Apparent Molar Volume Measurements on Polyelectrolytes and Their Model Compounds in Aqueous Solutions

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Density measurements at sensitivites of a few parts-per-million have been performed at 25 °C with a vibrating tube densimeter on dilute aqueous solutions of strong, anionic-type and cationic-type polyelectrolytes, respectively. The densities of solutions of the respective model compounds for these polyelectrolytes were also determined. The concentration dependence of the derived apparent volumes per monomole, ϕ_v, of the polyelectrolyte solutions was compared with predictions from the cell-theory, and from the infinite-line-charge theory. The apparent molar volumes of the model compounds were fitted to the Redlich–Meyer equation. The ϕ_v values for sodium polystyrenesulfonate approached the theoretically predicted logarithmic dependence on concentration at high dilutions with the correct slope. Large differences between the ϕ_v values for the polyelectrolytes and their respective model compounds were found suggesting the onset of cooperative hydration in the former.

No general agreement has existed up to this time as to the nature of the concentration dependence of the apparent molar volumes, ϕ_v, of high molecular weight polyelectrolytes when they are dissolved in dilute aqueous solution. Several investigators (*10, 15, 22*) have reported a linear dependence of ϕ_v on monomolar concentration, but recently measurements carried to slightly greater dilutions (*20*) have indicated a logarithmic concentration dependence. The functional form of the dependence is of interest because, by analogy with simple electrolyte solutions, additivity of the limiting apparent molar volumes, ϕ_v^0, of the counterions and polyions at infinite dilution might be expected. Thus, for an anionic polyelectrolyte

$$\phi_v^0(\text{total}) = \phi_v^0(\text{cation}) + \phi_v^0(\text{polyanion}) \qquad (1)$$

Apparent molal volumes at infinite dilution for simple electrolytes in aqueous solutions usually may be determined with fair accuracy by extrapolation using the Redlich–Meyer (*19*) equation

$$\phi_v = \phi_v^0 + S_v c^{1/2} + b_v c \qquad (2)$$

Electrostatic theory (*1, 8, 17*) predicts that for strong polyelectrolytes in solvents with high dielectric constant, ϕ_v will vary with the logarithm of c, the monomolar concentration. If such a dependence holds, extrapolation to infinite dilution is not possible, and the potential usefulness of eq 1 for estimating ion binding cannot be realized.

This research was carried out to determine the correct dilution law for the apparent molar volumes of strong polyelectrolytes and to compare the ϕ_v values for these compounds with the apparent molar volumes of their respective monomers, or, model compounds. It was hoped that an increased insight as to the nature of polyion hydration might be derived in this way.

Experimental Section

Pure *p*-ethylbenzenesulfonic acid, H-*p*-EBS, and its sodium, cesium, and tetramethylammonium salts were employed as model compounds for the anionic polyelectrolyte, poly(styrenesulfonic acid), while benzyltrimethylammonium chloride, $BzMe_3NCl$, served as a model compound for the cationic polyelectrolyte, poly(vinylbenzyltrimethylammonium) chloride. The synthesis, purification, and analysis of H-*p*-EBS has been described (*2, 16*) as has the source, purification, and analysis of $BzMe_3NCl$ (*3*).

The poly(styrenesulfonic acid) and poly(vinylbenzyltrimethylammonium) chloride which were used were taken from the same source as in previous work (*4*). Care was devoted to the purification, salt preparation, and isolation of the dry, lyophilized polyelectrolytes in the light of Zana's (*22*) recommendations. Equivalent weights (and hence the degree of substitution) were determined by analysis of the pure, anhydrous preparations.

Aqueous stock solutions of all the compounds were prepared by weight with distilled water that had been further purified by subboiling condensation (*14*). The concentrations of these solutions were determined by weight titration which with the polystyrenesulfonates and the *p*-ethylbenzene sulfonate salts involved conversion to the acid with a cation-exchange column. Potentiometric titration of the chloride ion content with standard $AgNO_3$ solution was employed to determine concentrations of the poly(vinylbenzyltrimethylammonium) chloride and the quarternary ammonium model compound chloride solutions.

Densities at 25 °C were determined with a vibrating tube densimeter (*13*) as embodied in a commercial density meter (Digital Densimeter DMA 02C, manufactured by Anton Paar K. G.). This instrument, which will measure the densities, *d*, of small samples (ca. 0.7 mL) of viscous mixtures rapidly and reproducibly, is particularly convenient for work with polyelectrolyte solutions. Determinations sensitive to ±1.5 ppm can be made limited only by the precision of the frequency meter of the instrument. Thus as estimated with the equation (*9*)

$$\delta\phi_v = -1000\delta d/cd_0 \qquad (3)$$

the uncertainty in the apparent molar volume, ϕ_v, for a millimolar solution ($c = 0.001$ M) will be ±1.5 mL mol^{-1}. Temperature control of the densimeter to better than 0.005 °C must be maintained to achieve measurements reliable to 1 ppm, because the density of water changes by ca. 0.25 ppm per millidegree in the temperature interval from 20 to 30 °C (*11*). A 60-L water bath regulated to better than ±0.001 °C was employed in this work. The exit temperature of the water circulated from the bath through a massive metal block which enclosed the vibrating sample tube was constant to 0.001 °C as measured with a Beckmann thermometer.

Freshly boiled, ultrapure water from a Millipore Q-2 system, and standard NaCl solutions prepared by weight dilution of saturated NaCl stock solution at 25.00 °C ($m = 6.1443$) were employed to determine the densimeter apparatus constant and to monitor the reproducibility of the instrument on a daily basis. The density of pure water at 25 °C was taken from Kell (*11*) as $d_0 = 0.997075_1$ g mL^{-1} with a standard error of 1 ppm. The densities, d_s, of the standard NaCl solutions were interpolated to 1×10^{-6} g mL^{-1} from a least-squares fit of the extensive, high-precision density data of Vaslow (*23*) to a polynomial in square root of the solution molality

$$1000(d_s - d_0) = 41.670m - 1.5131 - 0.9722m^2 \qquad (4)$$

up to $m = 1.00$. These data, which are reported to seven decimal places, were first examined by fitting them to a polynomial in the square root of the volume concentration

$$1000(d_s - d_0) = A_1c - S_vc^{3/2} - A_2c^2 - A_3c^{5/2} \qquad (5)$$

based on the addition of a second virial coefficient, A_3, to the Redlich-Meyer equation. The value of S_v in eq 5 was taken as 1.868 as predicted by the Debye-Hückel theory for 1-1 strong electrolytes. The standard deviation, $\sigma(d_s)$, of the fit was 1.3 × 10^{-6} g mL^{-1} using 53 of 57 total density-concentration measurements up to c = 1.0003 M.

The estimation of densities is based on measurements of the period, T, of resonant frequency of the mechanical oscillation of the sample cavity of the densimeter when it is filled with a sample of density, d

$$T^2 = Ad + B \qquad (6)$$

where A and B are empirical constants. In our application of eq 6 the unknown density, d_x, of the model compound or polyelectrolyte solution is related to that of pure water or to that of a salt solution of known density, d_s, as follows

$$d_x = d_s + (T_x^2 - T_s^2)/A \qquad (7)$$

where T_x and T_s are the respective resonant periods. The constant A was determined periodically by measurements with NaCl solutions of known density and least-squares fitting to eq 6. A typical value was A = 2.316 00 × 10^{12} precise to ±0.1% and constant over extended periods.

An analysis of the propagation of experimental error in eq 7 reveals that a 10-μs uncertainty in the measurement of T_x and T_s, respectively, contributes a standard deviation of ±1.3 × 10^{-6} g mL^{-1} to d_x. The standard deviation, $\sigma(d_x)$ = 1.8 ppm, follows on taking the standard deviation of the interpolated salt solution density to be $\sigma(d_s)$ = 1.3 ppm. The estimate, $\sigma(d_x)$ = 1.8 × 10^{-6} g mL^{-1}, may be compared with an absolute precision of ±1.5 × 10^{-6} g cm^{-3} and a practical precision of ±5 × 10^{-6} g cm^{-3} quoted by the manufacturer of the densimeter.

One group of investigators (*7*) has reported that the period of their densimeter was sensitive to changes in barometric pressure. In measurements of T for air and for pure water carried out daily for several months, however, we have observed no atmospheric pressure dependence. Changes in the period of the vibrating sample tube filled with air agreed with the values estimated from the changes in the density of air with pressure and humidity. Kiyohara and Benson (*12*) also have reported the absence of any clear-cut pressure dependence.

Measurement Procedure

The sequence followed in the determination of the unknown densities of a solution consisted in alternately measuring the frequencies of the sample solution and of a NaCl solution of approximately the same density as the sample solution while the frequency of freshly boiled water was measured at the beginning and end of the series.The final value of d_s was chosen to be as close to d_x as possible so that the second term in eq 7 would be made as small as possible. The minimum time for the samples to come to temperature equilibrium in the sample tube appeared to be approximately 15 min. The solutions of the model compounds of varying concentration were prepared by successive weight dilutions of their more concentrated stock solutions.

Results and Treatment of Data

Densities of the aqueous model compound solutions at 25 °C are presented in Table I while Table II gives the values for the strong polyelectrolytes. Molar concentrations, c, listed in column 2 were computed with the equation

$$c = 1000md/(1000 + mM) \qquad (8)$$

Table I. Densities of Aqueous Solutions of Model Compounds at 25 °C

m, mol/ kg of H_2O	c, mol/L	$10^3(d - d_0)$, g/mL	ϕ_v, mL/mol
H-*p*-EBS			
0.05046	0.05030	2.581	135.0
0.08870	0.08838	4.488	135.3
0.30158	0.29989	14.838	135.3
0.49302	0.48914	23.636	135.3
1.0109	0.99474	45.091	135.8
Na-*p*-EBS			
0.00996	0.00991	0.737	134.3
0.01993	0.01982	1.476	134.1
0.05113	0.05063	3.764	134.3
0.10216	0.10049	7.452	134.9
0.18950	0.18426	13.626	134.9
0.30421	0.29139	21.472	135.1
0.51983	0.48436	35.553	135.3
1.1279	0.97527	70.688	136.2
Cs-*p*-EBS			
0.00929	0.00924	1.509	155.4
0.01780	0.01770	2.882	155.8
0.04519	0.04474	7.270	156.1
0.20142	0.19470	31.490	156.9
0.49908	0.46155	74.560	157.1
Me_4N-*p*-EBS			
0.01004	0.00999	0.354	224.6
0.02016	0.02001	0.711	224.5
0.05029	0.04959	1.764	224.5
0.10029	0.09780	3.346	224.7
0.20088	0.19168	6.834	224.4
0.50084	0.44905	15.998	224.4
0.79869	0.67609	24.784	223.4
0.92486	0.76472	28.118	223.3
Me_3BzNCl			
0.05150	0.05091	0.847	169.5
0.10027	0.09831	1.641	169.5
0.20232	0.19506	3.286	169.3
0.39675	0.37079	6.366	169.0
0.59033	0.53542	9.319	168.8
0.98846	0.84526	15.005	168.4
$Me_2(EtOH)BzNBr$			
0.05017	0.04955	3.404	192.0
0.10067	0.09847	6.739	192.3
0.20369	0.19549	13.557	191.4
0.40252	0.37263	25.602	192.0
0.60465	0.54034	37.148	192.0
0.99389	0.83272	57.424	191.8
2.1959	1.5426	106.75	191.5

where M is the gram-molecular weight of the compound. Apparent molar (or monomolar) values, ϕ_v, were derived from the relation (*9*)

$$\phi_v = (M/d) - 1000(d - d_0)/md_0d \qquad (9)$$

and are plotted in Figures 1-3. The plots in Figures 1 and 2 were constructed according to eq 2 and show the constants in this equation together with the standard error (SE) of the fit. The apparent monomolar volumes for sodium poly(styrenesulfonate) are plotted against the logarithm of its molarity in Figure 3. It may be seen that a significant uncertainty in ϕ_v exists at concentrations below c = 0.005 monomolar.

Discussion

The experimental data on the model compounds appear to agree quite well with the Redlich-Meyer equation (eq 2) up to concentrations as large as 1 M. Reliable extrapolations of ϕ_v to zero concentration can be made, and accurate estimates of the

Table II. Densities of Aqueous Solutions of Strong Polyelectrolytes at 25 °C

m, mol/kg of H_2O	c, mol/L	$10^3(d - d_0)$, g/mL	ϕ_v, mL/monomole
		HPSS	
0.02226	0.02214	1.569	112.95
0.05141	0.05096	3.636	113.4
0.09903	0.09764	6.952	113.9
0.20292	0.19774	13.932	114.7
0.34643	0.33213	23.021	115.8
		NaPSS	
0.00295 (2)	0.00294	0.287	109.9 ± 0.2
0.00591	0.00559	0.569	110.5
0.01182	0.01177	1.137	110.5
0.01975	0.01965	1.885	111.2
0.02958 (2)	0.02940	2.818	111.3 ± 0.1
0.05973	0.05916	5.642	111.7
0.12096 (3)	0.11900	11.331	112.5 ± 0.1
		Bu_4NPSS	
0.01008 (2)	0.01001	0.221	385.5 ± 0.1
0.02062 (2)	0.02040	0.420	386.3 ± 0.1
0.05066 (2)	0.04954	0.839	387.4 ± 0.1
0.10438	0.10003	1.982	388.4
0.33775	0.29782	3.971	388.2
		PVR_4NCl	
0.00102	0.00101	0.045	185.0
0.00495	0.00493	0.200	188.7
0.01000	0.00996	0.390	190.2
0.03026	0.03000	1.118	192.1
0.10208	0.09982	3.560	193.7
0.29875	0.28160	9.931	194.1

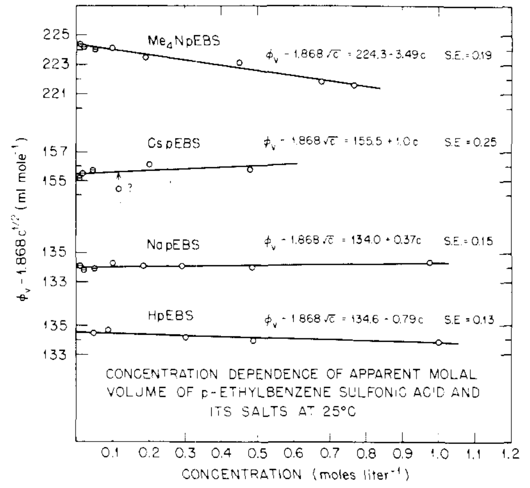

Figure 1. Concentration dependence of the apparent molar volume of *p*-ethylbenzenesulfonic acid and its salts at 25 °C.

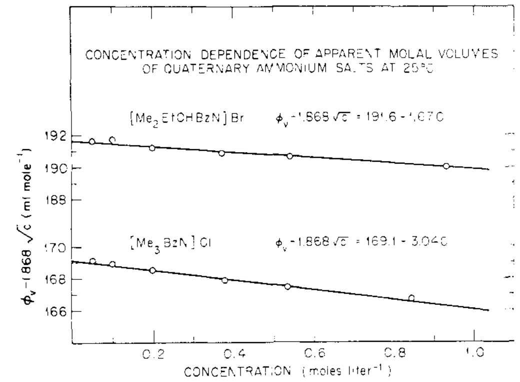

Figure 2. Concentration dependence of the apparent molar volumes of quaternary ammonium salts at 25 °C.

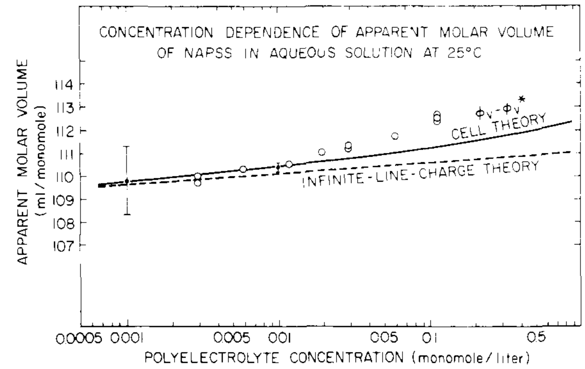

Figure 3. Concentration dependence of the apparent monomolar volume of NaPSS in aqueous solution at 25 °C (note log scale on abscissa).

first virial coefficient, b_v, for concentration dependence of ϕ_v therefore are possible. The values for ϕ_v^0 indicated in Figure 1 may be employed to estimate the limiting apparent molar volume of the anion, p-EBS$^-$, assuming additivity of ionic volumes at infinite dilution. Thus taking the values (*18*) 0.0, −1.2, 21.3, and 89.6 mL mol^{-1} for H^+, Na^+, Cs^+, and Me_4N^+ ions, respectively, the value $\phi_v^0(p\text{-EBS}^-) = 134.7 \pm 0.2$ mL mol^{-1} is found. Subtraction of the values 17.8 and 24.7 mL mol^{-1} for Cl^- and Br^- ion from ϕ_v^0 for the quaternary ammonium salts of Figure 2 gives $\phi_v^0(BzMe_3N^+) = 151.3$ and $\phi_v^0(BzMe_2EtOHN^+) = 166.9$ mL mol^{-1}, respectively. Only an approximate comparison between the limiting apparent molar volumes of the model compound ions and the monomolar volumes of the corresponding polyelectrolyte is possible. This, of course, is because of the logarithmic concentration dependence of ϕ_v for the latter substances (cf. Figure 3). If values at a concentration of $c = 0.01$ monomolar polyelectrolyte are taken, the data of Table II lead to a value of $\phi_v(PSS^-)_{0.01} = 110.4 \pm 1.0$ mL monomole^{-1} while for the cationic polyelectrolyte, $\phi_v(BzMe_3N^+)_{0.01} = 172.4 \pm 1.1$ mL monomole^{-1}. Both polyelectrolyte ϕ_v values are significantly smaller than for their corresponding model compounds. Our average value for the apparent monomolar volume of the poly(styrenesulfonate) anion appears to agree well with the average, $\phi_v(PSS^-)_{0.01} = 110.3 \pm 1.4$ mL mol^{-1}, which may be derived from measurements by Zana (*22*) on the acid and its Li, Na, K, Rb, Cs, and tetramethylammonium salts. This comparison involves a short, linear extrapolation of the data of ref 22, as these measurements do not extend below $c = 0.04$ M.

The data for the concentration dependence of the apparent monomolar volumes of sodium poly(styrenesulfonate) are compared in Figure 3 with predictions from the cell theory (*1*, *8*) and from the infinite-line-charge theory (*17*) of strong polyelectrolyte properties. Both theories assume that electrostatic forces alone determine solution behavior. The cell theory gives (*20*)

$$\phi_v - \phi_v^* = -(\alpha z_p V_m / z_c \lambda) u (\mathrm{d} \ln \epsilon / \mathrm{d} \ln P) - (\alpha z_p V_m / 2 z_c \lambda) v (\mathrm{d} \ln V / \mathrm{d} \ln P) \quad (10)$$

where ϕ_v^* is the apparent monomolar volume of the polyelectrolyte in an uncharged solution, α is the degree of ionization ($\alpha = 1$), z_p and z_c are the numbers of charges per ionized group of the polyion and on the counterion, respectively, λ is the charge density parameter (*20*), and u and v are dimensionless functions proportional to the electrostatic energy of the solution. The quantity, $(\mathrm{d} \ln \epsilon / \mathrm{d} \ln P) = 4.71 \times 10^{-5}$, gives the change in the dielectric constant of water with pressure, while $(\mathrm{d} \ln V / \mathrm{d} \ln P) = -4.54 \times 10^{-5}$.

The *infinite-line-charge* theory (*20*) gives the dependence of ϕ_v on ln *c* at extreme (but not infinite) dilution

$$(d\phi_v/d \ln c) = (\alpha z_p V_m/2z_c\lambda)(d \ln \epsilon/d \ln P) = 0.429 \text{ mL mol}^{-1} \quad (11)$$

It can be demonstrated that eq 10 will approximate eq 11 in the limit of extremely small values of *c*. The value of ($d\phi_v$/d log *c*) for vinyl type strong polyelectrolytes ($\alpha = 1$, $z_p = z_c = 1$) with λ 2.832 is 0.429 mL mol^{-1}. The apparent molar volumes of NaPSS appear to approach the curve computed from eq 10 for concentrations at and below $c = 0.012$ monomolar. Deviations from cell theory predictions at and above these concentrations also have been observed in measurements of the heats of dilution of NaPSS (*5*, *21*) and presumably reflect polyion-polyion interactions. The theory shows the need for density measurements to at least 0.1 ppm, or better than ten times more sensitive than can be attained by the vibrating tube densitometer used in this research.

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Isobaric Binary Vapor–Liquid Equilibria Systems Acetonitrile–Ethylbenzene and Acetonitrile–*p*-Xylene

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Isobaric vapor–liquid equilibrium data for the wide boiling systems acetonitrile–ethylbenzene and acetonitrile–*p*-xylene were obtained at 760 mmHg pressure using a vapor recirculating type of equilibrium still. The *t–x–y* data for these systems were tested for thermodynamic consistency and correlated by the Wilson equation.

Isobaric vapor–liquid equilibrium data, which forms part of a program on the evaluation of nonideality characteristics for mixtures of C_8 aromatics and other types of compounds, were obtained for the systems acetonitrile–ethylbenzene and acetonitrile–*p*-xylene at 760 ± 2 mmHg pressure using a vapor recirculating type of equilibrium still. These systems have boiling ranges of 56.6 and 56.8 °C, respectively. Experimental data for these systems have not been reported in literature. The system acetonitrile–ethylbenzene did not form any azeotrope which confirms the observations made by Horsley (*4*). The system acetonitrile–*p*-xylene also did not form any azeotrope. Horsley has reported (*4*) the system acetonitrile–mixed xylenes as nonazeotropic.

Experimental Section

Analytical Techniques. Ethylbenzene from British Drug Houses, England, acetonitrile from British Drug Houses Ltd., India, and *p*-xylene from Riedel, Germany, were dried using suitable drying agents and then further purified by distillation in a glass column described elsewhere (*14*). Table I summarizes some of the physical properties of the compounds employed.

A modified version of the equilibrium still described by Rao and co-workers (*12*) was used for obtaining the vapor–liquid equilibrium data. The equilibrated mixtures were analyzed by the refractive index method using a Bausch and Lomb Abbe-3L refractometer. The apparatus, modifications, and analytical techniques have already been described (*14*). The estimated uncertainities in the measurements were composition, 0.002 mole fraction, temperature, 0.1 °C, and pressure, ±2.0 mmHg. Table II gives the refractive index–composition data. Figures 1 and 2 represent the boiling point–composition diagrams for the two systems acetonitrile–ethylbenzene and acetonitrile–*p*-xylene.

Results and Discussion

The liquid-phase activity coefficients were estimated from the experimental data taking into consideration the nonideality of the vapor phase employing the following equation (*1*, *6*)

$$\gamma_i = \pi y_i / P^0{}_i x_i \exp[(\pi - P^0{}_i)(B_i - V_i)/RT]$$

Table III gives the correlations used for the estimation of pure component vapor pressures, second virial coefficients, and liquid molar volumes. These correlations gave close fit (*8*) with the experimental pure component data from the literature.

Table I. Physical Properties of Pure Compounds

		Ethylbenzene	*p*-Xylene	Acetonitrile
Normal bp, °C	Exptl	136.20	138.40	81.60
	Lit. (*5*, *15*)	136.19	138.40	81.60
Refractive index	Exptl	$1.4910^{30°C}$	$1.4908^{30°C}$	$1.3385^{30°C}$
	Lit. (*15*)	$1.4905^{30°C}$	$1.4905^{30°C}$	$1.3415^{25°C}$
Density, $d_4{}^t$	Exptl	$0.8497^{35°C}$	$0.8433^{35°C}$	$0.7707^{30°C}$
	Lit. (*15*)	$0.8583^{30°C}$	$0.8523^{30°C}$	$0.7766^{25°C}$