layer: The substrate should be a polymer (preferably soluble in water, and non-carbohydrate in nature) that is easily hydrolyzable at moderate temperatures. Such peculiar model systems would attract very little interest in scientific literature because of their limited practical value. For example, one possible variant of a suitable model substrate that comes to mind is poly(vinyl lactate); however, scientific literature reveals no mention of such compound. It is clear that experimental characterization of diffuse proton layers in gelular electrolytes will have to be a dedicated research project in fundamental science, something that is far outside of the scope of the present study.

4 Conclusion

Our theory of autodissociative double layers began as an attempt of explaining the catalytic interaction between solid acid catalysts and solid cellulose, and it successfully explained a number of previously known experimental facts.^[20] The theory keeps gaining supportive evidence: In the present paper it is shown that generation of negative charge on pore walls of a sulfonic ionomer membranes due to dissociation of the acid groups can adequately (even semi-quantitatively) explain both high cation selectivity of sulfonic ionomer membranes, and decline of this selectivity at high concentration of a strong acid background solution.^[36]

While our model assumes complete absence of the background electrolyte, its predictions can be expected to be approximately valid for the case where the background electrolyte concentration is very low (i.e., lower than the predicted near-surface proton concentration by at least an order of magnitude). It would be interesting to compare the model predictions to experimental data from literature, but there are not many known experiments with appropriate design for such comparison. Specifically, there should not be any pH buffering in the background solution. Atomic force microscopy probing of surface potential on montmorillonite in 1 mM NaCl postulates the surface potential value of $\approx -63 \text{ mV}$,^[54] which is quite close by magnitude to the predicted potential 69 mV^2 at the distance 14.8 nm at which the predicted diffuse proton concentration attains the same value as the background electrolyte in the cited experiment (Fig. 4c "only surface layer, no gel" pK 3; this curve corresponds to a planar solid electrolyte with relatively far-spanning open space in front of it, which is an adequate model for the cited AFM experiment). Known data concerning typical surface area,^[55] acid sites content and their strength^[56] in montmorillonite suggest that our model's numeric parameters like acid sites surface concentration and their pK (see caption of Fig. 4) are reasonably accurate to describe the real mineral. The model as presented in this paper should not be expected to provide quantitatively accurate results for more concentrated EDL of a strongly acidic surface. The main reason for this is that the presented model does not account for the existence of the inner and outer Helmholtz planes which become increasingly more important as the surface potential magnitude grows. On semi-quantitative level, we can take a look at a more easily measurable EDL

²the sign differs because in electrochemistry the reference point is the background solution, whereas we use the solid surface for this purpose.

characteristic: zeta potential. For montmorillonite in 1 mM NaCl, $\zeta \approx -7 \text{ mV}^{[57]}$ which is many times smaller than the aforementioned surface potential. For materials based on sulfonated carbon, $\zeta \approx -55 \text{ mV}$ was reported.^[58,59] Based on this value, a surface potential on the order of hundreds of millivolts should be expected, considering how surface potential is considerably greater than zeta potential. Our model satisfies this expectation, providing the potential value of 194 mV at the distance 19.7 nm where the diffuse proton concentration 1 mM is attained.

Since hydrolysis of cellulose over solid acids was where we started, we believe that the results obtained in the present study should be put into the context of cellulose hydrolysis mediated by EDLs. Based on the presented model, it appears that using gelular acids as a catalyst of this process is detrimental in every aspect: in addition to known problems with chemical stability of such catalysts,^[48,49] the diffuse layer of protons outside the gel is (at best) not more concentrated in comparison to a solid acid with rigid impenetrable skeleton (e.g., sulfonated carbons).

High porosity and surface area of a heterogeneous catalyst are important for obtaining high specific activity towards conversion of soluble substrates (e.g., soluble glucan oligomers that are detached from a solid cellulose particle in the process of hydrolysis). However, the catalytic effect on a solid particle can only manifest in the vicinity of a catalyst particle outer surface. Can a more concentrated diffuse layer of protons be formed at a pore orifice in comparison to a smooth catalyst surface, thereby improving the rate of cellulose hydrolysis? Within the scope of the present paper, no conclusive answer is possible because a pore orifice cannot be satisfactorily approximated as a unidimensional system. However, on speculative level, formation of such more concentrated region appears possible. Comparison of near-surface proton concentrations for pK -1 inside a pore (Fig. 3a) and near a solid surface (Fig. 4a, "only surface layer, no gel") shows that the former is higher by approximately one-third. This difference creates a concentration gradient that is naturally prone to even itself out, creating a possibility for some of the protons inside the pores to leave their confines through the orifice. A more substantiated answer will require at least a two-dimensional model, which will constitute an additional step in complexity of our theory.

As a concluding remark, we would like to name a few points of potential interest that may arise in catalysis due to the existence of a diffuse layer near the surface of a solid electrolyte catalyst, and represent a potential research subject:

- whether any non-dissociated acid groups exist in strong solid acids in water, and consequentially, whether a reaction catalyzed by such acid mostly occurs in the diffuse layer rather than on the surface acid species (Table 1);
- the possibility of obtaining high specific catalytic activity due to high proton concentration in the diffuse layer in reactions that have high kinetic order in proton (e.g.^[35]);
- action of electrostatic forces on the substrate molecules. E.g., attraction of protonated cellulose to the catalyst surface is theorized to play an important role in its hydrolysis over solid acids.^[20] Attraction of the substrate is particularly important for bifunctional catalysis where some of the catalytic centers are unconditionally surface-bound (e.g., metal-augmented solid acids for combined hydrolysis and hydrogenation of polysach-harides^[60–63]). Another possibility is preferential orientation of polar molecules in the electric field of EDLs.

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Keywords

Acid-base catalysis; electrical double layer; electroosmosis; gels; porosity.

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