

## Review

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## Zeta potential of microfluidic substrates: 2. Data for polymers

Zeta potential data are reviewed for a variety of polymeric microfluidic substrate materials. Many of these materials currently used for microchip fabrication have only recently been employed for generation of electroosmotic flow. Despite their recent history, polymeric microfluidic substrates are currently used extensively for microchip separations and other techniques, and understanding of the surface  $\zeta$  potential is crucial for experimental design. This paper proposes the use of  $pC$  (the negative logarithm of the counterion concentration) as a useful normalization for the  $\zeta$  potential on polymer substrates in contact with indifferent univalent counterions. Normalizing  $\zeta$  by  $pC$  facilitates comparison of results from many investigators. The sparseness of available data for polymeric substrates prevents complete and rigorous justification for this normalization; however, it is consistent with double layer and adsorption theory. For buffers with indifferent univalent cations, normalization with the logarithm of the counterion concentration in general collapses data onto a single  $\zeta/pC$  vs.  $pH$  curve, and (with the exception of PMMA) the repeatability of the data is quite encouraging. Normalization techniques should allow improved ability to predict  $\zeta$  potential performance on microfluidic substrates and compare results observed with different parameters.

**Keywords:** Microfluidic substrates / Miniaturization / Review / Zeta potential

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### 1 Introduction

The growth of microfluidic technologies with widely varying substrate requirements has led to increased interest in polymeric materials. Polymers offer a wide range of mechanical and electroosmotic properties as well as fabrication techniques [1], and hence are ubiquitous in microchip analytical systems. However, because the surface chemistry of most polymeric substrates is less well-known than for silica or silicon, this introduces practical difficulties and possible opportunities for zeta potential ( $\zeta$ ) modeling. While only a small amount of work (as compared to that for silica) has been performed on most polymeric materials, the large number of potential polymeric substrates has led to many investigations along these lines. Much of this work is listed in Table 1.

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**Abbreviations:** PA, polyamide; PDMS, poly(dimethyl siloxane); PE, polyethylene; PET, poly(ethylene terephthalate); PETG, poly(ethylene terephthalate glycol); PMMA, poly(methylmethacrylate); PS, polystyrene; PTFE, poly(tetrafluoroethylene); PU, polyurethane; PVC, poly(vinyl chloride); RMS, root-mean-square

**Table 1.** Selected zeta potential references

Ref.	Substrate	Technique	Counterion	Buffer ion	Comments
[10]	PETG, PS, PMMA	EOM	Na <sup>+</sup> /K <sup>+</sup>	Phosphate	
[13]	PDMS/S	EOM	Na <sup>+</sup>	Phosphate	Sylgard 184; hybrid glass/PDMS channels
[14]	PDMS	EOM	K <sup>+</sup>	Phosphate	Shows effects of hydrophobic additives: TBA, SDS
[15]	S, PDMS	SP	K <sup>+</sup> , La <sup>3+</sup>	None	Shows effect of counterion valency on PDMS
[16]	PMMA, PDMS, PC, S	EOM	Na <sup>+</sup> /K <sup>+</sup> a)	Carbonate	Shows dependence in plastics to exposure to caged dye;
[17]	PDMS, oxidized PDMS	EOM			qualitative – used charged tracer
[18]	PDMS/S	EOM	Tris <sup>+</sup>	Tris-borate	Sylgard 184; hybrid glass/PDMS channels
[19]	PDMS	EOM	Na <sup>+</sup> /K <sup>+</sup>	Phosphate	Cured silicone oil coating on capillaries;
[20]	PC, PETP	EOM	Na <sup>+</sup>	Acetate	Composite microchannels
[23]	PDMS	EOM	Na <sup>+</sup>	Borate	Sylgard 184; plasma-oxidized; measurements in buffer with methanol and SDS; stability measurements
[24]	PETG, PS, PC	EOM	Na <sup>+</sup> /K <sup>+</sup>	Phosphate, citrate, borate	pH 10 data ignored here due to heating concerns; PET lids for all substrates
[25]	PC	EOM	Na <sup>+</sup> /K <sup>+</sup> a)	Carbonate	
[26]	PETG, PC, PS, PMMA, PDMS	EOM	Na <sup>+</sup> /K <sup>+</sup> a)	Phosphate	Composite microchannels
[28]	PMMA, PC	EOM	Na <sup>+</sup> /K <sup>+</sup> a)	Acetate, borate	Chemical modification of PMMA, PC
[30]	PMMA	EOM	Na <sup>+</sup> /K <sup>+</sup> a)	Acetate, borate	Chemical modification of PMMA
[31]	S, PMMA	EOM	ACES <sup>+</sup> /Na <sup>+</sup>	Phosphate, ACES	
[32]	PETG	EOM	Tris <sup>+</sup>	TBE	Shows effects of alkaline hydrolysis
[33]	PETG	EOM	Na <sup>+</sup> /K <sup>+</sup> a)	Phosphate	Shows effects of hydrolysis and variation between imprinting and laser-ablation
[34]	S, polyester	EOM	Na <sup>+</sup>	Borate, citrate, phosphate	Most measurements in presence of SDS
[35]	S, C, PA, PE, PU	SP, SC	Na <sup>+</sup>	None	SP and SC results do not match – authors postulate formation of thick gel layer; results of zeta scaling with ionic strength do not match those of other investigators
[38]	PTFE, P(TFE-co-HFP)	EOM	Na <sup>+</sup>	Citrate	A number of anomolous results reported, including deformation of capillaries and violation of no-slip condition at wall
[39]	P(TFE-co-HFP), PE, PVC	EOM	Na <sup>+</sup>	Phosphate, borate	CAPS, betaine zwitterions in buffer; investigate dependence of zeta on organic solvents
[42]	PMMA, S	SP	K <sup>+</sup>	None	Results for both PMMA and S are well below other reported results
[43]	PDMS	EOM	Na <sup>+</sup> /K <sup>+</sup> Ca <sup>2+</sup> /Mg <sup>2+</sup>	Phosphate, HEPES	Sylgard 184; native and plasma-oxidized PDMS; effects of aging and NaOH treatment on EOF
[44]	PDMS	EOM	Na <sup>+</sup>	MES	Sylgard 184; dynamic coating effects of MES buffer
[46]	S, PTFE	SP	Various	Various	
[47]	S, PTFE	EOM	K <sup>+</sup>	Various	

Substrates: S, silica; PC, polycarbonate. Others defined in text. Techniques: EOM, electroosmotic mobility; EPM, electrophoretic mobility; SP, streaming potential; SC, streaming current.

ACES, *N*-(2-acetamido)-2-aminoethanesulfonate; TBE, Tris-borate-EDTA; TBA, tetrabutylammonium; C, cellulose acetate

a) Cation unspecified, assumed Na<sup>+</sup> or K<sup>+</sup>

The difficulty of obtaining accurate and precise zeta potential (or electroosmotic mobility) measurements means that the data show a great deal of scatter in addition to study-to-study variation. Thus, one of the major goals of this paper is to compare the data from numerous studies on a single graph, which is essential to establish conclusions based on the ensemble of data obtained by the research community. However, the data are often reported for cases with large differences in counterion concentration, as well as significant differences in other fluid properties as well, and  $\zeta$  depends strongly on these properties. The purpose of this paper is twofold: (i) to develop a model-based framework for reporting  $\zeta$  of polymeric substrates, and (ii) to use this framework to summarize and compare existing data on  $\zeta$  of polymer microfluidic substrate materials. The companion to this paper [2] has detailed theory and experimental techniques for measuring the zeta potential, presented data for silica, and reported the effects of  $\zeta$  and its variation on separations. This paper is organized to first apply these theoretical foundations to deduce a useful scaling of zeta potential, so that cases with different counterion concentrations may be compared. This framework is then utilized to present data for the zeta potential of a variety of microfluidic substrates.

## 2 Theory of zeta potential and electroosmosis

This section summarizes key conclusions from [2] and serves to motivate the techniques used to graph and report data in later sections. In particular, two relations are crucial for the sections to come. The first is the relationship between the electroosmotic mobility and  $\zeta$ . The second is the dependence of  $\zeta$  on the counterion concentration.

The net charge density on a microfluidic substrate in contact with an aqueous solution gives rise to an electrical double layer and electroosmosis. Discussion of double layer structure can be found in many sources [2–8]. The net surface charge density,  $q''$  (units charge per unit area, e.g., C/cm<sup>2</sup>), is dictated primarily by pH and, for counterions that adsorb, the counterion type and adsorption equilibria. In the Guoy-Chapman-Stern (GCS) model of the double layer [3], the electrical double layer (EDL) is comprised of a diffuse layer and a Stern layer. The diffuse layer gives rise to electroosmosis and is the region of the EDL most pertinent to calculations of electroosmosis in microchip separation devices.

For microchip separation devices, the most important consequence of the EDL is electroosmosis in microchip channels. An electric field introduced down the length of an electrolyte-filled capillary or microchannel induces the

net charge in the EDL to migrate, carrying the rest of the fluid in the capillary with it by the action of viscosity. For flow past an infinite plate with infinitely thin double layers, the flow speed past the plate surface,  $u$ , is

$$u = \frac{\varepsilon\zeta}{\eta} E \quad (1)$$

where  $\varepsilon$  is the electrical permittivity, and  $E$  is the electric field. Hence the factor  $\varepsilon\zeta/\eta$  is known as the electroosmotic mobility,  $\mu_{eo}$ . Equation (1) is typically used to relate electroosmotic mobility to the zeta potential. Relations for the dependence of  $\zeta$  on counterion concentration, surface charge density, and temperature follow from the GCS double layer model:

$$\sinh(-e\zeta/2kT) = q''\lambda_D e/2\varepsilon kT \quad (2)$$

where  $k$  is the Boltzmann constant,  $T$  is the temperature,  $e$  is the elementary charge, and  $\lambda_D$  is the Debye length. If the surface charge density is unaffected by the counterion and the counterion concentration, and all the shielding is performed by the diffuse portion of the double layer, then the dependence of  $\zeta$  on counterion concentration  $c$  (given constant temperature, dielectric constant, and assuming a symmetric electrolyte of valency  $z$ ) can be shown to be

$$\zeta \sim \lambda_D \sim c^{-1/2} z^{-1} \quad \text{when } \zeta \ll 2kT/e \quad (3)$$

$$\zeta \sim \log \lambda_D \sim a_0 + a_1 \log(cz^2) \quad \text{when } \zeta \gg 2kT/e \quad (4)$$

In [2] the applicability of the simplified relations in Eqs. (3) and (4) is addressed. The low- $\zeta$  scaling ( $\zeta \sim 1/c^{1/2}$ ) is rarely useful for microchip separation systems, since it requires counterion concentrations that are too high for most electroosmotic applications. The high- $\zeta$  scaling ( $\zeta \sim -\log c$ ) works well for a wide range of concentration, and continues to work in the presence of surface adsorption since adsorption also leads to a logarithmic functional form. Defining  $pC$  equal to  $-\log c$ , then,  $\zeta = a_0 + a_1 pC$  for univalent electrolytes.

The relations summarized above can be used to develop an initial framework for investigating the electroosmotic properties of polymeric substrates, which is necessary given the complexity of the system when considered in complete detail. This paper uses  $\zeta$  to describe the surface since  $\zeta$  is a surface property – unlike electroosmotic mobility,  $\zeta$  is independent of both viscosity and (excepting second-order effects on double layer thickness) dielectric constant. Unfortunately, the  $\zeta$  potential of a surface is still determined by both surface reaction equilibria as well as shielding phenomena, and is thus a function of pH, counterion concentration, counterion type and valency, ionic strength, chemical and mechanical surface modification, and ionic and nonionic surfactants. This fact, combined with the wide variety of polymeric substrates, leads to an

immensely complex system. A first attempt at summarizing the body of knowledge of  $\zeta$  on polymeric substrates requires that this be simplified. To this end, this paper will ignore data from experiments with surface-modified or surfactant-treated substrates (although brief mention will be made of references along these lines) and will focus on indifferent univalent electrolytes (e.g., sodium, potassium) to avoid specific binding issues and therefore eliminate ionic strength as a binding-related variable. For native surfaces in contact with indifferent univalent electrolytes, then the key variables are pH and counterion concentration. In general,  $\zeta$  can be plotted as a function of pC at every pH and  $a_0$  and  $a_1$  from Eq. (4) may be inferred. However, the system can fortunately be further simplified by noting that, for indifferent univalent electrolytes at conditions used for microchip separations,  $|a_0|$  is typically much smaller than  $|a_1 pC|$  and thus  $a_0$  can be neglected. This result does not follow from any fundamental physical argument (and, in fact, is a fortunate result of the unit system chosen – here  $c$  is in M). However, the fact that  $\zeta$  vs. pC data are well-approximated by lines through the origin implies that, as an engineering approximation,  $\zeta/pC$  can be assumed independent of concentration over the range  $10^{-1}$  M to  $10^{-6}$  M; thus,  $\zeta/pC$  may be used as a tool to generalize the pH-dependence of zeta over a wide range of materials, including silica [2] and all of the polymers discussed here. The errors associated with this approximation will be discussed in the context of the observed results. Once this normalization is performed, the magnitude and relative pH-dependence of  $\zeta$  can be summarized for each substrate material, despite rather wide variation in experimental techniques, and results can be compared despite large variations in both the counterion concentration and the absolute value of  $\zeta$ . Since zeta potential (or electroosmotic mobility) measurements tend to show a great deal of scatter and study-to-study variation, summarizing the results of numerous investigators on a single axis is essential to establish conclusions based on the preponderance of the evidence.

The available data for polymers is often sparse enough that the normalization proposed here can only be tentatively supported by the data. Despite this limitation, the success of normalization of  $\zeta$  by pC in facilitating summary of existing data should help identify which experimental conditions are well or poorly understood and, in so doing, highlight where further experimentation is necessary.

### 3 Measurement techniques for zeta potential in polymeric substrates

Techniques for measuring  $\zeta$  are summarized in [2], and consist primarily of streaming potential/current measurements, electroosmotic mobility measurements, and parti-

cle electrophoretic mobility measurements. This paper intentionally constrains its focus primarily to measurements in capillaries and microfluidic substrates, and will attempt to minimize the discussion of measurements in filtration membranes, polymer fibers, and colloidal dispersions. The reasons for this are as follows: first, measurements of electrokinetic properties in porous media are very difficult – the geometric requirements are strict and the uncertainties are large. Hence, measurements in filtration membranes and packed fibers have led to widely varying results; in the present work we hope to eliminate this source of uncertainty. Second, measurements in colloidal dispersions are affected by curvature effects, which can lead to great uncertainty in data interpretation. Finally, the chemical and mechanical nature of polymer colloids, fibers, and membranes can result in significant hydrodynamic-mechanical interaction leading to conformation changes in the material which would not be present in microfluidic substrates. Hence, data for these materials introduce additional ambiguity. By focusing primarily on results obtained from monolithic substrates, results shown and conclusions drawn here should be directly applicable to microfluidic systems.

### 4 Zeta potential on polymer substrates: reported data

A number of general comments can be made regarding fundamental differences between silica and polymer surfaces. Silica surfaces are usually high charge density, hydrophilic surfaces, with extensively studied properties and surface chemistry [9]. Polymer surfaces typically show lower surface charge density, they can be very hydrophobic, and their surface charge often comes from unknown sources or is affected by fabrication techniques. These three major differences all impact interpretation of  $\zeta$  data on polymers when viewed in comparison to silica: (i) lower surface charge makes the Debye-Hückel approximation more generally applicable to polymer systems than to silica systems, and makes the region of applicability of Eq. (4) narrower. (ii) The hydrophobic nature of many polymer surfaces means that hydrophobic buffer additives have the potential to greatly impact the observed zeta potential. In particular, ionic detergents (e.g., SDS) at  $> 1$  mM concentration are expected to dominate the zeta potential performance of hydrophobic polymer substrates through adsorption at the surface (iii) Organic polymers, in addition to the aforementioned dependences on pH, counterion concentration, etc., can show dependence on the vendor that produced the plastic (due to changes in polymer composition or additives) as well as the method of fabricating channels. Although vendor variations are not well-established, fabrication tech-

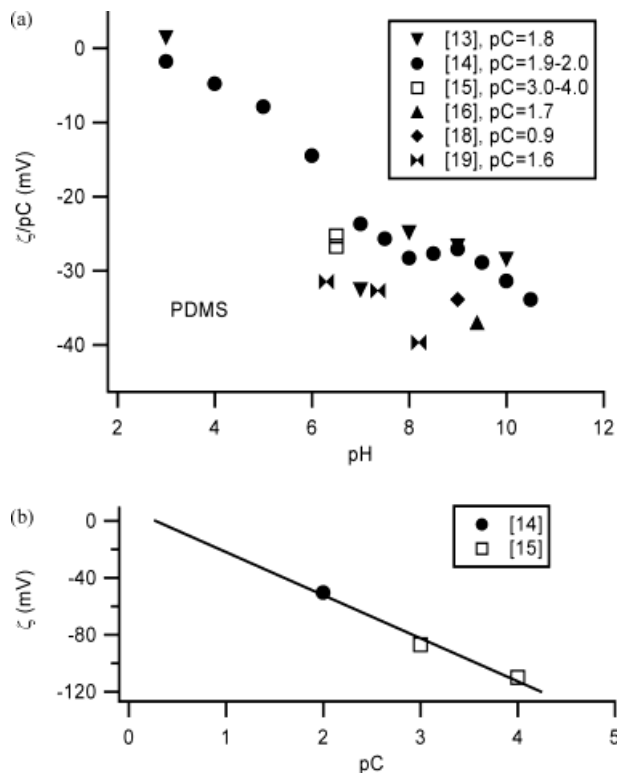
niques such as laser ablation in air can chemically alter  $\zeta$  by introducing charges from reactive oxygen species [10]. Surface charge density, as measured by fluorescent labeling, has been shown to be dependent on laser ablation processes and postablation sonication [11].

Despite the concerns raised by the preceding comments, significant progress has been made toward characterizing  $\zeta$  for polymers. The following paragraphs summarize results for a number of polymeric substrates.  $\zeta$  vs. pH is presented using normalization by pC. When data is available, the dependence of  $\zeta$  with counterion concentration is also shown to indicate the validity of this normalization as a way to combine  $\zeta$  measurements from many sources. Work on surface modification is briefly summarized but is not discussed in detail. All results are room temperature results (20–25°C) unless specified otherwise. Polymers are grouped here primarily for convenience and also with some attention to general chemical structure.

#### 4.1 Poly(dimethyl siloxane)

Poly(dimethyl siloxane) (PDMS; silicone) has become a very common substrate for microfluidic systems. Its advantages include rapid, inexpensive fabrication [12] achieved by pour-casting onto molds. Plasma-oxidation has been used in some experiments to facilitate bonding of PMDS to PDMS or glass, and has been shown to affect  $\zeta$ ; polyelectrolytes [13] have also been used to modify  $\zeta$ . However, this section will summarize zeta on PDMS only in its native state.

Measurements of  $\zeta$  in native (*i.e.*, not plasma-oxidized) PDMS are shown in Fig. 1a, with  $\zeta$  normalized by pC. The most thorough data is from [14]; more limited results from [13, 15–19] are in rough agreement. A number of data processing steps are required to plot the data as shown on this graph (these steps apply to the graphs that follow for other materials as well). Raw data is usually obtained as measurements of the electroosmotic mobility, which must be converted to  $\zeta$  through Eq. (1) at the experimental temperature (and therefore permittivity and viscosity) of the solution and interface, which is often not recorded; this is further complicated since applied voltage often leads to an unreported level of Joule heating. On some occasions, the reported electroosmotic mobility values have been converted to  $\zeta$  despite incomplete fluid property information. For example, absent information on temperature, 20°C has been assumed; this will lead to overreporting of  $\zeta$  if any heating effects are present, since both  $\zeta$  and  $\varepsilon/\eta$  increase with temperature. Further, a number of measurements have been made using PDMS molds bonded to glass surfaces (*e.g.*, [13, 18]). For these studies, the



**Figure 1.** (a)  $\zeta$ /pC vs. pH for PDMS. (b)  $\zeta$  vs. pC for PDMS (6.5 < pH < 7). For this and all of the following figures, closed symbols denote electroosmotic or electrophoretic measurements, open symbols denote streaming current or streaming potential measurements.

observed electroosmotic mobility is roughly equal to a surface-area-weighted average of the individual PDMS and glass  $\zeta$  values (see [20] for limits of this approximation and results of more detailed modeling), and an assumed value for glass combined with the microchannel dimensions must be used to infer the PDMS  $\zeta$  value. When a  $\zeta$  for silica was measured in the same study, that value was used; when this value was unavailable, a value for silica was assumed by phenomenologically approximating  $\zeta$  for silica (see data in Fig. 6 of [2]) as  $\zeta$ /pC [mV]  $\approx$  2 + 7 · (pH-3). This technique for inferring approximate PDMS  $\zeta$  values leads to greatly increased uncertainty, and was not used within the pH 4–6 region, in which the  $\zeta$  of silica can be history-dependent [21, 22]. However, unless a correction of this type is made, data from hybrid glass/PDMS chips cannot be compared to data in all-PDMS microchannels. The counterion concentration was calculated from the specifications in each reference using low-concentration buffer pK<sub>a</sub>. References for which the counterion concentration was ambiguous or unspecified are not presented. For experiments that use two buffers to monitor current changes caused by EOF, the geometric mean of the two concentrations was used.

Figure 1b shows  $\zeta$  vs. pC for PDMS in the pH range  $6.5 < \text{pH} < 7$  along with the best-fit line ( $a_0 = 6.75$  mV,  $a_1 = -29.75$  mV). The quality of the fit to the data can be evaluated in several ways, with particular attention to the appropriateness of normalizing  $\zeta$  by pC. Normalizing  $\zeta$  by pC is equivalent to setting  $a_0 = 0$  in Eq. (4), or, from a curve fitting standpoint, to forcing the linear fit to go through the origin. Key issues to be addressed include the quality of the linear fit, the degree of error introduced by forcing the linear fit through the origin, and the ability of a linear fit through the origin to match the data over the observed range. For the data in Fig. 1b, the coefficient of determination of the linear fit is 0.98, indicating a good linear fit in this range. The values provided by the best-fit line and a best-fit line that is forced to go through the origin ( $a_0 = 0$  mV,  $a_1 = -27.65$  mV) differ by less than 4.8% over the region studied, indicating that assuming that  $a_0 = 0$  in Eq. (4) leads to small errors. The best-fit line through the origin leads to root-mean-square (RMS) RMS errors of 6.1% for this data.

While the results from linear fitting on semilog axes are encouraging, conclusions drawn from linear fits to this  $n = 3$  data set are at best tentative. Any variety of functional forms could also successfully fit this data. However, the logarithmic form is successful for this data, and it is the most promising form for treating data over a wide range because of the wide applicability of Eq. (4). Results for other polymers in the coming sections are more extensive, and will lead to similar conclusions that further support this claim.

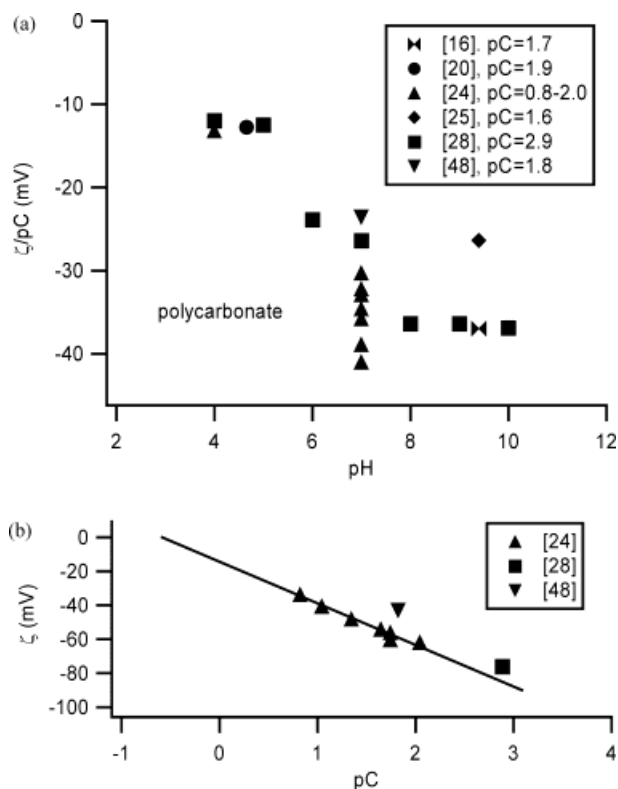
Normalizing the measured  $\zeta$  values by pC collapses the (rather limited) data onto a single curve with scatter contained within  $\pm 15\%$  of the average observed value. The quality of the agreement is no worse than that for silica [2], despite the sparse and recent nature of PDMS results as compared to decades of measurements and study on silica. The  $\zeta$  inferred from the data of [14, 19] differ by approximately 40% despite coming from the same research group; this is likely due primarily to Joule heating since the electroosmotic mobility measured for silica capillaries in [19] under similar conditions is approximately 40% above the value typically observed at 20°C. This discrepancy can be explained by a  $\sim 13^\circ\text{C}$  temperature increase in [19] as compared to [14], which would be unsurprising since the former used capillaries and the latter planar microchips. Such discrepancies are the unfortunate result of translating electroosmotic mobility measurements to  $\zeta$  in an attempt at generality. While only five sources are compared and the scatter is significant, the collapse onto a single curve is of note since concentrations varying over four orders of magnitude have all been plotted on the same  $\zeta/\text{pC}$  vs. pH graph.

The functional form of the  $\zeta/\text{pC}$  vs. pH curve inferred from the data of [14] is sigmoidal and indicative of a surface  $\text{p}K_a$  near 5. In this sense, the curve resembles that of many measurements on silica (though it should be noted that roughly half of the measurements reported on silica show a sigmoidal curve and half show a strictly linear dependence). It has been argued that the resemblance between the  $\zeta$  vs. pH curve of PDMS and that of silica supports the hypothesis that the  $\zeta$  of PDMS comes from silica filler in the most common (Sylgard 184) PMDS formula [14]; however, [17] has claimed that PDMS formulas without silica filler perform similarly, and the chemical source of the  $\zeta$  vs. pH response is as yet undetermined. Plasma oxidation [12, 17] has been shown to create surface O-H groups and increase the charge density to roughly that of silica; it is hypothesized that silanol groups with similar  $\zeta$  vs. pH behavior are responsible for the charge on plasma-oxidized PDMS. Plasma oxidation facilitates permanent bonding of PDMS substrates; however, the  $\zeta$  observed has been shown to change with time under dry storage, and repeatability in this configuration is poor.  $\zeta$  observed in plasma-oxidized PDMS is also a function of degree of oxidation, which varies from investigation to investigation. Because of this, no attempt has been made here to summarize results for plasma-oxidized PDMS. In the native state, the  $\zeta$  of PDMS is relatively constant with time [14].

Systematic investigation of the effects of surfactants of various degrees of hydrophobicity have shown that  $\zeta$  in native PDMS in standard buffers is attributable primarily to the surface itself, not adsorption of buffer ions or low concentrations of weakly hydrophobic molecules such as fluorescein or tetrabutylammonium [14]. However, since native PDMS is strongly hydrophobic, charged hydrophobic molecules can affect  $\zeta$ . Surfactants such as SDS, CTAB, Tween 20, and Brij 35 adhere to PDMS and change  $\zeta$  and its pH dependence [14, 19, 23], as do other compounds not normally thought of as ionic surfactants, e.g., large hydrophobic charged dyes such as some caged dyes [16].

## 4.2 Polycarbonate

Polycarbonate is a commonly used rigid polymer substrate [1], fabricated *via* laser-ablation [24] or stamping and thermal bonding [16, 25]. Polycarbonate surfaces have been used in their native state, and have been modified by deposition of polyelectrolyte multilayers [26] and exposure to sulfur trioxide [27, 28]. Figure 2a shows  $\zeta$  measurements on native polycarbonate substrates. As has been observed for silica and PDMS,  $\zeta$  increases in magnitude as pH is increased. The scatter is significant enough that the detailed functional form of the pH-

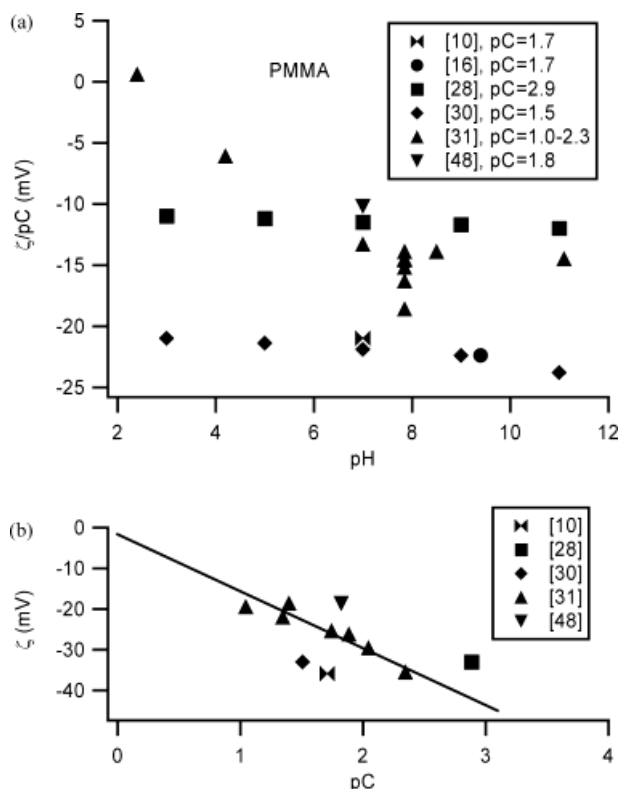


**Figure 2.** (a)  $\zeta$ /pC vs. pH for polycarbonate. (b)  $\zeta$  vs. pC for polycarbonate ( $6.8 < \text{pH} < 7.2$ ). Linear fit is to data of [24].

dependence is still ambiguous; however, the results of the six sources shown agree to within  $\pm 30\%$  around the mean. Figure 2b shows  $\zeta$  vs. pC for polycarbonate at pH 7 along with the best-fit line for the data of [24] ( $a_0 = -15.42$  mV,  $a_1 = -23.79$  mV). The coefficient of determination of the linear fit is 0.97. The values provided by the best-fit line and a best-fit line that is forced to go through the origin ( $a_0 = 0$  mV,  $a_1 = -33.46$  mV) differ by less than 21.4% over the region studied. The best-fit line through the origin leads to RMS errors of 10.0% for this data.

### 4.3 Poly(methyl methacrylate)

Poly(methyl methacrylate) (PMMA) is perhaps the most commonly used rigid polymer substrate, is easily machined or stamped, and has excellent optical properties [1]. It has been used both in its native state and modified after or during fabrication. Subablation fluences from pulsed lasers have been used to locally modify the  $\zeta$  in PMMA [29]. PMMA has also been modified by reacting the pendant ester of the PMMA with diamines [28, 30] to aminate the surface and generate a change toward positive  $\zeta$  potentials.



**Figure 3.** (a)  $\zeta$ /pC vs. pH for PMMA. (b)  $\zeta$  vs. pC for PMMA ( $7 < \text{pH} < 8$ ). Linear fit is to data of [31].

Figure 3a shows  $\zeta$  measurements on native PMMA substrates. PMMA shows perhaps the worst agreement between investigators of all of the polymers reviewed here. No clear agreement appears from the data regarding either the pH-dependence, concentration-dependence, or relative magnitude of the  $\zeta$  potential. Two studies have shown  $\zeta$  that is quite independent of pH; others show a pH-dependence similar to that of polycarbonate, perhaps indicative of deprotonation of carboxylic acid sites with  $\text{pK}_a$  near 5. Two investigations performed similarly and in the same laboratories [28, 30] show nearly identical data despite vastly different buffer concentrations – it is unclear if this is an anomalous measurement result or simply an editorial error when reporting buffer concentrations. Finally, the variation in magnitude of the measured  $\zeta$  for PMMA is the largest of all the polymers summarized here.

Figure 3b shows  $\zeta$  as a function of counterion concentration for  $7 < \text{pH} < 8$  along with the best-fit line for the data of [31] ( $a_0 = -4.06$  mV,  $a_1 = -12.57$  mV). The coefficient of determination of the linear fit is 0.90, and clearly some curvature can be observed in the data. The values provided by the best fit line and a best-fit line that is forced to go through the origin ( $a_0 = 0$  mV,  $a_1 = -14.84$  mV) differ

by less than 9.9% over the region studied. The best-fit line through the origin leads to RMS errors of 9.9% for this data. [31] specifically addresses different scaling approaches for silica and PMMA and claims that PMMA is better fit with a functional form  $\zeta = a_0 + a_1 c^{1/2}$ . This functional form does fit the data of [31] slightly better than a logarithmic form; however, the statistical significance of this is not well established given the limited number of data points and the rather limited concentration range. Also, the physical model used to justify the scaling relation requires postulation of extremely thick ( $> 100 \text{ \AA}$ ) Stern layers. It is clear that a number of functional forms successfully fit  $\zeta$  vs. concentration data, especially within narrow ranges of concentration; however, the body of evidence on many materials indicates that logarithmic scaling is of more general application.

#### 4.4 Polyesters, particularly poly(ethylene terephthalate)/poly(ethylene terephthalate glycol)

Microfluidic substrates have been fabricated in poly(ethylene terephthalate)/poly(ethylene terephthalate glycol) (PET/PETG), using primarily imprinting and hot embossing techniques [1]. PET/PETG films have also been used to construct microfluidic systems [20, 24]. Modification of  $\zeta$  in PETG substrates has been achieved through alkaline hydrolysis [32, 33], reaction with diamines [33], dynamic coating [32], and polyelectrolyte multilayers [26]. Ionic detergents such as SDS are expected to increase  $\zeta$  in PET/PETG due to wall adsorption and reduce pH dependence due to the low  $pK_a$  of the sulfate group. Effects of SDS in an unspecified polyester have been shown in [34]. Figure 4 shows  $\zeta$  potential measurements on native PET/PETG substrates. Among the limited data, results of different investigations with like materials agree rea-

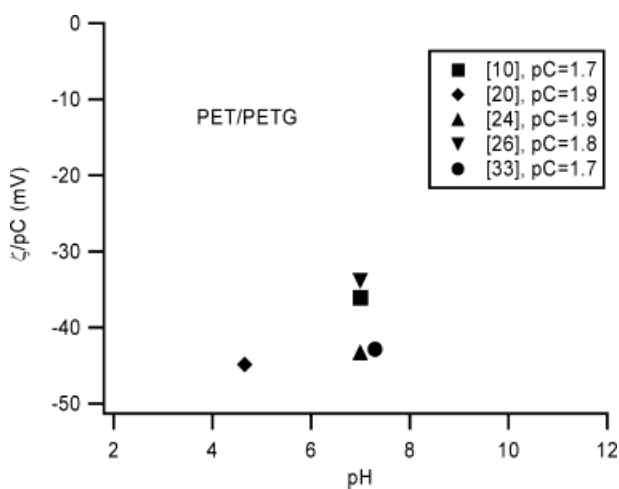


Figure 4.  $\zeta/pC$  vs. pH for PET/PETG.

sonably well; however, the data is so limited and within such a narrow range of conditions that few conclusions can be drawn. Despite no direct evidence for or against logarithmic scaling of  $\zeta$  with concentration, results are shown in terms of  $\zeta/pC$  for consistency.

#### 4.5 Polyethylene, polystyrene, and poly(vinyl chloride)

Microfluidic substrates have been fabricated in polyethylene (PE), polystyrene (PS), and poly(vinyl chloride) (PVC), using primarily imprinting and hot embossing techniques [1]. PE, PS, and PVC films and film adhesives are also available and have been used for sealing microchannels [20, 35]. While most results are on native materials, PS has been modified through the use of polyelectrolyte multilayers [26]. Figure 5 shows  $\zeta$  potential measurements on native PE/PS/PVC substrates. Among the limited data, results of different investigations with like materials agree reasonably well, and the  $\zeta$  of PVC is quite similar to that observed for PE. The average data observed for PS matches that of PE and PVC, though the data is limited and scatter is large. As was the case for polycarbonate, a functional form consistent with titration of carboxylic acid sites is observed; however, the chemical path to generation of carboxylic acid sites is unclear for these substrates, and the chemical nature of this surface charge is currently unknown.

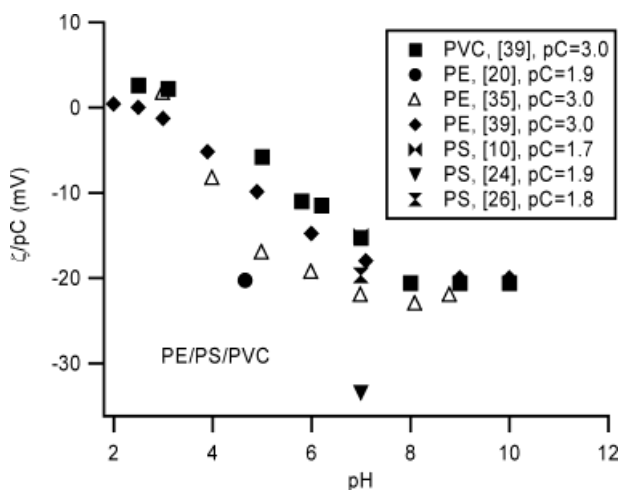
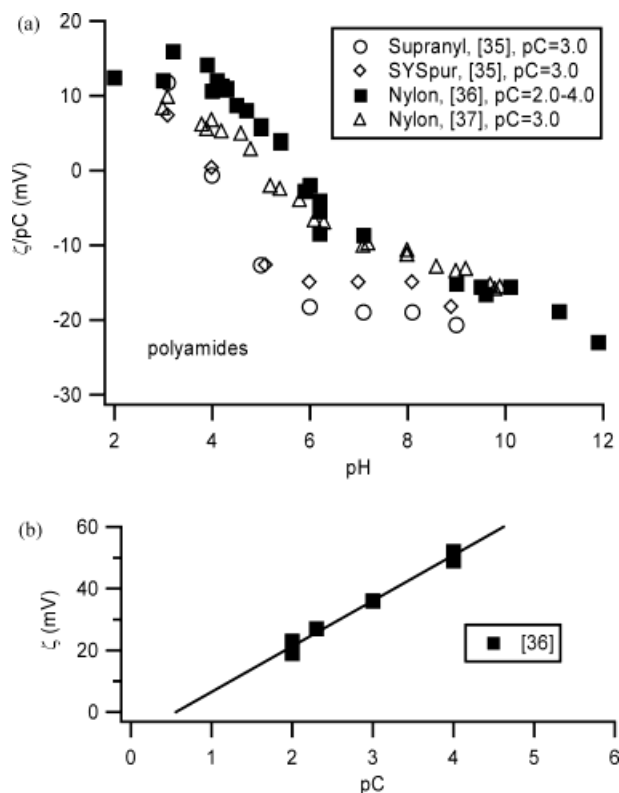


Figure 5.  $\zeta/pC$  vs. pH for PE/PS/PVC.

#### 4.6 Polyamides: nylon (PA), Kapton (polyimide), and polyurethane

Polyamide films and film adhesives are available and have been used for sealing microchannels [35], and polyimide tubing is available and commonly used. Figure 6a shows





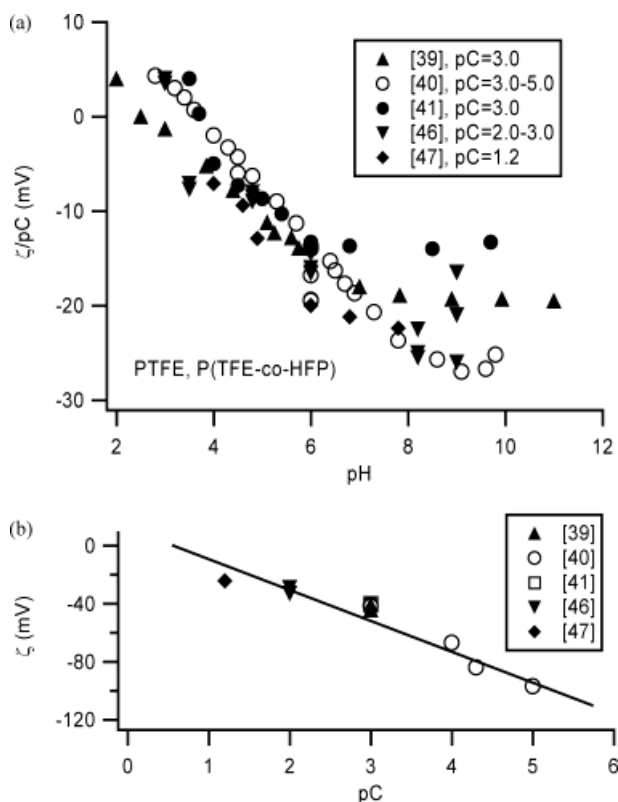
**Figure 6.** (a)  $\zeta/pC$  vs. pH for polyamides. (b)  $\zeta$  vs. pC for nylon ( $4 < \text{pH} < 4.5$ ).

$\zeta$  measurements on several different polyamide substrates. As compared to silica, and polymers such as PDMS, PE, PS, polycarbonate, and PVC, the polyamides that have been studied (nylon (PA) and polyurethane (PU)) show a higher  $pI$  ranging from pH 4–6 and significant positive charge at low pH. Higher  $pI$  and formulation-specific  $pI$  are both to be expected due to the presence of amine functionalities at varying concentration and of varying  $pK_a$ . One of the sources [36] measured  $\zeta$  of nylon colloids and one [37] measured  $\zeta$  of nylon grains. Both are included here (despite earlier comments that colloidal and porous measurements were to be avoided), in part because the errors attendant with porous and colloidal measurements typically do not affect measurement of the  $pI$ .

Figure 6b shows selected  $\zeta$  measurements from [36] as a function of pC for  $4 < \text{pH} < 4.5$  along with the best-fit line ( $a_0 = -7.61$  mV,  $a_1 = 14.55$  mV). The coefficient of determination of the linear fit is 0.98. The values provided by the best-fit line and a best-fit line that is forced to go through the origin ( $a_0 = 0$  mV,  $a_1 = 12.12$  mV) differ by less than 12.9% over the region studied. The best-fit line through the origin leads to RMS errors of 11.9% for this data.

#### 4.7 Polyfluorocarbons: poly(tetrafluoroethylene)

Poly(tetrafluoroethylene) (PTFE, Teflon) is available as capillary tubing, can be micromachined, and has also been used in sputter targets for deposition into microfluidic systems [38, 39]. PTFE has also been plasma-deposited on surfaces [40]. Teflon surfaces have been modified by  $O_2$  or  $NH_3$  plasma treatment and use of polyelectrolyte multilayers [41]. Figure 7a shows  $\zeta$  measurements on PTFE substrates. Quite good agreement is observed at moderate pH ( $4 < \text{pH} < 6$ ), although significant variation is present at high pH. Normalization by pC collapses the data rather well. Figure 7b shows  $\zeta$  measurements vs. pC for PTFE for  $5.5 < \text{pH} < 6$  along with the best-fit line ( $a_0 = 11.98$  mV,  $a_1 = -20.12$  mV). The coefficient of determination of the linear fit is 0.89, consistent with the observation that the data shows clear curvature. The values provided by the best fit line and a best-fit line that is forced to go through the origin ( $a_0 = 0$  mV,  $a_1 = 12.12$  mV) differ by less than 17.4% for pC  $> 2$ , but differ greatly at higher concentration – as much as 50% at 50 mM. The best-fit line through the origin leads to RMS errors of 16.6% for this data. Whether the curvature and resulting errors are real



**Figure 7.** (a)  $\zeta/pC$  vs. pH for perfluoropolymers. (b)  $\zeta$  vs. pC for PTFE ( $5.5 < \text{pH} < 6$ ). [40, 41] used plasma-deposited or treated PTFE; others used PTFE or P(TFE-co-HFP) capillaries (HFP, heafluoropropylene).

effects or just error exacerbated by the plotting of results from five separate experiments is unclear. The curvature in Fig. 7b is consistent with the functional form obtained if the large  $\zeta$  limit is not employed and the hyperbolic sine relation in Eq. (2) is used; however, the curvature occurs at  $\zeta$  values similar to those in silica and polymers at which no curvature is detected. Clearly this issue must be resolved by additional measurements at a wide variety of counterion concentrations.

## 5 Conclusions

The preceding sections have proposed the use of the negative logarithm of the counterion concentration (pC) to normalize  $\zeta$ , allowing results of experiments with widely varying solutions to be compared. Using this normalization, the reported data pertaining to the  $\zeta$  of polymer microfluidic substrates has been summarized. While the available data is too limited to draw firm and rigorous conclusions, the dependence of observed  $\zeta$  on counterion concentration for polymer substrates is consistent with the relation  $\zeta = a_0 + a_1 \log(c)$ , and for  $\zeta$  measurements relevant to most microfluidic systems the constant term may be neglected. Thus generality is achieved if  $\zeta$  is reported normalized by pC. Errors are likely introduced by this normalization, since  $a_0$  is not identically zero. However, these errors are moderate (typically < 10%, with possible exceptions for Teflon and polycarbonate). The investigator-to-investigator variation and uncertainty due to temperature is larger than these errors. For example, the error in electroosmotic mobility measurements of  $\zeta$  due to unrecorded heating is ~3% per °C; few electroosmotic mobility measurements would claim less than 5–10°C of heating. Directed measurements of the dependence of zeta potential with concentration on polymer substrates are required to support these conclusions and more clearly define their region of applicability.

The repeatability of the data is quite encouraging, and clear  $\zeta$ /pC vs. pH trends are observed for most of the polymers. With the exception of polyamides, which contain variable amine functionalities, and PMMA, for which results are unclear due to extensive discrepancies in the reported data, the polymer surfaces studied show  $\zeta$ /pC vs. pH functional forms quite similar to those observed for silica, perhaps due to the similarities between  $pK_a$  of silanols (silica) and carboxylic acids (polymers). PDMS, polycarbonate, and PET/PETG all show  $\zeta$ /pC roughly equal to –30 or –35 mV at high pH. PTFE, PE, PVC, and PS show roughly –20 to –25 mV. These  $\zeta$ /pC values are well below that of silica, for which typical  $\zeta$ /pC values are near –50 mV at high pH; however, these values are large enough to enable electrokinetic manipulation of fluids on

microchips, and polymer substrates will clearly continue to have increasing importance for microchip-based analysis.

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