and ammonium hexafluorophosphate by metathesis in aqueous solution. After recrystallization from acetone by the slow addition of water, the product melted at 248–51°.

Anal. Calcd. for $C_{19}H_{17}F_6IP_2$: I, 23.20. Found: I, 23.49.

Ylides. The air-sensitive ylides were prepared by reaction of the quaternary phosphonium salt with a freshly prepared solution of dimethylsulfinyl carbanion in DMSO (*1*, *5*).

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RECEIVED for review January 15, 1970. Accepted July 13, 1970. Research partially supported by the National Science Foundation under Grants GP4483 and GP7886. T. J. M. was a National Science Foundation Undergraduate Research Participant, 1964–5.

Partial Molal Volumes of *p*-Toluenesulfonic Acid, Sodium *p*-Toluenesulfonate, Iodic Acid, and Sodium Iodate in Aqueous Solutions at 25°C

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Partial molal volume data are reported for *p*-toluenesulfonic and iodic acid and their sodium salts. *p*-Toluenesulfonic acid exhibits strong acid behavior similar to that of hydrochloric acid, in that the partial molar volume of the sodium salt at infinite dilution is smaller than that of the acid. The behavior of iodic acid in very dilute solutions resembles somewhat that of acetic acid.

Ionization constants as calculated from Raman spectral data have been reported in recent years for both iodic acid (*1*) and *p*-toluenesulfonic acid (*2*). The molar volume of a weak electrolyte decreases upon ionization (*5*), and therefore it seemed desirable to investigate the behavior of these two acids which have ionization constants intermediate between those of a weak acid such as acetic and strong acids such as hydrochloric acid.

EXPERIMENTAL

Solutions of iodic acid, sodium iodate, and sodium *p*-toluenesulfonate were prepared by adding weighed amounts of the solids to known weights of triple-distilled water. Iodic acid and sodium iodate were reagent grade, used as received. The reagent-grade sodium *p*-toluenesulfonate was twice recrystallized from cold water and showed no trace of sulfate or chloride impurities. It was necessary to correct the iodic acid concentrations to account for the small amount of I_2O_5 which is present in dry HIO_3. This fraction was determined from the experimental equivalent weight found for HIO_3. *p*-Toluenesulfonic acid solutions were prepared by gravimetric dilution of a concentrated stock solution of the acid.

The volume of the Sprengel-Ostwald pycnometer was determined from its weight when filled with water. The capillary volumes were determined with mercury, using the handbook value for the density of mercury. After the filled pycnometer was weighed each time, it was placed in a water bath controlled to 25.00° ± 0.01° and the volume of the liquid was calculated from its level in the capillary arms. Density values for 0.5 and 1.0*m* NaCl, which were used as a check on the pycnometer calibration, varied from those in the literature by a maximum of 5 units in the last significant figure.

Apparent molal volumes were first calculated at the measured concentrations from the equation

$$\phi_v = 1000(\sigma_0 - \sigma)/mo\sigma_0 + M_2/\sigma$$

These data were plotted and partial molal volumes were calculated from the smoothed data by the equation

$$\bar{v}_2 = \phi_v + m^{1/2}/2\, d\phi/dm^{1/2}$$

The apparent molal volume calculated from the new data differed from the smoothed values by a maximum of 0.5% in one instance and by an average of 0.15%.

RESULTS AND DISCUSSION

Raw density data are presented in Table I and partial molal volume data at rounded concentrations, as calculated from the smoothed data, are given in Table II. Iodic acid with an ionization constant of 0.17 (*1*) and toluenesulfonic acid with an ionization constant of 11.6 (*2*) represent electro-

Table I. Densities of Aqueous Solutions[a] at 25° C

A		B		C		D	
m	σ	m	σ	m	σ	m	σ
0.0000	0.99707	0.0000	0.99707	0.00000	0.99707	0.00000	0.99707
0.5000	1.02159	0.5000	1.03228	0.01779	0.99974	0.04690	1.00514
1.0000	1.04334	0.9999	1.06354	0.03827	1.00275	0.09286	1.01300
1.5000	1.06260	1.4998	1.09107	0.06710	1.00703	0.27341	1.04341
2.0000	1.07970	2.0003	1.11544	0.09771	1.01154	0.38676	1.06224
2.4999	1.09495	2.5001	1.13702	0.13427	1.01693		
3.0000	1.10846	2.9994	1.15632	0.16939	1.02209		
3.5000	1.12067	3.4995	1.17361	0.18393	1.02421		
4.0003	1.13178	3.8745	1.18549	0.4910	1.06804		
4.5005	1.14187			0.6064	1.08449		

[a] A = p-toluenesulfonic acid, B = Na p-toluenesulfonate, C = HIO_3, D = $NaIO_3$.

Table II. Partial Molal Volumes at 25° C

A		B		C		D	
m	$\bar{v}_2$	m	$\bar{v}_2$	m	$\bar{v}_2$	m	$\bar{v}_2$
0.0	119.7	0.0	118.4	0.0	25.17[a]	0.0	24.78
0.5	120.4	0.5	119.6	0.1	27.25	0.1	26.50
1.0	121.1	1.0	120.8	0.2	28.65	0.2	27.56
1.5	121.8	1.5	121.8	0.3	29.68	0.3	28.20
2.0	122.4	2.0	122.9	0.4	30.56	0.4	28.52
2.5	123.0	2.5	123.9	0.5	31.40		
3.0	123.5	3.0	124.8				
3.5	124.0	3.5	125.4				
4.0	124.4	3.875	125.8				
4.5	124.6						

[a] Graphical extrapolation.

lytes intermediate between the almost completely un-ionized acetic acid and a completely ionized acid such as hydrochloric acid. The partial molal volume data for these four acids and the four sodium salts at various concentrations are shown in Figures 1 and 2.

The partial molal volume of NaCl is less than that of HCl at infinite dilution (*4*), but rises above it in more concentrated solutions. This is the normal behavior of completely dissociated acids and salts (*3*). The data for acetic acid and sodium acetate illustrate the decrease in volume upon dissociation of an electrolyte. An extrapolation to the molal volume of acetic acid at infinite dilution is obviously not possible and calculations must be made in the same manner as for the conductance of ions when weak electrolytes are involved. The data for HIO_3 and $NaIO_3$ follow a pattern similar to that of acetic acid and sodium acetate but not so extreme. The molal volume of HIO_3 at 0.5m, at which point it is about 55% ionized, is not

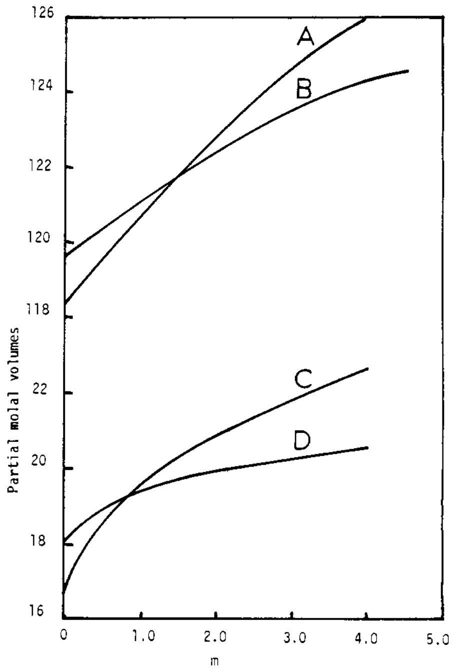

Figure 1. Partial molal volumes of sodium p-toluenesulfonate, p-toluenesulfonic acid, sodium chloride, and hydrochloric acid

- *A.* Sodium p-Toluenesulfonate
- *B.* p-Toluenesulfonic acid
- *C.* Sodium chloride
- *D.* Hydrochloric acid

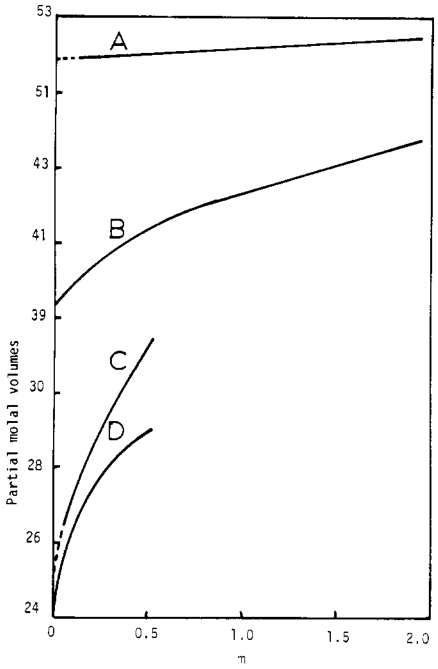

Figure 2. Partial molal volumes of acetic acid, sodium acetate, iodic acid, and sodium iodate

- *A.* Acetic acid
- *B.* Sodium acetate
- *C.* Iodic acid
- *D.* Sodium iodate

approaching that of $NaIO_3$ but is exceeding it by a larger amount than in more dilute solutions.

The behavior of *p*-toluenesulfonic acid and sodium *p*-toluenesulfonate resembled more closely that of HCl and NaCl, but in the more concentrated solutions there is evidence of incomplete ionization of the acid. The difference in partial molal volumes of the acids and corresponding salts at 4.0*m* is 2.1 ml for the chlorides but only 1.4 ml for the toluenesulfonates. A degree of ionization of 0.94 has been calculated of *p*-toluenesulfonic acid at 4.0*m*.

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RECEIVED for review January 16, 1970. Accepted June 11, 1970.

Apparatus for Measurement of Isobaric Dew and Bubble Points and Vapor-Liquid Equilibria

Methanol-Water and Water-Dioxane Systems

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A new apparatus for measurement of isobaric dew and bubble points and vapor-liquid equilibria makes it possible to measure dew and bubble points of any given composition without analysis. Vapor-liquid equilibrium relations may be measured at any vapor or liquid composition appointed and the apparatus can be applied to the usual Othmer-type measurements. With the apparatus, vapor-liquid equilibrium relations were determined at atmospheric pressure for methanol-water and water-dioxane systems.

Vapor-liquid equilibrium relations are important properties of liquid mixtures, and isobaric data in particular are required for practical use, such as in the design and operation of distillation equipment.

For measurements of isobaric vapor-liquid equilibria, several types of apparatus have been proposed by Othmer and other investigators (*1, 5, 10*). In these conventional apparatus, it is necessary to analyze the sample and it is difficult to measure the vapor-liquid equilibrium relation at the exact point desired.

For measurements of isobaric dew points, a unique apparatus was proposed by Kojima *et al.* (*7*). In the apparatus, it is necessary to analyze the sample and it is difficult to measure the dew point at the precise composition desired. Furthermore, the bubble points must be determined by separate measurements or by theoretical estimations.

For measurement of isobaric bubble points, Cottrell (*2*), Kojima *et al.* (*6, 8*), and Swietoslawski (*15*) have proposed some ebulliometers. However, in the general batch-type ebulliometer, it is necessary to correct for the difference between the liquid composition at steady state and the feed composition. The dew points must be determined separately.

The authors (*4*) previously proposed flow-type apparatus for measurement of isobaric dew and bubble points. However, it is not easy to measure dew and bubble points at the accurate composition desired, and for a multicomponent system this apparatus seems complex, because it is necessary to set each boiler for each component in the system studied.

In the present paper, a new apparatus for measurement of isobaric dew and bubble points and vapor-liquid equilibria is proposed, to eliminate as many disadvantages as possible.

EXPERIMENTAL APPARATUS

The apparatus for measurement of isobaric dew and bubble points and vapor-liquid equilibria is shown in Figure 1. It is constructed entirely of borosilicate glass. Its main parts are a dew point still, *D*, a bubble point still, *B*, three overflow tubes, *O*, a connecting tube, *C*, and a feeder, *F*.

The vapor from *D* does not return to that still but enters *B* after condensation. The internal construction of both stills is almost similar to that of the flow-type ebulliometer (*4*). Heat is supplied by Nichrome wires and a little glass dust is put on the wall of the heat transfer surface to stabilize boiling. The boiling vapor-liquid mixture rises through the Cottrell tube and flushes to the thermometer well. The amount of liquid contained in each still is about 15 cc; both stills are kept adiabatic with evacuated jackets and asbestos tapes. Using capillary connecting tube *C*, the liquid flows from *B* to *D*, as shown in Figure 1. Feeder *F* is 150 cc in volume and constructed like a general separating funnel.