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Densities and Apparent Molar Volumes of Na_2SO_4(aq) and K_2SO_4(aq) at Temperatures from 298 K to 573 K and at Pressures up to 30 MPa

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Densities of Na_2SO_4(aq) and K_2SO_4(aq) have been measured by vibrating-tube densitometry at concentrations of 0.01 mol·kg^{-1} to 1.0 and 0.5 mol·kg^{-1}, respectively, and at temperatures from 298.15 K to 572.7 K and pressures up to 30.7 MPa. Apparent molar volumes derived from these data were extrapolated using the Pitzer ion-interaction model to yield partial molar volumes of these electrolytes at infinite dilution. The two salts show similar behaviors over the whole range of conditions studied.

1. Introduction

The present paper is a contribution to the systematic study of the volumetric properties of aqueous electrolyte solutions at high temperatures and pressures started in the Laboratory of Thermodynamics and Chemical Engineering at the Blaise Pascal University in Clermont-Ferrand, France. Density differences between Na_2SO_4 and K_2SO_4 solutions and water and the apparent molar volumes derived from these data are reported for concentrations varying from approximately 0.01 mol·kg^{-1} up to 1.0 and 0.5 mol·kg^{-1}, respectively, and at temperatures ranging from 298 to 573 K and pressures of 10 and 30 MPa. The Pitzer volumetric equation was used for extrapolating the apparent molar volumes to infinite dilution.

Although the volumetric properties of both Na_2SO_4(aq) and K_2SO_4(aq) have been extensively investigated as a function of concentration, often up to quite high pressures, almost all the data refer to temperatures relatively close to 298 K. The major exceptions are the study of Phutela and Pitzer (1986) and, to a more limited extent, the pioneering work of Ellis (1968). The main literature sources reporting data at superambient conditions are listed below with the corresponding concentration, temperature, and pressure ranges of measurements. Na_2SO_4(aq): Ellis, 1968 ($0.05 \leq m$/mol·kg$^{-1} \leq 1.0$, $323 \leq T$/K ≤ 473, $p = 2$ MPa), smoothed values of densities; Chen et al., 1977 ($0.01 \leq m$/mol·kg$^{-1} \leq 0.33$, $273 \leq T$/K ≤ 323, $10 \leq p \leq 100$MPa); Lo Surdo et al., 1982 ($0.01 \leq m$/mol·kg$^{-1} \leq$ sat, $278 \leq T$/K ≤ 318, $p = 0.1$ MPa), recommended data based on a data base of experimental values; Phutela and Pitzer, 1986 ($0.06 \leq m$/mol·kg$^{-1} \leq 0.33$, $294 \leq T$/K ≤ 475, $2 \leq p \leq 10$ MPa); Connaughton et al., 1986 ($0.15 \leq m$/mol·kg$^{-1} \leq 1.7$, $298 \leq T$/K ≤ 368, $p = 0.10$ MPa); Saluja et al., 1992 ($0.02 \leq m$/mol·kg$^{-1} \leq 1.5$, $297 \leq T$/K ≤ 372, $p = 0.6$ MPa). K_2SO_4(aq): Ellis, 1968 ($0.05 \leq m$/mol·kg$^{-1} \leq 1.0$, $323 \leq T$/K ≤ 473, $p = 2$ MPa); Dedick et al., 1990 ($0.05 \leq m$/mol·kg$^{-1} \leq 0.65$, $278 \leq T$/K ≤ 368, $p = 0.1$ MPa); Saluja et al., 1992 ($0.01 \leq m$/mol·kg$^{-1} \leq 0.4$, $297 \leq T$/K ≤ 372, $p = 0.6$ MPa). In most cases, vibrating tube densitometers were used except for Ellis and Phutela and Pitzer who employed dilatometric methods and Chen and coworkers who used a magnetic float densitometer. From this survey it is apparent that, for both salts, there are no experimental data available above 473 K and no measurements have been made for temperatures greater than 323 K at pressures above 10 and 2 MPa for Na_2SO_4(aq) and K_2SO_4(aq), respectively. Thus, the primary objective of this study was to complete the data base of existing experimental values and to expand it toward higher temperatures and pressures.

Table 1. Calibration Constants K and Densities ρ of Calibration Fluids

		ρ/kg·m^{-3}		
T/K	p/MPa	H_2O	N_2 (NaCl)	K/kg·m^{-3}·ms^{-2}
298.2	10.0	1001.4	1109.1[a]	520.79[b]
298.2	30.2	1010.3	1116.4[a]	520.45[b]
369.4	10.3	965.6	90.6	307.76
369.4	30.5	974.5	238.6	307.22
369.5	10.6	965.8	96.4	512.45[b]
369.7	30.3	974.3	237.7	512.28[b]
450.1	10.2	896.2	73.4	299.89
450.1	30.7	908.4	196.7	299.67
517.0	10.3	814.8	64.2	293.23
517.0	30.4	833.7	170.7	293.02
572.7	10.4	716.8	58.5	286.95
572.7	30.3	751.6	154.1	287.16

[a] Density of NaCl(aq) of m = 2.989 28 mol·kg^{-1}. [b] Indicates measurements using Pt/Rh (20%) tubing (see text).

2. Experimental Section

Densities of the various salt solutions were measured using a vibrating tube flow densitometer which is an improved and automated version of those described previously (Albert and Wood, 1984; Majer et al., 1991a). Measurements of the vibration period (τ) of the tube with electrolyte solutions of increasing concentration were alternated throughout with measurements of pure water (τ_o) to ensure the existence of a stable baseline. The differences

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Table 2. Differences between Density of Solution and That of Water ($\Delta\rho = \rho - \rho_o$) and Corresponding Apparent Molar Volumes V_ϕ for $Na_2SO_4(aq)$ and $K_2SO_4(aq)$: $m^\circ = 1$ mol·kg^{-1}; $\rho^\circ = 1$ kg·m^{-3} [a]

p/MPa	T/K	m/m°	$\Delta\rho/\rho^\circ$	V_ϕ/cm^3·mol^{-1}	p/MPa	T/K	m/m°	$\Delta\rho/\rho^\circ$	V_ϕ/cm^3·mol^{-1}
				Na_2SO_4(aq)					
9.92	298.20	0.009983	1.27	15*	30.67	450.07	0.04983	6.37	1.5
9.92	298.20	0.009983	1.29	13*	30.32	450.10	0.09967	12.63	2.8
9.92	298.20	0.02507	3.21	14.3*	30.36	450.09	0.09967	12.56	3.5
9.92	298.20	0.02507	3.16	15.9*	30.39	450.09	0.2493	30.40	8.30
9.92	298.20	0.04966	6.28	15.6*	30.42	450.08	0.2493	30.41	8.26
9.92	298.20	0.04966	6.24	16.4*	30.52	450.08	0.4899	57.85	12.47
9.92	298.20	0.1003	12.61	16.2*	30.58	450.08	0.4899	57.85	12.46
9.91	298.20	0.1003	12.65	15.9*	30.52	450.07	1.0024	112.98	17.59
9.92	298.20	0.4889	58.73	20.83*	30.55	450.07	1.0024	113.03	17.54
9.92	298.21	0.4889	58.79	20.72*	10.30	517.04	0.004882	0.78	−65
9.87	298.18	1.0032	115.29	24.43*	10.30	517.03	0.004882	0.78	−66
9.89	298.18	1.0032	115.21	24.50*	10.30	517.04	0.009991	1.58	−64
30.60	298.20	0.02507	3.09	19.8*	10.31	517.03	0.009991	1.57	−63
30.60	298.20	0.02507	3.11	17.5*	10.24	517.04	0.02499	3.84	−56.7
30.60	298.21	0.02507	3.17	16.7*	10.25	517.03	0.02499	3.78	−53.4
30.20	298.19	0.04966	6.18	18.6*	10.25	517.03	0.04983	7.37	−47.8
30.23	298.19	0.04966	6.17	18.7*	10.26	517.03	0.04983	7.35	−47.4
30.30	298.19	0.1003	12.42	19.0*	10.26	517.03	0.09967	14.34	−41.6
30.37	298.20	0.1003	12.39	19.3*	10.27	517.02	0.09967	14.28	−40.7
30.45	298.20	0.4889	58.09	22.86*	10.27	517.02	0.2493	34.05	−30.1
30.50	298.20	0.4889	58.08	22.89*	10.27	517.02	0.2493	34.02	−29.9
30.54	298.20	1.0032	113.80	26.47*	10.27	517.02	0.4899	63.85	−20.3
30.57	298.20	1.0032	113.78	26.49*	10.28	517.02	0.4899	63.87	−20.4
10.16	369.36	0.009991	1.23	15.1	10.27	517.02	1.0024	122.79	−8.8
10.16	369.36	0.009991	1.23	15.1	10.27	517.02	1.0024	122.73	−8.7
10.17	369.36	0.009991	1.22	15.7	30.07	517.03	0.009991	1.49	−45
10.57	369.51	0.02499	3.07	15.4*	30.11	517.03	0.009991	1.48	−43
10.58	369.51	0.02499	3.08	15.0*	30.12	517.03	0.02499	3.62	−37.9
10.17	369.36	0.04983	6.02	17.4	30.09	517.03	0.02499	3.62	−37.6
10.18	369.36	0.04983	6.07	16.3	30.36	517.01	0.04983	7.08	−33.6
10.17	369.36	0.09967	11.98	18.00	30.31	517.01	0.04983	7.05	−32.8
10.16	369.36	0.09967	11.97	18.12	30.27	517.01	0.09967	13.73	−27.3
10.16	369.36	0.2493	29.36	20.17	30.27	517.01	0.09967	13.67	−26.5
10.14	369.36	0.2493	29.35	20.21	30.26	517.01	0.2493	32.74	−17.8
10.16	369.36	0.4899	56.38	22.38	30.25	517.01	0.2493	32.76	−17.9
10.16	369.36	0.4899	56.41	22.30	30.30	517.02	0.4899	61.76	−10.2
10.16	369.36	1.0024	110.73	25.68	30.30	517.02	0.4899	61.81	−10.4
10.16	369.36	1.0024	110.74	25.67	30.26	517.02	1.0024	119.11	−0.49
10.60	369.51	1.0024	110.80	25.63*	30.26	517.02	1.0024	119.14	−0.53
10.60	369.51	1.0024	110.85	25.58*	10.41	572.73	0.009991	1.99	−188
30.41	369.38	0.02499	2.98	20.0	10.41	572.73	0.009991	2.02	−194
30.42	369.39	0.02499	2.99	19.8	10.40	572.71	0.02499	4.80	−174
30.15	369.66	0.02499	3.03	17.72*	10.39	572.71	0.02499	4.77	−172
30.43	369.39	0.04983	5.95	19.8	10.38	572.71	0.04983	9.14	−156.5
30.43	369.38	0.04983	5.94	20.1	10.36	572.71	0.04983	9.09	−154.7
30.15	369.67	0.04983	6.03	18.3*	10.37	572.71	0.09967	17.30	−136.0
30.42	369.38	0.09967	11.84	20.48	10.40	572.71	0.09967	17.27	−135.5
30.43	369.38	0.09967	11.85	20.27	10.41	572.71	0.2493	40.21	−109.4
30.43	369.38	0.2493	29.04	22.43	10.41	572.71	0.2493	40.17	−109.1
30.44	369.38	0.2493	29.04	22.43	10.39	572.72	0.4899	73.63	−85.4
30.43	369.39	0.4899	55.76	24.50	10.39	572.72	0.4899	73.60	−85.3
30.43	369.38	0.4899	55.80	24.42	10.38	572.72	1.0024	137.60	−57.7
30.43	369.37	1.0024	109.54	27.59	10.39	572.72	1.0024	137.74	−58.0
30.44	369.37	1.0024	109.56	27.58	30.24	572.66	0.009991	1.78	−126
10.19	450.07	0.02499	3.32	−6.9	30.25	572.66	0.009991	1.78	−126
10.19	450.07	0.02499	3.28	−4.8	30.31	572.66	0.02499	4.24	−111
10.19	450.06	0.04983	6.46	−3.0	30.31	572.66	0.02499	4.24	−110
10.19	450.05	0.04983	6.47	−3.1	30.29	572.66	0.04983	8.14	−98.8
10.19	450.05	0.09967	12.68	0.1	30.26	572.66	0.04983	8.12	−98.3
10.19	450.05	0.09967	12.70	−0.2	30.26	572.66	0.09967	15.60	−86.0
10.19	450.05	0.2493	30.86	4.25	30.27	572.67	0.09967	15.58	−85.7
10.19	450.05	0.2493	30.82	4.42	30.28	572.67	0.2493	36.58	−67.3
10.12	450.07	0.4899	58.58	9.02	30.27	572.67	0.2493	36.60	−67.4
10.12	450.06	0.4899	58.66	8.84	30.28	572.67	0.4899	67.88	−51.5
10.12	450.05	1.0024	114.35	14.61	30.28	572.67	0.4899	67.86	−51.4
10.13	450.05	1.0024	114.38	14.58	30.27	572.67	1.0024	128.73	−32.6
30.70	450.07	0.04983	6.34	2.3	30.28	572.67	1.0024	128.84	−32.8
				K_2SO_4(aq)					
9.90	298.20	0.004834	0.64	41*	30.61	450.07	0.02492	3.45	24.2
9.91	298.20	0.004834	0.70	29*	30.62	450.07	0.04970	6.87	24.1
9.94	298.25	0.009999	1.34	40*	30.63	450.07	0.04970	6.89	23.7
9.96	298.25	0.009999	1.38	37*	30.64	450.07	0.09970	13.70	25.0
9.97	298.25	0.009999	1.41	34*	30.64	450.07	0.09970	13.64	25.7
9.98	298.24	0.02483	3.46	35.0*	30.64	450.07	0.2529	33.83	28.64
9.99	298.23	0.02483	3.44	35.6*	30.65	450.07	0.2529	33.85	28.54
9.94	298.25	0.04969	6.83	36.7*	30.66	450.07	0.5052	64.92	33.69

Table 2. (Continued)

p/MPa	T/K	$m/m°$	$\Delta\rho/\rho°$	V_{ϕ}/cm^3·mol^{-1}
9.94	298.25	0.04969	6.87	36.0*
9.95	298.23	0.09948	13.60	37.2*
9.95	298.23	0.09948	13.55	37.7*
9.96	298.20	0.2527	33.75	39.52*
9.96	298.20	0.2527	33.79	39.35*
9.88	298.20	0.5042	65.53	41.69*
9.89	298.20	0.5042	65.56	41.64*
30.15	298.21	0.009999	1.35	40*
30.14	298.21	0.009999	1.35	41*
30.14	298.21	0.02483	3.39	38.6*
30.15	298.20	0.02483	3.46	35.9*
30.14	298.20	0.04969	6.74	39.4*
30.14	298.20	0.04969	6.77	38.7*
29.75	298.20	0.09948	13.43	39.7*
29.76	298.20	0.09948	13.45	39.5*
29.91	298.21	0.2527	33.48	41.31*
30.00	298.21	0.2527	33.39	41.66*
30.00	298.21	0.5042	64.89	43.58*
30.03	298.20	0.5042	64.85	43.67*
10.61	369.51	0.009993	1.37	32.9*
10.61	369.51	0.009993	1.37	32.8*
10.22	369.36	0.02492	3.33	37.2
10.22	369.36	0.02492	3.38	35.0
10.22	369.36	0.04970	6.65	36.7
10.21	369.36	0.04970	6.65	36.7
10.21	369.36	0.09970	13.19	38.06
10.21	369.36	0.09970	13.21	37.88
10.22	369.36	0.2529	32.74	40.23
10.21	369.36	0.2529	32.75	40.19
10.22	369.36	0.5052	63.12	43.63
10.22	369.36	0.5052	63.14	43.58
10.61	369.51	0.5052	63.28	43.41*
10.60	369.51	0.5052	63.29	43.30*
30.15	369.66	0.009993	1.39	30.9*
30.14	369.66	0.02492	3.37	36.0*
30.59	369.37	0.04970	6.60	38.8
30.59	369.37	0.04970	6.59	39.0
30.60	369.37	0.09970	13.09	40.01
30.59	369.37	0.09970	13.08	40.12
30.59	369.36	0.2529	32.51	42.06
30.60	369.36	0.2529	32.49	42.14
30.60	369.37	0.5052	62.60	45.43
30.60	369.36	0.5052	62.59	45.45
10.02	450.04	0.009993	1.47	12
10.04	450.04	0.009993	1.46	12
10.04	450.04	0.02492	3.57	15.9
10.06	450.03	0.02492	3.57	15.9
10.07	450.03	0.04970	7.09	16.8
10.08	450.03	0.04970	7.05	17.6
10.08	450.03	0.09970	13.94	20.0
10.09	450.03	0.09970	13.94	20.1
10.02	450.14	0.2529	34.34	24.42
10.03	450.15	0.2529	34.34	24.41
10.04	450.15	0.5052	65.80	30.05
10.06	450.15	0.5052	65.81	30.02
30.60	450.07	0.02492	3.47	23.1
30.65	450.07	0.5052	64.40	34.89
10.32	517.04	0.004863	0.83	−45
10.33	517.04	0.009993	1.70	−42
10.29	517.04	0.02492	4.14	−35.9
10.30	517.04	0.02492	4.11	−34.3
10.30	517.04	0.04970	8.01	−28.6
10.30	517.04	0.04970	7.99	−28.1
10.25	517.03	0.09970	15.76	−23.7
10.26	517.03	0.09970	15.62	−21.6
10.28	517.03	0.2529	37.84	−10.9
10.29	517.03	0.2529	37.79	−10.7
10.30	517.03	0.5052	71.79	−0.1
10.29	517.03	0.5052	71.68	0.2
30.32	517.01	0.004863	0.83	−36
30.28	517.00	0.004863	0.81	−30
30.29	517.01	0.009993	1.67	−31
30.27	517.01	0.009993	1.59	−20
30.27	517.01	0.02492	3.92	−17.1
30.26	517.01	0.02492	3.92	−17.2
30.27	517.01	0.04970	7.62	−11.4
30.27	517.01	0.04970	7.61	−11.0
30.28	517.01	0.09970	14.97	−6.8
30.30	517.01	0.09970	14.97	−6.9
30.30	517.01	0.2529	36.44	1.7
30.31	517.01	0.2529	36.44	1.7
30.31	517.01	0.5052	69.38	10.6
30.31	517.01	0.5052	69.40	10.5
10.40	572.71	0.004863	1.11	−200
10.41	572.71	0.004863	1.10	−194
10.41	572.71	0.009993	2.12	−168
10.42	572.72	0.009993	2.15	−175
10.41	572.72	0.02492	5.13	−156
10.41	572.72	0.02492	5.15	−158
10.42	572.72	0.04970	9.80	−138.5
10.42	572.72	0.04970	9.83	−139.7
10.41	572.73	0.09970	18.90	−122.3
10.41	572.73	0.09970	18.88	−121.9
10.41	572.73	0.2529	44.54	−93.6
10.41	572.75	0.2529	44.62	−94.2
10.40	572.75	0.5052	82.80	−67.8
10.40	572.75	0.5052	82.85	−68.0
30.27	572.68	0.004863	0.91	−99
30.28	572.67	0.004863	0.93	−108
30.28	572.67	0.009993	1.88	−101
30.28	572.67	0.009993	1.87	−99
30.29	572.68	0.02492	4.57	−92
30.28	572.68	0.02492	4.60	−94
30.29	572.67	0.04970	8.80	−80.6
30.28	572.67	0.04970	8.69	−76.8
30.28	572.67	0.09970	17.02	−68.7
30.28	572.67	0.09970	17.01	−68.5
30.28	572.67	0.2529	40.65	−49.8
30.28	572.67	0.2529	40.71	−50.2
30.28	572.67	0.5052	76.66	−33.2
30.27	572.67	0.5052	76.64	−33.2

[a] Data marked by * were obtained on Pt/Rh (20%) alloy tubing (see text).

($\Delta\rho$) between the density of the electrolyte solutions (ρ) and that of pure water (ρ_o) were obtained from the relationship

$$\Delta\rho = \rho - \rho_o = K(\tau^2 - \tau_o^{\,2}) = K\Delta\tau^2 \qquad (1)$$

K is the calibration constant of the densitometer, which was determined by measuring τ for two fluids of known density under the desired conditions of temperature and pressure. Water and nitrogen were generally used, with the density of water being calculated from the equation of state of Hill (1990) and that of nitrogen (playing a minor role in the calculation) being derived from Perry, 1973. At 298 K, it is difficult to replace quantitatively water by nitrogen in a flow regime as H_2O drops tend to stick on the wall of the tube. For that reason water and 3 m NaCl(aq) were taken as the calibrating fluids at the lowest temperature. The density of the latter was calculated from the recommended values of Archer (1992). The calibration constants for the conditions employed in the present study are given in Table 1 along with other relevant information. We believe that the calibration constant has an error of 0.1−0.2%. The pressure dependence of the calibration constant is negligible.

As described in detail elsewhere (Hynek et al., in press) a digital control system maintained short term temperature fluctuations of the densitometer block to less than ±0.01 K. The temperature of the densitometer block was measured by a 500 Ω Burns industrial platinum resistance thermometer; the absolute error in the temperature of the vibrating tube is estimated to be less than 0.15 K. Pressure in the system was controlled by a Circle Seal back-pressure regulator and during the course of a typical experiment was maintained constant within ±0.02 MPa. The pressure was measured by a Druck DPI 260 (0−35 MPa) electronic manometer with an error of 0.15% of the full scale reading. Typical flow rates through the system were between 0.4 and 0.5 $\mathrm{cm^3 \cdot min^{-1}}$; the preheating system was able under these conditions to approximate closely the temperature of the incoming fluid to that of the block. The measured density differences were flow independent for the flow rates used. The vibration period was determined as the time for 2000 oscillations, corresponding to one reading every 12−15 s, depending on the nature of the metal of the vibrating tube. To provide a check on the functioning of the densitometer system, measurements were routinely made with a concentrated NaCl solution (concentration near 3 $\mathrm{mol \cdot kg^{-1}}$) for which accurate density data are available over a wide range of T and p (Archer, 1992). These results are discussed more fully elsewhere (Hynek et al., in press), and agreement with the literature data was always obtained within expected uncertainty limits.

The density data reported here for Na_2SO_4(aq) and K_2SO_4(aq) were measured over a 2 year period, commencing toward the end of 1992, during which time a number of modifications were made to the instrumentation. A complete description of the current version of the densitometer is given by Hynek et al. (in press); however, for convenience the main changes are briefly summarized here. Initial measurements were made with Hastelloy-C tubing (1.6 mm o.d., 0.2 mm wall thickness, $\tau \sim 6.1$ ms) in the hot zone of the densitometer. The original design of the vibrating unit was similar to that described previously by Albert and Wood (1984). The thermostating system, placed in an evacuated can, was of the same design as that described by Majer et al., 1991a. In addition, the apparatus contained a small actively-controlled preheater which was in good thermal contact with the tube delivering the incoming fluid and was positioned close above the densitometer block. The preheater input was adjusted such that the thermocouple signal measuring the temperature difference between the tube entering the block and a spot near the Burns thermometer was close to zero ($\Delta T \leq 0.1$ K). All temperature regulation was *via* a computer which also served for storage and retrieval of the vibration period. Drive and pick-up electronics were similar to those described by Wood et al. (1989).

Because of slow corrosion during measurements, the Hastelloy was eventually replaced by Pt/Rh (20%) tubing. The oscillating part of the latter ($\tau \sim 7.7$ ms) was 1.6 mm o.d. with a wall thickness of 0.25 mm and formed one piece with a transporting tube of 1.1 mm o.d. and 0.2 mm wall thickness. The design of the platinum vibrating tube unit represents a further development of previous designs (Albert and Wood, 1984; Majer et al., 1991a) and uses two permanent magnets and a pole piece which focuses the magnetic field onto the pickup and drive bars (for more details, see Hynek et al., in press).

Stock solutions of concentrated Na_2SO_4(aq) and K_2SO_4(aq) were prepared by mass from commercial samples (Fluka, analytical reagent grade, assay >99 mol %) used without further purification. Less concentrated solutions were prepared by mass dilution. All solutions were prepared using distilled, deionized water. Buoyancy corrections were applied throughout. The uncertainty in the molalities of the electrolyte solutions is estimated to be 0.1%. Because of the length of time over which the measurements were made and the replacement of the vibrating tube, many solutions, including the stock solutions, were prepared (and their densities measured) on more than one occasion. No significant differences were observed in such measurements obtained under the same conditions over the 2 year period.

Typically two to four measurements were performed at each concentration, temperature, and pressure, with a reproducibility about 0.1% in $\Delta\tau^2$ for the higher concentrations and better than 10% for the concentrations 0.01 $\mathrm{mol \cdot kg^{-1}}$ and below. Prior to filling the stainless steel sample loop used for introducing the solution to the densitometer, each sample was degassed manually in a plastic syringe. Vaporization of water due to this procedure was negligible, as no changes in density were noticed. It was, however, observed occasionally at concentrations below 0.025 $\mathrm{mol \cdot kg^{-1}}$ that the derived apparent molar volumes showed large positive deviations from the bulk of the data. This is almost certainly due to insufficient degassing and such points were discarded. Similar observations have been made previously in high-temperature densitometric studies with 1:1 electrolytes (Majer et al., 1988, 1989ab).

3. Results and Discussion

Table 2 summarizes the present results for Na_2SO_4(aq) and K_2SO_4(aq). The fourth column of each set of figures in the table gives the density differences $\Delta\rho$ calculated from eq 1 using the calibration constants from Table 1. The apparent molar volumes V_ϕ presented in the fifth column of each set of figures in Table 2 were calculated from the usual relation

$$V_\phi = \left[\frac{M}{\rho} - \frac{\Delta\rho}{m\rho\rho_o}\right] \tag{2}$$

where M is the molar mass of anhydrous Na_2SO_4 (0.142 042 $\mathrm{kg \cdot mol^{-1}}$) or K_2SO_4 (0.174 259 $\mathrm{kg \cdot mol^{-1}}$), m is the stoichiometric solute molality, and ρ is the density in $\mathrm{kg \cdot m^{-3}}$.

The uncertainties in both $\Delta\rho$ and V_ϕ depend strongly on m, T and p. At low salt concentrations random errors are dominant ($\delta\Delta\tau^2 \leq 0.1\Delta\tau^2$), whereas at high concentrations, where $\delta\Delta\tau^2$ is much smaller compared to $\Delta\tau^2$, the uncertainty in the calibration constant ($\delta K \leq 0.002K$) becomes more important. A detailed analysis of both random and systematic errors which is broadly valid for the present apparatus and data is given by Majer et al. (1988). As previously (Majer et al. 1991b), the reliability of $\Delta\rho$ and V_ϕ was expressed by printing a digit only if its absolute estimated error was <30.

The present data can be correlated using the Pitzer ion-interaction model (Pitzer, 1991). In its full form, the Pitzer expression for the apparent molar volume of a 1−2 or 2−1 aqueous electrolyte can be written as:

$$V_\phi = V_\phi^\infty + (3A_V/b)\ln(1 + bI^{1/2}) + 4RT(mB^V + 2m^2C^V) \tag{3}$$

where V_ϕ^∞ is the value of V_ϕ at infinite dilution which approximates here the $\bar{V}°$, the standard partial molar volume of a salt in an aqueous solution; $b = 1.2\ \mathrm{kg^{1/2} \cdot mol^{-1/2}}$; I is the stoichiometric ionic strength which is equal to $3m$ for these solutes. A_V, B^V, and C^V are respectively the Debye−Hückel limiting slope for apparent molar volume and the second and third virial coefficients of the Pitzer formulation for volume; and the other symbols have their usual meanings, with $R = 8.3144\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. Furthermore, the second virial coefficient is given by

$$B^V = \beta^{(0)V} + \beta^{(1)V}(2/\alpha^2 I)[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})] \tag{4}$$

where $\alpha = 2.0\ \mathrm{kg^{1/2} \cdot mol^{-1/2}}$.

The volumetric Debye−Hückel slope A_V is given by

$$A_V = -4RT(\partial A_\phi/\partial p)_T = 2A_\phi RT[3(\partial \ln \epsilon/\partial p)_T + (\partial \ln V_o/\partial p)_T] \tag{5}$$

where ϵ and $(\partial \ln V_o/\partial p)_T$ are respectively the dielectric

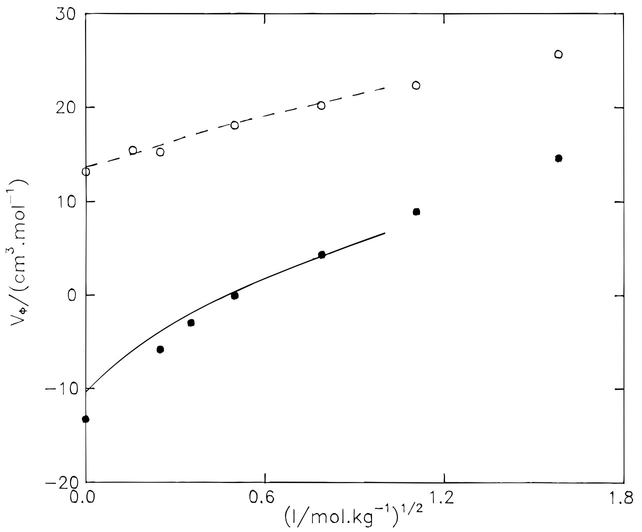

Figure 1. Comparison of apparent molar volume V_ϕ of Na_2SO_4(aq) with literature data (Phutela and Pitzer, 1986) at 10 MPa: (○) 369 K, this work; (●) 450 K, this work; (- - -) 369 K (lit. data); (—) 450 K (lit. data).

Table 3. Parameters $\bar{V}°$, A_V, and $\beta^{(0)V}$ Derived from the Experimental Apparent Molar Volumes V_ϕ of Na_2SO_4(aq) and K_2SO_4(aq) as a Function of Molality at Constant Temperature and Pressure

T/K	p/MPa	$\bar{V}°$/cm^3·mol^{-1}	A_V/cm^3·mol^{-1}	$10^3\beta^{(0)V}$/kg·mol^{-1}·MPa^{-1}
		Na_2SO_4(aq)		
298.20	9.91	13.9	1.799	0.5618
298.20	30.44	16.5	1.739	0.5146
369.36	10.17	13.1	3.775	0.1506
369.36	30.42	15.8	3.488	0.1514
450.06	10.17	−13.3	10.07	−0.0342
450.08	30.56	−7.47	8.749	0.0295
517.03	10.27	−75.4	28.04	−0.7919
517.03	30.22	−54.1	21.25	−0.5112
572.72	10.39	−246	98.90	−5.528
572.66	30.27	−153	58.19	−2.576
		K_2SO_4(aq)		
298.23	9.94	34.6	1.799	0.6031
298.22	30.03	36.9	1.739	0.5504
369.36	10.22	32.5	3.775	0.3916
369.36	30.59	35.0	3.488	0.3960
450.06	10.05	6.89	10.07	0.0171
450.08	30.63	13.87	8.749	0.0409
517.03	10.30	−55.5	28.04	−1.013
517.03	30.29	−32.8	21.25	−0.7966
572.72	10.41	−227	98.90	−7.597
572.66	30.28	−133	58.19	−3.699

constant (relative permittivity) and isothermal compressibility of water and A_ϕ is the Debye−Hückel slope for osmotic coefficients as given by Pitzer (1991). The values of A_V for each temperature and pressure were calculated using the dielectric constants of Archer and Wang (1990) and the equation of state by Hill (1990) for the isothermal compressibility.

For the present salts over the range of concentrations studied C^V was not found to be necessary. Table 3 lists the values of A_V along with the variables $\bar{V}° = V_\phi^\infty$ and $\beta^{(0)V}$ obtained from isothermal and isobaric fitting of the data in Table 2 (weighted least squares) to eqs 3 and 4, truncated after the second virial coefficient with $B^V = \beta^{(0)V}$. Inclusion of the $\beta^{(1)V}$ term produced signs of overfitting and so was omitted; this implies that the pressure derivative of the Pitzer B coefficient is independent of ionic strength for the conditions and measurements considered here. The estimated error in $\bar{V}°$ is about 0.5 cm^3·mol^{-1} near 298 K rising to about 10 cm^3·mol^{-1} at 573 K. It should be stressed that the standard molar volumes were derived without any consideration of real speciation in the solution. Aqueous sulfates hydrolyze somewhat and tend to ion-pair strongly with increasing temperature and concentration. The values of V_ϕ^∞ in eq 3 cannot be considered in fact as the standard volume of the fully dissociated salt (especially near the upper temperature limit of measurements) but rather as the semiempirical parameters reflecting infinite dilution volumes of the nominal salts.

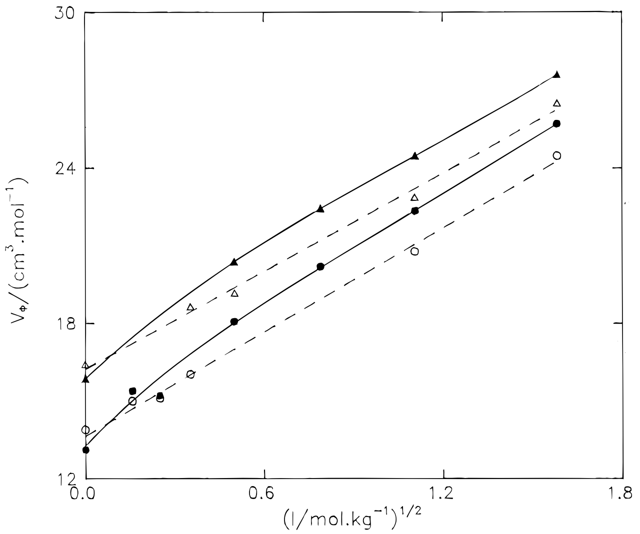

Figure 2. Dependence of the apparent molar volume V_ϕ of Na_2SO_4(aq) on the square root of ionic strength $I^{1/2}$ at two different temperatures and pressures. 298 K (- - -): (○) 10 MPa, (△) 30MPa. 369 K (—): (●) 10 MPa, (▲) 30 MPa.

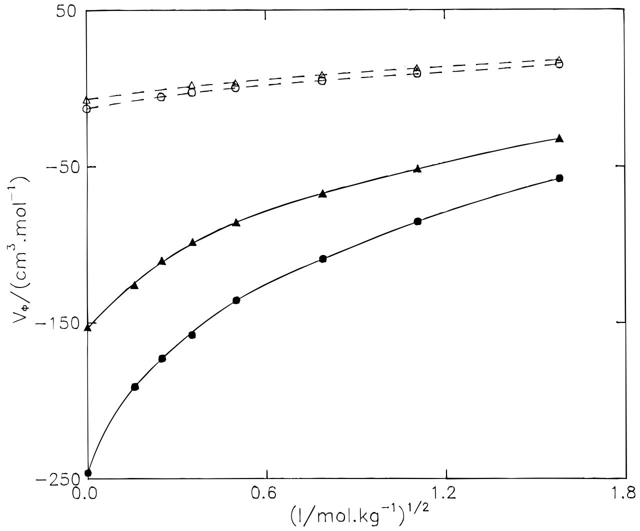

Figure 3. Dependence of the apparent molar volume V_ϕ of Na_2SO_4(aq) on the square root of ionic strength $I^{1/2}$ at two different temperatures and pressures. 450 K (- - -): (○) 10 MPa, (△) 30 MPa. 573 K (—): (●) 10 MPa, (▲) 30 MPa.

Figure 1 compares the present results for V_ϕ (points) with the rounded values of Phutela and Pitzer (lines) at 10 MPa and two temperatures. At 298 K the agreement is within the experimental uncertainty. At 450 K, as might be expected, the agreement is less close but still within likely experimental errors; Phutela and Pitzer report an estimated uncertainty of *ca.* ±2 cm^3·mol^{-1} in V_ϕ at $I \leq 0.4$ mol·kg^{-1} and $T = 473$ K, the expected error of our values in this range is probably somewhat lower.

Figure 2, which plots on a more sensitive scale the apparent molar volume of Na_2SO_4(aq) as a function of ionic strength, indicates that at relatively low temperatures both T and p have little effect on V_ϕ(Na_2SO_4(aq)). The intersection of the isobaric V_ϕ *versus* $I^{1/2}$ curves, corresponding to the temperatures of 298 and 369 K, at low salt concentrations is possibly a reflection of changes in the solution structure. The influence of temperature and pressure is seen more clearly in Figure 3 which plots V_ϕ *versus* $I^{1/2}$ at higher temperatures. As is usually found for (relatively) strong electrolytes, and as is expected on theoretical grounds (Wood et al., 1994), the apparent molar volume of the electrolyte changes significantly only when major changes occur in the properties of the solvent (water), particularly its compressibility and dielectric constant. These factors influence, respectively, the electrostriction of the solvent by the ions and the formation of ion pairs. Thus only at higher temperatures is there a significant pressure effect on $V_\phi(Na_2SO_4(aq))$. Interestingly, the 573 K data in Figure 3 also reveal a noticeable difference at higher concentrations in the ionic strength dependence of V_ϕ at 10 and 30 MPa. This is almost certainly a reflection of increased ion pairing at higher temperatures and concentrations and at lower pressures, as is further discussed elsewhere (Obšil et al., 1996).

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