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Electrical Conductances of Sodium Polystyrenesulfonate in 2-Ethoxyethanol (1) + Water (2) Mixed Solvent Media in the Presence of Sodium Chloride at (308.15, 313.15, 318.15, and 323.15) K

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The electrical conductances of solutions of an anionic polyelectrolyte sodium polystyrenesulfonate in 2-ethoxyethanol (1) + water (2) mixed solvent media containing (0.25, 0.40, and 0.50) mass fractions of 2-ethoxyethanol (w_1) have been reported at (308.15, 313.15, 318.15, and 323.15) K in the presence of sodium chloride. The conductance data have been analyzed on the basis of an equation developed in this study following the model for the electrical conductivity of salt-free polyelectrolyte solutions using the scaling description for the configuration of a semidilute polyion chain according to Dobrynin et al. (*Macromolecules* **1995**, *28*, 1859−1871). Excellent quantitative agreement between the experimental results and those obtained using the equation developed here was observed.

Introduction

We have reported the results of conductivity measurements on salt-free solutions of sodium polystyrenesulfonate in 2-ethoxyethanol (1) + water (2) mixtures in an earlier communication.[1] The addition of salts to a polyelectrolyte solution might change its conductivity behavior considerably, and hence studies on the conductivity of polyelectrolytes in the presence of a salt might help elucidate polyion−counterion interactions in polyelectrolytes with added salts.

Although the polyelectrolyte conductivities have been well-understood in salt-free solutions[2] using the scaling description for the configuration of a polyion chain according to Dobrynin et al.,[3] the situation is quite unsatisfactory for salt-containing polyelectrolyte solutions.

Devore and Manning[4] first attempted to describe the electric transport properties of polyelectrolyte solutions containing a simple salt using the Manning counterion condensation theory[5] without much success. In view of the inadequacy of the Manning theory of the electrical transport of salt-containing polyelectrolyte solutions, a phenomenological treatment of the results of conductance experiments in terms of the additivity (commonly known as the "primitive additivity") of contributions of the polyelectrolyte and the simple salt to the total specific conductance was made.[6−9]

Traditionally, this approach takes the form of an assumed additivity of the specific conductance of the polyelectrolyte and of the salt, which gives the specific conductance (κ) of the polyelectrolyte in a salt solution through the equation,

$$\kappa = \kappa_p + \kappa_s \tag{1}$$

where κ_p is the specific conductance of the polyelectrolyte in the absence of a simple salt and κ_s is the specific conductance of the simple salt in the absence of polyelectrolyte.

However, earlier investigations[10−14] suggest that the experimentally obtained specific conductances for salt-containing polyelectrolyte solutions do not, in general, agree with those predicted by simple additivity, eq 1.

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Ander et al.[10,11] modified the "primitive" additivity by taking into account the Debye−Hückel interactions between the polyion and the salt ions to give the polyelectrolyte specific conductance in a polyelectrolyte−salt solution as

$$\kappa = \kappa_p + \kappa_s(D_2/D_2^0) \tag{2}$$

where D_2 and D_2^0 are the co-ion self-diffusion coefficients in a salt-containing polyelectrolyte solution and in an infinitely dilute polyelectrolyte-free salt solution, respectively. The ratio of self-diffusion coefficients D_2/D_2^0 has been used as a quantitative measure[5] of the effective interaction of uncondensed small ions in the presence of the polyelectrolyte, and hence the effective specific conductance of the added simple salt would be $\kappa_s(D_2/D_2^0)$.

Although the "modified" additivity has been shown to be somewhat better than the "primitive" one, departures from the experimental results are still prominent.[10−14] Later Bordi et al.[15] evaluated equivalent conductances for a hydrophilic polyion in the presence of a salt in light of the scaling approach[3] and compared them with the experimental values. The agreement is rather good, although a quantitative description is still awaiting.

In this paper, a simple model is introduced to analyze the conductivity of the polyelectrolyte in the presence of an added electrolyte based on scaling theory for the conductivity of polyelectrolyte solutions.[2] This model has been extensively tested with data on sodium polystyrenesulfonate in the presence of sodium chloride in 2-ethoxyethanol−water mixed solvent media at different temperatures. The data set used here considers a number of parameters, for example, the relative permittivity of the medium, temperature, and concentration of the added salt. Moreover, three decades of concentration of the polyelectrolyte were covered. Very good quantitative agreement with only one adjustable parameter has been observed.

Theory

Here we introduce a simple equation for describing the conductivity behavior of polyelectrolyte in salt solutions fol-

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lowing the model for the electrical conductivity of solutions of polyelectrolytes without salt proposed by Colby et al.[2] using the scaling description for the configuration of a polyion chain according to Dobrynin et al.[3]

In semidilute solutions, the polyion chain is modeled as a random walk of N_ξ correlation blobs of size ξ_0, each of them containing g monomers. Each blob bears an electric charge $q_\xi = zefg$ (z being the counterion valence and e is the electronic charge), and the complete chain, of contour length $L = N_\xi \xi_0$, bears a charge $Q_p = N_\xi q_\xi = zefgN_\xi$, where f is the fraction of uncondensed counterions. Because of the strong electrostatic interactions within each correlation blob, the chain is a fully extended conformation of g_e electrostatic blobs of size ξ_e. This means that for length scales less than ξ_0, the electrostatic interactions dominate (and the chain is a fully extended conformation of electrostatic blobs of size ξ_e); for length scales greater than ξ_0, the electrostatic interactions are screened, and the chain is a random walk of correlation blobs of size ξ_0.

Following Colby et al.,[2] the specific conductivity of a salt-free semidilute polyelectrolyte solution (κ_p) is given by

$$\kappa_p = fc_p\left[\lambda_c^0 + \frac{c_p\xi_0^2 e^2 f}{3\pi\eta_0}\ln\left(\frac{\xi_0}{\xi_e}\right)\right] \tag{3}$$

where c_p is the number density of monomers, λ_c^0 the limiting equivalent conductivity of the counterions, and η_0 the coefficient of the viscosity of the medium.

The interactions between the polyion and the counterions will be modified in the presence of an electrolyte and this will result in a different level of counterion condensation, that is, in a different value of f (designated as f'). The effective specific conductivity due to the polyelectrolyte in the presence of a simple salt can be expressed as

$$\kappa_{p(eff)} = f'c_p\left[\lambda_c^0 + \frac{c_p\xi_0^2 e^2 f'}{3\pi\eta_0}\ln\left(\frac{\xi_0}{\xi_e}\right)\right] \tag{4}$$

Thus the total specific conductivity (κ) of a polyelectrolyte solution with added simple electrolyte should be equal to the sum of the specific conductivity of the simple salt in the absence of a polyelectrolyte and the effective specific conductivity due to the polyelectrolyte in the presence of a simple salt and is given by

$$\kappa = \kappa_s + f'c_p\left[\lambda_c^0 + \frac{c_p\xi_0^2 e^2 f'}{3\pi\eta_0}\ln\left(\frac{\xi_0}{\xi_e}\right)\right] \tag{5}$$

This equation (eq 5) has one adjustable parameter, f', and this could be obtained by the method of a least-squares fit of the experimental specific conductivity of the polyelectrolyte solution (κ) in the presence of a salt to eq 5 using the measured specific conductance (κ_s) of the salt in the absence of the polyelectrolyte. This value of f' takes care of the changed polyion−counterion interactions under the influence of the added salt. The second term in eq 5 is the actual contribution of the polyelectrolyte species toward the total specific conductivity in the presence of an added salt.

Experimental Section

2-Ethoxyethanol (Merck) was distilled with phosphorus pentoxide and then redistilled over calcium hydride. The purified solvent had a density of 0.92497 $g\cdot cm^{-3}$ and a coefficient of viscosity of 1.8277 mPa·s at 308.15 K; these values are in good agreement with literature values.[6] Triply distilled water with a specific conductance of about 10^{-6} $S\cdot cm^{-1}$ at 308.15 K was used for the preparation of the mixed solvents. The relative permittivities of 2-ethoxyethanol (1) + water (2) mixtures at the experimental temperatures were obtained with the equations as described in the literature[4] using the literature density and relative permittivity data of the pure solvents,[6,16] and the densities of the mixed solvents are given in Table 1.

Table 1. Properties of 2-Ethoxyethanol (1) + Water (2) Mixtures Containing 0.25, 0.40, and 0.50 Mass Fraction of 2-Ethoxyethanol at (308.15, 313.15, 318.15, and 323.15) K

T / K	density / $g\cdot cm^{-3}$	η_0 / mPa·s	ε
	$w_1 = 0.25$		
308.15	0.99758	1.8430	60.13
313.15	0.99245	1.5293	58.70
318.15	0.98807	1.2738	57.37
323.15	0.98394	1.0923	56.11
	$w_1 = 0.40$		
308.15	0.99747	1.9545	50.54
313.15	0.99101	1.7015	49.28
318.15	0.98696	1.4274	48.14
323.15	0.98378	1.2317	47.10
	$w_1 = 0.50$		
308.15	0.99361	1.9234	44.30
313.15	0.98514	1.7195	43.03
318.15	0.98004	1.4552	41.95
323.15	0.97610	1.2762	40.96

The sodium salt of polystyrenesulfonate (NaPSS) employed in these investigations was purchased from the Aldrich Chemical Co. The average molecular weight of the sample was about 70 000 $g\cdot mol^{-1}$, and a degree of sulfonation of 1.0 was purified by dialysis.[17,18] The molecular weight reported by the manufacturer agreed well with that determined in the present study obtained in the presence of 0.05 M sodium chloride (NaCl) at 298.15 K using the Mark−Houwink relationship,[19] $[\eta] = 1.39\cdot 10^{-4}M^{0.72}$, where $[\eta]$ is the intrinsic viscosity and M is the average molecular weight. The absorption coefficient of the NaPSS solutions used at 261 nm, which is considered to be a characteristic indicator of the sample purity,[18] is found to be 400 $dm^3\cdot cm^{-1}\cdot mol^{-1}$. A spectroscopic examination of the polyelectrolyte sample using this criterion was employed periodically to substantiate the sample purity. Sodium chloride (Fluka) was of puriss grade. This was dried in vacuo for a prolonged period immediately before use and was used without further purification.

Conductance measurements were carried out on a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell with a cell constant of 1.15 cm^{-1} and having an uncertainty of 0.01 %. The cell was calibrated by the method of Lind and co-workers[16] using aqueous potassium chloride solution. The measurements were made in a water bath maintained within ± 0.01 K of the desired temperature. The details of the experimental procedure have been described earlier.[9,20] Several independent solutions were prepared, and runs were performed to ensure the reproducibility of the results.

To avoid moisture pickup, all solutions were prepared in a dehumidified room with utmost care. In all cases, the experiments were performed at least in three replicates. The experimental uncertainties in density, viscosity, and conductivity were always within 0.02 %, 0.80 %, and 0.30 %, respectively.

Results and Discussion

The experimental values of specific conductivities (κ) of sodium polystyrenesulfonate in the presence of varying con-

Table 2. Specific Conductance Values of Sodium Polystyrenesulfonate (NaPSS) in the Presence of NaCl at Temperatures of (308.15, 313.15, 318.15 and 323.15) K in 2-Ethoxyethanol (1) + Water (2) Mixed Solvent Media

308.15 K		313.15 K		318.15 K		323.15 K	
$c_p \cdot 10^{-4}$ eqv·L^{-1}	κ μS·cm^{-1}	$c_p \cdot 10^{-4}$ eqv·L^{-1}	κ μS·cm^{-1}	$c_p \cdot 10^{-4}$ eqv·L^{-1}	κ μS·cm^{-1}	$c_p \cdot 10^{-4}$ eqv·L^{-1}	κ μS·cm^{-1}
$w_1 = 0.25$							
$c_{NaCl} = 0.0001$ mol·L^{-1}							
102.70	411.70	95.24	438.00	96.10	487.00	106.19	533.00
77.02	316.00	71.43	348.00	72.07	384.00	79.64	442.00
57.77	245.70	53.57	269.00	54.05	300.00	59.73	345.00
43.33	189.70	40.18	208.00	40.54	232.00	44.80	263.00
32.49	146.20	30.13	161.00	30.41	181.00	33.60	199.00
24.37	113.70	22.60	126.00	22.80	141.00	25.20	160.00
18.28	88.70	16.95	98.60	17.10	111.00	18.90	122.00
13.71	70.80	12.71	77.90	12.83	88.10	14.17	98.00
10.28	55.20	9.53	62.60	9.62	71.20	10.63	77.20
7.71	45.30	7.15	50.90	7.22	57.60	7.97	63.10
5.78	36.70	5.36	41.90	5.41	47.70	5.98	52.90
4.34	31.70	4.02	35.00	4.06	40.10	4.49	43.50
3.25	27.80	3.02	29.80	3.04	34.30	3.36	37.50
2.44	24.20	2.26	26.00	2.28	29.80	2.52	33.50
1.83	21.80	1.70	23.00	1.71	26.60	1.89	29.50
1.37	19.70	1.27	31.00	1.28	24.20	1.42	26.60
1.03	18.10	0.95	19.80	0.96	22.40	1.06	24.30
0.77	16.80	0.72	19.10	0.72	21.00	0.80	23.20
0.58	15.70	0	18.00	0.54	19.90	0.60	22.00
0.43	15.10			0.41	19.20	0.45	21.00
0.33	14.50			0	18.80	0.34	20.30
0.24	14.16					0.25	19.80
0.18	14.05					0.19	19.30
0.14	13.95					0	18.50
0	13.70						
$c_{NaCl} = 0.001$ mol·L^{-1}							
101.70	458.50	100.29	498.00	104.57	570.00	100.48	588.00
76.27	364.40	75.22	417.00	78.43	478.00	64.31	442.00
57.21	296.40	56.41	334.20	58.82	392.00	51.44	377.00
42.90	240.40	42.31	274.20	44.12	324.00	41.16	322.00
32.18	200.40	31.73	225.20	33.09	270.00	32.92	274.00
24.13	168.40	23.80	197.20	24.82	230.00	26.34	246.00
18.10	145.40	17.85	171.20	18.61	200.00	21.07	217.00
13.57	125.40	13.39	154.00	13.96	176.00	16.86	198.00
10.18	112.40	10.04	137.20	10.47	159.00	13.49	176.00
7.64	101.40	7.53	124.20	7.85	145.00	10.79	163.00
5.73	94.80	5.65	114.20	5.89	135.00	8.63	151.00
4.30	89.40	4.24	106.20	4.42	126.00	6.90	146.00
3.22	86.40	3.18	101.20	3.31	120.00	5.52	142.00
2.42	83.20	2.38	98.00	2.48	116.00	4.42	136.00
1.81	80.50	1.79	97.00	1.86	112.00	3.54	132.00
1.36	78.60	1.34	95.80	1.40	109.80	2.83	129.00
1.02	77.40	1.01	95.50	1.05	108.20	2.26	126.00
0.76	76.40	0.75	95.00	0.79	106.90	1.81	124.00
0.57	75.60	0.57	94.70	0.59	106.00	1.45	122.00
0.43	75.20	0.42	94.50	0.44	105.40	1.16	120.00
0.32	74.73	0.32	94.30	0.33	105.36	0.93	119.00
0.24	74.67	0.24	94.28	0.25	105.32	0.74	118.00
0.18	74.55	0.18	94.26	0.19	105.29	0.59	116.70
0.14	74.51	0.13	94.23	0.14	105.27	0.47	116.00
0	74.40	0.10	94.21	0.10	105.25	0	114.00
		0	94.20	0	105.00		
$c_{NaCl} = 0.01$ mol·L^{-1}							
108.00	1150.00	99.62	1250.00	95.90	1387.00	102.57	1610.00
81.00	1050.00	74.71	1174.00	71.93	1289.00	76.93	1510.00
60.75	979.00	56.04	1100.00	53.95	1210.00	57.70	1422.00
45.56	923.00	42.03	1042.00	40.46	1150.00	43.27	1346.00
34.17	885.00	31.52	1000.00	30.35	1110.00	32.45	1298.00
25.63	853.00	23.64	970.00	22.76	1070.00	24.34	1262.00
19.22	830.00	17.73	946.00	17.07	1044.00	18.26	1234.00
14.42	810.00	13.30	928.00	12.80	1027.00	13.69	1207.00
10.81	797.00	7.98	902.00	9.60	1012.00	10.27	1192.00
8.11	786.00	6.38	891.00	7.20	1002.00	7.70	1182.00
6.08	780.00	5.11	887.00	5.40	990.00	5.78	1176.00
4.56	776.00	4.09	881.00	4.05	984.00	4.33	1169.00
3.42	774.40	3.27	877.00	3.04	979.00	3.25	1165.00
2.57	772.50	2.61	875.00	2.28	976.00	2.44	1161.00
1.92	770.40	2.09	874.00	1.71	974.20	1.83	1159.00
1.44	769.60	1.67	873.00	1.28	972.60	1.37	1156.80

Table 2 Continued

308.15 K		313.15 K		318.15 K		323.15 K	
$c_p \cdot 10^{-4}$ eqv·L^{-1}	κ μS·cm^{-1}	$c_p \cdot 10^{-4}$ eqv·L^{-1}	κ μS·cm^{-1}	$c_p \cdot 10^{-4}$ eqv·L^{-1}	κ μS·cm^{-1}	$c_p \cdot 10^{-4}$ eqv·L^{-1}	κ μS·cm^{-1}
1.15	768.80	1.34	872.80	0.96	971.20	1.03	1155.00
0.90	768.00	1.07	872.60	0.72	970.30	0.77	1153.50
0	767.00	0.86	872.50	0.54	969.42	0.58	1152.00
		0.69	872.40	0.41	969.33	0.43	1151.30
		0.55	872.30	0.30	969.29	0.33	1151.10
		0.44	872.20	0.23	969.28	0.24	1150.80
		0.35	872.10	0.17	969.26	0.18	1150.62
		0.28	872.08	0.13	969.24	0.14	1150.22
		0.23	872.05	0.10	969.20	0.10	1150.16
		0.00	872.00	0	969.00	0	1150.00
$w_1 = 0.40$							
$c_{NaCl} = 0.0001$ mol·L^{-1}							
103.14	285.00	103.05	282.00	100.19	333.00	99.81	358.00
77.36	221.00	77.29	229.00	75.14	268.00	74.86	295.00
58.02	172.00	57.96	177.00	56.36	212.00	56.14	227.00
43.51	133.00	43.47	139.10	42.27	167.00	42.11	174.00
32.63	103.00	32.61	100.00	31.70	131.00	31.58	133.00
24.48	81.00	24.45	78.70	23.78	102.00	23.69	102.00
18.36	64.40	18.34	63.70	17.83	81.20	17.76	79.50
13.77	51.40	13.76	49.10	13.37	64.80	13.32	60.20
10.33	41.60	10.32	39.30	10.03	52.50	9.99	47.60
7.74	34.10	7.74	29.40	7.52	43.70	7.49	39.30
5.81	28.50	5.80	27.00	5.64	36.40	5.62	32.50
4.36	24.30	4.35	22.20	4.23	31.20	4.22	29.00
3.27	21.00	3.26	18.60	3.17	27.10	3.16	25.60
2.45	18.50	2.45	16.70	2.38	23.90	2.37	22.52
1.84	16.60	1.84	14.30	1.79	21.50	1.78	20.50
1.38	15.10	1.38	13.10	1.34	19.90	1.33	19.10
1.03	14.00	1.03	11.60	1.00	18.80	1.00	17.80
0.78	13.20	0.77	11.50	0.75	18.00	0.75	16.60
0.58	12.70	0.58	11.20	0.60	17.30	0.56	15.80
0.44	12.10	0.44	11.00	0.48	16.80	0.42	15.20
0.33	11.80	0.33	10.28	0.39	16.30	0.32	14.70
0.24	11.50	0.25	10.22	0.31	15.90	0.24	14.50
0.18	11.30	0.18	10.18	0.25	15.60	0.18	14.40
0.14	11.20	0.14	10.16	0.20	15.40	0.13	14.30
0.10	11.10	0.10	10.13	0.16	15.1	0.10	14.20
0	11.00	0	10.10	0	14.80	0	13.80
$c_{NaCl} = 0.001$ mol·L^{-1}							
104.85	308.00	98.10	317.00	101.71	377.40	104.29	426.90
78.64	239.00	73.57	270.00	76.28	307.00	78.22	358.90
58.99	199.00	55.18	222.00	57.21	253.00	58.66	296.90
44.23	161.00	41.38	188.00	42.91	207.00	44.00	242.10
33.17	131.00	31.04	150.00	32.18	172.00	33.00	198.00
24.88	111.00	23.28	132.00	24.14	149.00	24.75	169.00
18.66	96.00	17.46	113.00	18.10	130.00	18.56	144.70
13.99	82.80	13.09	107.00	13.58	118.00	13.92	132.80
10.50	73.20	9.82	96.00	10.18	107.00	10.44	120.70
7.87	65.60	7.37	87.40	7.64	101.00	7.83	109.00
5.90	60.20	5.52	82.70	5.73	96.40	5.87	104.00
4.43	56.10	4.14	79.60	4.30	92.50	4.40	101.00
3.32	53.00	3.11	74.60	3.22	88.70	3.30	98.00
2.49	50.70	2.33	74.50	2.42	85.50	2.48	95.40
1.87	48.70	1.75	72.00	1.81	83.60	1.86	93.30
1.40	47.40	1.31	70.60	1.36	82.20	1.39	91.90
1.05	46.40	0.98	70.50	1.02	81.10	1.05	90.40
0.79	45.70	0.74	70.50	0.76	80.40	0.78	89.40
0.59	45.35	0.55	70.20	0.57	79.70	0.59	88.50
0.44	44.83	0.41	69.90	0.43	79.20	0.44	87.90
0.33	44.61	0.31	69.60	0.32	78.62	0.33	87.50
0.25	44.39	0.23	69.57	0.24	78.40	0.25	87.30
0.19	44.21	0.17	69.55	0.18	78.00	0.19	87.20
0.14	44.13	0.13	69.59	0.14	77.92	0.14	87.10
0.11	44.07	0.10	69.51	0.10	77.67	0.10	87.00
0	44.00	0	69.50	0	77.40	0	86.70
$c_{NaCl} = 0.01$ mol·L^{-1}							
104.95	799.00	100.00	828.00	100.38	903.00	99.14	950.00
78.71	730.00	75.00	786.00	75.29	833.00	74.36	890.00
59.04	690.00	56.25	742.00	56.46	778.00	55.77	828.00
44.28	659.00	42.19	709.00	42.35	741.00	41.83	781.00
33.21	632.00	31.64	686.00	31.76	711.00	31.37	740.00
24.91	612.00	23.73	664.00	23.82	691.00	23.53	709.00

Table 2 Continued

308.15 K		313.15 K		318.15 K		323.15 K	
$c_p \cdot 10^{-4}$ eqv·L^{-1}	κ μS·cm^{-1}	$c_p \cdot 10^{-4}$ eqv·L^{-1}	κ μS·cm^{-1}	$c_p \cdot 10^{-4}$ eqv·L^{-1}	κ μS·cm^{-1}	$c_p \cdot 10^{-4}$ eqv·L^{-1}	κ μS·cm^{-1}
18.68	600.00	17.80	647.00	17.87	676.00	17.65	691.00
14.01	587.00	13.35	639.00	13.40	667.00	13.23	679.00
10.51	577.00	10.01	628.00	10.05	663.00	9.93	670.00
7.88	570.00	7.51	621.00	7.54	660.00	7.44	664.00
5.91	565.00	5.63	618.00	5.65	659.00	5.58	660.00
4.43	561.00	4.22	614.00	4.24	656.00	4.19	655.90
3.32	558.00	3.17	610.00	3.18	652.00	3.14	653.00
2.49	555.50	2.38	611.00	2.38	650.00	2.36	651.00
1.87	553.50	1.78	608.00	1.79	648.50	1.77	649.50
1.40	552.60	1.34	607.18	1.34	647.20	1.32	648.00
1.05	551.80	1.00	607.18	1.01	646.20	0.99	647.00
0.79	551.40	0.75	608.00	0.75	645.70	0.75	646.00
0.59	551.00	0.56	608.00	0.57	645.00	0.56	645.60
0.44	550.60	0.42	607.20	0.42	644.60	0.42	645.30
0.33	550.44	0.32	607.19	0.32	644.00	0.31	645.22
0.25	550.27	0.24	607.18	0.24	643.80	0.24	645.18
0.19	550.13	0.18	607.18	0.18	643.40	0.18	645.16
0.14	550.08	0.13	607.18	0.13	643.33	0.13	645.14
0.11	550.03	0.10	607.17	0.10	643.20	0.10	645.12
0	550.00	0	607.00	0	643.00	0	645.00
$w_1 = 0.50$							
$c_{NaCl} = 0.0001$ mol·L^{-1}							
114.38	236.00	96.38	217.00	105.90	254.00	107.24	298.00
85.79	182.00	72.29	176.00	79.43	206.50	80.43	232.90
64.34	142.00	54.21	137.00	59.57	162.50	60.32	181.00
48.25	110.00	40.66	107.00	44.68	125.00	45.24	140.00
36.19	86.90	30.50	85.30	33.51	100.00	33.93	110.00
27.14	68.30	22.87	68.30	25.13	79.60	25.45	86.00
20.36	54.20	17.15	55.30	18.85	62.60	19.09	66.90
15.27	43.50	12.87	45.00	14.14	51.70	14.31	55.20
11.45	35.10	9.65	37.40	10.60	41.10	10.74	45.00
8.59	28.60	7.24	31.40	7.95	34.10	8.05	37.40
6.44	23.60	5.43	26.70	5.96	29.00	6.04	31.60
4.83	19.90	4.07	23.30	4.47	25.00	4.53	26.80
3.62	17.00	3.05	20.60	3.35	22.10	3.40	23.60
2.72	14.90	2.29	18.60	2.52	19.50	2.55	21.40
2.04	13.20	1.72	16.90	1.89	18.40	1.91	19.60
1.53	12.00	1.29	15.70	1.42	16.70	1.43	18.00
1.15	11.00	0.97	14.70	1.06	15.90	1.07	16.70
0.86	10.20	0.72	13.80	0.80	15.00	0.81	15.90
0.64	9.70	0.54	13.00	0.60	14.30	0.60	15.10
0.48	9.25	0.41	12.80	0.45	13.80	0.45	14.60
0.36	8.90	0.31	12.40	0.34	13.48	0.34	14.20
0.27	8.69	0.23	12.15	0.25	13.30	0.26	13.90
0.20	8.52	0.17	11.98	0.19	13.05	0.19	13.70
0.15	8.41	0.13	11.74	0.14	12.88	0.14	13.64
0.11	8.31	0.10	11.68	0.11	12.76	0.11	13.63
0	8.21	0	11.40	0	12.50	0	13.60
$c_{NaCl} = 0.001$ mol·L^{-1}							
98.86	201.00	102.57	263.00	98.38	286.00	100.48	336.00
74.14	159.00	76.93	220.00	73.79	240.50	75.36	272.70
55.61	125.00	57.70	185.00	55.34	199.50	56.52	224.10
41.71	98.00	43.27	155.00	41.50	163.50	42.39	185.00
31.28	78.00	32.45	134.00	31.13	137.50	31.79	157.70
23.46	61.00	24.34	115.00	23.35	122.50	23.84	135.00
17.59	48.90	18.26	101.80	17.51	107.50	17.88	120.00
13.20	39.90	13.69	92.80	13.13	97.50	13.41	108.00
9.90	32.90	10.27	80.40	9.85	88.10	10.06	99.10
7.42	27.80	7.70	75.20	7.39	81.50	7.54	92.50
5.57	24.20	5.78	71.70	5.54	76.10	5.66	87.30
4.18	21.30	4.33	69.10	4.16	73.40	4.24	82.80
3.13	19.00	3.25	67.00	3.12	70.50	3.18	80.30
2.35	17.30	2.44	65.50	2.34	69.00	2.39	77.80
1.76	16.00	1.83	64.40	1.75	68.10	1.79	76.30
1.32	15.00	1.37	63.10	1.31	66.60	1.34	75.20
0.99	14.40	1.03	62.10	0.99	66.20	1.01	74.40
0.74	14.00	0.77	61.20	0.74	65.90	0.76	73.90
0.56	13.50	0.58	60.40	0.55	65.70	0.57	73.60
0.42	13.20	0.43	60.30	0.42	65.50	0.42	73.40
0.31	12.80	0.33	60.00	0.31	65.30	0.32	73.10
0.24	12.80	0.24	59.76	0.23	65.13	0.24	72.86
0	12.50	0.18	59.61	0.18	64.92	0.18	72.76

Table 2 Continued

308.15 K		313.15 K		318.15 K		323.15 K	
$c_p \cdot 10^{-4}$ eqv·L^{-1}	κ μS·cm^{-1}	$c_p \cdot 10^{-4}$ eqv·L^{-1}	κ μS·cm^{-1}	$c_p \cdot 10^{-4}$ eqv·L^{-1}	κ μS·cm^{-1}	$c_p \cdot 10^{-4}$ eqv·L^{-1}	κ μS·cm^{-1}
		0.14	59.42	0.13	64.80	0.13	72.72
		0.10	59.36	0.10	64.68	0.10	72.71
		0	59.10	0	64.50	0	72.70
$c_{NaCl} = 0.01$ mol·L^{-1}							
100.29	587.00	117.62	680.00	101.43	751.00	101.52	872.00
75.21	571.00	88.21	638.00	76.07	716.00	76.14	805.00
56.41	555.00	66.16	608.00	57.05	675.00	57.11	755.00
42.31	543.00	49.62	587.00	42.79	635.00	42.83	721.00
31.73	529.00	37.22	566.00	32.09	612.00	32.12	700.00
23.80	522.00	27.91	553.00	24.07	599.00	24.09	681.00
17.85	517.00	20.93	541.00	18.05	586.00	18.07	668.00
13.39	511.00	15.70	536.00	13.54	576.00	13.55	656.00
10.04	508.00	11.78	527.00	10.15	567.00	10.16	648.00
7.53	502.00	8.83	518.00	7.62	563.00	7.62	641.00
5.65	500.00	6.62	511.00	5.71	557.00	5.72	636.00
4.24	498.00	4.97	509.00	4.28	556.10	4.29	631.00
3.18	496.00	3.73	506.50	3.21	554.70	3.22	629.00
2.38	494.00	2.79	502.20	2.41	553.80	2.41	627.00
1.79	493.00	2.10	499.00	1.81	553.00	1.81	625.50
1.34	492.00	1.57	497.00	1.36	551.70	1.36	624.10
1.01	491.00	1.18	495.00	1.02	551.40	1.02	624.00
0.75	490.89	0.88	493.40	0.76	551.20	0.76	623.80
0.57	490.60	0.66	493.20	0.57	551.00	0.57	623.60
0.42	490.49	0.50	493.00	0.43	550.80	0.43	623.40
0.32	490.41	0.37	492.80	0.32	550.60	0.32	623.20
0.24	490.29	0.28	492.71	0.24	550.40	0.24	623.10
0.18	490.18	0.21	492.49	0.18	550.30	0.18	623.04
0.13	490.14	0.16	492.28	0.14	550.17	0.14	623.01
0.10	490.11	0.12	492.25	0.10	550.12	0.10	623.01
0	489.97	0	492.00	0	550.00	0.00	623.00

centrations of sodium chloride in 2-ethoxyethanol (1) + water (2) mixtures have been listed as a function of the equivalent polyelectrolyte concentration (c_p) at (308.15, 313.15, 318.15, and 323.15) K in Table 2. The specific conductivities of NaPSS as a function of the polymer concentration at given temperatures and solvent compositions in 2-ethoxyethanol (1) + water (2) mixtures with varying amounts of added NaCl are shown in the representative Figures 1 through 4. Figures 5 and 6, on the other hand, demonstrate the influence of temperature on the specific conductivity versus the polymer concentration profiles. From these figures and also from Table 2, it is apparent that for all of the solutions studied the specific conductivities increase with polyelectrolyte concentration. The addition of salt increases the specific conductances of the polyelectrolyte−salt solutions as expected. The specific conductances of the polyelectrolyte−salt systems are, in general, found to decrease with an increasing amount of 2-ethoxyethanol in the mixed solvent media (shown in the representative Figure 7).

Since the present 2-ethoxyethanol (1) + water (2) mixtures are poor solvents for the uncharged polymer polystyrene, the electrostatic blob is collapsed into a dense globule, and we use a value of 5 Å as the effective monomer size (b) as suggested by Colby et al.[2]

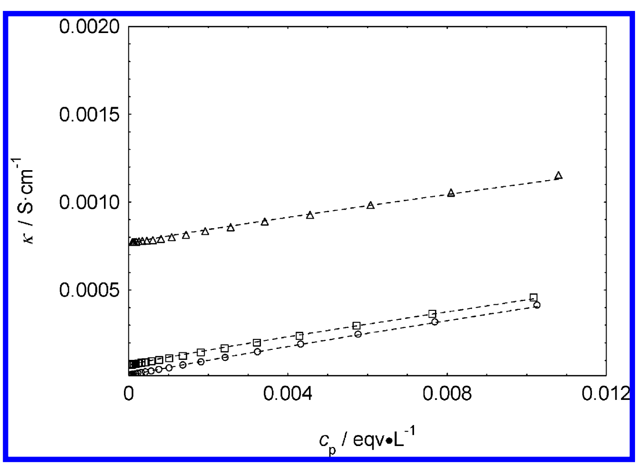

Figure 1. Specific conductivities of NaPSS as a function of the polymer concentration (c_p) at 308.15 K in a 2-ethoxyethanol (1) + water (2) mixture with $w_1 = 0.25$. Experimental: open symbols represent experimental values, whereas the dashed lines are according to eq 5. Circles, squares, and triangles represent the polyelectrolyte solutions in the presence of (0.0001, 0.001, and 0.01) mol·L^{-1} NaCl, respectively (see text).

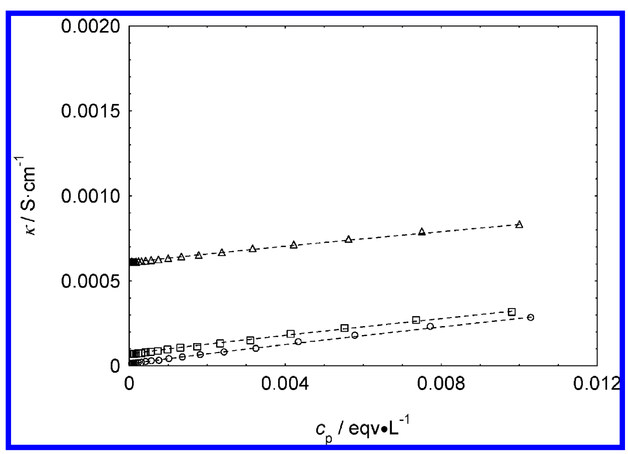

Figure 2. Specific conductivities of NaPSS as a function of the polymer concentration (c_p) at 313.15 K in a 2-ethoxyethanol (1) + water (2) mixture with $w_1 = 0.40$. Experimental: open symbols represent experimental values, whereas the dashed lines are according to eq 5. Circles, squares, and triangles represent the polyelectrolyte solutions in the presence of (0.0001, 0.001, and 0.01) mol·L^{-1} NaCl, respectively (see text).

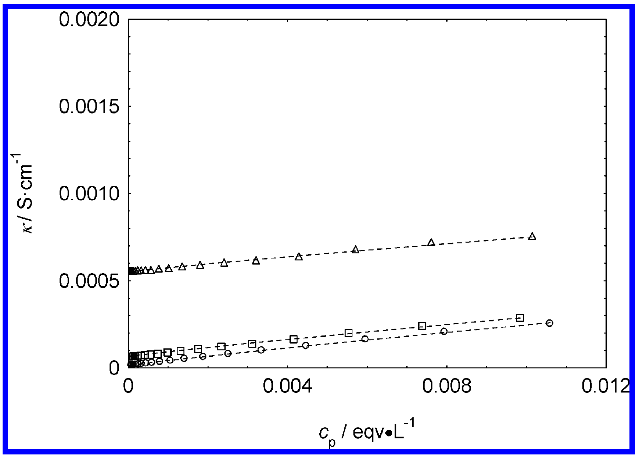

Figure 3. Specific conductivities of NaPSS as a function of the polymer concentration (c_p) at 318.15 K in a 2-ethoxyethanol (1) + water (2) mixture with $w_1 = 0.50$. Experimental: open symbols represent experimental values, whereas the dashed lines are according to eq 5. Circles, squares, and triangles represent the polyelectrolyte solutions in the presence of (0.0001, 0.001, and 0.01) mol·L^{-1} NaCl, respectively (see text).

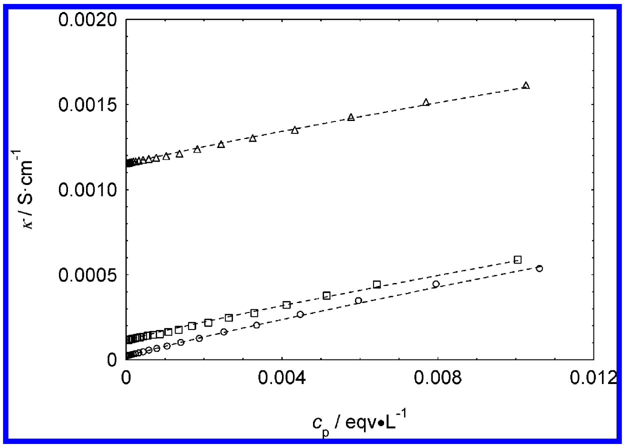

Figure 4. Specific conductivities of NaPSS as a function of the polymer concentration (c_p) at 323.15 K in a 2-ethoxyethanol (1) + water (2) mixture with $w_1 = 0.25$. Experimental: open symbols represent experimental values, whereas the dashed lines are according to eq 5. Circles, squares, and triangles represent the polyelectrolyte solutions in the presence of (0.0001, 0.001, and 0.01) mol·L^{-1} NaCl, respectively (see text).

Under poor solvent conditions, the electrostatic blob size (ξ_e) and the correlation blob size (ξ_0) are given by[2]

$$\xi_e = bf'^{-2}\xi^{-1/3} \tag{6}$$

$$\xi_0 = (cb)^{-1/2}f'^{-2}\xi^{-1/3} \tag{7}$$

The specific conductivity values of the polyelectrolyte−salt system as a function of polyelectrolyte concentration in a given solvent medium at a given temperature and for a given salt concentration were fitted to eq 5 by the method of least-squares analysis. The best-fitted f' values along with the standard deviations are reported in Table 3. In the representative Figures 1 to 4 we compare the calculated specific conductivities using the f' values obtained in the semidilute regime (reported in Table 3) with those obtained experimentally. From the standard deviations recorded in Table 3, as well as from an inspection of these figures, it is directly evident that the present method of analysis reproduced the experimental results even in dilute solutions quite satisfactorily. It should be noted that this vigorous test of the proposed model has been performed with 36 sets of data considering the effects of medium, temperature, and

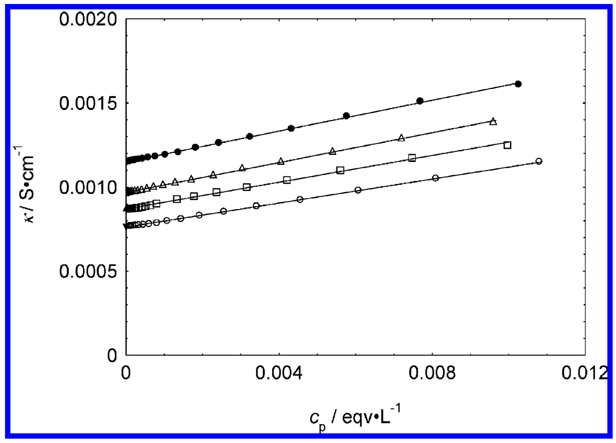

Figure 5. Specific conductivities of NaPSS as a function of the polymer concentration (c_p) at temperatures of ○, 308.15 K; □, 313.15 K; △, 318.15 K; and ●, 323.15 K in a 2-ethoxyethanol (1) + water (2) mixture with $w_1 = 0.25$ in the presence of 0.01 mol·L^{-1} NaCl. Lines are used to guide the eye.

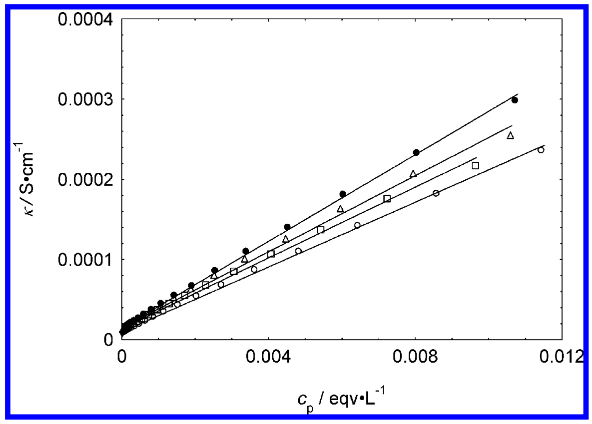

Figure 6. Specific conductivities of NaPSS as a function of the polymer concentration (c_p) at temperatures of ○, 308.15 K; □, 313.15 K; △, 318.15 K; and ●, 323.15 K in a 2-ethoxyethanol (1) + water (2) mixture with $w_1 = 0.50$ in the presence of 0.0001 mol·L^{-1} NaCl. Lines are used to guide the eye.

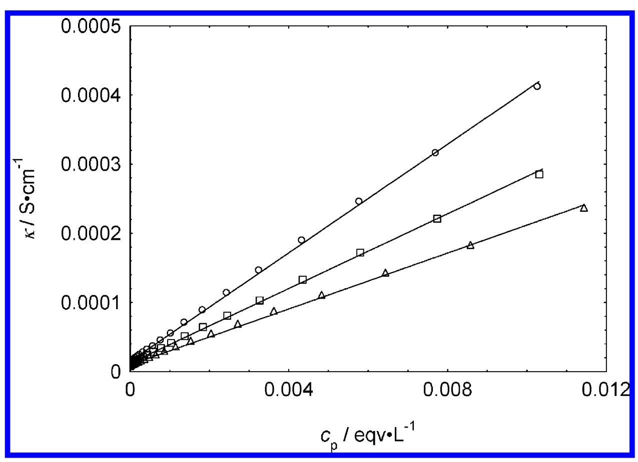

Figure 7. Specific conductivities of NaPSS as a function of the polymer concentration (c_p) at a temperature of 308.15 K in a 2-ethoxyethanol (1) + water (2) mixture with w_1 = ○, 0.50; □, 0.40; and △, 0.50 in the presence of 0.0001 mol·L^{-1} NaCl. Lines are used to guide the eye.

concentration of the added simple salt. We have, thus, been able to develop a simple model in describing the specific conductivity behavior of polyelectrolyte solutions with added salt. Further studies on the application of this model to other polyelectrolyte−salt systems in different mixed solvent media are presently under investigation.

Table 3. Fraction of Uncondensed Counterions (f') and the Standard Deviations (σ) of Fit for Sodium Polystyrenesulfonate (NaPSS) in the Presence of NaCl at Temperatures (308.15, 313.15, 318.15, and 323.15) K in 2-Ethoxyethanol (1) + Water (2) Mixed Solvent Media as Obtained According to Equation 5

temperature K	mass fraction (w_1)	C_{NaCl} mol·L^{-1}	f'	$\sigma \cdot 10^6$
308.15	0.25	$1 \cdot 10^{-4}$	0.40	3.09
		$1 \cdot 10^{-3}$	0.38	4.59
		$1 \cdot 10^{-2}$	0.34	10.06
	0.40	$1 \cdot 10^{-4}$	0.25	1.14
		$1 \cdot 10^{-3}$	0.23	1.82
		$1 \cdot 10^{-2}$	0.21	2.37
	0.50	$1 \cdot 10^{-4}$	0.25	0.74
		$1 \cdot 10^{-3}$	0.24	1.52
		$1 \cdot 10^{-2}$	0.21	2.91
313.15	0.25	$1 \cdot 10^{-4}$	0.40	5.19
		$1 \cdot 10^{-3}$	0.35	6.29
		$1 \cdot 10^{-2}$	0.33	6.82
	0.40	$1 \cdot 10^{-4}$	0.23	3.40
		$1 \cdot 10^{-3}$	0.21	4.01
		$1 \cdot 10^{-2}$	0.18	3.77
	0.50	$1 \cdot 10^{-4}$	0.25	1.13
		$1 \cdot 10^{-3}$	0.23	1.65
		$1 \cdot 10^{-2}$	0.18	5.60
318.15	0.25	$1 \cdot 10^{-4}$	0.38	3.84
		$1 \cdot 10^{-3}$	0.35	4.26
		$1 \cdot 10^{-2}$	0.32	5.67
	0.40	$1 \cdot 10^{-4}$	0.25	2.45
		$1 \cdot 10^{-3}$	0.22	3.62
		$1 \cdot 10^{-2}$	0.17	8.48
	0.50	$1 \cdot 10^{-4}$	0.23	1.69
		$1 \cdot 10^{-3}$	0.21	2.76
		$1 \cdot 10^{-2}$	0.18	5.08
323.15	0.25	$1 \cdot 10^{-4}$	0.34	6.33
		$1 \cdot 10^{-3}$	0.31	7.65
		$1 \cdot 10^{-2}$	0.28	7.57
	0.40	$1 \cdot 10^{-4}$	0.24	4.87
		$1 \cdot 10^{-3}$	0.22	5.61
		$1 \cdot 10^{-2}$	0.20	7.69
	0.50	$1 \cdot 10^{-4}$	0.23	2.32
		$1 \cdot 10^{-3}$	0.22	3.90
		$1 \cdot 10^{-2}$	0.19	5.10

Conclusions

The electrical conductances of the solutions of sodium polystyrenesulfonate in 2-ethoxyethanol (1) + water (2) mixed solvent media containing (0.25, 0.40, and 0.50) mass fractions of 2-ethoxyethanol (w_1) have been reported at (308.15, 313.15, 318.15, and 323.15) K in the presence of sodium chloride. The conductance data have been analyzed on the basis of a simple equation with only one adjustable parameter developed in the present study following the model for the electrical conductivity of solutions of semidilute polyelectrolytes without salt proposed by Colby et al.[2] using the scaling description for the configuration of a polyion chain according to Dobrynin et al.[3] Excellent agreement between the experimental results and those obtained using eq 5 has always been observed. We expect that the model proposed here provides a universal description of the specific conductivities of polyelectrolyte solutions in the presence of an added electrolyte. Further studies on the application of this model to other polyelectrolyte−salt systems in various other mixed solvent media are presently under investigation.

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