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Electrostatically-Driven Collapse of Polyelectrolytes:
The Role of the Solvent's Dielectric ConstantAnish Gulati¹  | Lingzi Meng²  | Takaichi Watanabe³  | Carlos G. Lopez² ¹Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany | ²Materials Science and Engineering Department, The Pennsylvania State University, State College, Pennsylvania, USA | ³Department of Applied Chemistry, Graduate School of Environmental, Life, Natural Science, and Technology, Okayama University, Okayama, Japan**Correspondence:** Carlos G. Lopez (cvg5719@psu.edu)**Received:** 21 May 2025 | **Revised:** 20 June 2025 | **Accepted:** 24 June 2025**Funding:** This work was supported by the Japan Society for the Promotion of Science (JP24K01236, JP20KK0325) and the Deutsche Forschungsgemeinschaft (GO 3250/2-1).**Keywords:** counterion | dipole | polyelectrolyte | SANS | SAXS | scattering

ABSTRACT

We experimentally confirm a longstanding theoretical prediction of counterion-induced polyelectrolyte collapse in low dielectric media. The scattering behavior of polystyrene sulfonate in different solvents with dielectric permittivities in the range of $\epsilon \simeq 12 - 180$ is investigated. For high and intermediate ϵ media, typical polyelectrolyte behavior is observed: the correlation length (ξ) scales with concentration (c) as $\xi \sim c^{-1/2}$, as predicted by various theories. When the dielectric constant of the solvent decreases below $\simeq 22$, a scaling of $\xi \sim c^{-1/3}$, characteristic of partially collapsed polyelectrolytes, is observed. For these solvents, the correlation peak disappears at high concentrations. Interestingly, polyelectrolyte collapse is observed under both solvophilic and solvophobic conditions, supporting the existence of attractive electrostatic interactions. These results are in qualitative agreement with theoretical predictions which expect chain collapse in low dielectric media due to the influence of condensed counterions, either via dipolar attraction and/or charge-correlation-induced attractions.

1 | Introduction

The dilute solution behavior of non-ionic polymers can be described in terms of two length scales: the Kuhn segment, which is a measure of backbone rigidity, and the thermal blob, which quantifies the excluded volume strength. For non-dilute solutions, an additional length scale, the correlation length, is necessary to describe excluded volume and hydrodynamic screening. The length of a Kuhn segment is usually a property of the polymer and not of the solvent [1, 2] and the thermal blob size depends on the solvent quality.

In the case of ion-containing polymers, the number of relevant lengthscales and experimental variables increases [3–10]. For example, the solvent quality cannot be quantified in terms of a

single parameter like the thermal blob size: instead, the interactions of the solvent with the backbone and counterions must be considered [11–13]. Additionally, the dielectric constant or solvent permittivity, which modulates electrostatic interactions in solution also plays an important role. Experimental studies on the influence of the solvent permittivity on the properties of polyelectrolyte solutions are sparse [10, 14–22], with most of the literature focusing on aqueous solutions [23–30] with fixed relative permittivity of $\epsilon_r \simeq 78$ or mixtures of water and organic solvents, which vary the relative permittivity to a limited degree [31–35].

Within the Debye-Huckel approximation, the potential between two charges separated by a distance r can be written as:

$$U(r) = \frac{l_B}{r} e^{-\kappa r}$$

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where l_B and κ are the Bjerrum length and inverse Debye-Huckel screening length, respectively.

The Bjerrum length is the distance at which the non-screened electrostatic energy between two monovalent charges is the same as the thermal energy:

$$l_B = \frac{e^2}{4\pi k_B T \epsilon_0 \epsilon_r}$$

where ϵ_0 is the vacuum permittivity, e the electrostatic unit of charge, k_B is the Boltzmann constant, and T the absolute temperature.

Counterions are entropically driven to dissociate from the backbone and explore the solution volume. This is opposed by the electrostatic attraction exerted by the oppositely charged groups along the polymer backbone. When the charge density of the backbone exceeds $\simeq e/l_B$, counterions adsorb or “condense” onto the backbone, becoming osmotically inactive and lowering the effective charge of the backbone [36–39]. This phenomenon is known as Oosawa-Manning condensation and has been observed for many highly charged polyelectrolytes in semidilute solutions [10, 37, 40, 41].

1.1 | Structure of Polyelectrolyte Solutions

Polyelectrolytes dissolved in salt-free solvent far below the overlap concentration (c^*) are strongly stretched by electrostatics, and their conformation is rod-like [10, 42]. As the concentration increases, the chain dimensions decrease and by the point where the overlap concentration is reached, their dimensions are significantly shrunken relative to the infinite dilution limit [10, 43]. Beyond the overlap concentration, interactions on lengthscales larger than the correlation length (ξ) are screened, but the polymer remains highly stretched (dilute-like) on distances smaller than ξ [44]. The correlation length decreases with concentration as $\xi \sim c^{-1/2}$ and electrostatic interactions become progressively screened as the concentration increases. Experimental studies on counterion condensation generally reveal that the fraction of free counterions is approximately independent of polymer concentration [32, 45–48]. This general picture, which applies to many polyelectrolyte/solvent systems, including highly sulfonated NaPSS [49] in water has been described extensively in earlier literature [25, 32, 50–56], see [4, 5, 10] and references therein for details.

Solvophobic polyelectrolytes are those for which the net non-electrostatic excluded volume of the backbone in a given solvent is negative. The balance of long-range repulsive interactions between like-charged dissociated groups and short-ranged attractive solvophobic forces between monomers dictates whether a polyelectrolyte chain exists in an extended, semi-collapsed or fully collapsed state [57–60]. In brief, when electrostatic repulsion dominates, the chains adopt extended conformations as described in the preceding paragraph. As the solvophobic forces become more dominant, the chain collapses into a “pearl-necklace” structure, where highly collapsed sections of the chains (beads or pearls) co-exist with

strongly stretched sections (strings). Partially collapsed chains are predicted to exhibit a different type of counterion condensation, where the fraction of free counterions decreases with polymer concentration, thereby leading to a progressive reduction of the effective charge of the backbone, which weakens of electrostatic repulsion between like-charged dissociated groups and further promotes the collapse of the chains [57]. Osmotic pressure data for solutions of partially sulfonated polystyrene sulfonate does not give evidence of this feature [61]. The primary structural features of hydrophobic polyelectrolyte collapse into pearl-necklace configurations were verified experimentally by Boue and co-workers for NaPSS in water [62–67].

The role of condensed counterions is often assumed to be only that of partially neutralizing the charge of the polyelectrolyte backbone. This appears to be a reasonable approximation in solvent media with high dielectric permittivity, where the fraction of condensed counterions is low and electrostatic interactions are weak. Schiessel and Pincus [68, 69] predicted that ionic groups with condensed counterions behave as dipoles, which attract each other with a strength proportional to l_B^2 . When the solvent's dielectric constant is sufficiently low, the attractive forces between condensed counterions become stronger and result in an electrostatically-induced chain collapse, a phenomenon which was later observed by Chertvy in a simulation [70]. Dobrynin and co-workers [71] on the other hand argued on the basis of simulation data that condensed counterions are too mobile to form permanent dipoles and instead consider charge correlations responsible for counterion-induced attraction. The effect of charge correlations was calculated in their model by using the Debye-Huckel theory for the weak interaction case and from an analogy to the Wigner crystal for the strongly interacting case. While different in the physical mechanism of chain collapse, the models of Schiessel and Pincus and Dobrynin et al. lead to qualitatively similar predictions. The model of Muthukumar considers both effects [72]. Experimental validation of the above theoretical and simulation results is lacking. This is probably because of the limited solubility of common polyelectrolytes such as NaPSS, NaPA or NaCMC in organic solvents. Large organic counterions are known to promote solubility in organic media [22, 73, 74]. Here we use the tetrabutylammonium (TBA^+) salt of polystyrene sulfonate which is soluble in polar, protic liquids.

In this article, we study the scattering properties of non-dilute polystyrene sulfonate with tetrabutyl-ammonium counterions (TBAPSS) in solvents of varying dielectric constant, covering a relatively broad range of relative permittivities between $\epsilon_r \simeq 12$ for pyridine to $\epsilon_r \simeq 180$ for N-methyl-formamide and N-methyl-acetamide. For solvents with high and intermediate dielectric constants ($\epsilon_r \gtrsim 28$), typical polyelectrolyte behavior is observed and the results are similar to earlier studies [25, 48, 75]. For lower dielectric constant solvents, chain collapse is observed, which could be attributed to either the solvophobic nature of the backbone and/or to counterion-induced attraction. Solutions in pyridine ($\epsilon_r \simeq 12$) are particularly interesting because chain collapse is observed but backbone solvophobicity is unlikely to be the origin of the attractive forces needed for chain collapse, because pyridine is a solvent for polystyrene.

2 | Results and Discussion

All the samples measured are above the overlap concentration (c^*). The overlap concentration was determined for TBAPSS in nine of the solvents used here in earlier studies. For DMF and 1-propanol solutions, we estimated c^* based on a plot of c^* vs. the solvent dielectric constant [76, 77]. SAXS measurements for solutions in ethylene glycol and propylene glycol gave a flat signal, presumably due to the lack of sufficient contrast. Measurements in 1,3-butanediol were not of sufficient quality to reliably extract the peak position, these are included in the [Supporting Information](#) but not discussed here.

We divide our discussion of the data between “high” dielectric constant solvents, corresponding to those with $\epsilon_r \gtrsim 24$ and those with “low” dielectric constant ($\epsilon_r \lesssim 22$). The criterion for this classification is discussed in more detail below. In brief, in the low dielectric constant solvents, we observe scattering behavior which is characteristic of partially or fully collapsed polyelectrolytes ($\xi \sim c^{-1/3}$, peak disappears at high concentrations). In the high dielectric constant solvents, on the other hand, the scattering properties of TBAPSS resembles those

of non-collapsed polyelectrolytes ($\xi \sim c^{-1/2}$, peak is observed over the entire concentration range). The dielectric constant of polyelectrolyte solutions usually decreases with increasing polymer content, but lacking such data for the systems studied, we use the dielectric constant of the pure solvents throughout this study.

2.1 | High Dielectric Constant Solvents

Figure 1a–d shows representative SANS profiles of TBAPSS in several high dielectric constant solvents at different concentrations. All solutions display a peak in their scattering function. The wave-vector at the peak (q^*) is obtained by fitting a polynomial around the local maxima. This involves a subjective choice of the q -region to be fitted. Fits by two authors yielded nearly identical results, see the [Supporting Information](#) for details. The intensity at the maxima increases with increasing concentration until $c \approx 0.2 - 0.3$ M and then decreases, see the [Supporting Information](#). The specific concentration at which this cross-over occurs depends weakly on the solvent and we do not observe any clear correlation with the dielectric constant.

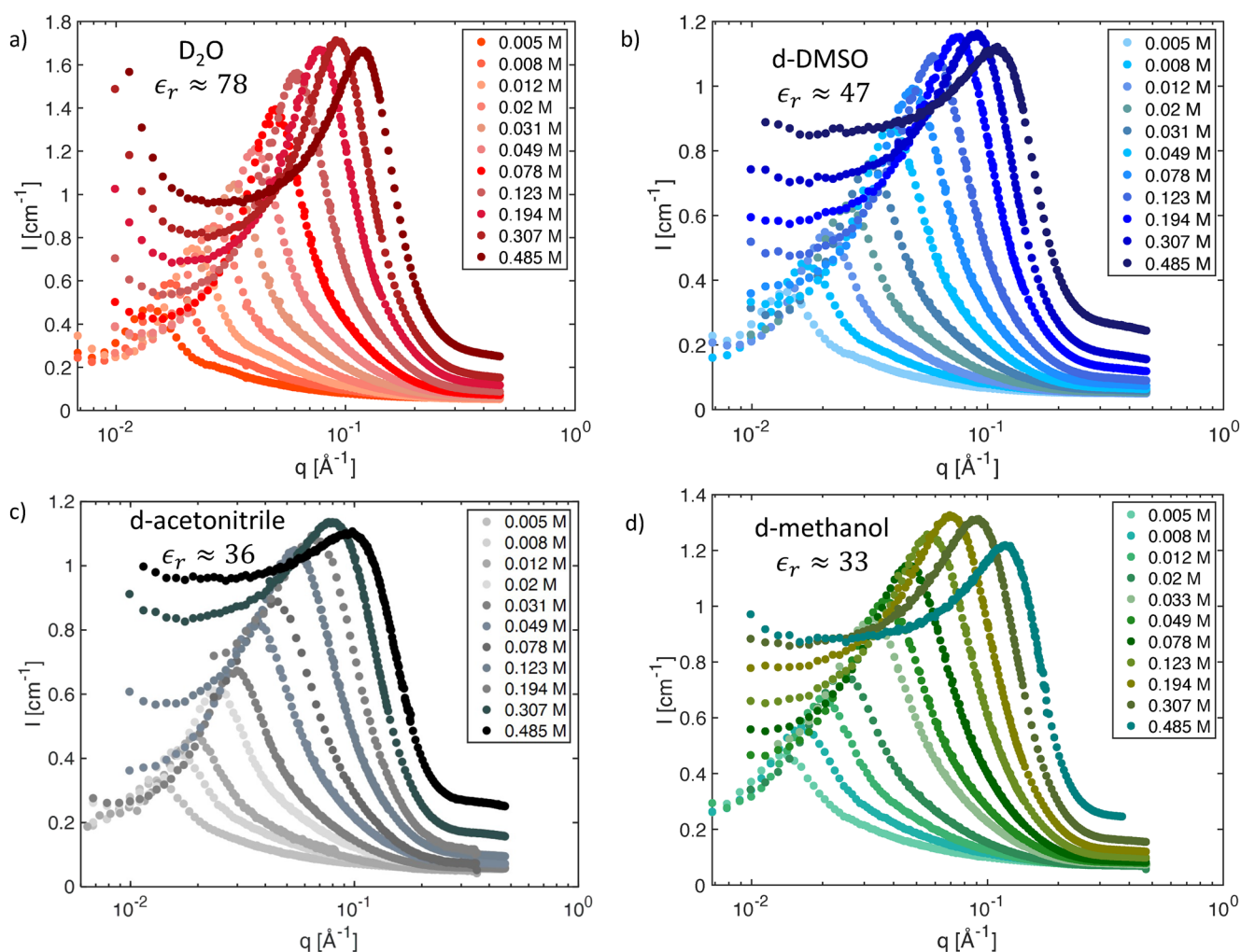


FIGURE 1 | SANS profiles for TBAPSS in different solvents: D₂O, d-DMSO, d-Acetonitrile, d-Methanol. Concentrations are indicated on the legend. Note that the peak intensity decreases with concentration beyond some critical concentration, the value of which is approximately the same for all solvents, see the [Supporting Information](#).

The correlation length is calculated as: [55, 78–80].

$$\xi \approx \frac{2\pi}{q^*} \quad (1)$$

The concentration dependence of the correlation length is plotted in Figure 2. For SAXS measurements, the scaling for all solvents is close to the $\xi \propto c^{-1/2}$ prediction of Dobrynin et al.'s scaling model, shown by the full line [81]. For SANS measurements, where the contrast is strongly dominated by the counterions, a slightly weaker dependence of ξ on c is observed. This is consistent with the behavior reported in earlier studies for TBACMC and TMAPSS in water [82–84].

The scaling theory predicts for the correlation length: [81, 85].

$$\xi = \left(\frac{B}{bc} \right)^{1/2} \quad (2)$$

where b is the monomer size, taken to be 0.25 nm for PSS [86] and B is the stretching parameter. $B = 1$ corresponds to chains

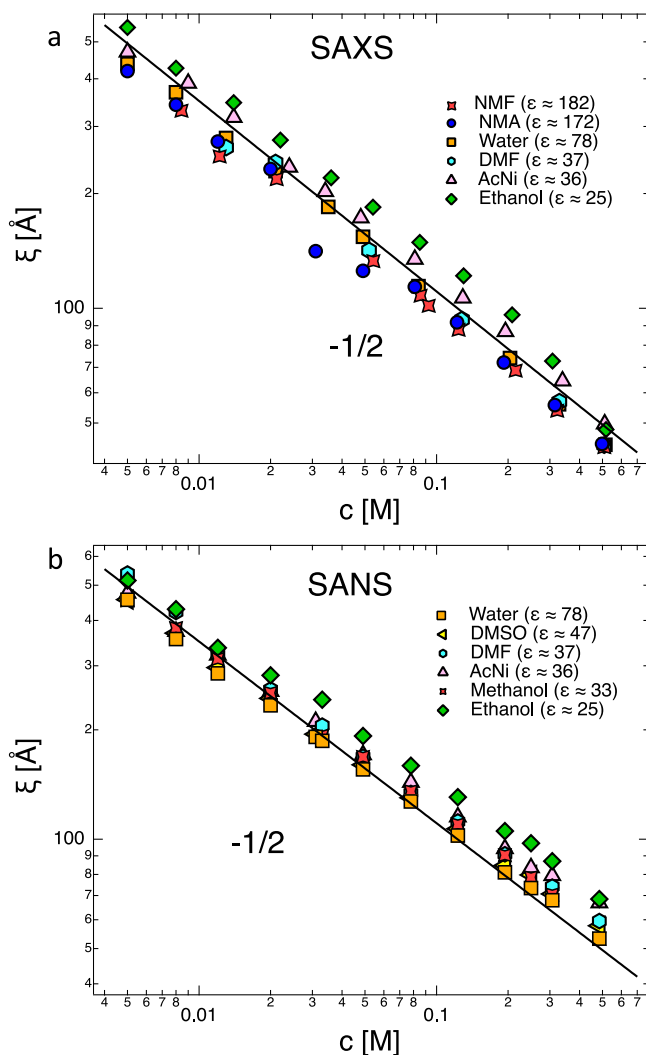


FIGURE 2 | Correlation length calculated from the position of the local maxima and Equation (1) for TBAPSS in different solvents. Top and bottom panels are for maxima obtained from SAXS and SANS spectra, respectively.

which are fully stretched inside the correlation blob and $B > 1$ corresponds to local folding inside the correlation blob [10, 81]. For reference, NaPSS in water displays $B \approx 1.5 - 1.8$ [48, 50, 75, 80, 87, 88].

According to the scaling model, each correlation blob is made up of several electrostatic blobs of size ξ_{el} . The electrostatic blob size is the lengthscale at which the electrostatic energy of a chain segment is equal to $k_B T$. On distances smaller than ξ_{el} , electrostatics do not perturb the chain and the polyelectrolyte adopts a neutral-like conformation: it is rigid on distances smaller than Kuhn length, Gaussian on distances larger than the Kuhn segment but smaller than the thermal blob size, and follows collapsed, ideal or excluded volume statistics on distances larger than the thermal blob size (ξ_T) but smaller than ξ_{el} . On distances larger than ξ_{el} and smaller than ξ , the chain is a stretched pole of electrostatic blobs [10, 81]. The dependence of the stretching parameter, which is the ratio of the contour length of g_{el} monomers making up the correlation blob and its end-to-end distance is:

$$B = \frac{bg_{el}}{\xi_{el}} \propto \begin{cases} l_B^{-2/3} f^{-4/3} & T \ll \theta \text{ (poor solvent)} \\ l_B^{-1/3} f^{-2/3} & T = \theta \text{ (theta solvent)} \\ \xi_T^{1/7} l_B^{-2/7} f^{-4/7} & T > \theta \text{ (good solvent)} \end{cases} \quad (3a)$$

$$B = \frac{bg_{el}}{\xi_{el}} \propto \begin{cases} l_B^{-2/3} f^{-4/3} & T \ll \theta \text{ (poor solvent)} \\ l_B^{-1/3} f^{-2/3} & T = \theta \text{ (theta solvent)} \\ \xi_T^{1/7} l_B^{-2/7} f^{-4/7} & T > \theta \text{ (good solvent)} \end{cases} \quad (3b)$$

$$B = \frac{bg_{el}}{\xi_{el}} \propto \begin{cases} l_B^{-2/3} f^{-4/3} & T \ll \theta \text{ (poor solvent)} \\ l_B^{-1/3} f^{-2/3} & T = \theta \text{ (theta solvent)} \\ \xi_T^{1/7} l_B^{-2/7} f^{-4/7} & T > \theta \text{ (good solvent)} \end{cases} \quad (3c)$$

where f is the fraction of monomers bearing a charge, which for polyelectrolytes with one ionic group per monomer is the fraction of dissociated counterions.

In deriving Equation (3) it is assumed that the electrostatic blob size is larger than the bare Kuhn segment of the polyelectrolyte ($l_K \approx 2$ nm for polystyrene sulfonate [10]). The scaling theory calculates ξ_{el} as the lengthscale where the Coulomb interactions are equal to the thermal energy ($k_B T$). When there is more than one dissociated charge per Kuhn segment, this should correspond to the Bjerrum length of the solvent. Since the Manning theory expects one charge per Bjerrum length, the scaling theory predicts that for PSS, when $l_B \lesssim 2$ nm, $\xi_{el} \lesssim l_K$. Under this condition, $B \sim \epsilon_r^0$ is expected [89]. When $l_B \gtrsim 2$ nm, Equation (3b) applies and $B \sim \epsilon_r^{-1/3}$ assuming θ solvent conditions.

Two qualifications to the argument above are needed: first, experimental measurements of the effective charge density of polyelectrolytes in semidilute solution typically yield values somewhat lower than the Manning condensation threshold, often corresponding to ≈ 1 charge per $1.5 l_B$ [46, 47, 90]. Second, intrinsic viscosity data of polyelectrolytes with varying charge density suggest that the electrostatic blob size may be an order of magnitude larger than that predicted by the scaling theory [10]. This is consistent with the analysis of viscosity data for NaPSS in water by Dobrynin and co-workers, who concluded that the electrostatic blob has a Coulomb energy of $\approx 9 k_B T$ [91].

In summary, we expect:

$$B \sim \begin{cases} \epsilon_r^0 & l_B < Al_K \\ \epsilon_r^{-1/3} & l_B > Al_K \end{cases} \quad (4a)$$

$$B \sim \begin{cases} \epsilon_r^0 & l_B < Al_K \\ \epsilon_r^{-1/3} & l_B > Al_K \end{cases} \quad (4b)$$

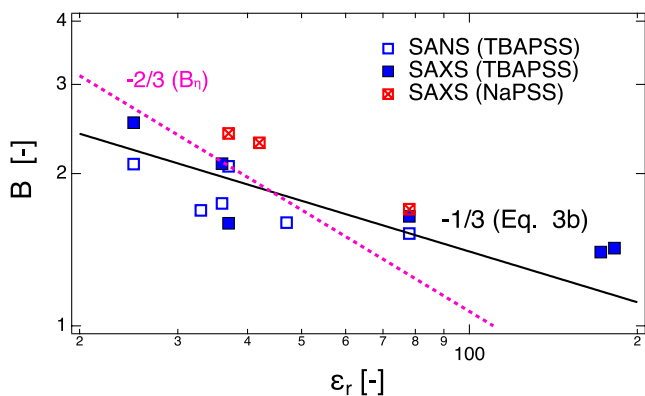


FIGURE 3 | Stretching parameter of TBAPSS as a function of relative permittivity of the solvent. Black line is power law with exponent of $-1/3$, corresponding to Equation (3b) for θ solvent conditions and $f \propto l_B^{-1}$ (Manning-Oosawa condensation). Purple line is the scaling of the stretching parameter obtained from viscosity measurements (B_η), see ref. [76]. Red symbols are data from [21] for NaPSS in water, ethylene glycol and glycerol.

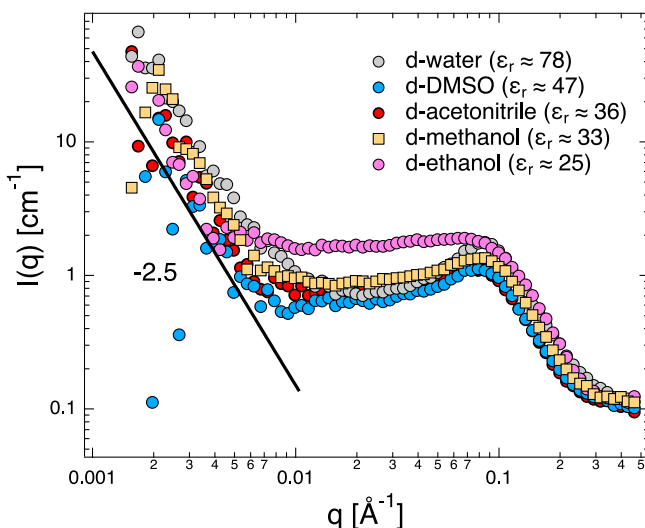


FIGURE 4 | SANS profiles for TBAPSS solutions with $c = 0.25$ M in five solvents, indicated in the legend. Line is power law with exponent of -2.5 .

where A is a constant. The scaling model uses $A = 1$ but experiments suggest that its value is somewhat lower.

We calculate B for each solvent by fitting Equation (2) to the entire concentration range for the SAXS data and for $c \lesssim 0.012$ M for the SANS data. The results are plotted as a function of the relative permittivity of the solvent in Figure 3. The stretching parameter obtained for TBAPSS in water is very similar to that of NaPSS reported in earlier studies [50, 75, 80, 87, 88]. The values of B measured by Han and Colby for NaPSS in glycerol ($\epsilon_r \approx 42$) and ethylene glycol ($\epsilon_r \approx 37$) are also included for comparison. The experimental values of B are compared with Equation (3b), shown by the full line, assuming Manning condensation ($f \propto 1/l_B$). The data display considerable scatter, presumably because the stretching parameter depends on the solvent quality, which does not correlate with its dielectric constant.

The weak dependence of the stretching parameter on solvent dielectric constant observed in Figure 3 contrasts with the scaling of the overlap concentration ($c^* \propto \epsilon_r^{-2}$) reported in two earlier studies [10, 76]. Since $c^* \propto B^3$ viscosity data imply $B \sim \epsilon_r^{-2/3}$, as indicated by the dashed purple line. This relationship does not agree with the scattering data.

A major limitation of the analysis presented above is that we assume that the dielectric constant of the solvent in the solution is the same as that of the pure solvent. It is possible that near the polymer backbone and/or near the counterions, the local solvent permittivity is significantly decreased due to increased solvent ordering. This point has been noted in earlier theoretical and simulation work [72, 92–94] and may be important for a full description of polyelectrolyte solution behavior, but we do not have a way of experimentally measuring the dielectric constant near the backbone.

The scattering intensity at the peak position increases linearly with the square root of the polymer concentration up to $c \approx 0.2$ M, beyond which the trend flattens and then reverses; see Figure S1. Nishida et al. for observed a similar trend for NaPSS in DI water but the concentration at which the cross-over occurred was significantly higher (≈ 1 M).

One of the most puzzling aspects of polyelectrolyte scattering is the presence of an upturn in the low- q region [95]. Such behavior is not expected because of the large energetic cost of long-ranged concentration fluctuations in charged systems [10]. Figure 4 compares the scattering intensity of TBAPSS solutions with $c = 0.25$ M in five high dielectric constant solvents. An upturn is observed for all samples. The power-law exponent is ≈ 2.5 for all samples, which is similar to values reported for other polyelectrolyte systems [55, 84, 96, 97]. No clear trend between the intensity of the upturn and the solvent properties is apparent.

2.2 | Low Dielectric Constant Solvents

Figure 5 plots the SANS and SAXS intensities of TBAPSS solutions in 1-butanol and pyridine. At low concentrations, the samples display a correlation peak. For $q > q^*$, the scattering intensity follows a power law of $I(q) \propto q^{-1.3}$, indicated by the black line on Figure 5a,b. A similar exponent is observed for the scattering profiles at higher concentrations except for samples displaying a shoulder, where the power-law exponent increases drastically, see below. The position of this peak is approximately the same in the SANS and SAXS spectra (see Figure 6). As the concentration increases beyond ≈ 0.04 M for pyridine and ≈ 0.08 M for 1-butanol, the correlation peak disappears and the curves instead display a broad shoulder feature. This behavior was also observed for isopropanol and acetone (data in Supporting Information). In 1-propanol solutions, the highest concentration studied was 0.12 M and a clear peak was observed. At the highest concentration measured for 1-butanol and pyridine (≈ 0.5 M), a peak reappears in the SAXS signal, but not in the SANS one, indicating a de-coupling of the concentration fluctuations of counterions and polymer backbone [84, 99], the SANS signal being dominated by the hydrogen-rich counterions. A similar but less drastic decoupling was

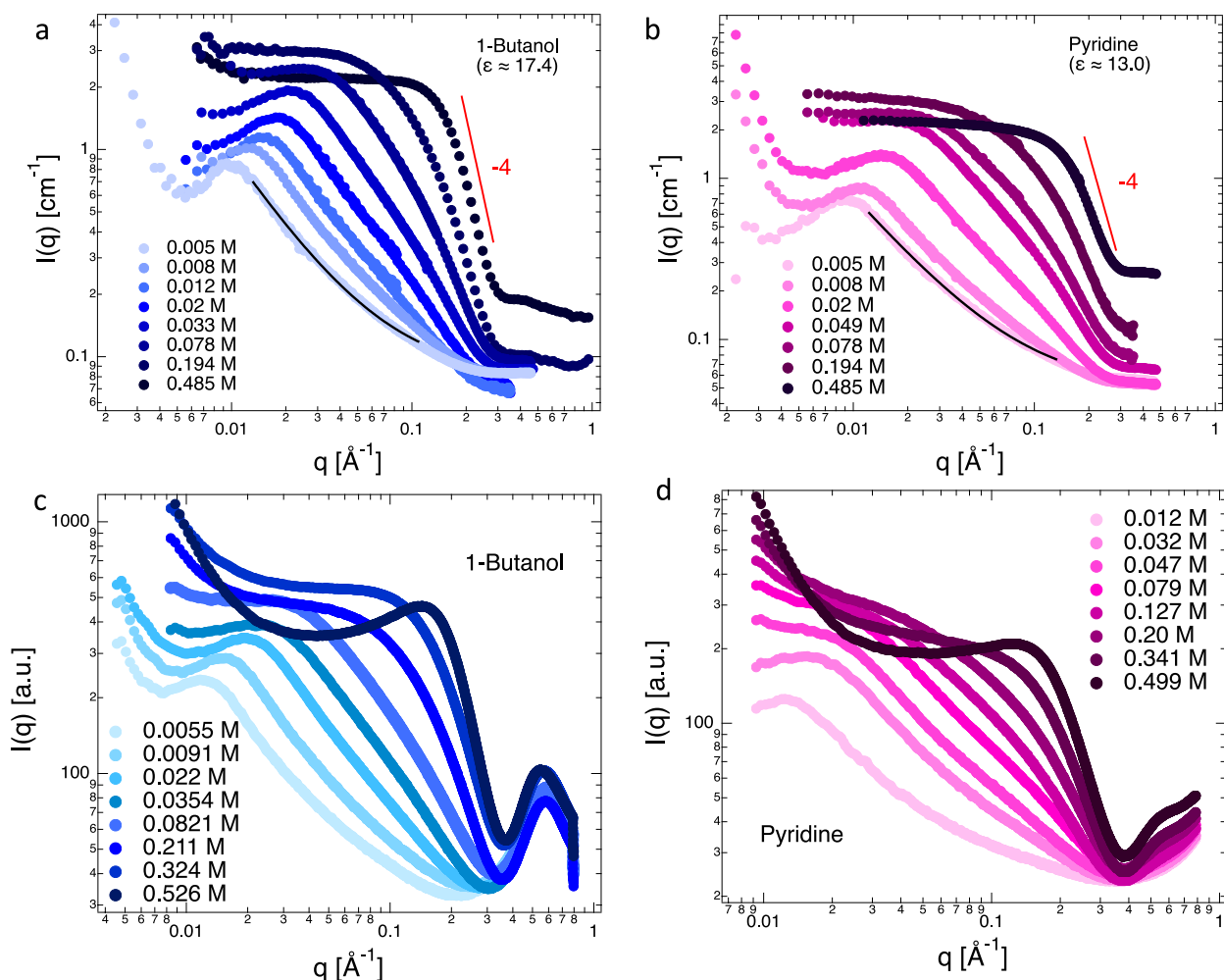


FIGURE 5 | (a, b) SANS curves for selected concentrations of TBAPSS in deuterated 1-butanol and deuterated pyridine. (c, d) SAXS curves for selected concentrations of TBAPSS in 1-butanol and pyridine. The high q peak observed in panel c arises from the 1-butanol. Red lines indicate power-law of -4 . Black lines on the top panels are best-fit to a power law with a background (q -independent) term. In both cases, the best-fit exponent is ≈ -1.3 .

observed for solutions of the tetra-alkyl-ammonium salts of carboxymethyl cellulose in water [84].

2.2.1 | The Bead Controlled Regime

Neglecting the influence of charge correlation interactions, the Dobrynin-Rubinstein model predicts the correlation length in the bead controlled regime (i.e., one bead per correlation blob) to scale as:

$$\xi \propto (1 - \bar{c})^{-2/3} \bar{c}^{-1/3} \quad (5)$$

where the constant of proportionality depends on the Kuhn segment, the fraction of charged monomers and the Bjerrum length of the solvent. $\bar{c}$ is the polymer concentration relative to that of a bead (c_{bead}). If the fraction of free counterions is concentration-independent, the mass per bead is also independent of concentration and $\xi \propto c^{-1/3}$. The term in brackets in Equation (5) accounts for the increase in counterion condensation with increasing c , which makes the beads grow in size and mass as the polymer concentration increases. Equation (5)

expects the $\xi - c$ scaling law to flatten and ξ to reach a minimum for $\bar{c} \approx 1/3$.

In the bead-controlled regime, the peak in the scattering function corresponds to the inter-bead distance and the correlation length can be calculated using Equation (1). The results for TBAPSS in acetone, 1-butanol, isopropanol and pyridine are plotted in Figure 6 and found to be compatible with Equation (5). At low concentrations, the data are consistent with a scaling of $\xi \propto c^{-1/3}$, though we cannot rule out the existence of a cross-over between $\xi \propto c^{-1/2}$ and $\xi \propto c^{-1/3}$ power-laws due to the limited concentration range studied. The correlation length reaches a minimum at a value of ≈ 40 nm for pyridine and ≈ 30 nm for isopropanol.

2.2.2 | Properties of Beads

The number of monomers per bead (g_B) in the bead-controlled regime is:

$$g_B = \xi^3 c \quad (6)$$

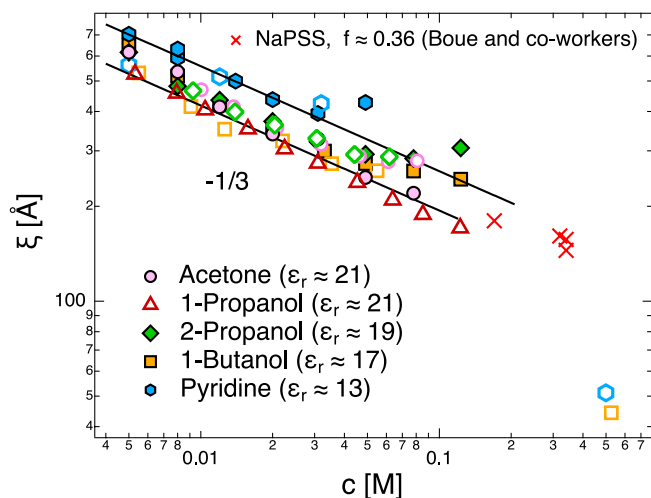


FIGURE 6 | Correlation length of TBAPSS in low dielectric constant solvents. Filled symbols are for SANS measurements and hollow symbols are for SAXS measurements. In both cases, the correlation length is calculated from the peak position. Lines are power-laws with exponents of $-1/3$. Note that there is a concentration range where the samples do not display a peak. Red crosses are results by Boue and co-workers for 36%–38% sulfonated NaPSS in water [62, 65, 98].

Equation (6) is expected to hold as long as there is one bead per correlation blob and the majority of the chains' mass is located in the beads, i.e., $g_B \approx g$, where g is the polymer mass per correlation blob. The top and bottom power-laws on Figure 6 correspond to $g_B \approx 1000$ and $g_B \approx 500$, respectively. These large values signal that the $g_B \approx g$ approximation may not hold. Similarly large values are obtained when comparing Equation (6) with Spiteri et al.'s data, for partially sulfonated NaPSS in water, shown as red crosses in Figure 6. Such values are incompatible with the small (≈ 2.5 nm [65]) radius of the pearls obtained by fitting the form factor of the chains: If the NaPSS pearls are assumed to contain no solvent ($\phi_{bead} = 1$), an upper limit of $g_B \approx 330$ is obtained.

If we assume that the minimum in the $\xi - c$ plots corresponds to $\bar{c} = 1/3$ as expected by Equation (5), we can estimate the concentration inside the beads as $c_{bead} \approx 0.12$ M for pyridine and $c_{bead} \approx 0.24$ M for isopropanol. These concentrations correspond to volume fractions of $\phi_{bead} = 0.034$ and $\phi_{bead} = 0.092$, respectively. The radius of the beads may then be estimated as ≈ 15 nm for pyridine and ≈ 9 nm for isopropanol. These values are almost an order of magnitude larger than those calculated by Spiteri et al. [65] for partially sulfonated NaPSS in water by analyzing the form factor of the chains, and therefore are judged to be incorrect.

2.2.3 | The Transition to the Bead Overlap Regime

The Dobrynin-Rubinstein model does not make a prediction for $1/3 \lesssim \bar{c} \lesssim 1$, which covers the transition between the bead-controlled semidilute and the bead-overlap concentrated regimes. Our data show that TBAPSS does not exhibit a correlation peak in this transition regime and instead the scattering

profiles display a broad shoulder feature. The disappearance of the correlation peak upon increasing the polymer or added salt concentration has been reported in earlier studies for non-collapsed polyelectrolytes [75, 84, 100–102], and these show a dependence of $I(q) \propto q^{-1}$ in the high- q region of the shoulder. Here, by contrast, the low- q plateau is followed by a strong decay in the scattering intensity: for example, the pyridine and 1-butanol samples at the highest concentrations measured display a power-law of $I(q) \sim q^{-4}$, suggesting strongly collapsed structures. The disappearance of the scattering peak at high concentrations matches the behavior observed by Waigh et al. [16] for a polyionic liquid in poor solvent. This behavior is similar to that observed for partially sulfonated polystyrene in water, see for example ref. [63]. The Dobrynin-Rubinstein model expects the scattering function to not display a peak if the volume fraction exceeds the fraction of free counterions ($\phi \gtrsim f$). In our case this would require $f \approx 0.02 - 0.03$ for pyridine and $f \approx 0.03 - 0.045$ for acetone, 1-butanol and isopropanol. These values are similar to those observed for aqueous solutions of NaPSS with a degree of sulfonation of 36% [61].

For $\bar{c} \gtrsim 1$, beads overlap and the solution is in the concentrated regime. Here, the model expects the appearance of a second peak. This second peak arises due to correlations between polymer chains and is not related to the inter-bead distance. Based on the discussion above we expect $\bar{c} \approx 1$ to correspond to $c \sim 0.12$ M for pyridine and 0.24 M for isopropanol.

For 1-butanol and pyridine solutions, we observe a re-appearance of the peak at around $c \approx 0.5$ M in the SAXS scattering function. This matches the behavior observed by Waigh et al. [16] for a poly(ionic liquid) in acetonitrile solution. The origin of this re-appearance is not understood at present. The Dobrynin-Rubinstein model expects a peak at high concentrations but only if $\phi \lesssim f$. In order for our results to be consistent with this, the fraction of free counterions should rise sharply at high concentrations. The decoupling of the SANS and SAXS signals observed for the $c \approx 0.5$ M sample is consistent with this, as it suggests that the counterions and backbone are not tightly correlated. We note that the emergence of a peak in the structure factor at high concentrations for a polyelectrolyte in poor solvent was reported in a simulation study by Chang and Yethiraj [103].

2.2.4 | What Drives Polyelectrolyte Collapse?

The canonical examples of polyelectrolyte collapse in solution are polymethacrylic acid and partially sulfonated polystyrene in water [104, 105]. In both cases, energetically unfavorable polymer-solvent interactions lead to attractive interactions between the polymer segments which drive collapse. These results are consistent with several simulation studies showing solvophobic polyelectrolyte collapse [106–110], though the specific mechanism remains the subject of discussion [111, 112].

The results observed here appear to have a different origin from the two examples mentioned above. Pyridine is a solvent for polystyrene and we expect it to display energetically

favorable interactions with tetrabutylammonium counterions [113]. Ruling out negative excluded volume as the cause of attractive forces, we conclude that the collapse is driven by attractive forces between condensed counterions, as predicted in earlier theoretical work [68, 69, 71, 72, 114]. Our results do not allow us to resolve whether the counterion-induced attraction originates from dipole formation or charge-induced correlations as both become stronger when the dielectric constant of the solvent decreases. The behavior observed here is qualitatively similar to the polyelectrolyte-to-ionomer transition for charged polymers in the bulk state [115, 116], but the systems studied here display additional features due to the presence of solvent molecules.

Several works predict electrostatically driven phase separation of polyelectrolyte solutions in good solvent [117–121]. All the solutions studied here were observed to be homogeneous and optically clear. The scattering data presented also do not show any evidence of phase separation. The reason why we do not observe phase separation is presumably that the concentrations and/or Bjerrum lengths studied are not sufficiently large.

3 | Conclusions

We have presented a comprehensive study of the scattering properties of a flexible polyelectrolyte in solvents of varying dielectric constant. Our results identify two distinct types of behavior: In high dielectric constant solvents, the correlation length scales as $\xi \propto c^{-1/2}$ as observed in many previous studies for solvophilic or weakly solvophobic polyelectrolytes. The dependence of the correlation length on dielectric constant is consistent with the prediction of the scaling model, but the data are too limited to provide a proper experimental test to the electrostatic blob theory.

For solutions in solvents with dielectric constants below $\epsilon_r \approx 24$, the scattering function of TBAPSS displays several features characteristic of polyelectrolytes in poor solvent. Specifically, a correlation length scaling of $\xi \propto c^{-1/3}$, previously reported for partially collapsed NaPSS in water is observed. Beyond a critical concentration the polyelectrolyte peak disappears until eventual re-emergence at high concentrations.

Interestingly, the “solvophobic” behavior is observed in media which are expected to be good solvents for the polystyrene backbone and the TBA⁺ counterions. This suggests that the polyelectrolyte collapse is not driven by unfavorable polymer-solvent interactions and is instead electrostatically-driven. This finding is consistent with theoretical predictions of counterion-induced polyelectrolyte collapse under good solvent conditions. Two mechanisms have been proposed as the source of counterion-induced attraction: dipole–dipole interactions and charge correlations. The experimental results presented here do not reveal which of these mechanisms is dominant.

Analytical treatment of the scattering function of polyelectrolytes remains a challenge and our analysis of the scattering data

is therefore limited. The scattering patterns for all samples are tabulated in the [Supporting Information](#) for further analysis.

4 | Experimental Methods

4.1 | Chemicals

NaPSS was purchased from Polymer Standard Service (Mainz, Germany). Details of the molar mass determination can be found in [91, 122]; the degree of polymerization for each sample is listed in the [Supporting Information](#). The procedure used to prepare and purify the TBAPSS salts is the same as in [76]; the hydrogenated solvents were also the same as in that study. Additionally, hydrogenated 1-propanol, 2-propanol, 1,3-butanediol, ethylene glycol, propylene glycol, and acetone were purchased from FUJIFILM Wako Pure Chemical Corp. Information about the deuterated solvents, purchased from Deutero, is listed in Table 1.

4.2 | SAXS

The SAXS measurements were mostly carried out at the BL40B2 beamline at the SPring-8 synchrotron facility, Hyogo, Japan (proposal numbers 2024A1203 and 2025A1060). Some of the measurements were also conducted using the in-house instrument at DWI—Leibniz-Institut für Interaktive Materialien e.V, Aachen, Germany. The beamline at SPring-8 provided a q -range of 0.023 to 2.0 nm^{−1} and temperature was maintained at 25°C using a Peltier heating unit. The in-house measurements were conducted on the Nano-inXider instrument from Xenocs. This instrument provided an accessible range of 0.011 to 4.4 nm^{−1} for the scattering vector. These measurements were also carried out at room temperature (~23°C). All the samples were measured in quartz capillaries with diameters of 1.5 or 2 mm. These capillaries were procured from either WJM Glass Muller GmbH (Germany) or Hampton Research (US). Upon loading, the samples were sealed using an epoxy glue gun to prevent any evaporation during the

TABLE 1 | Deuterated solvents used for SANS measurements.

Solvent (grade)	Purity [%]
Acetonitrile (d_3)	99
Acetone (d_6)	99
Butanol (d_{10})	99.5
D ₂ O	99.9
DMF (d_7)	99.5
DMSO (d_6)	99.8
Methanol (d_4)	99.8
Ethanol (d_6)	99
Isopropanol (d_8)	99.5
Pyridine (d_5)	99

measurements. Acquisition times were on the order of tens of seconds for synchrotron measurements and a few hours for the in-house instrument.

4.2.1 | Data Reduction

The data were reduced using the standard procedure:

$$I(q) = \frac{I_{\text{sample}}(q)}{t_{\text{sample}} T_{\text{sample}}} - \frac{I_{\text{capillary}}(q)}{t_{\text{sample}} T_{\text{capillary}}} \quad (7)$$

where are I_{sample} and $I_{\text{capillary}}$ are the count rates for the sample and the empty cell, t is the thickness and T the transmission. $I(q)$ is the scattering intensity from the sample after subtraction of the capillary signal in units of counts/(s mm). The I vs. q profiles after reduction with Equation (7) are tabulated in the [Supporting Information](#) for all samples along with the experiment date. Measurements of water capillaries, also after reduction with Equation (7) are also listed. The raw counts for the empty capillary used for each experiment (i.e., $I_{\text{capillary}}$) are also tabulated in the [Supporting Information](#).

4.3 | SANS

The SANS measurements were carried out at D11 at Institut Laue-Langevin (ILL), Grenoble, France, SANS2D and ZOOM instruments at the ISIS neutron and muon source, UK, SANS-1 at Paul Scherrer Institute (PSI), Switzerland and TAIKAN instrument at the J-PARC Center, Tokai, Japan. The measurements at D11 were conducted over a q -range of 0.002 to 0.55 Å⁻¹ using five different sample-to-detector (SDD) distances (1.7, 5.5, 8, 12, and 28 m). For the SANS2D instrument, SDDs of 2.4 and 4 m were used for the front and rear detectors, respectively. This combination, in the time-of-flight mode, provided a q -range of 0.0045 to 1 Å⁻¹. The SDD for the ZOOM instrument was kept at 4 m, covering a q -range of 0.0045 to 0.85 Å⁻¹. The SANS-1 instrument at PSI was operated at two SDD distances (3 and 11 m), which provided a q -range of 0.005–0.36 Å⁻¹. The measurements at the TAIKAN instrument were carried out at an SDD of 5.65 m encompassing a q -range of 0.005–0.7 Å⁻¹. Data were reduced according to the procedure recommended by the corresponding facility.

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Conflicts of Interest

The authors declare no conflicts of interest.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section. **Data S1.** Supporting Information. **Data S2.** Supporting Information.

Appendix A

Dielectric Constant of Solvents (See Table A1)

TABLE A1 | Dielectric constants and Bjerrum lengths of solvents used. Data are for $T = 298$ K except for NMA ($T = 308$ K). Data are from the CRC Handbook of Chemistry and Physics, 85th edition.

Solvent	ϵ_r [–]	l_B [nm]
N-methyl-formamide (NMF)	182	0.31
N-methyl-acetamide (NMA)	172	0.31
Water	78.4	0.71
Di-methyl sulfoxide (DMSO)	46.8	1.19
Di-methyl formamide (DMF)	37.2	1.50
Acetonitrile	35.7	1.56
Methanol	32.6	1.71
Ethanol	24.9	2.24
1-propanol	20.5	2.72
Acetone	20.5	2.72
2-propanol	19.3	2.88
1-butanol	17.4	3.20
Pyridine	13.0	4.28