THE PARTIAL MOLAR VOLUMES OF SIX ALKALI HALIDES AND THEIR IONS AS A FUNCTION OF CONCENTRATION

by

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The application of the technique of sedimentation equilibrium in density gradients to proteins requires a knowledge of the partial molar volumes of bound ions and water. Partial molar volumes of water and six alkali halides, CsCl, CsBr, CsI, RbCl, RbBr and RbI were computed as a function of concentration throughout the entire solubility ranges. These values were apportioned into partial molar volumes of the ions according to the cubes of Pauling's ionic radii. These data are tabulated as a function of density and water activity. The partial molar volumes of all of the salts and the ions increase with increasing salt concentration. Unique triple points are observed in the plots of the partial molar volumes of both the rubidium and cesium ions as a function of density.

1. INTRODUCTION

The technique of sedimentation equilibrium in density gradient in the analytical ultracentrifuge (14) as applied to the study of nucleic acids and proteins has been limited primarily to the use of one salt, CsCl. One study (10) has examined the buoyant density of bovine serum mercaptalbumin at its isoelectric point in CsCl, CsBr, CsI, KBr, RbBr, Cs₂SO₄ and CsAc, and buoyant densities of DNA are routinely reported for both CsCl and Cs₂SO₄. However, these investigations have been hampered by the lack of an adequate thermodynamic data base. Refractive index vs. density relations have been established for 8 aqueous salt solutions (8) and density gradient proportionality constants have been published for twenty 1:1 electrolytes (8).

The next step in our progress toward an understanding of the behavior of proteins in concentrated salt solutions appears to lie in the correct application of Equation [1].

$$\rho_0 = \frac{1 + z_X + z_Y + \Gamma_1'}{\bar{v}_3 + z_X \bar{v}_X + z_Y \bar{v}_Y + \Gamma_1' \bar{v}_1} \quad [1]$$

This equation has been used several times on an empirical basis (10, 23) and has recently been derived rigorously using thermodynamics by SHARP *et al.* (22). It states that the buoyant density (ρ_0) of a protein can be expressed in terms of the weight fractions z_X and z_Y of the bound cations and anions, the weight fraction of bound water, Γ_1' and the partial specific volumes, $\bar{v}_1$ and $\bar{v}_3$, of water and the protein respectively. In this paper, we have employed the subscripts 1, 2 and 3 to designate water, salt and protein respectively. At some point, it is to be hoped that the partial specific volumes of the protein-salt complex will be available. But until both the theoretical background and the experimental details of how to conduct these measurements have been resolved, it is necessary to treat the seven variables of Equation [1] separately.

The partial specific volume of the protein, $\bar{v}_3$, at the isoelectric point, which is assumed to be the same as the isoionic point, and the buoyant density, ρ_0 , are both directly available from experiment. The weight fractions of the bound ions can be computed under certain pH condi-

tions (7). If the partial specific volumes of the bound ions were known, the total hydration could be computed.

Unfortunately, values of $\bar{v}_{ions}$ as a function of concentration are available only for CsCl. Most investigations of partial molar volumes to date have dealt only with apparent molal volumes of the salt as a function of concentration (3) or the partial molar volumes of ions in dilute aqueous solution (25) or at infinite dilution (17). Therefore to continue the process of making the density gradient technique more generally useful to the protein chemist, we have calculated the $\bar{v}_{ions}$ in six salts throughout the entire solubility ranges.

Although these $\bar{v}$ values are strictly valid only in a two-component system, we expect the values in a salt solution containing 0.1% protein to be practically identical.

2. CALCULATIONS

2.1. Partial molar volumes of salts

Several methods are available for the computation of the partial molar volumes of molecules, such as salts, in solution. ZEN (25) has presented the case for using the method of apparent molar volumes, ϕ_2 . Value of ϕ_2 as a function of concentration are calculated directly from the original weight percent versus density data (6). This method can only be used when the apparent molar volumes can be expressed as a linear function of the square root of the concentration. Although this behavior has been observed for some salts over limited ranges of concentration by earlier workers (5), more recent work (3, 13) has demonstrated non-linearity at concentrations below even 0.5 m. For instance, DESNOYERS *et al.* (3) have experimentally redetermined the densities of aqueous alkali halides at 25°C at concentrations c , up to 0.75 molar and demonstrated that the relation:

$$\phi_2 = \phi_2^\circ + 1.86 \, c^{1/2} + hc \quad [2]$$

accurately describes the variation of ϕ_2 with concentration up to 0.5 M. The constants h were empirically determined for the alkali halides. More severe deviations from a linear relation can be expected at higher concentrations.

For this reason, the classical procedure of ROOZEBOOM (21), described as method IV by LEWIS and RANDALL (12) was employed. Inconsistencies in the data, as described by ZEN, will indeed give anomalous results which must be discarded and the quality of this method can be determined in part by the continuity of the data which result.

This method consists of plotting the reciprocal of the density, $1/\rho$, the specific volume of the solution in ml/g, versus the weight fraction of the salt, z_2 . As seen in Equation [3], the tangent to this curve, at a given molality, extrapolated to $z_2 = 1$, yields the partial specific volume of the salt, $\bar{v}_2$, and extrapolation of this same tangent to $z_2 = 0$ yields the partial specific volume of water, $\bar{v}_1$, both valid at that concentration.

$$1/\rho = (1 - z_2) \bar{v}_1 + z_2 \bar{v}_2 \quad [3]$$

Finally multiplication of these $\bar{v}$'s by the appropriate molecular weight yields the partial molar volume, $\bar{V}$.

The salts selected for this study are the six alkali halides, CsCl, CsBr, CsI, RbCl, RbBr and RbI which have high solubilities in water and provide solutions of high density and low viscosity. They were selected because the buoyant densities of the protein, ovalbumin, have recently been measured in each of these six salts as a function of pH (19) and the buoyant titrations of three homopolypeptides are currently being measured in these same solutions (9). The original density-weight fraction data selected for use were from the International Critical Tables (6).

In the previous study employing this method (11), the tangents to the $1/\rho$ vs. z_2 curve were obtained by constructing large scale plots of the data and graphically obtaining these tangents by the chord method. Because this method is time-consuming and because of inherent errors in graphical methods, a program was written for the Hewlett-Packard 9825 A computer (See Appendix A.) This program took three adjacent evenly-spaced data points, computed the slope of the straight line through the outer two points, applied this slope at the central data point and extrapolated this line to $z_2 = 0$ and $z_2 = 1$ to obtain $\bar{v}_1$ and $\bar{v}_2$ respectively. The partial speci-

fic volumes thus obtained were converted to their respective partial molar volumes by multiplying by the appropriate molecular weight.

2.2. Partial molar volumes of ions

The first method proposed for the calculation of ionic partial molar volumes was that of BERNAL & FOWLER (1). They assumed that the ratio of the volumes in solution was equal to the ratio of cubes of the crystallographic radii in CsCl. When values had been assigned to Cs^+ and Cl^- , all other ions could be obtained.

WIRTH (24) assumed that $\bar{V}(\text{K}^+) = \bar{V}(\text{F}^-)$ because the crystal radii of potassium and fluoride ions are similar. FAJANS & JOHNSON (4) assumed that $\bar{V}(\text{NH}_4^+) = \bar{V}(\text{Cl}^-) = \bar{V}(\text{H}_2\text{O}) = 18.0 \text{ cm}^3/\text{mole}$ because several of the properties of NH_4Cl solutions resemble those of H_2O .

All of the values referred to above are partial molar volumes of ions at infinite dilution, commonly referred to as $\bar{V}^\circ$. They serve as useful checks for $\bar{V}$ data obtained as a function of concentration when these data are extrapolated to zero concentration. However, they do not fulfill the need to provide values for use in Equation [1] at quite high concentration.

Since 1957, a number of other studies have appeared giving $\bar{V}$ values of ions at higher concentrations. These efforts have been summarized in the important review by MILLERO (15). Most approaches have been based on a search for the value of $\bar{V}(\text{H}^+)$. However, depending upon the approach used, values ranging between $-0.2 \text{ cm}^3/\text{mole}$ and $-7.6 \text{ cm}^3/\text{mole}$ have been reported by 24 different workers. Because of this ambiguity and because there is no thermodynamically rigorous method to compute $\bar{V}$'s of ions, we have chosen to apportion the partial molar volumes of the salts according to the cubes of the ionic radii of the ions in close-packed crystal lattices. The most accurate data for this purpose appears to be the original data of PAULING (18).

As noted above, earlier workers have apportioned the $\bar{V}$ of one salt according to the cubes of the ionic radii of its two ions and derived the volumes of all other therefrom. However, if the radius for the cation was too large (even by a few hundredths of an Ångström) and the corresponding anionic radius too small, all cation

volumes computed would be too large and all anion volumes too small. The *vice versa* could also obviously occur. For this reason, we have chosen to apportion all salt $\bar{V}$'s according to the cube of Pauling's radii of the constituent ions. These values are given in Table I. Thus any random errors in the crystal radii will be reflected in the ionic partial volumes but no systematic errors will be incurred.

2.3. Water activity and partial molar volumes of water

As described below, water activities, a_1 , were computed for each salt at each concentration. Values of a_1 were computed from the standard relation

$$\ln a_1 = \frac{-\nu \cdot m_2 \cdot M_1}{1000} \Phi \quad [4]$$

Values of the osmotic coefficients, Φ , were obtained from ROBINSON & STOKES (20). Large scale plots were made and values read from these plots at the appropriate densities. The value of ν , the number of ions per salt molecule, was two in each case and M_1 is the molecular weight of water.

The partial molar volumes of water in these salt solutions are also required for the correct application of Equation [1]. As is apparent from Equation [3], these values are readily obtained at $z_2 = 0$.

3. RESULTS AND DISCUSSION

3.1. Partial molar volumes of salts

The $\bar{V}$ values of the six salts investigated, CsCl, CsBr, CsI, RbCl, RbBr, and RbI are given in Figure 1 and in column 3 of Tables II-VII. The values displayed in the figure indicate continuous increases in $\bar{V}$ ranging from 4 to 16% from the lowest concentration up to the saturation limit of the salts. This conforms to the general trend reported for these and other salts (11, 2).

The data points displayed in Figure 1 correspond to the original data derived from the International Critical Tables and have not been smoothed. These points are connected by straight lines. For these reasons, the curves are rather angular and display some unusual dis-

continuities. Nevertheless they do indicate that the numerical technique employed in this paper does provide rather continuous curves.

In order to make these data more generally useful for other purposes, all of the raw data are given in the Tables. These data permit the construction of large scale plots by the reader if interpolation is required.

The data for CsCl can be compared with the data published earlier (11) which employed the graphical method of extrapolation. The data from both studies were plotted on the same graph and the differences between the two sets of data were negligible. The values of CHOI & BONNER (2) of 39.25, 41.44 and 42.36 ml/mole for CsCl at molalities of 0.0, 0.5 and 1.0 respectively compare with the values 39.94, 41.34 and 42.44 ml/mole in the present study. The infinite dilution value of 39.94 was obtained by an extrapolation of the data which end at 4% and is not considered to be as accurate as the other infinite dilution values (6).

DESNOYERS *et al.* (3) have observed that the difference between the partial molar volumes at infinite dilution, $\bar{V}^0$, of the alkali fluorides and chlorides, the chlorides and bromides, and bromides and iodides are constant to within 0.1 ml/mole. These values were compared with the $\bar{V}$'s at the lowest concentration presented in this paper. The differences between the iodides and bromides of rubidium and cesium are virtually identical in the two studies. The infinite dilution values for the bromides and chlorides are about 5% larger than the values in the present study.

The increase in $\bar{V}$ observed for all salts may be due to an increase in size of the anions and cations and/or to a decrease in electrostriction of the bound water. Further discussion of these effects is given below.

3.2. Partial molar volumes of ions

These values are displayed as a function of density in Figures 2 and 3 and as a function of water activity in Figures 4 and 5. The actual numerical data are given in columns 2, 4, 5 and 7 of Tables II-VII.

The data in Figures 2 and 3 constitute the necessary data for the application of equation [1] to the study of the behavior of proteins in gradients of density generated in these salt solu-

Figure 1. The partial molar volume in water $\bar{V}$, ml/mole, of the salts CsCl, CsBr, CsI, RbCl, RbBr and RbI versus the density d , g/ml, of the salt solution, 25°C.

Figure 2. The partial molar volume $\bar{V}$, ml/mole, of the cations Cs^+ and Rb^+ in the chloride, bromide and iodide salts versus the density d , g/ml, of the salt solution, 25°C.

tions. However, several aspects of these figures invite further comment.

Both Rb^+ and Cs^+ display a triple point in Figure 2. At densities of 1.167 g/ml and 1.223 g/ml, Rb^+ and Cs^+ ions respectively have identical partial molar volumes in all three salt solutions. There is no apparent reason why this should be true at a particular density but it did appear to us that a reasonable explanation might be that the three solutions share a common water activity at this density. As long as the ionic radius is invariant, the electrostriction might be expected to be identical if the water activity were the same in each solution. Therefore water activities were computed for the six salt solutions at the two triple points and values of a_1 of 0.934, 0.954, and 0.967 were obtained for RbCl , RbBr , and RbI solutions at $d = 1.167$ g/ml and a_1 values of 0.940, 0.955, and 0.961 for CsCl , CsBr , and CsI solutions of $d = 1.223$ g/ml. It is apparent that common water activities are not responsible for common $\bar{V}$ values at the triple points.

Although the data at one density for each cation did not provide an explanation, it was felt that perhaps some further clarification could be obtained if $\bar{V}$ values were plotted as a function of water activity. Figures 4 and 5 display these data. It is apparent that neither anions nor cations have common partial molar volumes at common water activities, the $\bar{V}$'s decrease with increasing water activity and the two triple points have vanished. Two aspects of these curves deserve comment.

First, the $\bar{V}$'s of the two ions in one salt change with the water activity of the salt solution. For instance, $\bar{V}_{\text{Cs}^+}$ increases from 18.25 ml/mole to 20.69 ml/mole in going from a 4 to a 55 wt.% CsCl solution. One explanation of this is that the ionic radius increased by 4.3% over this concentration range. In order to determine whether such a change was feasible, we have compared the $\bar{V}$ of CsCl with the molar volumes of the Cs^+ and Cl^- computed from Pauling's crystal radii. The latter values are 12.17 ml/mole and 14.95 ml/mole respectively giving a molar volume of CsCl of 27.12 ml/mole. This is appreciably smaller than the approximate value of 39.94 ml/mole derived for $\bar{V}^0$ in this study. Because ions are known to have an electrostricti-

Figure 3. The partial molar volume $\bar{V}$, ml/mole, of the anions Cl^- , Br^- and I^- in the cesium and rubidium salts versus the density d , g/ml, of the salt solution, 25°C.

Figure 4. The partial molar volume $\bar{V}$, ml/mole, of the cations Cs^+ and Rb^+ in the chloride, bromide and iodide salts *versus* the water activity, a_1 , in the salt solution, 25°C.

Table I

Ionic Crystal Radii^{x)}

Ion	Ionic Radius Å
Rb^+	1.48
Cs^+	1.69
Cl^-	1.81
Br^-	1.95
I^-	2.16

x) Data from Pauling (18)

Figure 5. The partial molar volume $\bar{V}$, ml/mole, of the anions Cl^- , Br^- and I^- in the cesium and rubidium salts *versus* the water activity, a_1 , of the salt solution, 25°C.

ve influence on the surrounding water (17), the relation

$$\bar{V} = I - E \quad [5]$$

where I is the intrinsic volume of the ion and E its electrostriction, indicates that the intrinsic volume must be even larger than 39.94 ml/mole. Thus it appears that the crystal ionic radii do increase dramatically upon entering an aqueous environment and the 4.3% further expansion required above may indeed be feasible.

The other possibility is that the value of E in Equation [5] decreases with decreasing water activity. Even if I remained constant, this would also lead to an increase in $\bar{V}$.

Secondly, Figures 4 and 5 demonstrate that at a particular water activity, the partial molar volumes of a given cation or anion vary significantly. Thus the nature of the counter ion is the dominant factor in modifying the $\bar{V}$ of a given ion at a given water activity by influencing the ionic radius and/or the electrostriction.

In conclusion, we are unable to apportion changes in partial molar volumes of ions in solution according to changes in ionic radii or electrostrictive effects, but it appears that either or both could be responsible for the observed changes. Furthermore, the nature of the counter ion plays a major role in determining the partial molar volume of an ion in solution.

3.3. Partial molar volumes of water

The partial molar volumes of water are tabulated in column 6 of Tables II-VII and are plotted in Figures 6 as a function of water activity. The $\bar{V}$'s of water are seen to vary monotonically for each salt and converge to a common value at infinite dilution. The pairs of salts with a common anion have similar $\bar{V}$'s, with the values of the cesium salts being slightly larger. In contrast to the partial molar volumes of the salts, the largest increase in $\bar{V}$ of water noted here is only 1.1% throughout the entire solubility ranges.

Figure 6. The partial molar volume of water $\bar{V}$, ml/mole, in the salts CsCl, CsBr, CsI, RbCl, RbBr and RbI versus the water activity, a_1 , of the salt solution, 25°C.

Table II

Partial Molar Volumes $\bar{V}$, ml/mole, in CsCl Solutions, 25°C.

Wt. %	Density d g/ml	$\bar{V}_{\text{CsCl}}$	$\bar{V}_{\text{Cs}^+}$	$\bar{V}_{\text{Cl}^-}$	$\bar{V}_{\text{H}_2\text{O}}$	Water activity a_1
4	1.02839	40.68	18.25	22.42	18.050	0.992
6	1.04472	41.05	18.42	22.63	18.049	0.988
8	1.06153	41.38	18.57	22.81	18.047	0.984
10	1.07884	41.69	18.70	22.98	18.043	0.980
12	1.09668	41.97	18.83	23.13	18.040	0.975
14	1.11507	42.24	18.96	23.29	18.034	0.971
16	1.13404	42.51	19.07	23.43	18.031	0.966
18	1.15362	42.73	19.17	23.55	18.025	0.961
20	1.17385	42.91	19.26	23.66	18.020	0.955
22	1.19476	43.13	19.35	23.77	18.014	0.950
24	1.21638	43.35	19.45	23.90	18.007	0.944
26	1.23874	43.61	19.57	24.04	17.998	0.937
28	1.26187	43.86	19.68	24.18	17.987	0.930
35	1.34960	44.51	19.98	24.54	17.957	0.903
40	1.41964	44.95	20.17	24.78	17.928	0.880
45	1.49688	45.37	20.36	25.01	17.896	0.851
50	1.58245	45.76	20.54	25.23	17.856	0.817
55	1.67776	46.11	20.69	25.42	17.815	

Table III

Partial Molar Volumes $\bar{V}$, ml/mole, in CsBr Solutions, 25°C.

Wt. %	Density d g/ml	$\bar{V}_{\text{CsBr}}$	$\bar{V}_{\text{Cs}^+}$	$\bar{V}_{\text{Br}^-}$	$\bar{V}_{\text{H}_2\text{O}}$	Water activity a_1
4	1.02918	47.31	18.65	28.73	18.052	0.994
6	1.04597	47.62	18.77	28.92	18.050	0.991
8	1.06328	47.92	18.89	29.10	18.049	0.987
10	1.08114	48.18	18.99	29.26	18.047	0.984
12	1.09958	48.41	19.08	29.40	18.043	0.980
14	1.11863	48.62	19.17	29.54	18.041	0.977
16	1.13832	48.82	19.25	29.66	18.038	0.973
18	1.15869	48.99	19.31	29.75	18.036	0.969
20	1.17978	49.14	19.37	29.85	18.032	0.965
22	1.20162	49.33	19.45	29.96	18.027	0.960
24	1.22425	49.50	19.51	30.07	18.023	0.956
26	1.24772	49.65	19.57	30.15	18.020	0.951
28	1.27208	49.80	19.63	30.25	18.014	0.946
35	1.36503	50.39	19.86	30.60	17.993	0.925
40	1.43986	50.75	20.01	30.82	17.973	0.907
45	1.52305	51.07	20.14	31.02	17.953	0.885
50	1.61610	51.39	20.26	31.13	17.930	0.859

Table IV

Partial Molar Volumes $\bar{V}$, ml/mole, in CsI Solutions, 25°C.

Wt. %	Density d g/ml	$\bar{V}_{\text{CsI}}$	$\bar{V}_{\text{Cs}^+}$	$\bar{V}_{\text{Cl}^-}$	$\bar{V}_{\text{H}_2\text{O}}$	Water activity a_1
4	1.02899	58.72	19.02	39.71	18.052	0.995
6	1.04570	58.95	19.09	39.85	18.052	0.992
8	1.06294	59.16	19.15	39.99	18.050	0.989
10	1.08074	59.36	19.23	40.14	18.049	0.987
12	1.09912	59.62	19.31	40.31	18.047	0.984
14	1.11811	59.81	19.37	40.44	18.045	0.981
16	1.13775	59.94	19.41	40.53	18.043	0.978
18	1.15808	59.99	19.43	40.56	18.043	0.974
20	1.17915	60.01	19.44	40.58	18.041	0.971
22	1.20099	60.12	19.47	40.64	18.040	0.968
24	1.22364	60.20	19.49	40.70	18.038	0.964
26	1.24715	60.25	19.51	40.74	18.038	0.960
28	1.27157	60.35	19.55	40.82	18.034	0.956
35	1.36497	60.61	19.63	40.99	18.027	0.940
40	1.44044	60.79	19.69	41.10	18.020	0.926
45	1.52460	61.00	19.75	41.24	18.009	0.911

Table V

Partial Molar Volumes $\bar{V}$, ml/mole, in RbCl Solutions, 25°C.

Wt. %	Density d g/ml	$\bar{V}_{\text{RbCl}}$	$\bar{V}_{\text{Rb}^+}$	$\bar{V}_{\text{Cl}^-}$	$\bar{V}_{\text{H}_2\text{O}}$	Water activity a_1
4	1.02693	33.68	11.90	21.77	18.050	0.989
6	1.04239	34.17	12.07	22.09	18.045	0.983
8	1.05823	34.59	12.22	22.37	18.041	0.977
10	1.07448	34.93	12.35	22.59	18.036	0.971
12	1.09117	35.24	12.45	22.78	18.031	0.965
14	1.10832	35.51	12.55	22.97	18.023	0.958
16	1.12595	35.79	12.65	23.14	18.016	0.951
18	1.14408	36.06	12.74	23.32	18.009	0.943
20	1.16273	36.34	12.84	23.49	18.000	0.935
22	1.18192	36.60	12.94	23.67	17.989	0.927
24	1.20167	36.87	13.03	23.84	17.977	0.918
26	1.22201	37.12	13.12	24.01	17.964	0.909
28	1.24296	37.38	13.21	24.17	17.950	0.899
35	1.32151	38.21	13.50	24.71	17.894	0.858
40	.38318	38.72	13.68	25.04	17.847	0.823
45	1.45018	39.18	13.85	25.34	17.797	

Table VI

Partial Molar Volumes $\bar{V}$, ml/mole, in RbBr Solutions, 25°C.

Wt. %	Density d g/ml	$\bar{V}_{\text{RbBr}}$	$\bar{V}_{\text{Rb}^+}$	$\bar{V}_{\text{Br}^-}$	$\bar{V}_{\text{H}_2\text{O}}$	Water activity a_1
4	1.02833	40.14	12.21	27.94	18.052	0.992
6	1.04464	40.46	12.30	28.16	18.050	0.988
8	1.06143	40.77	12.40	28.38	18.047	0.983
10	1.07872	41.10	12.50	28.60	18.043	0.979
12	1.09653	41.40	12.59	28.81	18.040	0.974
14	1.11489	41.66	12.67	29.00	18.036	0.969
16	1.13383	41.91	12.74	29.17	18.031	0.964
18	1.15338	42.14	12.81	29.33	18.025	0.959
20	1.17357	42.38	12.88	29.49	18.020	0.953
22	1.19443	42.57	12.95	29.63	18.013	0.947
24	1.21600	42.77	13.00	29.76	18.007	0.941
26	1.23832	42.94	13.06	29.89	18.002	0.934
28	1.26143	43.14	13.12	30.02	17.993	0.927
35	1.34917	43.70	13.29	30.41	17.966	0.899
40	1.41924	44.11	13.41	30.70	17.939	0.875
45	1.49654	44.49	13.53	30.97	17.906	0.847
50	1.58222	44.91	13.65	31.25	17.887	

Table VII

Partial Molar Volumes $\bar{V}$, ml/mole, in RbI Solutions, 25°C.

Wt. %	Density d g/ml	$\bar{V}_{\text{RbI}}$	$\bar{V}_{\text{Rb}^+}$	$\bar{V}_{\text{I}^-}$	$\bar{V}_{\text{H}_2\text{O}}$	Water activity a_1
4	1.02831	51.46	12.52	38.94	18.052	0.994
6	1.04464	51.68	12.58	39.11	18.050	0.990
8	1.06147	51.89	12.63	39.27	18.050	0.987
10	1.07883	52.06	12.66	39.39	18.049	0.983
12	1.09675	52.21	12.70	39.51	18.047	0.980
14	1.11525	52.40	12.75	39.65	18.045	0.976
16	1.13436	52.57	12.79	39.78	18.041	0.972
18	1.15411	52.76	12.84	39.92	18.038	0.968
20	1.17453	52.93	12.88	40.05	18.036	0.963
22	1.19566	53.08	12.91	40.16	18.032	0.959
24	1.21754	53.23	12.95	40.28	18.027	0.954
26	1.24020	53.42	13.00	40.43	18.022	0.949
28	1.26368	53.65	13.05	40.60	18.016	0.943
35	1.35307	54.06	13.15	40.91	18.000	0.922
40	1.42481	54.40	13.23	41.16	17.982	0.903
45	1.50428	54.71	13.31	41.41	17.962	0.880
50	1.59281	55.01	13.38	41.63	17.939	0.853

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Appendix A

Hewlett Packard 9825A program for the determination of partial molar volumes in 1:1 salt solutions.

```

0: dsp "CALC. OF PARTIAL MOLAR VOLUME";wait 1500
1: dim M[3],R[2],S$[10],W[23],D[23],P[8],Q$[3];cfg 13
2: "SALT":enp "SALT =" ,S$
3: ent "MOL.-WEIGHT OF CATION =" ,M[1]
4: ent "MOL.-WEIGHT OF ANION =" ,M[2]
5: M[1]+M[2]*M[3]
6: ent "CRYSTAL RADIUS OF CATION =" ,R[1]
7: ent "CRYSTAL RADIUS OF ANION =" ,R[2]
8: for I=1 to 2;R[I]^3*R[I];next I
9: dsp "PRINTER READY ?";stp
10: fmt "SALT:",cl0,/;wrt 6,S$
11: fmt "Mol.-weight of salt:",2x,f7.2;wrt 6,M[3]
12: fmt "Mol.-weight of cation:",f7.2;wrt 6,M[1]
13: fmt "Mol.-weight of anion:",1x,f7.2,/;wrt 6,M[2]
14: fmt "Wt.%" ,3x,"Density",4x,"Partial Molar Volumes of:";wrt 6
15: fmt 18x,"salt",4x,"cation",4x,"anion",4x,"water",/;wrt 6
16: for I=1 to 15;2I"W[I];next I
17: for I=1 to 8;5I+30"W[15+I];next I
18: 1"I
19: "D":fxd 0;dsp "WEIGHT%=",W[I],"DENSITY(25C) =" ;ent "" ,D[I]
20: if flgl3;cfg 13;I-1"N;gto "CALC"
21: 1/D[I]"D[I];1+I"I;gto "D"
22: "CALC":for I=2 to N-1
23: D[I]-W[I](D[I+1]-D[I-1])/(W[I+1]-W[I-1])"P[1]
24: D[I]+(100-W[I])(D[I+1]-D[I-1])/(W[I+1]-W[I-1])"P[2]
25: 18P[1]"P[5];M[3]P[2]"P[6]
26: M[3]P[2]R[1]/(R[1]+R[2])"P[7]
27: M[3]P[2]R[2]/(R[1]+R[2])"P[8]
28: fmt 1x,f2.0,4x,f7.5,4x,f5.2,4x,f5.2,4x,f5.2,4x,f6.3,/
29: if I#15;wrt 6,W[I],1/D[I],P[6],P[7],P[8],P[5]
30: next I;ent "ANOTHER SALT? yes or no",Q$
31: if cap(Q$)="YES";gto "SALT"
32: stp
33: end
*23817

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