

Viscosity, NMR Diffusometry and Light Scattering Data for Aqueous and Aqueous-Salt Solutions of Poly(1-butyl-3-vinylimidazolium bromide)

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Electronic Supplementary Information

Abstract Poly(1-butyl-3-vinylimidazolium bromide) is a polymerized ionic liquid (PILs), a relatively new class of materials that combines the attractive properties of ionic liquids (ILs) and polyelectrolytes and finds wide applications. The backbone of this PIL is composed of quaternary imidazolium salts, which are among the most promising and popular ILs. However, little is known about the physicochemical characteristics of the aqueous solutions of this PIL. In this study, we synthesized and characterized samples of this PIL and obtained experimental data on the viscosity, static and dynamic light scattering, and nuclear magnetic resonance diffusometry for aqueous and aqueous KBr solutions with varying polymer contents at $T=298.15$ K. We discuss the effects of the polymer concentration and salinity on the behavior of the solution.

Keywords Polymerized ionic liquid; Polyelectrolyte solutions; Viscosity; Light scattering; NMR diffusometry

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INTRODUCTION

Polymerized ionic liquids have attracted much attention as a new class of polymeric materials that combine a number of unique properties of conventional low-molecular-weight ionic liquids (ILs) with intrinsic polyelectrolyte features. Polymerized ILs (PIL) have numerous applications,^[1–7] ranging from the development of smart functional materials with tunable properties^[8,9] to the design of highly efficient aqueous biphasic extraction systems and bioseparation.^[10,11]

For specific applications, the rational design of novel polymerized ILs is required.^[3] Many polymerized ILs have been synthesized with various cation and anion structures and ionic centers in the main or side chains of polymers.^[2,4,7] Among them, poly(1-butyl-3-vinylimidazolium bromide) (poly[C₄Vim]Br) consists of 1,3-dialkylimidazolium halides as the side chain of the monomer unit. It is known that quaternary imidazolium salts are among the most promising and frequently used conventional ILs.^[12–16]

Most reviews on polymerized ILs summarize the state-of-the-art synthetic strategies or applications of polymerized ILs.^[3,4] However, to the best of our knowledge, little is known

about the behavior of aqueous poly[C₄Vim]Br solutions. Because low-molecular-weight ILs are prone to aggregation in solutions, it might be expected that the propensity for aggregation may also have an impact on the macroscopic behavior of polymerized ILs, particularly on the solution viscosity and interactions with the added salts, distinguishing polymerized ILs as a separate class from conventional polyelectrolytes.

The viscosity of a polymer solution is usually described by scaling laws (Fig. 1). For salt-free polyelectrolyte solutions as well as solutions of neutral polymers, $\eta_{sp} \sim c$ in the dilute

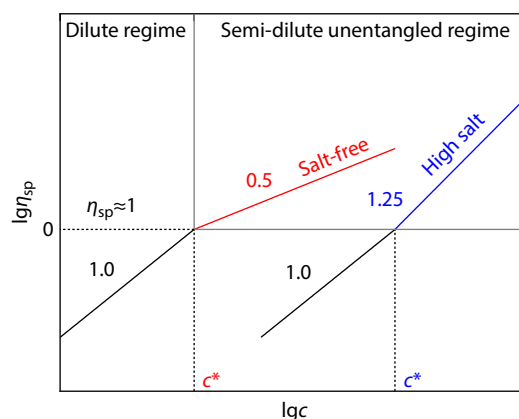


Fig. 1 Scaling exponents predicted theoretically for flexible polyelectrolyte in a good solvent without salt or at high salinity.

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regime according to the Zimm model.^[17] For polyelectrolytes in dilute regimes with high concentrations of added salt, the scaling law should be the same, that is, $\eta_{sp} \sim c$.^[18]

In the semi-dilute unentangled regime, $\eta_{sp} \sim c^{1/2}$ (Fuoss law^[19]) for salt-free polyelectrolyte solutions or $\eta_{sp} \sim c^{5/4}$ for polyelectrolytes at high salt limits.^[18,20] These scaling laws are valid for flexible polyelectrolytes in good solvents, and may be violated for semi-flexible and/or polydisperse polymers.^[21]

Fig. 2 shows the typical behavior of polyelectrolytes in good solvents. As one can see, an increase of molecular mass of sodium polystyrene sulfonate (NaPSS) leads to an increase of solution viscosity (Fig. 2a). Simultaneously, the scaling exponent in the semi-dilute regime practically does not change. Fig. 2(b) illustrates the effect of incorporating an ionic group into poly(2-vinylpyridine) (poly[2Vpyr]), yielding 55% quaternized poly(*N*-methyl-2-vinylpyridinium chloride) (poly[C₁-2Vpyr]Cl). As a result, scaling exponent in dilute regime remains the same, but for semi-dilute unentangled regime it differs in accordance with theory: from 1.3 for neutral polymer to 0.5 for polyelectrolyte without salt.^[22,23] Shown in Fig. 2(c) behavior of the salt-free sodium carboxymethyl cellulose (NaCMC) solution and the solution of this polyelectrolyte in 0.5 M NaCl in the semi-dilute unentangled regime are shown in Fig. 1. The observed deviation may be due to the chain rigidity and/or polydispersity.^[21]

In this work, we measure the viscosity of two samples of poly[C₄Vim]Br in water and aqueous salt at $T=298.15$ K and report the results of static and dynamic light scattering (SLS, DLS) and the data of nuclear magnetic resonance (NMR) diffusometry for this PIL. The samples were synthesized by free-radical polymerization and characterized by NMR, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). From our viscosity and diffusion measurements, we obtained the concentration thresholds for the semi-dilute regime, average molecular weight of the polymer, hydrodynamic radii, second virial coefficients, and diffusion coefficients. We discuss the dependence of these quantities on the concentration of the polymerized IL and solution salinity.

EXPERIMENTAL

Materials

1-Vinylimidazole ($\geq 99\%$, Aldrich, Germany) was double-distilled under reduced pressure. 1-bromobutane (99%, Sigma-Aldrich, India) and *N,N*-dimethylformamide (DMF, $>99.9\%$, Vekton, Russia) were distilled under ambient and reduced pressure, respectively. The chemicals were stored in A3 molecular sieves in sealed vessels. Ethyl acetate ($\geq 99.7\%$ for HPLC; Honeywell, Germany), acetonitrile ($\geq 99.9\%$ for HPLC; Cryochrom, Russia), methanol ($>99.5\%$; Vekton, Russia), and acetone ($>99.8\%$; Vekton, Russia) were used as received. 2,2'-Azobis(2-methylpropanitrile) (AIBN, 99 %, Sigma-Aldrich, USA) was recrystallized from methanol and dried under vacuum before use. Potassium bromide ($>99.0\%$; Reahim, Russia) was used without further purification. Water was double-distilled. Deuterated water ($\geq 99.8\%$, Chemical Line, Russia) was used for the NMR studies.

Synthesis of 1-Butyl-3-vinylimidazolium Bromide ([C₄Vim]Br)

1-Butyl-3-vinylimidazolium bromide was synthesized by the

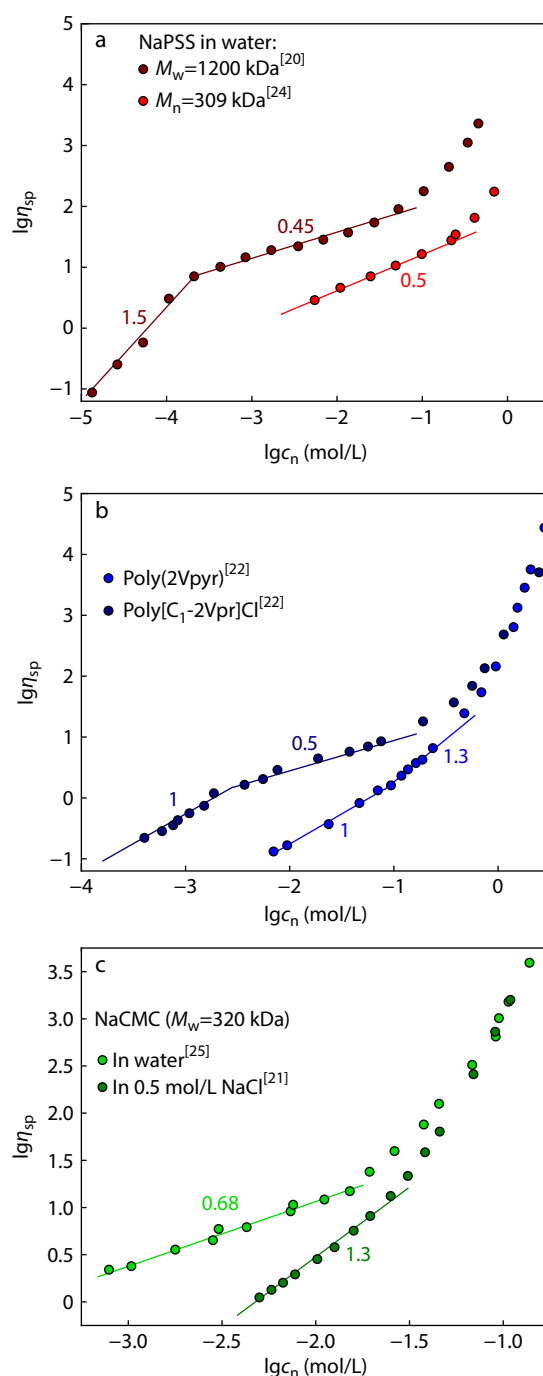
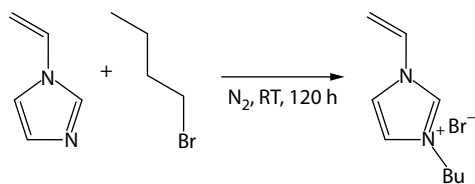


Fig. 2 Factors affecting the viscosity: a) molecular mass of polyelectrolyte, b) addition ionic group to neutral polymer, c) salt addition to polyelectrolyte solution. References to experimental data: "Boris & Colby 1998",^[20] "Fernandez Prini & Lagos 1964",^[24] "Dou & Colby 2006",^[22] "Lopez et al 2014",^[25] "Lopez et al 2016".^[21]

quaternization of 1-vinylimidazole (Scheme 1), similar to the method described by Chen *et al.*^[26] 31.54 g (335 mmol) of 1-vinylimidazole and 53.61 g (391 mmol) of 1-bromobutane were separately degassed by sparging with nitrogen for 40 min. Then 1-bromobutane was added dropwise to 1-vinylimidazole under constant stirring. The reaction mixture was shielded from the outside light and stirred for 5 days at ambient temperature



Scheme 1 Synthesis of 1-butyl-3-vinylimidazolium bromide.

(22–25 °C) in a nitrogen atmosphere. The obtained white crystals of [C₄Vim]Br were washed with ethyl acetate and recrystallized three times with ethyl acetate from an acetonitrile solution. The precipitate was dried using a rotary evaporator at 60 °C under vacuum. As a result, 68.10 g of [C₄Vim]Br was obtained (yield: 88%). This IL was used as a monomer for the synthesis of the polyelectrolyte.

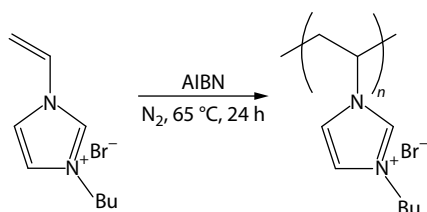
¹H- and ¹³C{¹H} NMR spectra confirmed the absence of precursors and other impurities in the synthesized IL (Figs. S1 and S2, ESI). The concentration of water measured by the Karl Fischer method (Mettler Toledo V20 titrator) was 0.03 wt%.

Synthesis of Poly(1-butyl-3-vinylimidazolium bromide) (Poly[C₄Vim]Br)

The synthetic procedure was based on the method described by Green *et al.*^[27] Poly(1-butyl-3-vinylimidazolium bromide) was obtained *via* free-radical polymerization of 1-butyl-3-vinylimidazolium bromide (Scheme 2). The polymerization reaction was performed in a nitrogen atmosphere using a Schlenk line. Details of the air-sensitive technique have been described elsewhere (e.g., Ref. [28]).

In this study, we synthesized two poly[C₄Vim]Br samples. For the first one 20.30 g (87.8 mmol) of [C₄Vim]Br and 1.4425 g (8.78 mmol) of AIBN were dissolved in 129 mL of DMF. For the second one 20.10 g (87.0 mmol) of [C₄Vim]Br and 0.1428 g (0.87 mmol) of AIBN were dissolved in 127 mL of DMF.

The basic procedure was the same for both the samples. Oxygen was removed from the prepared solution by three freeze-pump-thaw cycles. At the same time, the reaction flask was heated to 65 °C in an oil bath, and the atmosphere in the flask was changed to nitrogen. After degassing, the solution was transferred to a reaction flask using the cannula technique.^[28] The reaction mixture was shielded from the outside light and stirred at 65 °C in a nitrogen atmosphere. After 24 h, the reaction was stopped by precipitation of the polyelectrolyte into acetone. The resulting yellowish solid was dissolved in methanol and precipitated with acetone three times. After the last precipitation, polyelectrolyte was washed with acetone and dried at 40 °C in a vacuum oven for 3 days. The amounts of poly[C₄Vim]Br obtained in the first and the second syntheses are 17.4 g (yield: 86 %) and 13.3 g (yield: 66%), respectively. The synthesized two polymers are denot-



Scheme 2 Free-radical polymerization of 1-butyl-3-vinylimidazolium bromide.

ed “sample 1” and “sample 2” in this work.

¹H- and ¹³C{¹H} NMR spectra showed the absence of monomers in the synthesized polymers (Figs. S3 and S4, in the electronic supplementary information, ESI). The concentrations of water (3.0 wt% for **sample 1** and 3.6 wt% for **sample 2**) measured by Karl Fischer method was taken into account in all further experiments. The synthesized polyelectrolyte was soluble in water, dimethylformamide, methanol, and acetonitrile, and insoluble in acetone and ethyl acetate.

Methods

TGA and DSC measurements

TGA was carried out on a NETZSCH TG 209F1 Libra instrument at a heating rate of 10 °C/min in an inert argon atmosphere. By analyzing the thermogravimetric curves, the temperatures corresponding to the onset of sample decomposition (*T*_{onset}) were obtained. DSC was performed on a NETZSCH DSC 204F1 Phoenix instrument in an argon atmosphere at a heating rate of 10 °C/min.

Viscosity measurements

All viscosity measurements were performed using an Anton Paar Lovis 2000 M microviscometer. The measurements are based on the rolling ball principle: a ball rolls through a closed, liquid-filled capillary inclined at different angles. The viscometer measured the rolling time of the ball, which is directly proportional to the viscosity of the sample. We used a capillary with inner diameter of 1.59 mm (viscosity range 0.7–15 mPa·s) and a gold-coated ball with a diameter of 1.5 mm. The capillary was calibrated with double-distilled water.

In order to ensure that dust particles do not affect the measurements, the samples were filtered through a Sartorius Minisart RC 15 syringe filter (pore size 0.45 μm) prior to filling the capillary. The solution densities (needed for the determination of the dynamic viscosity) were measured using a Mettler Toledo DM45 Density Meter.

Polymer solutions may exhibit non-Newtonian behavior at relatively high shear rates.^[29] In our experiments, shear rates were less than 500 s^{−1} (according to viscometer readings), and the studied polyelectrolytes had relatively low molecular weights; therefore, shear thinning was unlikely. We measured the viscosity at different inclination angles of the capillary and ensured that there was no pronounced shear thinning effect (an example is presented in Fig. S5 in ESI).

In a typical experiment, solution with the highest concentration was prepared by dissolution of solid polyelectrolyte in water or aqueous KBr (*C*_{KBr} = 0.1 or 0.5 mol/L). Solutions of lower concentrations were obtained by diluting the initial solution with water or KBr solution. All the studied solutions were prepared using the gravimetric method.

The standard expressions for the relative (*η*_r), specific (*η*_{sp}), and reduced (*η*_{red}) viscosities are given by:

$$\eta_r = \frac{\eta}{\eta_s} \quad (1)$$

$$\eta_{sp} = \eta_r - 1 \quad (2)$$

$$\eta_{red} = \frac{\eta_{sp}}{c} \quad (3)$$

where *η* and *η*_s are the dynamic viscosities of the sample and solvent in mPa·s, respectively, and *c* is the concentration of polyelectrolyte in g/mL.

To determine the intrinsic viscosity of poly[C₄Vim]Br, the experimental data on aqueous-salt solutions of polyelectrolytes were fitted using the Huggins and Kraemer equations:^[30,31]

$$\eta_{\text{red}} = [\eta] + k_{\text{H}}[\eta]^2 c \quad (4)$$

$$\frac{\ln \eta_r}{c} = [\eta] + k_{\text{K}}[\eta]^2 c \quad (5)$$

where $[\eta]$ is the intrinsic viscosity and k_{H} and k_{K} are the Huggins and Kraemer coefficients, respectively. The intrinsic viscosities determined using Eqs. (4) and (5) must be the same, implying that the coefficients are related:^[30,31]

$$k_{\text{H}} - k_{\text{K}} = 0.5 \quad (6)$$

Eq. (4) can only be applied for the interval of the relative viscosities between 1.2 and 2.5^[29] and Eq. (5) is valid for the interval of relative viscosities between 1.2 and 1.6.^[29]

The overlap concentration (transition from the dilute to semi-dilute regime) is assumed to be the reciprocal of the intrinsic viscosity:^[21,22]

$$c^* = \frac{1}{[\eta]} \quad (7)$$

The intersection of straight lines corresponding to the scaling laws is related to the overlap concentration c^* (Fig. 1), which reflects the transition from a dilute to a semi-dilute regime.

Since Eqs. (4) and (5) are not applicable to polyelectrolytes in salt-free solutions because of the polyelectrolyte effect;^[29] the overlap concentration c^* is usually determined by the empirical criterion $\eta_{\text{sp}}(c^*) = 1$ (Fig. 1).^[20,23]

Static and Dynamic Light Scattering

Light scattering experiments were performed using a PhotoCor Complex instrument (PhotoCor, Russia). A heat-stabilized diode laser operating at 654 nm (25 mW power) was used as the light source. Light scattering was measured at scattering angles from 30° to 140° with 10° increments. The solutions were cleared of dust particles by filtering through a PTFE 0.2 μm pore-size filter.

The weight average molecular mass (M_w) was obtained from the measured Rayleigh ratio:^[17,30]

$$\left\langle \frac{Hc}{R(\theta, c)} \right\rangle = \frac{1}{M_w} + 2A_2c \quad (8)$$

where H is the scattering constant, c is the mass concentration of the polymer solution, A_2 is the second virial coefficient, $R(\theta, c)$ is the Rayleigh ratio of the scattering intensity determined for each solution concentration and at different scattering angles θ . The molecular weight was determined by extrapolating the angle-averaged Hc/R values to zero concentration. The second virial coefficient A_2 is obtained from the slope of the concentration dependence, Eq. (8).

In dynamic light scattering experiments, the diffusion coefficient of the particles is determined using an approximation of the autocorrelation function of the intensity of the scattered light, I :

$$g_2(\tau) = \langle I \rangle^2 \left(1 + \beta |g_1(\tau)|^2 \right) = B_1 + Ae^{-2\tau/t_c} \quad (9)$$

where $g_1(\tau)$ is the autocorrelation function of the electric field, B_1 is the baseline, A is the amplitude of the signal, and t_c is the characteristic time (lifetime of concentration fluctuation). For the relaxation rate, we have

$$\frac{1}{t_c} = Dq^2 \quad (10)$$

where D is the translation diffusion coefficient of the scattering particles and q is the modulus of the wave vector of concentration fluctuations, which in the case of quasielastic scattering is given by

$$q = \frac{4\pi n_0}{\lambda_0} \sin\left(\frac{\theta}{2}\right) \quad (11)$$

where n_0 is the refractive index of the solvent, and λ_0 is the wavelength of the laser.

The hydrodynamic radius R_h is calculated according to the Stokes-Einstein relation:

$$R_h = \frac{kT}{6\pi\eta D_0} \quad (12)$$

where k is the Boltzmann constant, T is the temperature, η is the dynamic viscosity of solvent, D_0 is the value of the diffusion coefficient obtained by extrapolation to zero polymer concentration.

NMR Diffusometry

¹H-NMR diffusion experiments were performed on a 500 MHz Bruker Avance III spectrometer equipped with a GREAT 1/60A gradient amplifier and a 5 mm MIC DIFF/30 probe with ¹H insert. The self-diffusion coefficients were measured using pulse gradient stimulated echo (PGSTE).^[32]

The self-diffusion coefficient D is directly related to the decaying intensities of the NMR signal according to:

$$I/I_0 = e^{-D(2\pi\gamma G\delta)^2(\Delta-\delta/3)} \quad (13)$$

where I and I_0 are the intensities of the NMR signal in the presence and absence of field gradient pulses, respectively, G is the gradient strength, Δ is the diffusion time, δ is the gradient pulse length, γ is the gyromagnetic ratio.

In all the experiments, the gradient strength was varied, and the maximum value of the gradient strength was about 52 Gauss/cm. The gradient pulse length (δ) was 6 ms. The diffusion time (Δ) was optimized for the sample and its value was in the range of 200–600 ms.

The self-diffusion coefficient of poly[C₄Vim]Br was determined as the average value of the data from the following peaks: 8.00–7.10 (m, 2H), 4.63–3.64 (m, 3H), 2.02–1.59 (m, 2H), 1.58–1.15 (m, 2H), 1.15–0.60 (m, 3H) (Figs. S3 and S4 in ESI). The self-diffusion coefficient of water ($D_{\text{H}_2\text{O}}$) was determined from the peak at 4.70 ppm.

The decaying intensities ($\ln(I/I_0)$) of the signals were fitted to a single exponential function. Fig. 3 shows an example of the decaying intensities and an approximation curve for peaks at 8.00–7.10 ppm and 1.15–0.60 ppm for **sample 2** of poly[C₄Vim]Br (5 mg/mL) in D₂O+KBr (0.5 mol/L).

RESULTS AND DISCUSSION

Static Light Scattering Data

For the studied samples, the dependence of Hc/R on the scattering angle θ lies within the experimental error, which makes it impossible to obtain the gyration radius from our data. The molecular weight was determined by extrapolating the average Hc/R value to zero (Fig. 4). This extrapolation was performed in the concentration range where the integral intensity of the scattered light depended linearly on the concentration of the poly-

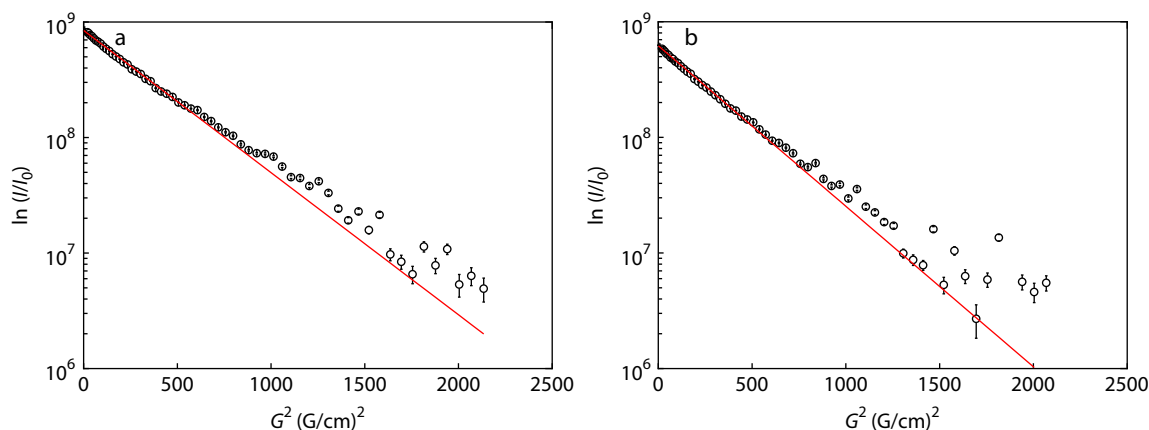


Fig. 3 The plot of decaying intensities ($\ln(I/I_0)$) versus the gradient strength squared (G^2) and an approximation curve for **sample 2** poly[C₄Vim]Br (5 mg/mL) in D₂O+KBr (0.5 mol/L): (a) for the peak at 8.00–7.10 ppm, (b) for the peak at 1.15–0.60 ppm.

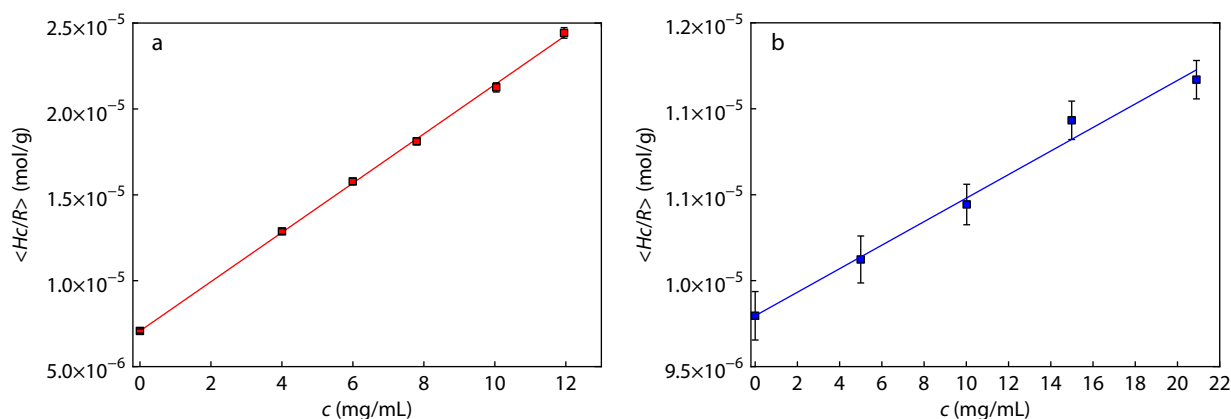


Fig. 4 Concentration dependences of Hc/R values for poly[C₄Vim]Br (**sample 2**) in 0.1 mol/L (a) and 0.5 mol/L (b) KBr. In the left graph the error bars are equal or less than the symbol size.

Table 1 Values of the weight average molecular mass M_w and the second virial coefficient A_2 .

C_{KBr} (mol/L)	M_w (Da)	A_2 ($\times 10^{-7}$ dm ³ ·mol·g ⁻²)
0.1 (sample 1)	133000 $\pm$ 10000	6.6 $\pm$ 0.3
0.1 (sample 2)	141000 $\pm$ 1000	7.2 $\pm$ 0.2
0.5 (sample 1)	94000 $\pm$ 4000	0.24 $\pm$ 0.01
0.5 (sample 2)	102000 $\pm$ 4000	0.34 $\pm$ 0.01

electrolyte. The results are presented in Table 1.

The salt concentration affected the molecular weight values obtained by SLS. The large experimental error inherent in this method makes it practically impossible to distinguish the molecular weights of **samples 1** and **2**. In addition, gel permeation chromatography using a TSKgel G5000PWLX-CP column (Tosoh Bioscience) gave no results due to the strong interaction of the PIL with the column. However, we believe that the molecular weight of **sample 2** was larger than that of **sample 1**. Note that **sample 2** was synthesized using 10 times less AIBN, which theoretically should have increased the molecular weight by three times compared to **sample 1**.

TGA and DSC Characterization

The TGA thermograms of the synthesized PIL (poly[C₄Vim]Br) and its monomer ([C₄Vim]Br) are presented in Fig. S6 (in ESI). The thermograms show that the decomposition of samples pro-

ceeds similarly with T_{onset} =260 °C for the monomer [C₄Vim]Br and T_{onset} =275 °C and T_{onset} =270 °C for **samples 1** and **2** of poly[C₄Vim]Br, respectively. The decomposition temperature of poly[C₄Vim]Br is in agreement with the data of Ke *et al.*,^[10] who reported T_{onset} from the interval 246–327 °C for the samples with different molecular masses.

The DSC curves of [C₄Vim]Br and poly[C₄Vim]Br are shown in Fig. 5. The DSC study of [C₄Vim]Br showed a pronounced

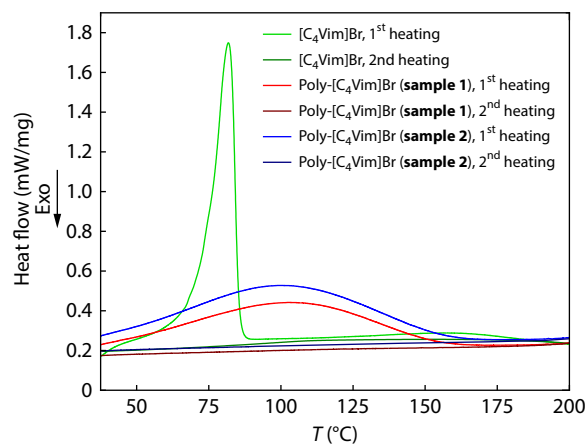


Fig. 5 DSC thermograms for [C₄Vim]Br and poly[C₄Vim]Br.

Table 2 Viscosity of salt-free aqueous poly[C₄Vim]Br solutions at 298.15 K.

Sample	<i>c</i> (mg/mL)	ρ (g/cm ³)	η^a (mPa·s)	η_{sp}
Poly[C ₄ Vim]Br (sample 1)	0	0.99704	0.8904	–
	0.599	0.99727	1.211	0.3602
	1.201	0.99747	1.384	0.5544
	2.410	0.99790	1.642	0.8440
	4.821	0.99871	1.988	1.233
	9.679	1.00033	2.492	1.799
	19.50	1.00361	3.280	2.684
	29.35	1.00682	3.977	3.467
	39.09	1.00998	4.649	4.222
	48.06	1.01290	5.262	4.910
Poly[C ₄ Vim]Br (sample 2)	0	0.99704	0.8904	–
	0.160	0.99707	1.0164	0.1415
	0.320	0.99717	1.0691	0.2007
	0.650	0.99727	1.1626	0.3057
	1.300	0.99752	1.3808	0.5507
	2.610	0.99794	1.5885	0.7841
	5.170	0.99878	1.9960	1.2417
	10.15	1.00043	2.4080	1.7044
	20.44	1.00374	3.4855	2.9145
	40.45	1.00988	4.8463	4.4429

^a Relative uncertainty of dynamic viscosity was less than 0.5%.

endothermic effect with $T_{\text{onset}}=73.3$ °C and $T_{\text{peak}}=81.8$ °C, which corresponds to the melting of the sample. The obtained melting point was close to that of [C₄mim]Br (73–79 °C).^[33] The absence of the endothermic effect during the 2nd heating is because the sample remains in the form of a metastable melt after the 1st heating.

At the same time, poly[C₄Vim]Br (both samples) showed no significant effects in the temperature range of 25–200 °C. This indicates a higher melting point of these polyelectrolytes. The broad peaks at $T \approx 100$ °C for PIL samples may be attributed to dehydration of the polyelectrolytes since the 2nd heating does not show any effects.

Viscosity of Salt-free Aqueous Solutions of Poly[C₄Vim]Br

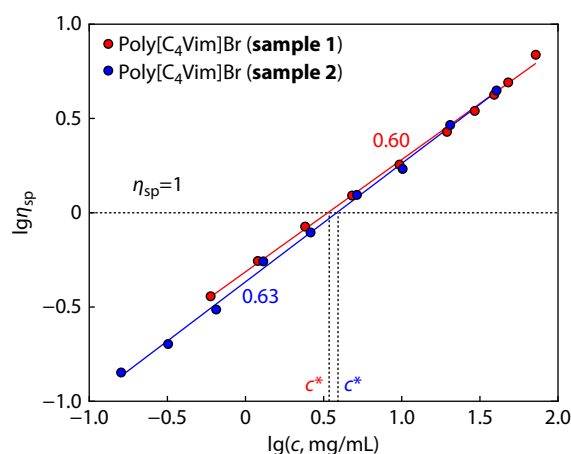
The viscosity data for salt-free aqueous solutions of poly[C₄Vim]Br are presented in Table 2 and Fig. 6.

We found that the scaling exponents for salt-free solutions in dilute and semi-dilute unentangled regimes are 0.60 and 0.63 for **samples 1** and **2**, respectively. This is slightly higher than the exponent of 1/2 predicted by Fuoss's law.^[19] Polydispersity can yield a higher apparent exponent owing to the co-existence of chains in the dilute and semi-dilute regimes, for which power laws of 1 and 1/2 are expected, respectively.^[21] The consistency of the exponents below the overlap concentration c^* (Fig. 6) may also be due to the polydispersity of the sample.

For the salt-free solution, the overlap concentration c^* was experimentally determined using the empirical criterion $\eta_{sp}(c^*)=1$ (Fig. 6). For poly[C₄Vim]Br (**sample 1**), $c^*=3.36 \pm 0.07$ mg/mL and for poly[C₄Vim]Br (**sample 2**), $c^*=3.84 \pm 0.07$ mg/mL.

Viscosity of Aqueous-salt Solutions of Poly[C₄Vim]Br

The experimental data on the viscosity of aqueous-salt (0.1 and 0.5 mol/L KBr) solutions of poly[C₄Vim]Br at 298.15 K are presented in Table 3. It should be noted that the densities and vis-

**Fig. 6** Determination of the overlap concentrations for aqueous solutions of poly[C₄Vim]Br at 298.15 K.

cosities of the aqueous KBr solutions are close to the values reported in the literature ($\rho=1.00540$ g/cm³, $\eta=0.8862$ mPa·s for 0.1 mol/L KBr and $\rho=1.03821$ g/cm³, $\eta=0.8692$ mPa·s for 0.5 mol/L KBr).^[34]

Plots of η_{red} and $\ln(\eta_r)/c$ versus c were constructed based on the experimental data (Fig. 7). The intrinsic viscosity was determined by interpolation of the linear dependences $\eta_{\text{red}}-c$ and $\ln(\eta_r)/c-c$ to zero concentrations (see Eqs. 4 and 5, respectively). For this interpolation, we only used the data points that belong to the validity regions of the Huggins equation ($\eta_r=1.2-2.5$), and of the Kraemer equation ($\eta_r=1.2-1.6$), which is shown in Fig. 7 by black curves.

The results of treating the experimental data using the Huggins and Kraemer equations are compared in Table 4. The overlap concentration, c^* was calculated using Eq. (7), where the intrinsic viscosity $[\eta]$ is the average of the values given by the Huggins and Kraemer equations ($[\eta]_H$ and $[\eta]_K$).

Table 3 Viscosity of aqueous-salt (0.1 and 0.5 mol/L KBr) solutions of poly[C₄Vim]Br at 298.15 K.

Sample	<i>c</i> (mg/mL)	ρ (g/cm ³)	η^a (mPa·s)	η_{sp}	η_{red} (mL/g)	$\ln(\eta_r)/c$ (mL/g)
Poly[C ₄ Vim]Br (sample 1) in 0.1 mol/L KBr	0	1.00557	0.8774	—	—	—
	6.244	1.00753	1.0684	0.2177	34.86	31.54
	10.36	1.00885	1.2056	0.3740	36.11	30.67
	14.38	1.01006	1.3446	0.5325	37.02	29.68
	19.25	1.01159	1.5267	0.7400	38.44	28.77
	24.14	1.01314	1.7223	0.9630	39.89	27.94
	27.95	1.01428	1.8816	1.1445	40.96	27.30
	31.91	1.01548	2.0423	1.3276	41.61	26.48
Poly[C ₄ Vim]Br (sample 1) in 0.5 mol/L KBr	0	1.03909	0.8728	—	—	—
	4.919	1.04069	0.9577	0.0973	19.78	18.87
	9.843	1.04224	1.0461	0.1986	20.18	18.40
	14.85	1.04353	1.1423	0.3088	20.79	18.12
	19.87	1.04501	1.2501	0.4323	21.76	18.08
	24.86	1.04642	1.3641	0.5629	22.64	17.96
	29.90	1.04787	1.4906	0.7079	23.68	17.91
	34.90	1.04921	1.6303	0.8680	24.87	17.90
	39.91	1.05064	1.7810	1.0406	26.08	17.87
	49.09	1.05305	2.0853	1.3893	28.30	17.74
Poly[C ₄ Vim]Br (sample 2) in 0.1 mol/L KBr	0	1.00557	0.8774	—	—	—
	13.97	1.01028	1.4562	0.6597	47.22	36.27
	17.90	1.01234	1.6401	0.8693	48.56	34.95
	22.76	1.01444	1.8425	1.0999	48.33	32.60
	26.97	1.01548	2.0492	1.3356	49.52	31.45
	30.43	1.01703	2.2410	1.5542	51.07	30.82
	36.35	1.01816	2.5124	1.8634	51.26	28.94
	41.18	1.01933	2.7131	2.0922	50.81	27.41
	53.97	1.02396	3.4407	2.9215	54.13	25.32
	64.32	1.02961	3.9220	3.4700	53.95	23.28
Poly[C ₄ Vim]Br (sample 2) in 0.5 mol/L KBr	0	1.03909	0.8728	—	—	—
	9.860	1.04352	1.0682	0.2239	22.70	20.49
	20.07	1.04646	1.2673	0.4520	22.52	18.58
	30.31	1.04912	1.5258	0.7482	24.68	18.43
	40.16	1.05208	1.7474	1.0021	24.95	17.29
	50.04	1.05507	2.0504	1.3492	26.96	17.07
	57.20	1.05593	2.3119	1.6488	28.83	17.03
	64.37	1.05981	2.6318	2.0154	31.31	17.15

^a Relative uncertainty of dynamic viscosity was less than 0.5%.

Fig. 7 and Table 4 show some deviations between the intrinsic viscosities obtained using the Huggins and Kraemer methods. The coefficients k_H and k_K are not in exact agreement with Eq. (6), although it closely follows. The observed deviations may be due to uncertainty in the experimental data.

Based on the data obtained, the following conclusions can be drawn: with increasing salt concentration, the intrinsic viscosity diminishes and the overlap concentration increases. As the salt concentration increased, the positive charge on the polymer chain was better shielded; therefore, the electrostatic repulsion decreased. This leads to the compression of the polyelectrolyte coil and a decrease in the pervaded volume. As a result, the overlap concentration increased.

For **sample 1** in 0.1 mol/L KBr and **sample 2** in 0.1 and 0.5 mol/L KBr, the Huggins coefficient $k_H < 0.4$, which means the flexible polymer in a good solvent.^[31] For **sample 1** in 0.5 mol/L KBr, $k_H > 0.5$, which indicates a poor solvent.^[31] An increase in the Huggins coefficient with increasing salinity signifies a worsening of the quality of the solvent (salting-out effect), which is in agreement with our light-scattering data on

the second virial coefficient (see Table 1).

In the case of polyelectrolyte in 0.5 mol/L KBr, the observed dependences of η_{red} and $\ln(\eta_r)/c$ are not strictly linear (Figs. 7b and 7d), especially for **sample 2**, for which deviations are observed even in the validity region of the Huggins and Kraemer equations. The deviations from the linear behavior are due to the intermolecular interactions between the highly coiled polymer, which leads to an additional increase in the viscosities compared to those predicted by the Huggins and Kraemer equations.^[20]

Fitting these data with smooth curves provides the values of the intrinsic viscosities with much better convergence (Fig. 8). The values obtained in this way are $[\eta] = 19.61$ mL/g for **sample 1** and $[\eta] = 21.96$ mL/g for **sample 2**, which are greater than the Huggins and Kraemer equation gives (Table 4). The correct overlap concentrations therefore should be $c^* = 50.99$ mg/mL and $c^* = 45.54$ mg/mL for **samples 1** and **2**, respectively.

The overlap concentrations in salt-free solutions are 10 times lower (3.36 ± 0.07 mg/mL for **sample 1** and 3.84 ± 0.07 mg/mL for **sample 2**, see previous Section) than in aqueous-

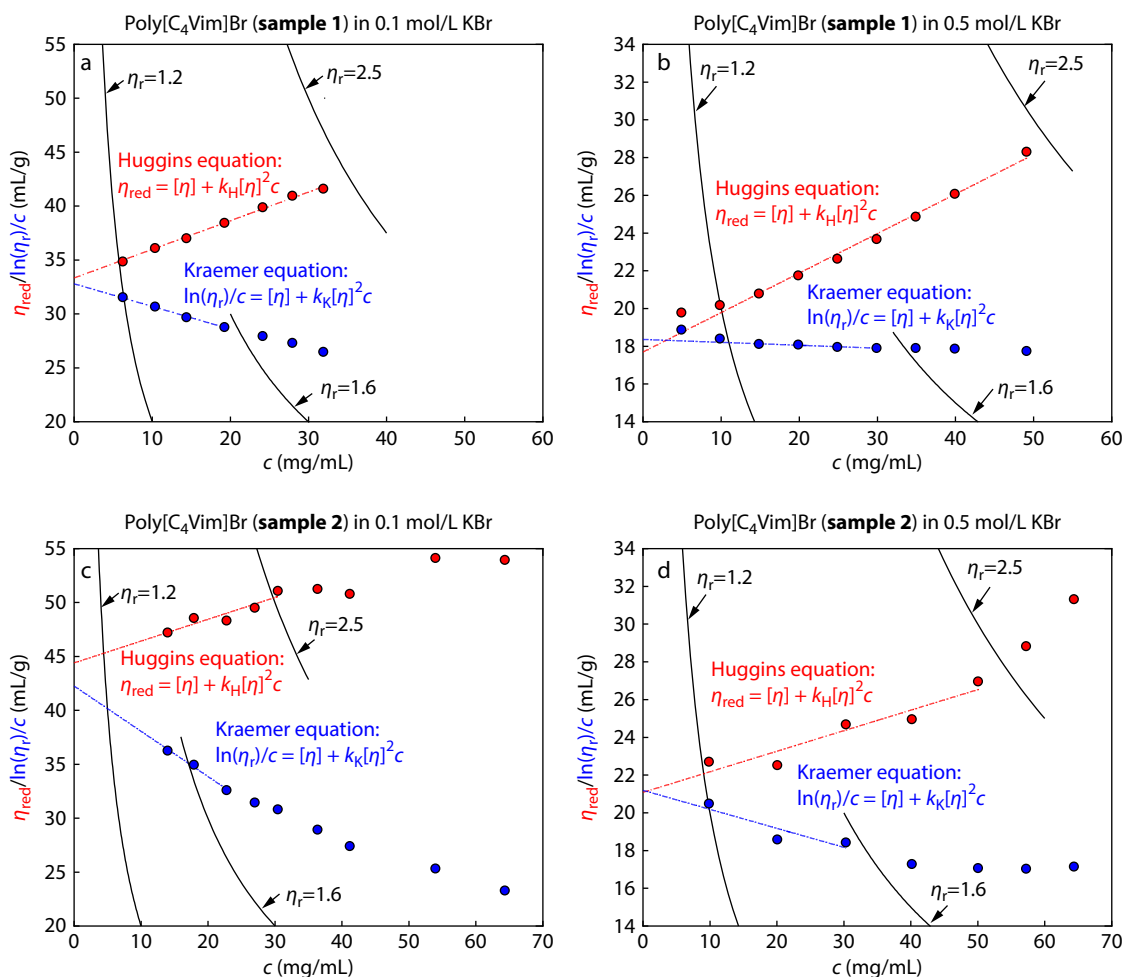


Fig. 7 Determination of the intrinsic viscosity of **sample 1** (a,b) and **sample 2** (c,d) of poly[C₄Vim]Br in 0.1 mol/L and 0.5 mol/L aqueous KBr solutions at 298.15 K. Black curves represent the validity regions of the Huggins and Kraemer equations.

Table 4 The intrinsic viscosities ($[\eta]_{\text{H}}$, $[\eta]_{\text{K}}$) determined by the Huggins and Kraemer equations, the Huggins and Kraemer coefficients (k_{H} , k_{K}) and the overlap concentrations (c^*) for aqueous-salt (0.1 and 0.5 mol/L KBr) solutions of poly[C₄Vim]Br at 298.15 K.

Sample	c_{KBr} (mol/L)	$[\eta]_{\text{H}}$ (mL/g)	$[\eta]_{\text{K}}$ (mL/g)	k_{H}	k_{K}	$k_{\text{H}} - k_{\text{K}}$	c^* (mg/mL)
Poly[C ₄ Vim]Br (sample 1)	0.1	33.3±0.2	32.8±0.2	0.239±0.009	-0.181±0.005	0.42±0.01	30.2±0.3
	0.5	17.7±0.2	18.36±0.05	0.67±0.03	-0.046±0.007	0.71±0.03	55.5±1.0
Poly[C ₄ Vim]Br (sample 2)	0.1	44.4±1.1	42.3±0.8	0.10±0.02	-0.24±0.03	0.34±0.04	23.1±1.1
	0.5	21.1±0.7	21.2±1.1	0.25±0.05	-0.22±0.11	0.43±0.06	47.3±1.4

salt solutions due to the extension of charged polyelectrolyte chain.

A logarithmic plot of the specific viscosity versus concentration yielded scaling exponents (Fig. 9). At high salinities, there was no significant difference between the PIL samples. At low salinity, where the extension of chains due to electrostatic repulsion is stronger, the specific viscosity is somewhat greater for **sample 2**, which probably has a higher molecular mass.

Fig. 9 also illustrates the application of the empirical criterion of the overlap concentration threshold $\eta_{\text{sp}}(c^*)=1$.

As shown in the introduction (see Fig. 1), the theoretically predicted scaling exponents for polyelectrolytes with high salt concentrations in dilute and semi-dilute unentangled regimes are 1 or 5/4.^[18,20] Our data (Fig. 9) shows that the ex-

perimental exponents are the averages of these two predictions. Moreover, the scaling exponents were the same before and after overlap concentration c^* . The observed behavior may be due to the polydispersity of the samples; while the lower molecular-weight fraction is in the dilute regime, the other fractions are in the semi-dilute regime. As a result, the scaling exponents 1 and 1.25 are averaged.

For the polyelectrolyte in 0.5 mol/L KBr, the scaling exponents are somewhat greater than in 0.1 mol/L KBr. This may be attributed to charge shielding, which is stronger at high salt concentration.

Diffusion Coefficients from DLS

DLS data on the diffusion coefficient were obtained based on the dependence of the inverse characteristic times on the

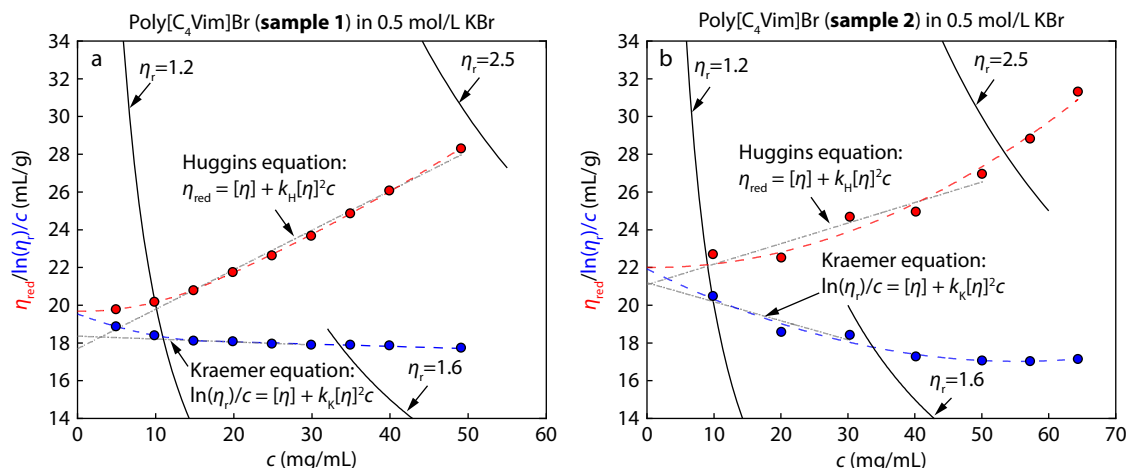


Fig. 8 Determination of intrinsic viscosity of poly[C₄Vim]Br in 0.5 mol/L aqueous KBr solutions at 298.15 K by fitting the data with smooth curves. Black curves represent the validity regions of the Huggins and Kraemer equations.

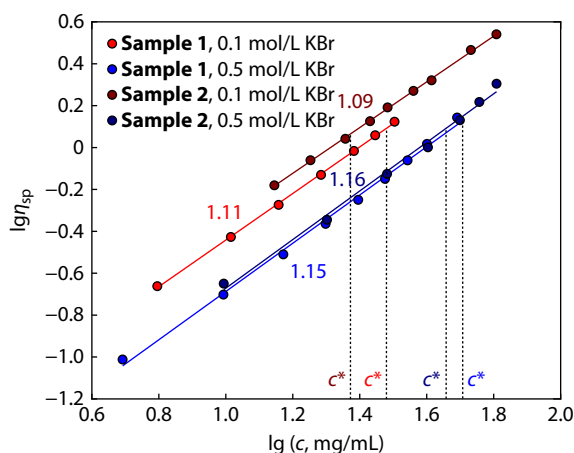


Fig. 9 Determination of the scaling exponents for poly[C₄Vim]Br with added salt at 298.15 K. Numbers shown in color represent the scaling exponents.

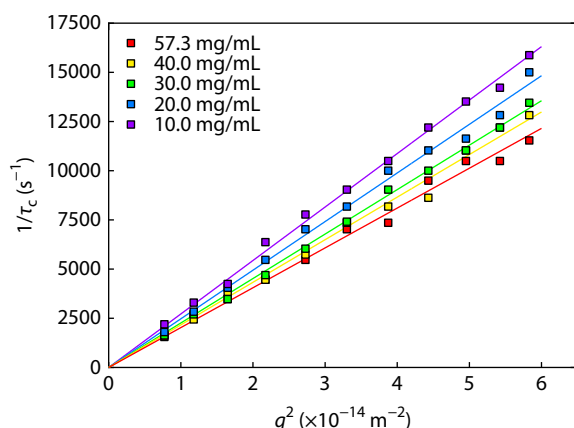


Fig. 10 Dependence of the inverse relaxation time on the square of the wave vector for different concentrations of poly[C₄Vim]Br (sample 2) with 0.5 mol/L added KBr at 298.15 K.

square of the wave vector (Eq. 10). As shown in Fig. 10, the curves were linear for all concentrations of poly[C₄Vim]Br under investigation. The slopes correspond to the values of the trans-

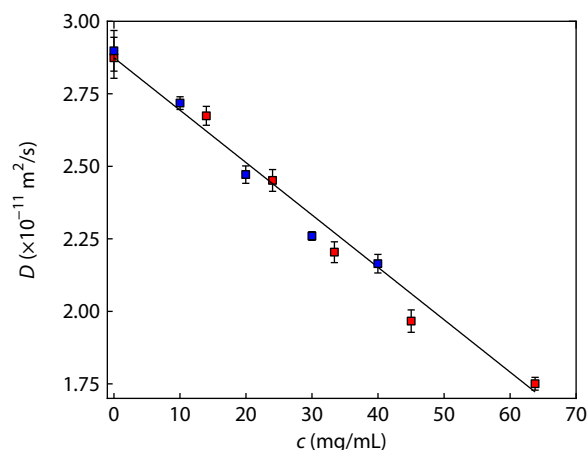


Fig. 11 Dependence of the translational diffusion coefficient on the concentration of poly[C₄Vim]Br (sample 2) with 0.5 mol/L added salt at 298.15 K. Line has been drawn to guide the eye. Different colors correspond to the two independent sets of measurements.

lational diffusion coefficients.

The obtained data on translational diffusion coefficients are presented in Fig. 11 and Table 5 for different concentrations of poly[C₄Vim]Br (sample 2) in 0.5 mol/L KBr aqueous salt solutions. Fig. 12 shows the intensity distribution at a scattering angle of 90°. As one can see the intensity distribution over the hydrodynamic radii is monomodal.

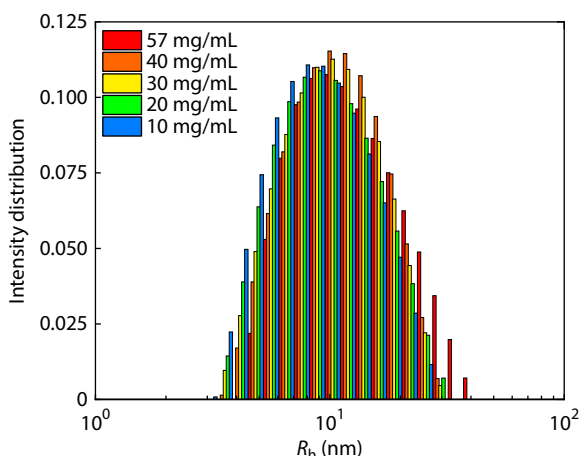
In the case of 0.5 mol/L added salt, the diffusion coefficient decreased with increasing polyelectrolyte concentration. It should be mentioned that according to the viscosity data, this system can be described as uncharged polyelectrolyte in a good solvent. This agrees with the positive value of the second virial coefficient obtained from the SLS experiment (see Table 1).

The diffusion coefficient at infinite dilution is $D_0 = (2.9 \pm 0.1) \times 10^{-11} \text{ m}^2/\text{s}$, and the hydrodynamic radius is $8.6 \pm 0.2 \text{ nm}$.

When studying the polyelectrolyte solution with 0.1 mol/L KBr added, the relaxation times were also determined for different concentrations of poly[C₄Vim]Br, and the dependence of the inverse relaxation time on the square of the wave vec-

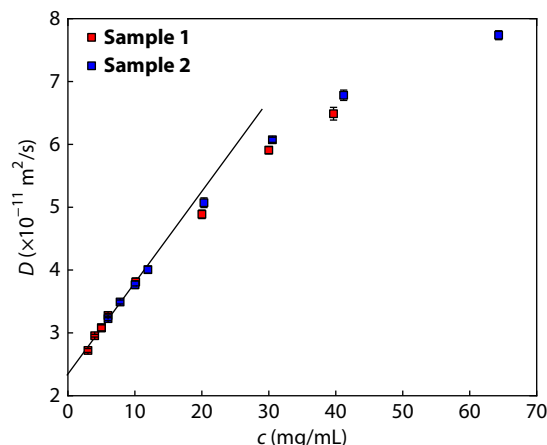
Table 5 Translational diffusion coefficients (D) and hydrodynamic radii of equivalent spheres (R_h) of poly[C₄Vim]Br in aqueous-salt solutions with 0.5 mol/L KBr at 298.15 K.

Sample	c (mg/mL)	D ($\times 10^{11}$ m ² /s)	R_h (nm)
Sample 1	58.3	2.11 $\pm$ 0.06	11.8 $\pm$ 0.3
	40.0	2.32 $\pm$ 0.04	10.7 $\pm$ 0.2
	30.0	2.61 $\pm$ 0.04	9.5 $\pm$ 0.1
	20.0	2.78 $\pm$ 0.03	9.0 $\pm$ 0.1
	15.0	2.87 $\pm$ 0.04	8.7 $\pm$ 0.1
	10.0	2.92 $\pm$ 0.03	8.5 $\pm$ 0.1
	5.0	3.12 $\pm$ 0.04	8.0 $\pm$ 0.1
Extrapolation to zero		3.17$\pm$0.03	7.9$\pm$0.1
Sample 2	1 st Set of measurements		
	57.3	2.03 $\pm$ 0.03	12.3 $\pm$ 0.2
	40.0	2.16 $\pm$ 0.03	11.5 $\pm$ 0.2
	30.0	2.26 $\pm$ 0.01	11.0 $\pm$ 0.1
	20.0	2.47 $\pm$ 0.03	10.1 $\pm$ 0.1
	10.0	2.72 $\pm$ 0.02	9.2 $\pm$ 0.1
	Extrapolation to zero		2.90$\pm$1.0
	2 nd Set of measurements		
	63.8	1.75 $\pm$ 0.02	14.7 $\pm$ 0.2
	45.8	1.97 $\pm$ 0.04	13.1 $\pm$ 0.3
	33.4	2.20 $\pm$ 0.04	11.7 $\pm$ 0.2
	24.0	2.45 $\pm$ 0.04	10.5 $\pm$ 0.2
	14.0	2.67 $\pm$ 0.03	9.6 $\pm$ 0.1
Extrapolation to zero		2.87$\pm$0.07	9.0$\pm$0.3

**Fig. 12** Distribution of the intensity of light scattered at an angle of 90° over the hydrodynamic radii for different concentrations of poly[C₄Vim]Br (**sample 2**) in aqueous-salt solutions with 0.5 mol/L KBr at 298.15 K.

tor was plotted (Fig. S7, in ESI). As in the case of 0.5 mol/L KBr, the intensity distribution function is monomodal (Fig. S8, in ESI). Additionally, polydispersity indices of the particles were determined based on DLS data by analyzing the correlation function with the aid of the cumulant method (Table S1, in ESI). This analysis shows that there is practically no difference between the polydispersities of **samples 1** and **2** of the PIL. A weak increase in the polydispersity index with polyelectrolyte concentration occurs. On the other hand, the polydispersity of the samples found for 0.5 mol/L KBr solution was slightly lower than that for 0.1 mol/L KBr.

Fig. 13 and Table 6 show the diffusion coefficient data obtained for different concentrations of poly[C₄Vim]Br in aque-

**Fig. 13** Dependence of the translational diffusion coefficient on the concentration of poly[C₄Vim]Br with 0.1 mol/L added salt at 298.15 K. Line has been drawn to guide the eye.**Table 6** Translational diffusion coefficients (D) and hydrodynamic radii of equivalent spheres (R_h) of poly[C₄Vim]Br in aqueous-salt solutions with 0.1 mol/L KBr at 298.15 K.

Sample	c (mg/mL)	D ($\times 10^{11}$ m ² /s)	R_h (nm)
Sample 1	39.7	6.5 $\pm$ 1.0	3.8 $\pm$ 0.1
	30.0	5.91 $\pm$ 0.06	4.2 $\pm$ 0.1
	20.0	4.89 $\pm$ 0.07	5.0 $\pm$ 0.1
	10.1	3.81 $\pm$ 0.06	6.4 $\pm$ 0.1
	6.0	3.28 $\pm$ 0.03	7.5 $\pm$ 0.1
	5.0	3.08 $\pm$ 0.05	8.0 $\pm$ 0.1
	4.0	2.96 $\pm$ 0.02	8.3 $\pm$ 0.1
	3.0	2.72 $\pm$ 0.03	9.0 $\pm$ 0.1
	extrapolation to zero		2.21$\pm$0.07
			11.1$\pm$0.4
Sample 2	64.3	7.74 $\pm$ 0.07	3.2 $\pm$ 0.1
	41.2	6.78 $\pm$ 0.08	3.6 $\pm$ 0.1
	30.5	6.07 $\pm$ 0.04	4.1 $\pm$ 0.1
	20.3	5.07 $\pm$ 0.08	4.9 $\pm$ 0.1
	12.0	4.01 $\pm$ 0.06	6.2 $\pm$ 0.1
	10.0	3.77 $\pm$ 0.06	6.5 $\pm$ 0.1
	7.8	3.49 $\pm$ 0.03	7.1 $\pm$ 0.1
	6.0	3.23 $\pm$ 0.03	7.6 $\pm$ 0.1
extrapolation to zero		2.45$\pm$0.06	10.1$\pm$0.3

ous salt solutions with KBr (0.1 mol/L KBr at 298.15 K).

In the case of the 0.1 mol/L added salt, the diffusion coefficient decreases with decreasing polyelectrolyte concentration. These data indicate the opening of the polyelectrolyte chain with dilution, which is in agreement with our viscosity data. A possible reason for this behavior is that the charge of the polyelectrolyte chain is not completely screened.^[35]

The diffusion coefficient at infinite dilution is $D_0 = (2.45 \pm 0.06) \times 10^{-11}$ m²/s, and the hydrodynamic radius is (10.1 ± 0.3) nm. The agreement with our NMR diffusometry data of $(2.5 \pm 0.1) \times 10^{-11}$ m²/s (see below) is excellent. For the lower salt concentration, the hydrodynamic radii (extrapolated to zero polymer content) are slightly larger than those for higher salinity, which also indicates incomplete charge shielding in 0.1 mol/L KBr.

Self-diffusion Coefficients by NMR Diffusometry

NMR diffusometry was employed to measure the self-diffusion coefficients of poly[C₄Vim]Br and water for dilute solutions (5

Table 7 NMR diffusometry data for poly[C₄Vim]Br (5 mg/mL) in D₂O and D₂O+KBr at 298.15 K.

c_{KBr} (mol/L)	D ($\times 10^{11}$ m ² /s)	$D_{\text{H}_2\text{O}}$ ($\times 10^9$ m ² /s)
0 (sample 1)	1.7 ± 0.1	1.75 ± 0.05
0 (sample 2)	1.3 ± 0.1	1.7 ± 0.1
0.1 (sample 1)	2.0 ± 0.1	1.80 ± 0.05
0.1 (sample 2)	2.5 ± 0.1	1.83 ± 0.01
0.5 (sample 1)	3.0 ± 0.2	1.74 ± 0.01
0.5 (sample 2)	3.3 ± 0.2	1.95 ± 0.05

mg/mL of PIL) in D₂O and in D₂O-salt solutions (0.1, 0.5 mol/L KBr). The results are presented in Table 7.

The self-diffusion coefficients of poly[C₄Vim]Br increase with increasing salt concentration, leading to a decrease in the size of the polyelectrolyte coils (see DLS data, Tables 5 and 6). As mentioned above, this was due to the screening of electrostatic repulsion with the added salt. At 0.5 mol/L KBr, all positive charges on the polymer chain are shielded, and there is no essential difference in the diffusion for **samples 1** and **2**.

In salt-free solutions, a minor difference in diffusion for the poly[C₄Vim]Br samples is most likely caused by a small difference in molecular weights. The obtained D values (Table 7) are in good agreement with the DLS data for aqueous salt solutions of PIL (Tables 5 and 6).

The diffusion of water is sensitive to salt as an additive. The water self-diffusion coefficients were $(2.02 \pm 0.01) \times 10^{-9}$ m²/s and $(2.00 \pm 0.01) \times 10^{-9}$ m²/s for 0.1 and 0.5 mol/L D₂O+KBr, respectively (and 2.3×10^{-9} m²/s for pure water). In dilute salt-free solutions of PIL, a certain fraction of water molecules is bound to the polymer chain (hydration). This leads to a decrease in the observed value of the water self-diffusion coefficient compared to that of pure water (2.3×10^{-9} m²/s). For **sample 2**, the water self-diffusion coefficient increased with increasing salt concentration, while a decrease in the size of the polymer coil occurred. The same effect was observed for **sample 1** in 0.1 mol/L KBr. For **sample 1** in 0.5 mol/L KBr, where our viscosity data reveal the salting-out effect ($k_H=0.67$, Table 4), $D_{\text{H}_2\text{O}}$ value is lower and equal to $D_{\text{H}_2\text{O}}$ in the salt-free solution. This is probably an indication of the same effect of solvent quality: in the bad solvent scenario, water molecules do not bind to the polymer and are free to move, as in the pure liquid state.

CONCLUSIONS

Two samples of poly(1-butyl-3-vinylimidazolium bromide) with slightly different molecular weights were synthesized and characterized using NMR, TGA, and DSC methods. The viscosity of solutions of poly[C₄Vim]Br in water and in aqueous salt (0.1 and 0.5 mol/L KBr) has been measured as function of polymer concentration for both samples at $T=298.15$ K. From our viscosity data, the scaling exponents, the Huggins and Kraemer coefficients, and the concentration thresholds to the semi-dilute regime have been determined. Light Scattering and NMR diffusometry techniques were applied to obtain the average molecular weight of the polymers, hydrodynamic radii, second virial coefficients, and coefficients of translational diffusion of water and polymer. Our data obtained using the different techniques

are in agreement. The observed dependence of the measured characteristics on the concentration of the polymer and salinity of the solution may be attributed to the effects of salting out and screening of electrostatic repulsion by the mobile charge. In summary, the obtained experimental data demonstrate no peculiarity in the behavior of the studied polymerized IL, which may distinguish it from a typical polyelectrolyte.^[36]

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-025-3269-y>.

Data Availability Statement

Any related data are available from the authors upon request. The author's contact information: e.a.safonova@spbu.ru.

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