

Apparent Molar Volumes of Electrolytes

Part 2.—Some 1-1 Electrolytes in Aqueous Solution at 25°C

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The apparent molar volumes of NaCl, KCl, KBr, KI, and $n\text{-Bu}_4\text{NBr}$ in the concentration range 0.001-1.0 M and at 25°C have been determined using a magnetically-operated dilatometer. The theoretical Debye-Hückel apparent molar volume limiting slope for 1-1 electrolytes at 25°C is satisfactorily approached by each electrolyte in the very dilute solution region.

Investigation of the apparent molar volume behaviour of electrolytes in very dilute solutions has been hampered by experimental difficulties. Consequently, reliable data for a wide variety of electrolytes in this concentration region have not been available to test the theoretical predictions of Redlich and Rosenfeld.¹ These authors have shown that the theoretical apparent molar volume limiting slope for an electrolyte at a fixed temperature is independent of the nature of the electrolyte except for its valency type. The theoretically-predicted² apparent molar volume limiting slopes for 1-1, 2-1, 3-1 and 4-1 electrolytes in aqueous solution at 25°C are 1.868, 9.706, 27.453 and 59.066 ml mole⁻¹ respectively. Using a dilatometric method,³ these values are observed experimentally in very dilute aqueous solutions at 25°C for a number of electrolytes of each of these valency types.^{3, 4} Data are reported here for some additional 1-1 electrolytes at 25°C.

EXPERIMENTAL

The theory and operation of the dilatometer have been described previously,³ as has the constant temperature bath.⁴ As a check on the previous estimate of the temperature control of the bath, the temperature of the contents of the dilatometer was measured with a Hewlett-Packard model DY-2801A quartz oscillator thermometer. The dilatometer was set up as described previously³ with the exception that the probe of the quartz thermometer was inserted in place of the capsule. After temperature equilibrium had been reached, the temperature variation of the contents of the dilatometer was found to be only 0.0004°C over a 2-h period. The dilatometer is clearly a very sensitive thermometer.

A.R. sodium chloride was twice recrystallized from conductance water and dried to constant weight at 500°C. Stock solutions were prepared by weight. A.R. potassium chloride was twice recrystallized from conductance water and dried to constant weight at 450°C. Stock solutions were prepared by weight and checked conductimetrically using the data of Chambers.⁵ Excellent agreement (0.02%) was obtained between the two methods of analysis. A.R. potassium bromide was twice recrystallized from conductance water containing a trace of HBr, and dried to constant weight at 130°C. Stock solutions were prepared by weight. Conductivity checks on a few solutions, using the conductance data of Jones and Bickford,⁶ yielded results in excellent agreement (0.02%) with the weight data. A.R. potassium iodide was twice recrystallized from conductance water and dried to constant

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weight at 130°C. Stock solutions were prepared by weight and were stored under dry nitrogen to prevent oxidation to free iodine. Conductivity checks on a few solutions, using the conductance data of Chambers,⁵ yielded results in excellent agreement (0.02%) with the weight data. Eastman Chemical Company tetra(n-butyl) ammonium bromide was recrystallized three times from acetone and dried to constant weight at 90°C *in vacuo* for several days. Stock solutions were prepared by weight. The purity of the salt, as estimated by duplicate (0.02%) gravimetric analyses as AgBr, was 99.72%.

In the conductance analyses, suitable deviation functions were employed. The cells and conductance equipment have been described previously.⁷

RESULTS

The apparent molar volumes of the concentrated solutions were calculated⁴ from density measurements using two 50 ml Ostwald pyknometers. Duplicate densities agreed to $\pm 1 \times 10^{-5}$ g ml⁻¹. Using 0.99707 g ml⁻¹ as the density of water at 25°C,

TABLE 1.—DENSITIES AND APPARENT MOLAR VOLUMES OF CONCENTRATED ELECTROLYTE SOLUTIONS AT 25°C

solution	$c/\text{mole l.}^{-1}$	d_4^{25}	$\phi^V/\text{ml mole}^{-1}$
1, NaCl	0.8089 ₁	1.02959 ₁	18.29
2, NaCl	0.2091 ₃	1.00564 ₄	17.50
3, KCl	0.7927 ₅	1.03356 ₄	28.60
4, KCl	0.2077 ₁	1.00682 ₅	27.67
5, KBr	0.8880 ₂	1.07128 ₉	35.54
6, KBr	0.7794 ₃	1.06230 ₁	35.42
7, KBr	0.7672 ₄	1.06127 ₁	35.44
8, KBr	0.6930 ₈	1.05514 ₈	35.32
9, KBr	0.5953 ₁	1.04701 ₃	35.22
10, KBr	0.4937 ₅	1.03855 ₀	35.10
11, KBr	0.3091 ₃	1.03149 ₅	34.97
12, KBr	0.2886 ₉	1.02142 ₀	34.77
13, KBr	0.2341 ₁	1.01684 ₁	34.66
14, KBr	0.1977 ₂	1.01378 ₁	34.59
15, KI	0.8981 ₅	1.10425 ₅	46.80
16, KI	0.7641 ₉	1.08837 ₄	46.67
17, KI	0.7412 ₄	1.08564 ₁	46.65
18, KI	0.7029 ₃	1.08109 ₂	46.61
19, KI	0.5784 ₁	1.06627 ₄	46.50
20, KI	0.4957 ₇	1.05643 ₆	46.40
21, KI	0.3971 ₈	1.04467 ₃	46.29
22, KI	0.3014 ₅	1.03323 ₂	46.18
23, KI	0.1935 ₈	1.02032 ₄	46.02
24, KI	0.1894 ₄	1.01983 ₈	45.96
25, n-Bu ₄ NBr	0.4465 ₆	1.00870 ₅	297.19
26, n-Bu ₄ NBr	0.1557 ₂	1.00078 ₀	299.43
27, n-Bu ₄ NBr	0.1018 ₆	0.99944 ₃	299.97

the pyknometers were regularly calibrated with conductance water. Table 1 gives the densities and apparent molar volumes of the concentrated solutions, while table 2 gives the dilatometer data and the apparent molar volumes of the dilute solutions of each electrolyte. The limiting apparent molar volume of each electrolyte given in table 3 has been obtained by plotting the function $\phi^V - 1.868 \nu^{\frac{1}{2}} c^{\frac{1}{2}}$ against c and extrapolating to zero concentration.⁴ From fig. 1-3, the theoretical limiting slope is again satisfactorily approached for each electrolyte studied.

The data for NaCl and KCl were obtained while testing the dilatometer technique, and are included for completeness. The NaCl data are in excellent agreement with

the data of Kruis,⁸ as are the KCl data with those of Kruis⁸ and Geffcken and Price.⁹ The data for KBr and KI are in good agreement with the data of Geffcken¹⁰ in the high concentration region, and below 0.5 M, with the KBr data of Desnoyers and Arel.¹¹ Above 0.2 M the data for $n\text{-Bu}_4\text{NBr}$ are in good agreement with the data of Wen and Saito,¹² and in the dilute solution region with the data of Conway, Verrall and Desnoyers¹³ and Franks and Smith.¹⁸

TABLE 2.—APPARENT MOLAR VOLUMES OF DILUTE ELECTROLYTE SOLUTIONS AT 25°C

solution in capsule	mole solute	$-\frac{\Delta v}{\text{ml}}$	$\frac{c}{\text{mole l.}^{-1}}$	$\frac{\phi v}{\text{ml mole}^{-1}}$
1, NaCl	0.002017	0.00317	0.004095	16.73
3, KCl	0.006825	0.01010	0.02292	27.12
3, KCl	0.008677	0.01405	0.007766	26.98
4, KCl	0.000518	0.00042	0.001053	26.86
7, KBr	0.006606	0.00932	0.02227	34.03
7, KBr	0.004939	0.00741	0.009889	33.94
13, KBr	0.002016	0.00153	0.006796	33.90
13, KBr	0.001507	0.00122	0.003017	33.85
17, KI	0.006382	0.00752	0.02152	45.48
17, KI	0.004771	0.00603	0.009554	45.39
24, KI	0.001631	0.00099	0.005499	45.35
24, KI	0.001219	0.00081	0.002442	45.29
25, $n\text{-Bu}_4\text{NBr}$	0.003844	-0.01318	0.01297	300.62
25, $n\text{-Bu}_4\text{NBr}$	0.004888	-0.01625	0.004378	300.52
26, $n\text{-Bu}_4\text{NBr}$	0.001705	-0.00180	0.001527	300.49

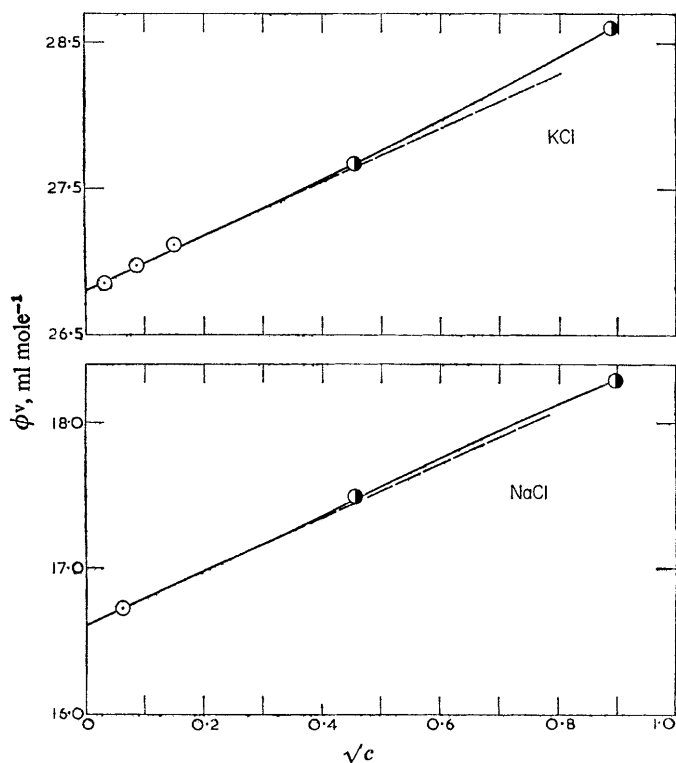


FIG. 1.—Apparent molar volumes of NaCl and KCl in water at 25°C.

●, pycnometer; ○, dilatometer; - - - - - 1-1 theoretical slope.

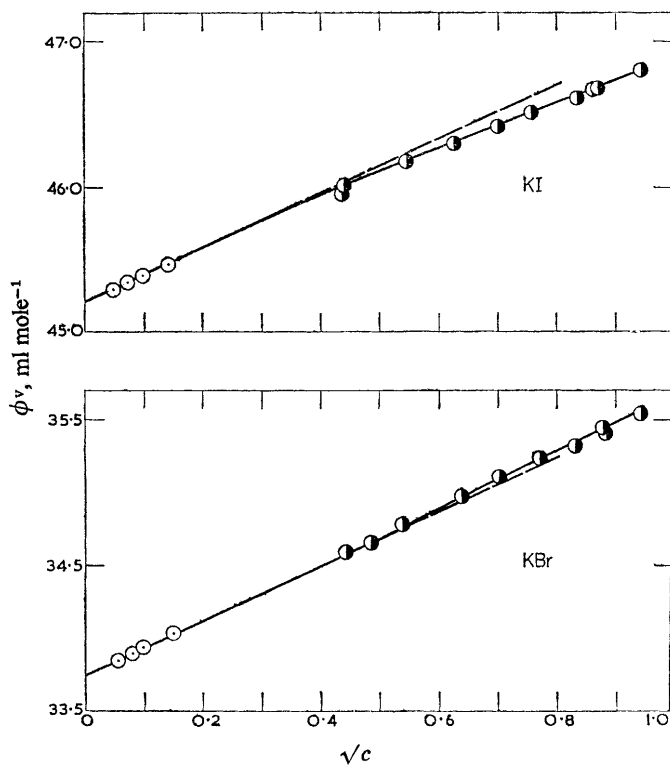


FIG. 2.—Apparent molar volumes of KBr and KI in water at 25°C.
 ●, pycnometer; ○, dilatometer; - - - - - 1-1 theoretical slope.

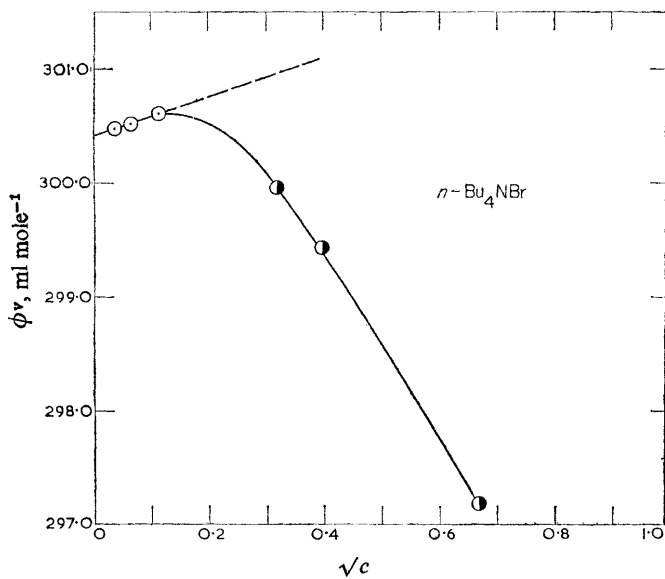


FIG. 3.—Apparent molar volume of $n\text{-Bu}_4\text{NBr}$ in water at 25°C.
 ●, pycnometer; ○, dilatometer; - - - - - 1-1 theoretical slope

DISCUSSION

Evaluation of individual ionic contributions to the transport properties of an electrolyte, such as conductance and diffusion, rests on sound experimental and theoretical foundations. No such basis exists for the separation of individual ionic partial molar thermodynamic quantities. For partial molar volumes, this is important if ion-solvent interactions are to be completely understood. Many workers^{13, 14} advocate non-thermodynamic approaches to the subject.

In the absence of a reliable method for calculating individual ionic partial molar volumes, the best method of comparing the limiting apparent molar volume data of various workers seems to be comparison of differences in ionic partial molar volumes. Since ionic partial molar volumes are additive, differences are readily calculated from experimental data for complete electrolytes. Clearly, for a given pair of ions, the wider the variety of oppositely charged ions used in determining the difference in ionic volumes, the more reliable will be the value of the difference.

TABLE 3.—SOME LIMITING APPARENT MOLAR VOLUMES AND LIMITING IONIC PARTIAL MOLAR VOLUME DIFFERENCES IN WATER AT 25°C

electrolyte	$\phi_0^y/\text{ml mole}^{-1}$	ions	$\Delta\phi_0^y/\text{ml mole}^{-1}$
NaCl	16.61	$\text{K}^+ - \text{Na}^+$	10.20
KCl	26.81	$\text{I}^- - \text{Cl}^-$	18.40
KBr	33.75	$\text{I}^- - \text{Br}^-$	11.46
KI	45.21	$\text{Br}^- - \text{Cl}^-$	6.94
n-Bu ₄ NBr	300.40		

Some ionic partial molar volume differences are given in table 3. The value for $\phi_0^y(\text{K}^+) - \phi_0^y(\text{Na}^+)$ compares favourably with that obtained previously⁴ using the ϕ_0^y data of K_2SO_4 and Na_2SO_4 . It is also in excellent agreement with the value of 10.25 ml mole⁻¹ obtained by Desnoyers and Arel¹¹ from ϕ_0^y data for KBr and NaBr, and with the value of 10.26 ml mole⁻¹ obtained by Vaslow¹⁵ from ϕ_0^y data for KCl and NaCl. The value for $\phi_0^y(\text{I}^-) - \phi_0^y(\text{Cl}^-)$ compares favourably with an average value of 18.3 ml mole⁻¹ calculated from the data of Conway, Verrall and Desnoyers¹³ for some tetraalkylammonium iodides and chlorides. The value for $\phi_0^y(\text{I}^-) - \phi_0^y(\text{Br}^-)$ is in excellent agreement with an average value of 11.4 ml mole⁻¹ calculated from the data of Conway, Verrall and Desnoyers¹³ for some tetraalkylammonium iodides and bromides. It also agrees favourably with the value of 11.5 ml mole⁻¹ calculated from the ϕ_0^y data of Verrall and Conway¹⁶ for n-propylamine hydrogen iodide and the ϕ_0^y data of Desnoyers and Arel¹¹ for n-propylamine hydrogen bromide. The value for $\phi_0^y(\text{Br}^-) - \phi_0^y(\text{Cl}^-)$ is in excellent agreement with the value of 6.87 ml mole⁻¹ obtained by using the ϕ_0^y data of Desnoyers and Arel¹¹ for NaBr and the ϕ_0^y data of Kruis⁸ for NaCl. Likewise, it is in good agreement with the average value of 6.9 ml mole⁻¹ calculated from the ϕ_0^y data of Conway, Verrall and Desnoyers¹³ for some tetraalkylammonium bromides and chlorides, and with the value of 7.01 ml mole⁻¹ calculated from the ϕ_0^y data of Desnoyers and Arel¹¹ for methylamine hydrogen bromide and the ϕ_0^y data of Verrall and Conway¹⁶ for methylamine hydrogen chloride. It would seem that the ϕ_0^y data of table 3 are consistent with literature values.

Wen and Saito¹² have determined the apparent molar volume of n-Bu₄NBr in the concentration range 0.1–10 M, and have extrapolated to infinite dilution using the experimentally observed negative slope. Since n-Bu₄NBr should show a positive limiting slope of 1.868 ml mole⁻² 1.^{1/2}, the apparent molar volume behaviour of this salt was investigated at much lower concentrations than those used by Wen and Saito.¹² From fig. 3, the theoretical limiting slope² is approached in very dilute solutions. Conway, Verrall and Desnoyers¹³ and Wirth¹⁷ have also observed

positive limiting slopes of 1.868 for other tetraalkylammonium bromides, for which Wen and Saito¹² have used negative slopes in their extrapolations to infinite dilution. Consequently, the ϕ_0^y data of these authors¹² are in error by 1–2 ml mole⁻¹. The ϕ_0^y value for n-Bu₄NBr given in table 3 is in excellent agreement with the value of 300.35 ml mole⁻¹ obtained by Franks and Smith.¹⁸

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