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Partial Molar and Specific Volumes of Polyelectrolytes: Comparison of Experimental and Predicted Values in Salt-free Solutions[†]

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The partial molar volume, \bar{V} , and the partial specific volume, \bar{v} , were estimated for more than 25 polyelectrolyte structures. The materials investigated by density measurements in highly diluted aqueous solutions ($c < 10^{-2}$ monomol/L) included both synthetic polyelectrolytes and chemically modified natural polymers. Through a detailed analysis, related to the chemical structure and macromolecular parameters, a linear dependence between the copolymer composition and the partial volumes could be identified for diallyldimethylammonium chloride/acrylamide copolymers. Additivity could also be shown for sodium cellulose sulfate having various degrees of substitution. For a homologous series of poly(vinylbenzyltri-alkylammonium chloride)s, a linear correlation between the molar mass of the monomer unit and the partial molar volume was obtained. No influence of the degree of polymerization was observed as long as the contour length exceeds the Debye length. The experimental results were used to evaluate the general applicability of the additivity schemes of Durchschlag and Zipper, as well as Gianni and Lepori, to polyelectrolytes. Agreement between experimental and calculated partial volumes strongly depends on the chemical structures. In the case of the synthetic polycations, the deviations are in a similar range for both models though somewhat smaller for the Gianni/Lepori model. The use of the Durchschlag/Zipper model yields much better agreement for the anionic biopolymers with deviations generally less than 3%. The tendency of the empirical models is correct; however, the precision may be improved by regressing of parameters from the experimental results. The new experimental data may also be useful in polyelectrolyte characterization.

Introduction

A detailed understanding of the solution behavior of polyelectrolytes requires information on a variety of chemical and physical parameters. The partial molar and specific volumes are two important thermodynamic properties which may be helpful in the identification of solvent–solute, as well as solute–solute, interactions. Moreover, these volumes are necessary for the application of characterization methods and physicochemical techniques including preparative and analytical ultracentrifugation, as well as small-angle X-ray and neutron scattering. Thus far, a molecular theory of partial volumes of polyelectrolytes which considers all types of interactions in polyelectrolyte solutions has not been available. Recently, empirical procedures have been developed to calculate and predict partial specific and partial molar volumes for nonionic and ionic organic compounds in aqueous solutions.^{1,2} However, the evaluation of these procedures for polyelectrolytes is limited by the lack of availability of reliable experimental data of a broad variety of chemical structures and macromolecular characteristics.

Partial volumes can be determined experimentally, for example, through density measurements. Unfortunately, much of the data provided in the literature results from measurements carried out prior to the development of high-precision techniques,^{3–8} or via extrapolations based on an insufficient number of data points.⁹ Often different values are reported for the same chemical structure.^{3,5,6}

Inaccuracies may result from insufficient purity, uncertainties in sample concentration and sample composition, or handling problems such as incomplete dissolution particularly of high molar mass polyelectrolytes. The effect of concentration and molar mass on the partial volumes has been studied for several polyelectrolyte structures; however, only limited systematic dependencies have been identified.^{5,6,9}

It is the objective of this contribution to present partial volumes for both synthetic polyelectrolytes and chemically modified natural ionic polymers and to compare the experimental results and calculated data. The results are discussed and analyzed based on the general solution behavior of polyelectrolytes and related to their chemical structure.

Calculation of Partial Volumes

Definitions. Detailed definitions and explanations of the partial molar and specific volumes have been provided in several papers.^{10–12} Therefore, only the basic relations pertinent to discussion of two-component solute–solvent systems, such as those studied herein, will be summarized.

The partial specific volume, \bar{v} , of the solute is then defined as the change in total volume, ∂V , per unit mass

[†] Presented at Polyelectrolytes '98, Inuyama, Japan, May 31–June 3, 1998.

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upon adding an infinitesimal amount, ∂g , of the solute at constant temperature, T , and pressure, p

$$\bar{v} = (\partial V / \partial g)_{T,p} \quad (1)$$

The partial molar volume, \bar{V} , is defined in an analogous way by substituting the number of grams, g , by the number of moles, n

$$\bar{V} = (\partial V / \partial n)_{T,p} \quad (2)$$

The partial specific volume is often provided in units of cm^3/g while the partial molar volume is expressed in terms of cm^3/mol . The two partial volumes are related by

$$\bar{v} = \bar{V}/M \quad (3)$$

where M is the molar mass of the solute in g/mol . Usually, for polyelectrolytes, M is the molar mass of one monomer unit. Under such circumstances the unit g/monomol is used as measure to avoid confusion.

Calculation from Experiments. If there is no concentration dependence of the partial volumes, the value of the partial specific volume at infinite dilution can be obtained directly from the experimental density increment in eq 4 plotting the density vs the concentration¹³

$$\rho = \rho_0 + (1 - \bar{v}\rho_0)c \quad (4)$$

where ρ denotes the density of the solution, ρ_0 the density of the solvent, and c the concentration of the solute in g/cm^3 .

If there is a concentration dependence, the partial volumes have to be extrapolated to concentration zero using one of the following two equations which calculate the apparent volumes at the finite concentrations c^9

$$\bar{v} = \frac{1}{\rho_0} - \frac{1}{c} \left(\frac{\rho}{\rho_0} - 1 \right) \quad (5)$$

with c in g/cm^3 or

$$\bar{V} = \frac{M}{\rho_0} - \frac{10^3}{c} \left(\frac{\rho}{\rho_0} - 1 \right) \quad (6)$$

with c the equivalent concentration in monomol/L .

Empirical Calculations. Two different empirical procedures have been applied to calculate the partial volumes for the polyelectrolyte structures of this study. The first, developed by Durchschlag and Zipper,¹ is based on Traube's additivity principle and concept of volume increments for atoms.^{14,15} However, a number of appropriate adaptations and corrections and completion of the initial concept were introduced in the basic concept to enable comprehensive calculations. The second model published by Gianni and Lepori² is an extension of an additivity scheme already adopted for nonelectrolytes.¹⁶ Using the experimental data of several hundreds of organic electrolytes, a least-squares procedure yielded increments for diverse functional nonionic and ionic groups. Both approaches are valid for aqueous solutions at 25 °C and yield volumes at infinite dilution. The following section summarizes the basic equations for both models.

Procedure of Durchschlag and Zipper (D/Z). The partial molar volume of an organic electrolyte in aqueous solution of infinite dilution may be calculated from

$$\bar{V} = \sum \bar{V}_c + \sum V_{\text{ion}}^* \quad (7)$$

with

$$\bar{V}_c = \sum V_i + V_{\text{CV}} - \sum V_{\text{RF}} - \sum V_{\text{ES}} \quad (8)$$

$V_{\text{ion}}^* = V_{\text{ion}}$ in the case of inorganic cations, however, $V_{\text{ion}}^* = V_{\text{ion}} - ZV_{\text{CV}}$ for inorganic anions, where V_i is the volume increment for any atom or atomic group, V_{CV} is the correction due to the covolume, and V_{RF} and V_{ES} take into account the decrease of volume caused by ring formation and ionization, respectively. Z is the number of electric charges per ion. It should be mentioned that, in the case of polymers, the contribution of V_{CV} has to be neglected if the volume of the monomer unit is to be calculated. For volume corrections at temperatures other than 25 °C, a value, $\Delta\bar{v}/\Delta T$, of $5 \times 10^{-4} \text{ cm}^3 \text{ g}^{-1} \text{ K}^{-1}$ has been proposed.¹

Procedure of Gianni and Lepori (G/L). The Gianni and Lepori method provides the following relationship to calculate the partial molar volume at infinite dilution:

$$\bar{V} = A + \sum_i n_i B_i \quad (9)$$

Here B_i denotes the contribution of the i th structural group (arrangement of one or more atoms) which appears n_i times in the ion under consideration. A is a constant term.² The constant A has to be taken into account only once for each molecule. For polymers (with N the degree of polymerization) where \bar{V} is related to one monomer unit, eq 10 is valid

$$\bar{V} = \frac{A + N \sum_i n_i B_i}{N} \quad (10)$$

Clearly, for $N \gg 1$ the constant A can be neglected. Equation 10 does not consider the contribution by the two terminal groups of the polymer. Obviously, the effect on the final numbers is small for $N \gg 1$. However, the B values may be different depending on the initiation and termination of the polymer chain. This could be significant for oligomers. Therefore, eq 11 contains the appropriate correction.

$$\bar{V} = \frac{A + (N-2) \sum_i n_i B_i + \sum_i m_i B_i + \sum_i k_i B_i}{N} \quad (11)$$

Experimental Section

Materials. Poly(sodium styrenesulfonate) (NaPSS) samples with narrow molar mass distributions were obtained from Polymer Standards (Mainz, Germany, $M_w = 8000, 46\,400, 66\,000$ g/mol) or Pressure Chemical Corp. (Pittsburgh, PA, $M_w = 35\,000, 200\,000, 780\,000$ g/mol). The M_w/M_n was < 1.2 for the three samples with lower molar masses and < 1.1 for the remaining polymers. The samples were designated as NaPSS-8, -35, -46, -66, -200, and -780. Following purification by ultrafiltration to remove small amounts of low molecular salt, all samples were analyzed by ^{13}C NMR spectroscopy and elementary analysis. Complete sulfonation was detected within the experimental error of the methods. Poly(allylamine) hydrochloride samples (PAHCl-10, PAHCl-50) with weight average molar masses of 10 000 and 50 000–60 000 g/mol were purchased from Aldrich Chemical Co. Poly(diallyldimethylammonium chloride) (PDADMAC) samples

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Table 1. Molecular Characteristics of DADMAC-AA and PDADMAC Samples

sample	cationic content		$M_n \times 10^{-3}$ ^a (g/mol)	$M_w \times 10^{-3}$ ^b (g/mol)
	mol %	mass %		
DADMAC-AA-0	0	0	550	
DADMAC-AA-15	15.2	29.0	643	
DADMAC-AA-38	37.6	57.8	476	
DADMAC-AA-41	41.3	61.7	481	
DADMAC-AA-56	55.5	73.9	198	
DADMAC-AA-69	68.7	83.3	100	
DADMAC-AA-100	100	100	170	
PDADMAC-31	100	100	31	45
PDADMAC-226	100	100	226	296
PDADMAC-240	100	100	240	574
PDADMAC-325	100	100	325	781

^a Determined by membrane osmometry in 0.5 N NaCl. ^b Determined by light scattering in 0.5 N NaCl.

and copolymers with acrylamide (AA) were synthesized, purified, and analyzed as described previously.^{17,18} The copolymer composition and the molecular characteristics are given in Table 1. Therein, the number at the end of the abbreviation indicates the molar content of the ionic component in the copolymers and the number average molar mass for the homopolymers, respectively.

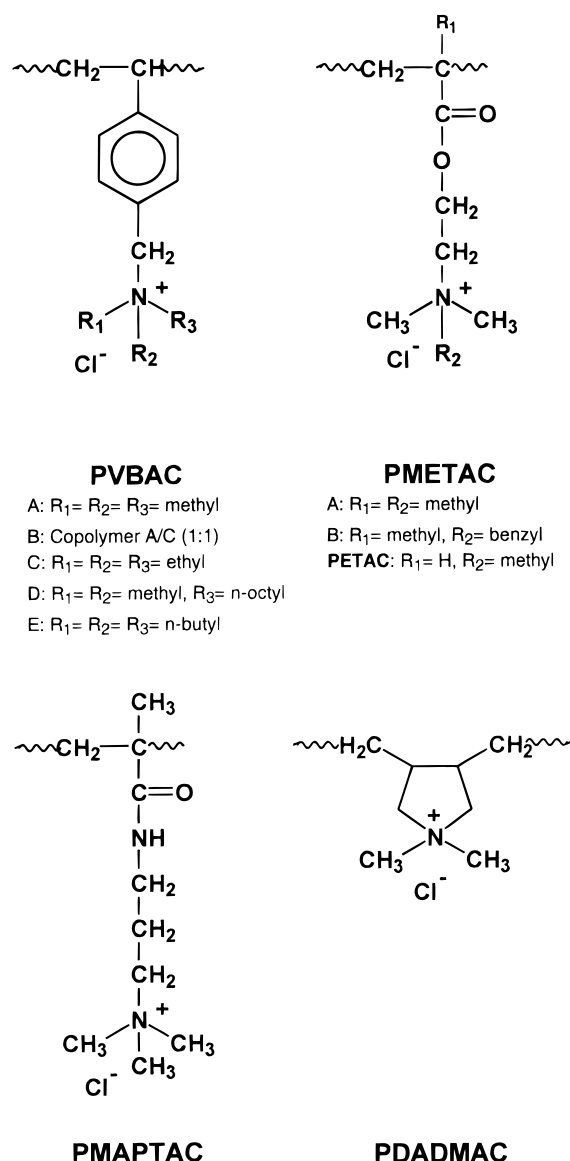
The synthesis, preparation, and characterization of poly(vinylbenzyltrialkylammonium chloride)s (PVBAC)s have been described in detail.¹⁹ The poly(methacryloyloxyethyltrialkylammonium chloride)s (PMETAC)s, -trimethyl- (PMETAC-A) and -benzyltrimethyl- (PMETAC-B), as well as poly(methacryloylamidopropyltrimethylammonium chloride) (PMAPAC) and the acryloyloxyethyltrimethylammonium chloride/acrylamide copolymer (PETAC-AA-40) were synthesized by radical solution polymerization of the appropriate monomers.²⁰ Sodium cellulose sulfates (NaCS) with low degrees of substitution (DS < 1) were heterogeneously prepared laboratory samples from H. Dautzenberg's laboratory.^{21,22} The highly substituted NaCS sample (DS = 2.4) was purchased from Acros Organics (New Jersey, USA). The degree of substitution of all NaCS samples was determined by direct potentiometric complex titration (692 pH/Ion Meter, Metrohm, Switzerland) with PDADMAC.²³ Sodium alginates were gifts from The NutraSweet-Kelco Co. (U.K.) and Pronova Biopolymers (Norway). Carrageenans were purchased from Fluka (Switzerland). The degrees of substitution of alginates and carrageenans were tested by the same complexation method. Table 2 contains the molecular characteristics of the alginates, cellulose sulfates, and carrageenans.

All polyelectrolytes were purified by ultrafiltration (Hollow-Fiber Concentrator CH2A, Amicon). Solids were obtained by vacuum freeze-drying (Beta 1-16, Christ, Germany). The concentrations of the stock solutions of the polycations with known chemical structure were analyzed by potentiometric determination of the counterions (736 GPTitrino, Metrohm, Switzerland). UV-vis spectroscopy (Lambda 2, Perkin-Elmer, International Inc.) was used to receive the concentration of the NaPSS solutions. The concentrations of the alginate and carrageenan solutions were calculated from the solid content of these biopolymers. All polyelectrolytes were dissolved in highly purified deionized water from a Milli-Q PF (Millipore, Switzerland). The stock solutions were freshly prepared for each concentration series to avoid problems of aging and microorganism contamination, which was found to occur with diluted polyelectrolyte solutions.²⁴ The purification, characterization, analytical investigation, and preparation of polyelectrolyte solutions have comprehensively

Table 2. Molecular Characteristics of Sodium Alginates, Sodium Cellulose Sulfates, and Sodium Carrageenans

sample	degree of substitution	$[\eta]^a$ (cm ³ /g)	$M_w \times 10^{-3}$ ^b (g/mol)	source
Keltone LV	1	470	261	Kelco
Protanal LF	1	534	304	Pronova
Manugel	1	785	471	Kelco
Keltone HV	1	846	514	Kelco
NaCS-0.36	0.36	401		Dautzenberg
NaCS-0.43	0.47	278		
NaCS-0.6	0.57	264		
NaCS-0.9	0.81	177		
NaCS-2.4	2.4	387		Acros
κ -carrageenan	0.5	c		Fluka
ι -carrageenan	1.0	c		Fluka

^a Determination by dilution viscometry in 0.5 N NaCl. ^b Calculated from: Smidsrød, O. *Carbohydr. Res.* **1970**, 13, 359. ^c Gelling in 0.5 N NaCl.

Scheme 1. Chemical Structures of the Synthetic Cationic Polyelectrolytes

been described elsewhere.²⁵ Schemes 1–3 present the chemical basic structures of the investigated polyelectrolytes.

Measurements. Density measurements were carried out at 20 °C using a Digital precision density meter DMA60/DMA602

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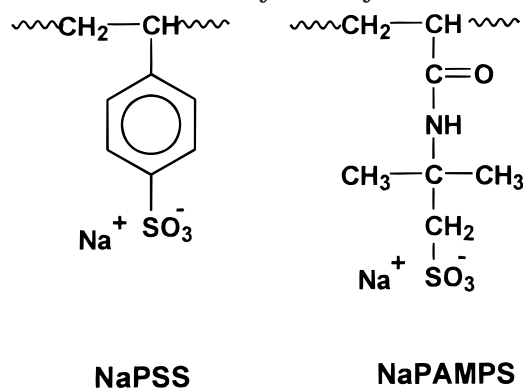
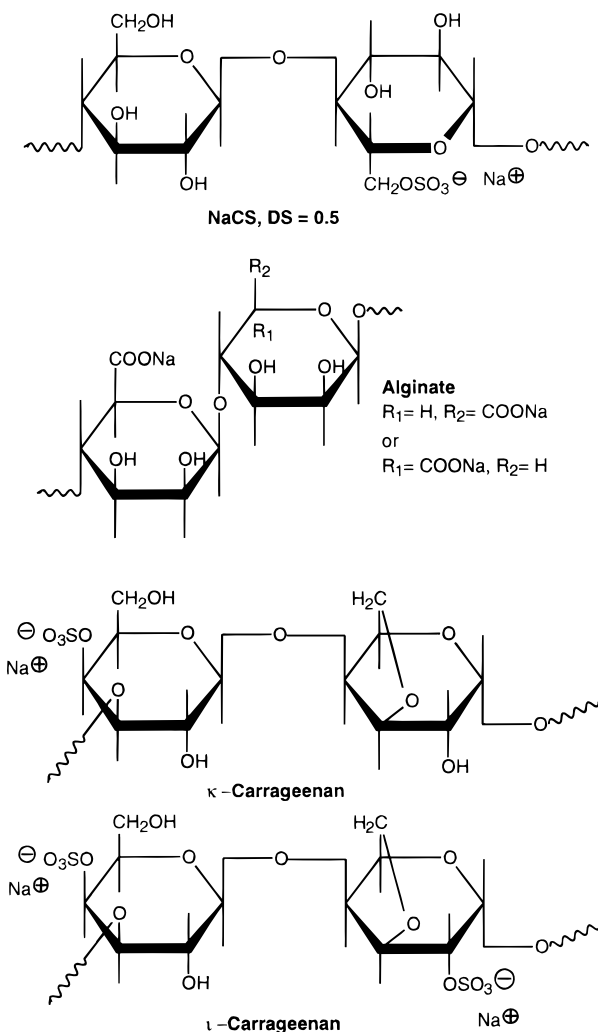
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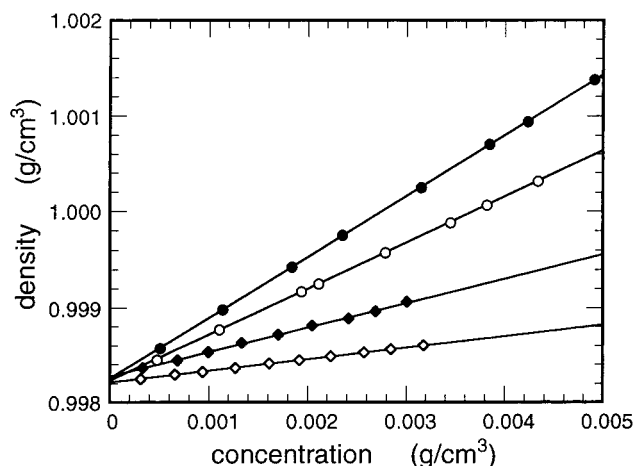
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Scheme 2. Chemical Structures of the Synthetic Anionic Polyelectrolytes**Scheme 3. Chemical Structures of the Modified Biopolymers**

(Anton Paar, Graz, Austria). Calibrations were performed with water and at least one calibration standard. The temperature was controlled with a calibrated precision thermometer CKT 100 (Anton Paar, Graz, Austria) having a resolution of 0.001 °C. Dependent on the thermal expansion coefficient, the density measurements of aqueous solutions are precise within $\pm 5 \times 10^{-6}$ g/cm³ at a temperature accuracy of ± 0.01 K.

Results

V and \bar{v} were estimated for more than 35 polyelectrolytes samples. Table 3 summarizes all experimental and calculated values of the partial molar and the partial specific volumes.

**Figure 1.** Concentration dependence of the density for various polyelectrolyte structures: ●, NaCS-2.4; ○, NaCS-0.36; ◆, PMETAC-A; ◇, PVBAC-E.

The partial specific volumes \bar{v}_{exp} have been determined from dilution series with at least seven dilutions using eq 4. For these calculations only the series with regression coefficients > 0.999 have been considered. This applied to approximately 95% of all measurements. Examples for these plots, related to eq 4, are presented in Figure 1. Experimental data for two sodium cellulose sulfates having various degrees of substitution, one poly(methacryloyl-ammonium) structure and one poly(vinylbenzylammonium) compound are shown. The different slopes reflect differences in the partial specific volumes. By means of eq 3 the partial molar volumes, \bar{V}_{exp} , could be obtained.

Dependent on the polyelectrolyte type, the concentration of the stock solution has been adjusted in the range of 1×10^{-3} to 5×10^{-3} g/cm³. If there is any concentration dependence of the partial volumes, the quality of the extrapolation to zero concentration will be clearly affected by the concentration range, the accuracy of the experimental data therein, and the absolute value of the partial volume at a given chemical structure. Table 4 demonstrates this for the assumption of two various \bar{v} values and two limits for experimental errors if the precision of the density measurements is $\pm 5 \times 10^{-6}$ g/cm³. Hence, it follows that for higher partial specific volumes higher concentrations are necessary in order to receive results of comparable precision. It has to be mentioned that the accuracy of partial volumes is more strongly influenced by the purity of the polyelectrolytes, the solution preparation, and the concentration determination than by the density measurements themselves. These problems have been generally discussed for polyelectrolytes elsewhere.²⁵ The resulting error can be minimized only by careful sample preparation and the use of high-performance analytical methods. For the data presented herein the standard deviation of \bar{v} was $< \pm 1\%$ for identical stock solutions and $< \pm 2.5\%$ if the preparation and concentration determination were included.

For all polyelectrolytes the partial volumes decreased by extrapolation to zero concentration. The extent of these changes was observed to depend on the chemical structure. In particular for the cationic polyelectrolytes investigated herein, the differences between the extrapolated and nonextrapolated values in the experimental concentration range were less than 2%. Figure 2 demonstrates these findings for various polycationic structures.

A stronger concentration dependence has been observed for some polyanions. However, a detailed analysis and discussion of the structural influence on the concentration

Table 3. Comparison of Experimental and Calculated Partial Molar and Partial Specific Volumes of Synthetic Polyelectrolytes and Modified Biopolymers in Water^a

sample	polymer	M (g/monomol)	experimental volumes		calculated volumes					
			\bar{V}_{exp} (cm ³ /mol)	\bar{v}_{exp} (cm ³ /g)	$\bar{V}_{\text{cal,DZ}}$ (cm ³ /mol)	$\bar{v}_{\text{cal,DZ}}$ (cm ³ /g)	$\Delta \bar{V}_{\text{DZ}}$ (%)	$\bar{V}_{\text{cal,GL}}$ (cm ³ /mol)	$\bar{v}_{\text{cal,GL}}$ (cm ³ /g)	$\Delta \bar{V}_{\text{GL}}$ (%)
Synthetic Polyelectrolytes										
1	cationic PVBAC-A	211.73	174.0	0.822	181.1	0.855	4.1	178.9	0.845	2.8
2	PVBAC-B	232.77	192.7	0.828	205.2	0.882	6.5	203.8	0.875	5.8
3	PVBAC-C	253.81	214.7	0.846	229.4	0.904	6.8	226.3	0.892	5.4
4	PVBAC-D	309.92	281.4	0.908	293.8	0.948	4.4	289.5	0.934	2.9
5	PVBAC-E	337.98	297.1	0.879	326.0	0.965	9.7	321.1	0.950	8.1
6	PMETAC-A	207.70	154.5	0.744	170.5	0.821	10.4	172.3	0.829	11.5
7	PMETAC-B	283.80	194.1	0.684	234.2	0.825	20.7	232.6	0.820	19.8
8	PMAPTAC	220.74	169.1	0.766	188.2	0.853	11.3	189.0	0.856	11.8
9	PETAC-AA-40	120.12	81.2	0.676	93.4	0.777	15.0	93.1	0.775	14.7
10	PAHCl-10	93.56	61.7	0.660	69.1	0.738	12.0	67.9	0.726	10.0
11	PAHCl-50	93.56	58.9	0.630	69.1	0.738	17.3	67.9	0.726	15.3
12	DADMAC-AA-0	71.08	48.6	0.684	52.7	0.741	8.4	51.25	0.721	5.4
13	DADMAC-AA-15	84.85	59.8	0.705	65.6	0.773	9.7	64.6	0.761	8.0
14	DADMAC-AA-38	105.14	78.1	0.743	84.5	0.804	8.2	84.35	0.803	8.0
15	DADMAC-AA-41	108.21	80.5	0.744	87.6	0.810	8.8	87.6	0.810	8.8
16	DADMAC-AA-56	121.36	92.8	0.765	99.7	0.821	7.4	100.1	0.825	7.9
17	DADMAC-AA-69	133.32	104.1	0.781	110.8	0.831	6.4	111.7	0.838	7.3
18	DADMAC-AA-100	161.67	130.6	0.808	137.3	0.849	5.1	139.3	0.861	6.7
18a	DADMAC ¹⁷	161.67	134.0	0.829	137.3	0.849	2.5	139.3	0.861	4.0
anionic										
19	NaPSS-8	206.19	114.6	0.556	108.0	0.524	-5.8	114.75	0.556	0.1
20	NaPSS-35	206.19	110.5	0.536	108.0	0.524	-2.3	114.75	0.556	3.8
21	NaPSS-46	206.19	109.9	0.533	108.0	0.524	-1.7	114.75	0.556	4.4
22	NaPSS-66	206.19	110.7	0.537	108.0	0.524	-2.4	114.75	0.556	3.7
23	NaPSS-200	206.19	111.3	0.540	108.0	0.524	-3.0	114.75	0.556	3.1
24	NaPSS-780	206.19	109.5	0.531	108.0	0.524	-1.4	114.75	0.556	4.8
25	NaPAMPS	229.2	118.5	0.517	131.2	0.572	10.7	134.7	0.587	13.7
Modified Biopolymers										
26	NaCS-0.36	198.59	102.5	0.516	102.5	0.516	0	117.1	0.590	14.2
27	NaCS-0.4	210.11	104.0	0.495	104.5	0.497	0.5	119.6	0.569	15.0
28	NaCS-0.6	220.31	106.4	0.483	106.2	0.482	-0.2	121.8	0.552	14.5
29	NaCS-0.9	244.81	110.4	0.451	110.3	0.450	-0.1	127.0	0.519	15.1
30	NaCS-2.4	407.10	146.1	0.359	146.3	0.359	0.1	161.3	0.396	10.4
31	Keltone LV	198.11	79.8	0.403	80.9	0.408	1.4	93.3	0.471	16.9
32	Protonal	198.11	81.4	0.411	80.9	0.408	-0.6	93.3	0.471	14.6
33	Manugel	198.11	81.8	0.413	80.9	0.408	-1.1	93.3	0.471	14.1
34	Keltone HV	198.11	79.2	0.400	80.9	0.408	2.1	93.3	0.471	17.8
35	k-carrageenan	424.31	196.9	0.464	207.8	0.504	5.5	241.5	0.569	22.6
36	i-carrageenan	526.36	220.0	0.418	223.1	0.436	1.4	263.3	0.500	19.7

$$^a \Delta \bar{V} = (\bar{V}_{\text{cal}} - \bar{V}_{\text{exp}}) / \bar{V}_{\text{exp}} \times 100.$$

Table 4. Precision of Density Measurements

\bar{v} (cm ³ /g)	error (%)	ρ_1 (g/cm ³)	C_{min}^a (g/cm ³)	C_{min}^a (monomol/L)
0.3	1	0.998 702	7×10^{-4}	3.5×10^{-3}
0.3	3	0.998 369	2×10^{-4}	1×10^{-3}
0.9	1	0.998 702	5×10^{-3}	2.5×10^{-2}
0.9	3	0.998 369	1.6×10^{-3}	8×10^{-3}

^a The lowest reliable concentration was calculated from eq 4 with $\rho_0 = 0.998\,202\text{ g/cm}^3$ (H₂O at 20 °C) and $M = 200\text{ g/monomol}$.

dependence is not the topic of this contribution. It will be presented in a separate paper.²⁶

Discussion

A comparison of the experimental values among themselves shows partial specific volumes in the range of approximately 0.3–0.9 cm³/g. Basically, for the polycations the \bar{v}_{exp} values (0.630–0.908 cm³/g) are higher than those for the polyanions including the anionic modified biopolymers (0.359–0.556 cm³/g). This may result from different intensities of the interaction with the water. With the exception of the experimental values for NaPSS (samples

19–24) and some biopolymers (samples 28, 29, 32, 33) all experimental partial volumes were found to be less than the values calculated by the D/Z model. The G/L model (with $B_i = -6.6$ for Na⁺ and 23.2 for Cl⁻) always yields higher values. The fact that the both models are valid for 25 °C, while the measurements were carried out at 20 °C, does not influence the comparison on the whole. The error is between 0.7 and 0.3%, through this dependence on the value of \bar{v} .¹

Chemical Structure. For the case of the polycations, the deviations from the calculated data are in a similar range (acrylic samples 6–9 and DADMAC samples 12–18) or somewhat smaller for the G/L model (PVBAC samples 1–5 and amine hydrochloride samples 10–11). Related to the chemical structures, the deviations seem to increase with an increase of the size of the substituents at the quaternary ammonium group (samples 1–5) and by the introduction of aliphatic groups into the polymer side chains, comparison of samples 1–5 and samples 6–9. For only a few structures were the deviations of experiment and calculation less than 5% (samples 1, 4, and 18a). In the case of PDADMAC the extent of the cyclopolymerization influences the experimental value.^{17,18} The agreement is better if the sample is extremely linear (sample 18a).¹⁷ For the synthetic polyanions the influence of the

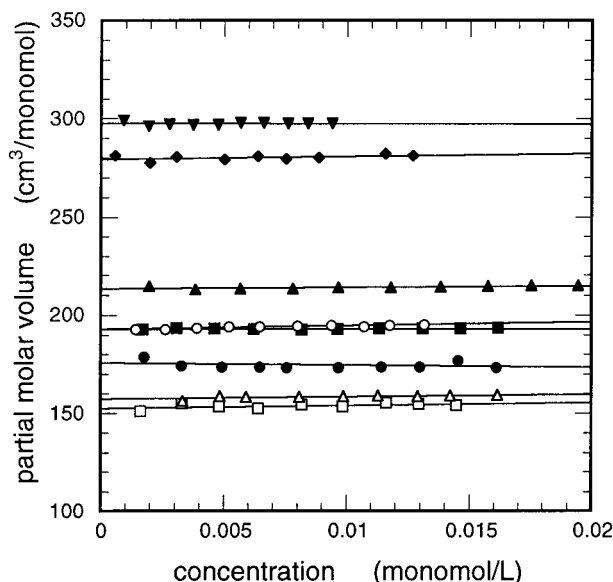


Figure 2. Concentration dependence of the partial molar volume for poly(vinylbenzyltrialkylammonium chloride)s (●, trimethyl; ■, trimethyl/triethyl (50/50); ▲, triethyl; ◆, dimethyl-*n*-octyl; ▼, tri-*n*-butyl) and poly(methacryloylammonium chloride)s (□, oxyethyltrimethyl; ○, oxyethylbenzyl dimethyl; △, amidopropyltrimethyl).

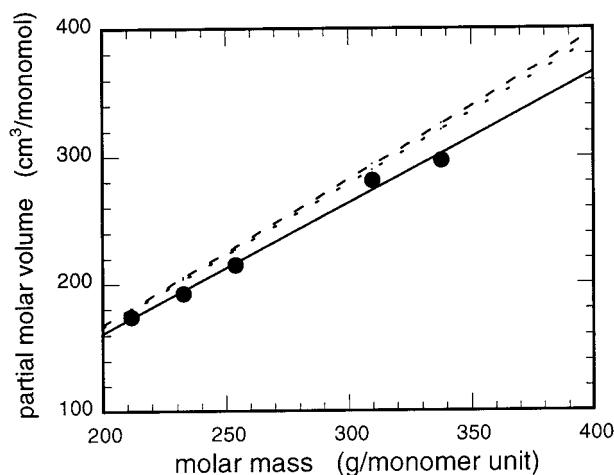


Figure 3. Additivity of partial molar volumes for PVBACs: ●, experimental data; — — —, Durchschlag/Zipper; ···, Gianni/Lepori. Influence of increasing $-\text{CH}_2-$ number in the substituents at the ionic group.

chemical structure applies in the same way. There is a relatively good agreement for NaPSS which is in a certain way similar to the structure of sample 1. However, there exists also a stronger deviation for an aliphatic side chain (sample 25) similar as in the case of sample 6. Remarkably different results from the two models were obtained for the anionic biopolymers. Here, the use of the D/Z model yields much better results with deviations mostly less than 3%.

Additivity. The incremental methods of Durchschlag/Zipper as well as Gianni/Lepori predict the additivity of partial volumes for an homologues series. Assuming noninteracting monomeric units, this additivity should also be valid for copolymers. Figures 3 and 4 show the experimental and calculated partial molar volumes as a function of molar masses of the monomeric units for poly(vinylbenzyltrialkylammonium chloride)s and DADMAC/acrylamide copolymers. Although the absolute values differ, linearity is observed experimentally.

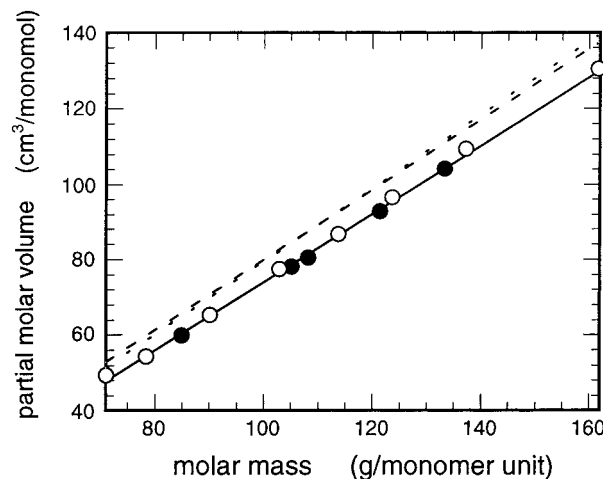


Figure 4. Additivity of partial molar volumes for DADMAC/AA copolymers: ●, experimental data; ○, data taken from Brand (Brand, F. Thesis, TU Berlin, 1995); — — —, Durchschlag/Zipper; ···, Gianni/Lepori.

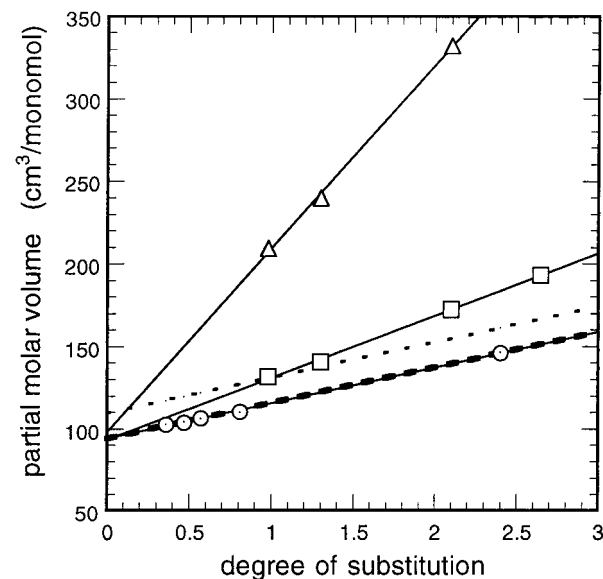


Figure 5. Influence of the degree of substitution on the partial molar volume: ○, NaCS; □, carboxymethyl cellulose protonated;⁹ △, tetramethylammonium carboxymethyl cellulose;⁹ — — —, Durchschlag/Zipper; ···, Gianni/Lepori.

Additivity could also be proved for the cellulose derivatives having different degrees of substitution. This fits to the proposed additivity for other cellulosic structures.⁹ The partial molar volumes from the literature and the results of this work are summarized in Figure 5.

It is clearly shown that the three curves meet in one point, which is related to the nonsubstituted cellulosic basic structure. However, this value cannot be evaluated by any experiment since cellulose is insoluble in water. Furthermore, the graph illustrates the good agreement with the D/Z model.

Molar Mass. Generally, there is consent that the molar mass of the polyelectrolytes does not influence the partial volumes as long as it is sufficiently high.⁹ The results of the present work support this opinion as long as the contour length exceeds the Debye length. The latter is determined by the polyelectrolyte concentration for the solutions investigated herein. Additionally, in the concentration range of these experiments, the polyelectrolyte concentrations for the low molar mass samples were calculated to be below the overlap concentration, whereas

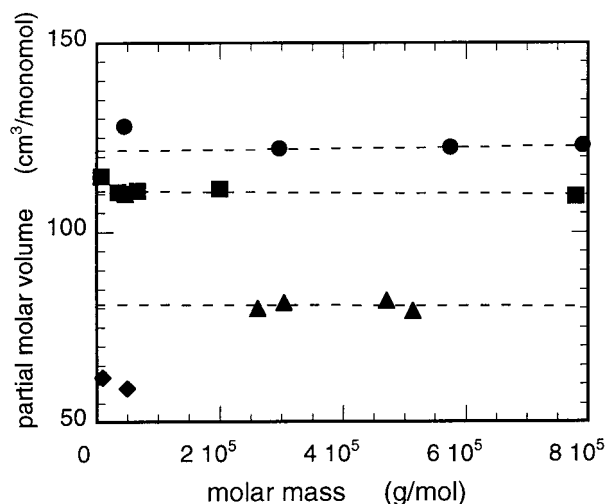


Figure 6. Influence of the molar mass of the polyelectrolytes on the partial molar volume: ●, PDADMAC; ■, NaPSS; ▲, alginate; ◆, poly(allylamine)HCl.

those of the high molar mass samples were above this critical parameter. These results are in correlation with the molar mass influence on other parameters, such as counterion activity or electrolytic conductivity.^{25,27,28} Figure 6 demonstrates the molar mass influence for various polyelectrolyte structures.

Concentration. Although, as already mentioned above, the concentration influence will be discussed in a separate publication in detail, some general remarks seem to be necessary. On the basis of available polyelectrolytes theories^{29–31} a decrease of the partial molar volume of approximately 0.5 mL/monomol for each order of magnitude has been predicted for a charge distance of 0.25 nm.³² The experiments yield, indeed, higher changes. However, at this point it could not be determined whether the dependencies follow a linear or logarithmic function-

ality. Furthermore, all theoretical predictions for polyelectrolytes are based on a constancy of the solvent properties. This implies that a change of the water structure in the environment of the polyion has not been considered. The influence of the polyions is expected to be much stronger than that of low molar mass ions. Derived from the experimental findings, theoretical approaches should include changes for all components as has been discussed for philic and phobic systems.¹² Furthermore, it has to be taken into account to which extent a denser water structure will lead to an increase of the dielectric constant. This again would have consequences on the characteristic values such as the Manning parameter.

Since all measurements of this work were carried out at very low concentrations, a concentration influence on the partial volumes has not been considered for the comparison with the empirical models. Such a correction would result in slightly smaller volumes and, therefore, generally in an appropriate increase of the deviations between experimental and calculated partial volumes.

Conclusions

The recently developed empirical additivity schemes of Durchschlag and Zipper as well as Gianni and Lepori permit the calculation of partial molar or partial specific volumes for polyelectrolytes. Although the additivity could be proven for various structures, the absolute values differ and are dependent on the chemical structure. The new experimental data and analysis presented here should, therefore, be useful in improving the empirical models and in stimulating new theoretical approaches. At the current time the results may be helpful to evaluate the reliability of partial volumes calculated from these models for polyelectrolytes.

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