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Surface charge and adsorption properties of polyethylene in aqueous solutions of inorganic electrolytes

I. Streaming potential measurement

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With 6 figures and 1 table

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Introduction

Adsorption of elements from their very dilute solutions on the walls of containers may cause significant difficulties in many branches of science (1-3). Among the most important container materials is polyethylene, the adsorption properties of which are not yet fully understood (4). E.g., there remains an open question about the mechanism of ion adsorption on polyethylene. Although it has been assumed that simple ions are adsorbed in an electric double layer on the surface of polyethylene (5-8), little information exists on the properties and origin of such a layer. Since the surface charge might be important not only for the adsorption of ionic species, it seemed interesting to investigate the relation between the charge and adsorption properties of polyethylene. In the present work, electrokinetic (zeta) potential of polyethylene was measured using the streaming potential method due to minimum experimental difficulties included. The results, discussed here, will be compared in the next paper with the adsorption properties of polyethylene, as determined by the radiotracer technique.

Experimental

Materials

Three sorts of polyethylene powder were used in this work: 1. Low-pressure (linear structure) Manolene 6035 (U.S.A.) having the specific gravity of 0.96 g/cm³. Fraction of particles with the diameter of 0.09-0.25 mm was used. 2. High-pressure (cross-linked) Bralen RA-2-19, product of Slovnaft Bratislava (ČSSR), of the same size as given above, and of specific gravity 0.92 g/cm³. 3. Polyethylene powder with the grain size above 0.25 mm, obtained by reprecipitation from commercial polyethylene

foil, having the same composition as given at 2. Control experiments have shown that preliminary treatment of the polyethylene powder with acid or hydroxide solution had no effect on the results.

The crushed and sized glass powder ("Sial"), which was used for the comparison purposes, had the grain size from 0.2-0.3 mm and composition 74.6% SiO₂, 6.8% B₂O₃, 6.0% Al₂O₃, 6.6% Na₂O, 1.5% CaO, 4.4% BaO.

All the solutions used were prepared from analytical grade reagents and single or twice distilled water. The difference in the purity of water was shown to have no effect on the results. p_H of the solutions was adjusted using hydrochloric acid or sodium hydroxide. Since the results should represent the usual laboratory conditions, no effort was made to free the solutions from aerial CO₂.

Apparatus and procedure

The streaming apparatus was of similar type as described elsewhere (9, 10). It was made of glass and fitted with two bright flat platinum electrodes (2 cm²). The dry polyethylene powder was packed between two platinum wire gauzes in the streaming cell in such a manner as to give a porous plug. Then solution was filled in, using suction of water jet pump or nitrogen pressure.

Prior to each experiment, the porous plug was washed with the solution of desired composition until the steady conditions were reached (p_H and concentration of the eluate). Then the solution was forced through the plug under controlled nitrogen pressure (*P*) and streaming potential (*E_s*) was measured between the platinum electrodes using digital p_H-meter PHM 52 (Radiometer, Copenhagen) with very high input resistance (> 10¹² Ω). Each experiment consisted of several measurements at different pressures. The results were plotted in *E_s* - *P* coordinates and straight lines were obtained. After each experiment the resistance (*R*) of the solution including the plug was determined with RLC bridge TM-393 (Tesla, Brno). Parallely, conductivity measurements were made at 25 °C in the conventional conductivity cell.

Electrokinetic (zeta) potentials were calculated from the equation

$$\xi = -9,69 \cdot 10^4 \frac{C \Delta E_s}{R \Delta P}$$

where C is resistance constant of the cell (determined with 0.020 M KCl solution at 25 °C) and ζ is in millivolts if $\Delta E_s/\Delta P$ (the slope of the lines) is given in mV/cm Hg. The value $9.69 \cdot 10^4$ includes the dielectric constant of the solution and thus is temperature-dependent. However, this dependence is rather slight (11), therefore the temperature at the experiments was maintained only in the region 22–25 °C.

Results and discussion

Relevance of the zeta potential data

Since some difficulties are often associated with streaming potential measurement (12, 13) it would be useful to comment briefly their significance in the present experiments. We have found that neither the compressibility nor the pore size of the polyethylene plug substantially influenced the results. The first fact follows from the linearity of E_s vs. P plots; some of those are shown in fig. 1.

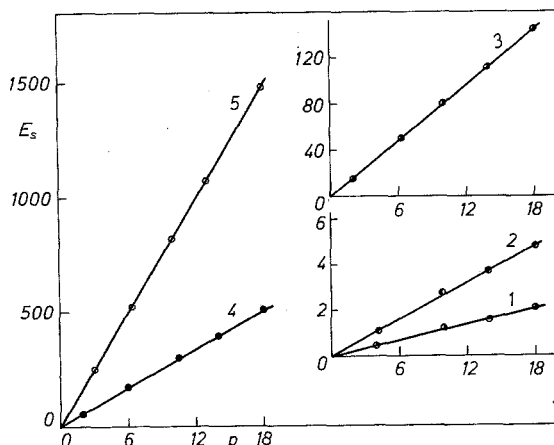


Fig. 1. The streaming potential E_s (in mV) against pressure P (in cm Hg) plots for polyethylene Nr. 3: 1. p_H 2.7, 2. p_H 3, 3. p_H 4, 4. p_H 4.5, 5. p_H 5

The second conclusion is supported by the low effect of the grain size and manner of packing of polyethylene on the slope of these lines, as revealed by control experiments. Similarly, the influence of electrode polarisation and time on zeta potential of polyethylene has been shown to be negligible. The slopes of the lines were the same even if parallel experiments were carried out in the time interval of several weeks. This indicated that the surface charge on polyethylene did not change significantly with time. The polarisation of the platinum electrodes caused only a shift of the line.

One of the mostly encountered complication at streaming potential measurements is the surface conductivity of the porous plug. In our case,

the values of the conductivity determined with the conventional conductivity cell coincided within several percents with the C/R values in the streaming cell even in the most dilute solutions. Hence, the surface conductivity of the polyethylene plug was very low.

Since the calculation of zeta potential from streaming potential data is subject to less uncertainty than other methods (9, 12), all these facts point to the reliability of the zeta potentials of polyethylene determined at low electrolyte concentration (less than 10^{-2} M). When examining the influence of an electrolyte, the measurements were conducted up to its concentration of 0.1–1 M, although the actual significance of corresponding values of zeta potential is low. These values can therefore be used only for qualitative comparison.

Origin of the surface charge on polyethylene

From the results presented in figs. 1–3 it is clear that an electric double layer exists on the surface of polyethylene in contact with aqueous solutions. The p_H -dependence of the zeta potential of polyethylene points to the potential-determining role of H^+ and OH^- ions. Similar conclusions were made also with other hydrophobic organic substances, as teflon (5), polystyrene (13), paraffin (14), etc. However, the opinions of various authors on the origin of the double layer on these substances considerably differ. According to Ottewill and Shaw (13) the surface of polystyrene latices is charged due to the primary dissociation of carboxyl groups, which are formed on polystyrene in course of its polymerization (15). Some authors have also pointed out the possibility of dissociation of foreign inorganic impurities contained in polymers (16, 17). On the other hand, Starik and coworkers (5) suggested that the negative charge on teflon is formed by the *van der Waals* or hydrogen bond adsorption of OH^- ions from the solution. Similar assumption was made by Parreira and Schulman (14) in the case of paraffin.

When analysing such possibilities for polyethylene, the dissociation of foreign inorganic impurities can be probably rejected as a cause of the double layer formation. If this was the case, the surface charge should be substantially greater on the low-pressure polyethylene, which usually contains rests of polymerization catalysators, than on high-pressure polyethylene, polymerized

without inorganic additives. As seen from fig. 2, the zeta potential and its p_H -dependence on both the polymers is virtually the same. It means that the surface charge on the different sorts of polyethylene is due to the dissociation of or adsorption on the identical surface groups. These groups might be most probably identified with carboxyl or other oxygen-containing groups, derived from both the initial synthesis and subsequent fabrication conditions, and as a result of normal temperature oxidation of polyethylene (18). It has been found by the infrared spectroscopy (19) that if polyethylene is oxidized by ozone or electric discharge, 30–40% of the oxidation products are carboxyl groups. The proportion of the carboxyl groups is probably much lower in polyethylene that was not specially oxidized. Infrared analysis failed to prove their presence in significant amounts (20). However, it must be kept in mind that the infrared analysis gives the average values from the whole volume and the situation on the surface may be rather different.

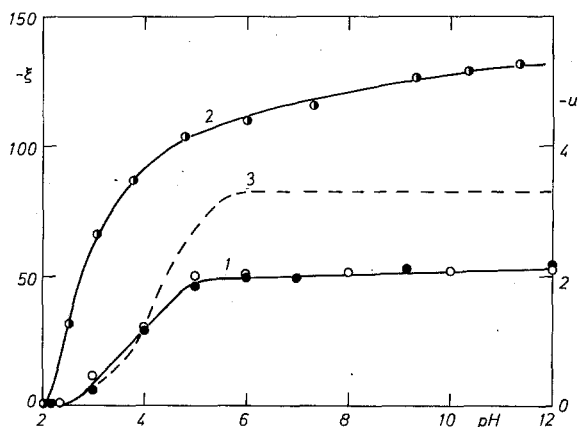


Fig. 2. The p_H -dependence of zeta potential (in mV) of: 1. polyethylene Nr. 1 (●) and Nr. 2 (○), 2. glass. Curve, 3. electrophoretic mobility u of polystyrene latices [in μ /sec V, according to (13)].

As known (21), the p_H -dependence of electrokinetic phenomena may serve to elucidate the origin of the surface charge. Therefore, the p_H -dependence of zeta potential on polyethylene found, has been compared with similar data concerning the materials with the known mechanism of surface charge formation. Quite good correspondence has been found with glass and polystyrene (see fig. 2), which are charged due to the dissociation of $\equiv\text{SiOH}$ and $-\text{COOH}$ groups, respectively. On the other hand, electrokinetic properties of teflon (5), hydrocarbon oil droplets (21) and paraffin (14), admittedly as-

cribed to the adsorption of OH^- ions, depend on p_H in entirely another manner. It can be inferred from the above that the increase in zeta potential of polyethylene over the p_H range 2.5–5 is consistent with the ionization of carboxyl groups. Above p_H 5, the potential increases only little, this probably indicating the ionization is complete. A cause of the little increase should be sought in ionisation of other (minor) groups or more probably in adsorption of OH^- ions on them. From the comparison with the similar increase in zeta potential of glass it appears that active surface groups on polyethylene are more homogeneous than those on glass (22), which might be of some importance for the adsorption properties of polyethylene.

In order to provide further argument in favour of the conclusion made above, zeta potential has been determined of the polyethylene that was previously oxidized by chromic acid and proved by infrared analysis to contain many carboxyl groups. As seen from curve 2 in fig. 3, very similar increase in zeta potential has been found in the region p_H 2.5–5. This seems to be a good evidence that our interpretation is correct. The different shape of the curve above p_H 5 is not relevant here, since it may be due to some secondary products of the reaction of polyethylene with chromic acid. Surprising at first sight might be that the zeta potential of oxidized polyethylene is lower than that of non-oxidized, although the content of carboxyl groups and therefore the surface charge is higher in the former case. To explain this situation one must realize that zeta potential is a function not only of the surface charge but also of the structure of interfacial layer.

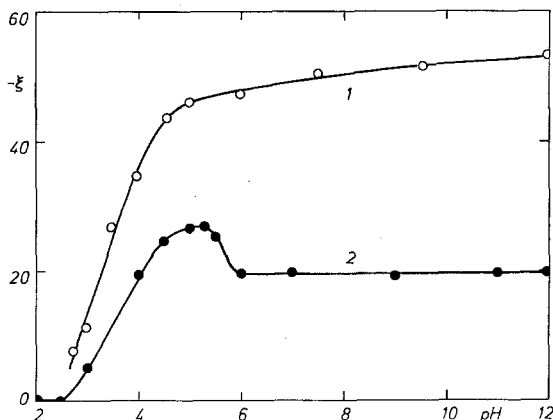


Fig. 3. The p_H -dependence of zeta potential (in mV) of: 1. polyethylene Nr. 3, 2. polyethylene Nr. 3 oxidized for 24 h at 25°C by the mixture of 50 g $\text{K}_2\text{Cr}_2\text{O}_7$ in 1000 ml of cc. H_2SO_4 .

Structure of the interfacial layer between polyethylene and aqueous solutions

An interaction between a hydrophilic surface and aqueous solutions, which includes the action of London dispersion forces, hydrogen bonds, electrostatic and dipole-dipole interactions, and other forces, results in a formation of firmly adhered layer of oriented molecules of water close to the surface. This layer is very important for electrokinetic phenomena because it can determine the position of slipping plane, where zeta potential is measured. It is clear that when this layer is thick, e.g. on hydrophilic oxidized polyethylene, it contains a considerable part of counter ions and consequently the zeta potential is low. On the other hand, if this layer is thin or lacking, the zeta potential may be high even at low surface charge. This is probably the case of hydrophobic saturated hydrocarbons which interact with the aqueous phase mostly due to weak dispersion forces (23). These facts can explain the relatively high zeta potential of non-oxidized polyethylene. [The lack of the adhered layer on polyethylene would be also consistent with the fast kinetics of adsorption (4).] Similar reasoning applies when comparison of zeta potential of hydrophilic glass and hydrophobic polyethylene is made.

Further information about the properties of the interfacial layer on polyethylene can be obtained by investigating the effect of electrolytes. The results of such an investigation are presented in figs. 4 and 5, and in table 1. For comparison, similar effect of an electrolyte on zeta potential of glass has been determined and is demonstrated in fig. 6. In all the figures, the first points, attached to the curves by dotted lines, relate to the case

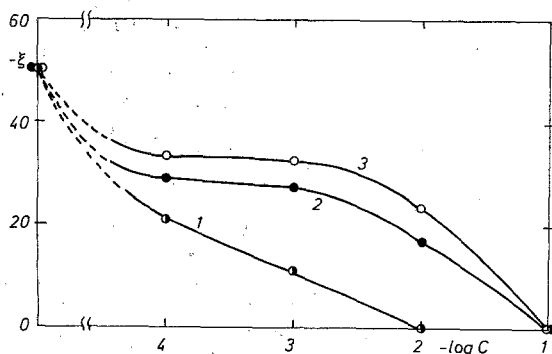


Fig. 4. Zeta potential of polyethylene Nr. 2 (in mV) as a function of the concentration c (in M/l) of electrolyte: 1. p_H 9, $CaCl_2$, 2. p_H 5, $NaCl$, 3. p_H 9, $NaCl$

when no electrolyte was added and the solution contained only hydrochloric acid or sodium hydroxide used for the adjustment of p_H .

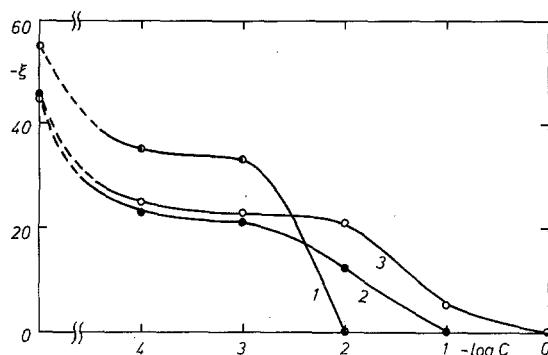


Fig. 5. Zeta potential (in mV) of polyethylene Nr. 1 (curve 2) and 3 (curves 1, 3) as a function of the concentration c (in M/l) of sodium chloride: 1. p_H 12, 2. and 3. p_H 5

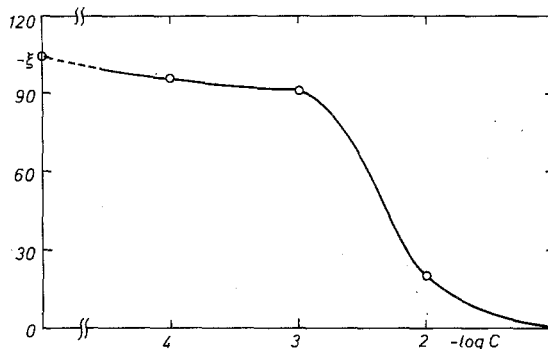


Fig. 6. Zeta potential of glass (in mV) at p_H 5 as a function of the concentration c (in M/l) of sodium chloride

It has been known that an increase in concentration of an electrolyte may generally cause: a) an increase in the charge density at surface, due to its effect on the primary ionization of surface groups or on the adsorption of OH^- ions (24 to 27); b) a decrease of the Stern potential ψ_0 , due to stronger adsorption of counter ions in the Stern layer; c) an increase in the potential drop between the Stern plane and the slipping plane, due to compression of diffuse part of the double layer. The first factor may have a positive effect on zeta potential, the others suppress it. It cannot be excluded that an electrolyte also influences the thickness or compactness of the adhered layer of water molecules, i.e., the position of the slipping plane. We believe that the rather complicated dependence of zeta potential on ionic strength of the solution, shown in figs. 4–6, can be explained by the superposition of these four effects. It is difficult to give their quantitative evaluation,

however, at least a qualitative picture will be presented here.

The initial decrease of zeta potential of polyethylene with the addition of low concentrations of electrolyte is probably caused by the adsorption of cations of the electrolyte in the *Stern* layer.

Table 1. Zeta potential of polyethylene Nr. 3 at p_H 9 in 0.0001 M solutions of various electrolytes

Electrolyte	Zeta potential (in mV)
LiCl	-43.8
NaCl	-35.2
NH ₄ Cl	-34.1
CaCl ₂	-21.3

It is supported by the dependence of this decrease on the quality of cations. As seen from table 1, Li⁺ ions depress the zeta potential less than Na⁺ ions. The same sequence has been found for hydrophobic colloids of AgJ (28), but inverse sequence applies for strongly hydrated surface of rutile (27). The logical explanation of this is that the more hydrated lithium ions, which are less likely to destroy the local structure of the surface liquid layer, are more strongly adsorbed on rutile than Na⁺ ions (27). The inverse adsorption occurs on polyethylene and argent iodide, where partial dehydration is necessary. Implicitly, this includes an assumption that the innermost part of the double layer can be identified with the surface of polyethylene and not with the layer of (at least partially) hydrated OH⁻ ions, which would be a part of the solution. Thus, the lyotropic sequence found provides an indirect evidence that the charge on polyethylene is due to the dissociation of carboxyl groups. All these findings point to some analogy between the structure of interfacial layers on polyethylene and argent iodide and support our concept that the adhered layer of water on polyethylene is thin or lacking.

At higher concentrations of electrolyte (0.0001 to 0.001 M), the effect of adsorption of counterions is probably counterbalanced by the inverse effect of increasing the surface charge. Therefore, zeta potential of polyethylene depends on the concentration of electrolyte only slightly. At still higher concentrations, compression of the double layer prevails and the zeta potential definitely falls. When calcium chloride is added as an electrolyte, the adsorption of Ca²⁺ ions and/or compression of the double layer is so strong that it cannot be counterbalanced by the increase in the surface

charge and therefore the usual (14, 29) concentration dependence is found.

As seen from figs. 4 and 5, zeta potentials of the different sorts of polyethylene are affected by the electrolyte in almost the same manner. The only exception is at higher electrolyte concentrations, where zeta potential of polyethylene Nr. 3 decreases less steeply. More pronounced differences have been found between the effects of the electrolyte at various p_H -values, which probably indicates that the structure of the interfacial layer also depends on p_H .

From the comparison of figs. 4 and 6 it follows that the decrease of zeta potential of glass above $c = 0.001$ M is more steep than that of polyethylene; the opposite is true for lower electrolyte concentrations. The former fact is probably consistent with the findings of *Stumm* and co-workers (30) that an increase in the differential capacity of double layer with the increasing concentration of electrolyte is greater on more polar substrates. Since the capacity of double layer is inversely proportional to its mean effective thickness and therefore to the zeta potential, these quantities will be more affected by electrolyte on glass than on polyethylene. The logical explanation of the latter fact seems to be that the *Stern* potential of glass is little sensitive to low concentrations of electrolyte.

The authors are indebted to Dr. *P. Skřivan* for helpful discussion of the streaming potential method and to Dr. *J. Hradil* for kindly supplying the polyethylene samples.

Summary

The streaming potentials of several sorts of polyethylene were determined as a function of p_H and composition of aqueous solutions and the electrokinetic (zeta) potentials were calculated. The results were compared with the electrokinetic properties of glass and polystyrene. It has been found that H⁺ and OH⁻ ions are potential-determining on polyethylene. The surface of polyethylene is charged negatively above p_H 2.5, probably due to dissociation of carboxyl groups, contained on polyethylene as a result of its oxidation during its polymerization and/or further processing. The zeta potentials depend in a rather complicated way on the concentration of various 1:1 inorganic electrolytes. The probable interpretation of this dependence has been given and conclusion was derived about the absence of compact adhered layer of water molecules at the surface of polyethylene. The results of the present work may be of some importance for elucidating the adsorption properties of polyethylene.

Zusammenfassung

Die Strömungspotentiale verschiedener Arten von Polyäthylen wurden als Funktion des p_H -Wertes und der Zusammensetzung wäßriger Lösungen bestimmt und aus diesen die elektrokinetischen Potentiale (Zeta) berechnet. Die Ergebnisse wurden mit den elektrokinetischen Eigenschaften von Glas und Polystyrol verglichen. Es zeigt sich, daß H^+ - und OH^- -Ionen auf Polyäthylen potentialbestimmend sind. Die Oberfläche des Polyäthylen ist oberhalb p_H 2,5 negativ geladen, vermutlich entsprechend der Dissoziation von Carboxylgruppen, die als Ergebnis der Oxydation während der Polymerisation und/oder weiterer Verarbeitungsprozesse im Polyäthylen enthalten sind. Die Zeta-Potentiale hängen in ziemlich komplizierter Weise von der Konzentration verschiedener ein-einwertiger anorganischer Elektrolyte ab. Die wahrscheinlichste Interpretation dieser Abhängigkeit wurde gegeben und Schlüsse über die Abwesenheit kompakter adsorbierter Schichten von Wassermolekülen auf der Oberfläche des Polyäthylens gezogen.

Die Ergebnisse der vorliegenden Arbeit mögen von einiger Bedeutung für die Erkenntnisse der Adsorptionseigenschaften von Polyäthylen sein.

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