Registry No. Me_2SO, 67-68-5; LiCl, 7447-41-8; H_2O, 7732-18-5.

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Supplementary Material Available: Table entitled "Viscosity of Water–Me_2SO Mixtures at 25 °C"; it reports viscosities of 38 different mole fractions and is compiled from four separate works (1 page). Ordering information is given on any current masthead page.

Densities and Apparent Molar Volumes of Aqueous Magnesium Sulfate and Sodium Sulfate to 473 K and 100 bar

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Densities of aqueous solutions of $MgSO_4$ and Na_2SO_4 have been measured up to 473 K, 100 bar, and 1 *m* ionic strength. The derived apparent molar volumes along with the available literature data on these substances have been analyzed by using the ion-interaction (Pitzer) approach. $\bar{V}_2^0$ for $MgSO_4$ is obtained indirectly from values for $MgCl_2$, Na_2SO_4, and NaCl. The term in $\beta^{(2)}$ represents adequately the ion-association effect in $MgSO_4$ up to 473 K. The present results yield the pressure effect on various thermodynamic properties.

Introduction

Recently we (*1*) completed a study which yielded a comprehensive equation for the thermodynamic properties of aqueous magnesium sulfate at low pressure based on our own heat capacity measurements and heats of dilution and osmotic coefficients from the literature. In the present study we present the measurements of densities of aqueous magnesium sulfate and sodium sulfate to 473 K, 100 bar, and 1 *m* ionic strength. In addition to the intrinsic interest of the volumetric properties, they also yield the pressure dependence of the thermodynamic properties already determined for low pressure.

Sodium sulfate behaves as a normal strong electrolyte and the present results are readily fitted to the same form of ion-interaction (Pitzer) equations used earlier by Rogers and Pitzer (*2*) for the heat capacity of aqueous Na_2SO_4. Magnesium sulfate, however, shows significant electrostatic ion-pairing. Our study of the heat capacity (*1*) showed that it was possible to use the ion-interaction equations up to 473 K provided that a special binary interaction term was included. Also, one cannot unambiguously extrapolate the $MgSO_4$ data to zero molality to obtain $\bar{V}_2^0$; rather this quantity for $Mg^{2+} + SO_4^{2-}$ is obtained indirectly from the values of $\bar{V}_2^0$ for $MgCl_2$, Na_2SO_4, and NaCl. Values for NaCl are taken from the recent comprehensive studies (*3*, *4*) from this laboratory. For Na_2SO_4, we have generated equations based on Pitzer's equations using our measurements and literature values (*5–15*). For $MgCl_2$, we have fitted the recent measurements of Saluja (*15*) along with the other available literature data to the same equations. The details of the $MgCl_2$ calculations will be presented separately (*16*) along with the similar results for $CaCl_2$ and $SrCl_2$, and their heat capacities.

With the infinitely dilute values fixed, our measurements along with literature data (*5*, *7–10*, *12*, *13*) on aqueous $MgSO_4$ were satisfactorily fitted by the ion-interaction equations. This type of equation has been very successful for mixed electrolytes. Thus it is valuable to have the required parameters for Na_2SO_4 and $MgSO_4$ since these ions are prominent in sea water and in other natural or industrial waters.

Experimental Method

A dilatometer has been used to measure the changes in the volume of a solution as a function of temperature. The volume at room temperature is known from the literature. The constructional details and operation of the dilatometer are described elsewhere (*17*).

The pressure vessel, which contains about 5.75 cm^3 of solution, was modified in design and rebuilt to stand higher pressures. The pressure vessel is connected through a stainless-steel capillary to a mercury reservoir made of a coil of stainless-steel tubing which in turn is connected to a glass capillary column. The entire system can be pressurized with nitrogen gas.

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Table I. Experimental Density of Aqueous Na_2SO_4

T/K	P/bar	m/mol·kg^{-1}	ρ/g·cm^{-3}	$^{\phi}V$/cm^3·mol^{-1}	T/K	P/bar	m/mol·kg^{-1}	ρ/g·cm^{-3}	$^{\phi}V$/cm^3·mol^{-1}
294.87	20.2	0.0578	1.00608	14.49	293.99	20.5	0.2025	1.02424	16.57
325.16	20.4	0.0578	0.99503	18.25	324.39	20.7	0.2025	1.01261	20.41
374.17	21.0	0.0578	0.96553	17.42	374.14	21.0	0.2025	0.98258	18.93
423.52	21.2	0.0578	0.92487	6.17	423.72	21.6	0.2025	0.94208	10.25
474.89	21.8	0.0578	0.87076	−12.04	475.64	22.1	0.2025	0.88830	−7.89
424.22	21.2	0.0578	0.92427	4.92	424.10	21.5	0.2025	0.94178	9.79
375.01	21.0	0.0578	0.96497	16.58	374.60	21.0	0.2025	0.98228	18.75
325.09	20.5	0.0578	0.99507	18.08	324.05	20.8	0.2025	1.01282	20.22
295.18	20.3	0.0578	1.00604	14.08	294.33	20.4	0.2025	1.02423	16.22
295.67	48.8	0.0578	1.00717	14.96	294.12	48.4	0.2025	1.02543	16.91
325.01	49.1	0.0578	0.99634	18.33	324.17	48.8	0.2025	1.01392	20.63
374.00	49.7	0.0578	0.96705	16.62	374.08	49.4	0.2025	0.98397	18.96
423.26	50.9	0.0578	0.92681	6.20	423.44	50.2	0.2025	0.94400	10.19
474.68	51.9	0.0578	0.87335	−12.47	475.15	51.4	0.2025	0.89112	−7.29
424.17	50.7	0.0578	0.92601	4.73	424.23	50.4	0.2025	0.94326	10.19
374.09	49.9	0.0578	0.96703	15.97	374.29	50.0	0.2025	0.98380	19.19
325.11	49.3	0.0578	0.99631	18.28	324.42	49.1	0.2025	1.01380	20.67
296.28	48.7	0.0578	1.00702	14.83	294.35	48.4	0.2025	1.02540	16.83
295.47	95.3	0.0578	1.00928	15.42	294.61	96.0	0.2025	1.02730	17.84
325.08	96.6	0.0578	0.99833	18.99	324.34	96.9	0.2025	1.01582	21.24
374.04	97.4	0.0578	0.96928	15.71	373.99	98.4	0.2025	0.98662	19.65
423.16	99.5	0.0578	0.92967	4.89	423.19	100.7	0.2025	0.94695	11.06
474.80	101.4	0.0578	0.87703	−14.94	475.32	102.3	0.2025	0.894.62	−5.96
424.32	99.3	0.0578	0.92866	3.42	424.11	99.9	0.2025	0.94614	10.49
374.71	98.1	0.0578	0.96881	16.27	374.12	98.8	0.2025	0.98617	19.47
324.67	96.4	0.0578	0.99854	18.33	325.13	96.6	0.2025	1.01546	21.10
295.09	95.5	0.0578	1.00939	15.43	294.52	95.9	0.2025	1.02739	17.50
295.12	20.1	0.1085	1.01239	15.25	295.12	20.4	0.3303	1.03930	18.17
324.94	20.4	0.1085	1.00123	19.15	325.27	20.8	0.3303	1.02705	21.55
374.84	20.6	0.1085	0.97110	17.44	374.45	21.2	0.3303	0.99702	20.12
423.60	21.3	0.1085	0.93094	8.35	423.81	21.6	0.3303	0.95693	12.06
475.07	21.8	0.1085	0.87710	−10.56	475.81	22.3	0.3303	0.90377	−4.83
423.54	21.3	0.1085	0.93104	7.93	424.67	21.8	0.3303	0.95615	11.92
374.87	20.7	0.1085	0.97110	17.17	374.89	21.3	0.3303	0.99671	20.06
324.73	20.1	0.1085	1.00138	18.51	325.18	20.8	0.3303	1.02709	21.55
296.35	20.0	0.1085	1.01207	15.40	294.99	20.3	0.o303	1.03936	18.09
294.85	47.6	0.1085	1.01366	15.63	295.08	47.7	0.3303	1.04041	18.69
324.86	48.3	0.1085	1.00245	19.53	325.33	48.2	0.3303	1.02810	21.98
374.48	49.3	0.1085	0.97265	18.16	374.46	49.2	0.3303	0.99822	20.58
423.53	50.1	0.1085	0.93265	8.48	423.69	50.3	0.3303	0.95849	12.88
475.14	51.2	0.1085	0.87929	−10.41	475.76	51.1	0.3303	0.90590	−3.83
424.53	50.4	0.1085	0.93175	8.06	424.02	49.5	0.3303	0.95828	12.38
375.00	49.4	0.1085	0.97230	17.90	375.33	48.7	0.3303	0.99765	20.26
324.75	47.9	0.1085	1.00252	19.21	324.61	47.9	0.3303	1.02848	21.84
295.25	47.5	0.1085	1.01356	15.62	294.86	47.1	0.3303	1.04053	18.42
295.18	95.5	0.1085	1.01567	16.34	296.26	95.6	0.3303	1.04203	19.55
324.65	96.7	0.1085	1.00463	19.66	324.65	96.5	0.3303	1.03041	22.45
374.29	98.1	0.1085	0.97514	17.40	374.55	98.0	0.3303	1.00038	20.89
423.89	100.5	0.1085	0.93519	7.94	423.97	100.0	0.3303	0.96103	13.10
475.25	102.5	0.1085	0.88313	−11.26	475.78	102.4	0.3303	0.90959	−2.65
423.93	100.3	0.1085	0.93518	7.47	425.02	100.0	0.3303	0.96011	12.80
375.37	98.7	0.1085	0.97437	17.58	375.72	98.7	0.3303	0.99957	20.82
325.28	96.6	0.1085	1.00436	19.46	325.42	97.0	0.3303	1.03005	22.49
294.87	95.7	0.1085	1.01576	16.32	296.28	95.6	0.3303	1.04205	19.50

The mercury reservoir and most of the capillary connecting tube are thermostated with a water bath and a circulation pump at 30 °C. The solution cell is surrounded by a large aluminum block and is placed in a high-temperature bath. The aluminum block serves as a heat sink to reduce temperature fluctuations. Thus the temperature of the sample cell is stable to ±0.01 K over a period of 30 min.

The density of the solution is determined by measuring the change in volume of the solution as the temperature is raised. Special care was taken to fill the sample cell with solution without introducing any air bubble. The cell was filled and emptied 6–7 times to eliminate any contamination by any old solution in the cell. The mercury and thereby also the solution was then pressurized with nitrogen gas. Any air bubbles in the solution could be detected by large displacement in the level of mercury column. The sample cell was then enclosed in the aluminum jacket and the solution was equilibrated at room temperature. The pressure of the system and the level of mercury were monitored overnight to check for any leakage. The temperature of the solution was then raised in increments of 25 or 50 °C and the heights of mercury column were measured to ±0.01 mm at each step with a Wilde cathetometer. The level of mercury menisci were noted at different temperatures until 200 °C. Then the temperature of the cell was decreased at the same intervals and the level of menisci noted until the initial temperature was reached. This sequence of measurements is followed in Tables I and II. The temperature of the solution cell was measured by using a 25-Ω platinum resistance thermometer using a G-2 Mueller Bridge. A bourdon-tube pressure gauge was used to determine the pressure of the system to ±0.1 bar. The temperatures of the water bath and the room were measured with mercury-in-glass thermometers.

Experimental Results

The density of the solution can be related to the change in the height of the mercury column as follows. Let *t* be the

Table II. Experimental Density of Aqueous $MgSO_4$

T/K	P/bar	m/mol·kg^{-1}	ρ/g·cm^{-3}	ϕV/cm^3·mol^{-1}
323.90	22.3	0.0723	0.997 20	0.20
374.18	23.2	0.0723	0.967 13	−1.45
422.84	24.1	0.0723	0.926 95	−8.35
474.80	24.6	0.0723	0.872 14	−21.01
423.58	24.0	0.0723	0.926 35	−10.07
374.65	23.0	0.0723	0.966 89	−3.01
324.48	22.3	0.0723	0.996 99	−0.53
324.24	49.1	0.0723	0.998 19	0.58
373.64	49.8	0.0723	0.968 82	−2.24
423.17	50.6	0.0723	0.928 30	−10.82
474.60	51.8	0.0723	0.874 55	−22.53
423.08	50.7	0.0723	0.928 37	−10.63
374.62	49.7	0.0723	0.968 17	−3.04
324.17	49.0	0.0723	0.998 22	0.52
324.26	98.3	0.0723	1.000 20	2.24
374.49	100.0	0.0723	0.970 43	−0.47
423.30	102.1	0.0723	0.930 86	−7.77
475.57	104.1	0.0723	0.877 14	−18.94
424.20	101.9	0.0723	0.930 09	−8.92
374.94	100.0	0.0723	0.970 18	−1.55
324.56	98.3	0.0723	1.000 13	1.28
294.21	21.9	0.1693	1.019 27	0.26
324.63	22.5	0.1693	1.008 14	1.68
374.63	22.6	0.1693	0.978 15	−1.79
423.58	23.3	0.1693	0.937 76	−9.27
475.77	24.2	0.1693	0.882 48	−20.39
424.24	24.0	0.1693	0.937 12	−8.90
374.80	23.5	0.1693	0.978 02	−1.47
324.91	23.1	0.1693	1.007 99	2.00
294.23	23.1	0.1693	1.019 24	0.70
293.84	47.6	0.1693	1.020 43	0.90
324.76	47.5	0.1693	1.009 17	1.81
374.41	48.2	0.1693	0.979 49	−1.56
423.90	48.8	0.1693	0.938 97	−9.56
475.55	50.0	0.1693	0.884 77	−20.35
294.23	94.9	0.1693	1.022 34	1.82
325.27	95.6	0.1693	1.010 83	2.99
374.17	97.4	0.1693	0.981 69	0.31
423.34	99.1	0.1693	0.941 95	−6.84
475.38	101.5	0.1693	0.888 50	−17.05
294.72	21.1	0.2503	1.028 49	1.59
325.06	21.6	0.2503	1.017 09	2.90
374.24	22.0	0.2503	0.987 78	−1.28
295.01	47.8	0.2503	1.029 54	2.06
324.20	48.1	0.2503	1.018 63	3.10
374.16	49.2	0.2503	0.988 87	−0.15
423.81	49.9	0.2503	0.948 33	−7.57
475.10	51.0	0.2503	0.894 79	−18.58
424.15	49.9	0.2503	0.948 02	−7.65
375.00	48.9	0.2503	0.988 32	−0.48
324.57	48.0	0.2503	1.018 49	2.94
294.88	47.6	0.2503	1.029 61	1.85
294.90	95.2	0.2503	1.031 56	2.78
324.57	96.0	0.2503	1.020 41	3.70
374.48	97.7	0.2503	0.990 80	0.46
423.65	99.5	0.2503	0.951 14	−6.73
475.10	101.5	0.2503	0.898 49	−17.47
423.74	99.3	0.2503	0.951 09	−6.92
375.02	97.9	0.2503	0.990 43	0.37
324.74	96.3	0.2503	1.020 33	3.80
295.03	95.4	0.2503	1.031 56	2.71

experimental temperature, t_R the reference temperature, and t_B the water-bath temperature in degrees centigrade. At the experimental temperature, the density of the solution is given by

$$\rho_t = g_t / V_t \qquad (1)$$

where g_t is the mass of the solution and V_t is the volume of the solution. The mass of the solution in the sample cell at any temperature is equal to the mass in the cell at the reference temperature, t_R, less the amount that has expanded from the cell. The mass of the solution expanded is given by

$$\Delta m = \Delta h A \rho_{t_B} \qquad (2)$$

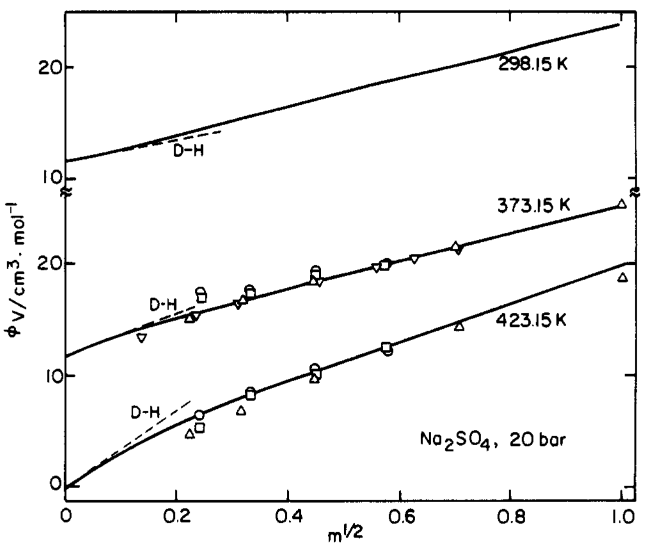

Figure 1. The apparent molar volume, $^{\phi}V$, for Na_2SO_4: ○, this study at 20 bar, rising temperature; □, this study at 20 bar, falling temperature; △, Ellis (*7*) at 20 bar; ▽, Saluja (*15*) at 6 bar. Solid curves are calculated from the present fit (eq 19) at 20 bar; dashed lines are the Debye–Hückel slopes taken from Bradley and Pitzer (*22*).

Table III. Parameters for Eq 19 and 20 for Apparent Molar Volume of Aqueous Na_2SO_4 and $MgSO_4$

Na_2SO_4[a]	$MgSO_4$[b]
$P_1 = -5.11686 \times 10^5$	$q_1 = -7.97433 \times 10^5$
$P_2 = 5.43000 \times 10^3$	$q_2 = 8.94735 \times 10^3$
$P_3 = -2.18218 \times 10^1$	$q_3 = -3.78219 \times 10^1$
$P_4 = 3.99915 \times 10^{-2}$	$q_4 = 7.15424 \times 10^{-2}$
$P_5 = -2.83513 \times 10^{-5}$	$q_5 = -5.14523 \times 10^{-5}$
$P_6 = 1.79274 \times 10^{-2}$	$q_6 = 7.42784$
$P_7 = 1.28610$	$q_7 = -6.12133 \times 10^{-2}$
$P_8 = -1.06978 \times 10^{-2}$	$q_8 = 1.77378 \times 10^{-4}$
$P_9 = 2.96022 \times 10^{-5}$	$q_9 = -1.82737 \times 10^{-7}$
$P_{10} = -2.70365 \times 10^{-8}$	$q_{10} = 2.06777 \times 10^3$
$P_{11} = 4.59690 \times 10^{-1}$	$q_{11} = -2.39043 \times 10^1$
$P_{12} = -1.31097 \times 10^{-3}$	$q_{12} = 1.03110 \times 10^{-1}$
	$q_{13} = -1.96675 \times 10^{-4}$
	$q_{14} = 1.40527 \times 10^{-7}$
	$q_{15} = 1.18481 \times 10^{-4}$

[a] Range: 0–200 °C; 0–1 m, to 20 bar; 0–0.33 m, to 100 bar.
[b] Range: 0–200 °C; 0–0.25 m, to 100 bar.

where Δh is the total change in the height of the mercury column between temperatures t_R and t, A is the cross-sectional area of the mercury column, and ρ_{t_B} is the density of the solution at the temperature of the water bath. Then the density of the solution is given by

$$\rho_t = (1/V_t)[\rho_{t_R} V_{t_R} - \Delta h A \rho_{t_B}] \qquad (3)$$

We assume the temperature dependence of the volume of the cell as

$$V_t = V_0 e^{\alpha t} \qquad (4)$$

where V_0 is the volume of the cell at 0 °C and α is the unknown expansivity of the cell. Substituting eq 4 into eq 3 we get

$$\rho_t = \rho_{t_R} e^{-\alpha(t - t_R)} - (A/V_0)\Delta h \rho_{t_B} e^{-\alpha t}$$

$$= \rho_{tR}[1 - \alpha(t - t_R)] - \Delta h (A/V_0)\rho_{t_B}[1 - \alpha t]$$

or

$$\rho_t = \rho_{t_R} - \frac{A}{V_0}\Delta h \rho_{t_B} + \alpha\rho_{t_R}(t_R - t) + \alpha\frac{A}{V_0} t \Delta h \rho_{t_B} \qquad (5)$$

Equation 5 was used to obtain the values of the density of the

Table IV. Apparent Molar Volumes ($cm^3 \cdot mol^{-1}$) of Aqueous Na_2SO_4

A

		m/mol·kg^{-1}										
t/°C	P/bar	0.00	0.01	0.05	0.10	0.20	0.30	0.40	0.50	0.60	0.80	1.00
0.0	1.0	2.12	3.17	4.94	6.42	8.61	10.32	11.78	13.07	14.26	16.42	18.39
10.0	1.0	6.72	7.79	9.46	10.82	12.77	14.27	15.53	16.64	17.64	19.45	21.07
20.0	1.0	9.99	11.08	12.68	13.93	15.71	17.04	18.15	19.11	19.98	21.52	22.90
25.0	1.0	11.22	12.32	13.89	15.11	16.81	18.08	19.12	20.03	20.85	22.29	23.57
30.0	1.0	12.21	13.33	14.88	16.06	17.70	18.91	19.91	20.77	21.55	22.91	24.11
40.0	1.0	13.59	14.76	16.28	17.41	18.95	20.09	21.01	21.81	22.53	23.78	24.88
50.0	1.0	14.30	15.54	17.06	18.16	19.65	20.73	21.62	22.39	23.08	24.28	25.34
60.0	1.0	14.48	15.80	17.35	18.44	19.90	20.97	21.86	22.62	23.31	24.52	25.59
70.0	1.0	14.22	15.65	17.24	18.34	19.81	20.90	21.79	22.58	23.28	24.54	25.67
80.0	1.0	13.59	15.14	16.80	17.93	19.44	20.56	21.49	22.31	23.06	24.40	25.61
90.0	1.0	12.62	14.32	16.08	17.26	18.83	20.00	20.99	21.86	22.66	24.10	25.41
100.0	1.0	11.34	13.21	15.09	16.34	17.99	19.23	20.28	21.22	22.08	23.64	25.07
110.0	1.5	9.74	11.81	13.85	15.18	16.94	18.27	19.39	20.39	21.32	23.01	24.56
120.0	2.0	7.80	10.12	12.35	13.78	15.67	17.08	18.28	19.36	20.35	22.16	23.82
130.0	2.7	5.50	8.09	10.55	12.11	14.13	15.65	16.93	18.08	19.13	21.06	22.83
140.0	3.6	2.77	5.70	8.42	10.13	12.32	13.94	15.30	16.52	17.63	19.66	21.50
150.0	4.8	−0.43	2.88	5.93	7.81	10.19	11.92	13.37	14.64	15.81	17.91	19.81
160.0	6.2	−4.18	−0.41	3.02	5.11	7.70	9.55	11.08	12.41	13.62	15.77	17.68
170.0	7.9	−8.56	−4.24	−0.35	1.98	4.82	6.80	8.41	9.79	11.03	13.19	15.08
180.0	10.0	−13.64	−8.68	−4.24	−1.62	1.51	3.64	5.33	6.76	8.01	10.16	11.98
190.0	12.6	−19.53	−13.80	−8.70	−5.73	−2.25	0.06	1.83	3.30	4.56	6.66	8.37
200.0	15.6	−26.32	−19.67	−13.77	−10.36	−6.46	−3.95	−2.07	−0.56	0.70	2.71	4.28

B

		m/mol·kg^{-1}						
t/°C	P/bar	0.00	0.01	0.05	0.10	0.20	0.30	0.40
0.0	100.0	3.89	4.94	6.69	8.17	10.35	12.06	13.51
10.0	100.0	8.50	9.55	11.21	12.55	14.50	15.99	17.24
20.0	100.0	11.77	12.84	14.42	15.66	17.43	18.75	19.85
25.0	100.0	12.99	14.08	15.63	16.83	18.52	19.78	20.82
30.0	100.0	13.98	15.09	16.61	17.78	19.40	20.61	21.60
40.0	100.0	15.36	16.51	18.01	19.12	20.65	21.77	22.69
50.0	100.0	16.07	17.29	18.78	19.86	21.32	22.40	23.28
60.0	100.0	16.25	17.55	19.05	20.12	21.56	22.62	23.48
70.0	100.0	16.00	17.38	18.93	20.01	21.45	22.51	23.39
80.0	100.0	15.36	16.87	18.48	19.58	21.05	22.15	23.06
90.0	100.0	14.40	16.04	17.74	18.88	20.41	21.55	22.51
100.0	100.0	13.11	14.92	16.73	17.93	19.53	20.74	21.76
110.0	100.0	11.51	13.50	15.46	16.74	18.43	19.71	20.80
120.0	100.0	9.56	11.78	13.91	15.28	17.09	18.45	19.61
130.0	100.0	7.24	9.72	12.06	13.54	15.48	16.93	18.16
140.0	100.0	4.50	7.29	9.87	11.48	13.56	15.11	16.41
150.0	100.0	1.27	4.42	7.30	9.07	11.31	12.95	14.33
160.0	100.0	−2.50	1.07	4.29	6.24	8.67	10.42	11.86
170.0	100.0	−6.91	−2.84	0.80	2.97	5.61	7.46	8.96
180.0	100.0	−12.03	−7.37	−3.24	−0.81	2.08	4.05	5.61
190.0	100.0	−17.96	−12.60	−7.87	−5.14	−1.95	0.16	1.78
200.0	100.0	−24.80	−18.60	−13.15	−10.04	−6.49	−4.23	−2.53

solution from the height of the mercury column.

Corrections in the mercury column due to the variations in water-bath temperature, room temperature, and hydrostatic head pressure were small and were applied.

Calibration runs were carried out using pure water in the solution cell. The calibration constants, i.e., the expansivity of the sample cell, α, and the ratio of the cross-sectional area of the column to the volume of the cell at 0 °C, A/V_0, were evaluated as a function of pressure up to 100 bar by a least-squares regression of eq 5. Observed values of Δh from 25 to 200 °C were combined with the known values of the densities of water (*18*).

Observed values of Δh were used directly in eq 5 in combination with the known calibration constants to obtain densities of the solution. Measurements were made on solutions of magnesium sulfate and sodium sulfate up to 1 m ionic strength at approximately 20, 50, and 100 bar pressures up to 200 °C. The experimental values of densities obtained for aqueous sodium sulfate and magnesium sulfate are given in Tables I and II.

The values of reference densities of sodium sulfate and magnesium sulfate solutions at reference temperature and at the water bath temperature are required in eq 5. These were obtained from literature (*10*). The values of the apparent molar volume, ${}^{\phi}V$, have been calculated from the density data as

$$ {}^{\phi}V = \frac{1000 + mM_2}{m}\left(\frac{1}{\rho}\right) - \left(\frac{1000}{m}\right)\frac{1}{\rho_0} \qquad (6)$$

where M_2 is the molecular weight of the salt and ρ_0 is the density of pure water.

The uncertainty in the experimentally measured density increases with temperature, being $\pm 4 \times 10^{-5}$ $g \cdot cm^{-3}$ at 50 °C and $\pm 1 \times 10^{-4}$ $g \cdot cm^{-3}$ at 200 °C. This results in an uncertainty in the apparent molar volume of 0.1 $cm^3 \cdot mol^{-1}$ for the measurement at 0.33 $mol \cdot kg^{-1}$ to 0.7 $cm^3 \cdot mol^{-1}$ for the dilute solutions below 0.06 $mol \cdot kg^{-1}$ at 50 °C. The uncertainty increases with temperature and the corresponding values for the same solutions at 200 °C are 0.4 and 2.2 $cm^3 \cdot mol^{-1}$.

Table V. Apparent Molar Volumes ($cm^3 \cdot mol^{-1}$) of Aqueous $MgSO_4$

A

		m/mol·kg^{-1}							
t/°C	P/bar	0.00	0.01	0.02	0.05	0.10	0.15	0.20	0.25
0.0	1.0	-13.85	-10.26	-9.11	-7.39	-5.79	-4.64	-3.72	-2.94
10.0	1.0	-10.41	-7.18	-6.14	-4.57	-3.11	-2.08	-1.25	-0.55
20.0	1.0	-8.44	-5.26	-4.25	-2.77	-1.42	-0.48	0.27	0.89
25.0	1.0	-7.87	-4.63	-3.62	-2.16	-0.86	0.04	0.76	1.35
30.0	1.0	-7.54	-4.19	-3.16	-1.71	-0.44	0.42	1.10	1.67
40.0	1.0	-7.43	-3.74	-2.65	-1.19	0.02	0.82	1.45	1.97
50.0	1.0	-7.87	-3.75	-2.57	-1.06	0.11	0.86	1.44	1.92
60.0	1.0	-8.72	-4.09	-2.81	-1.23	-0.09	0.63	1.17	1.61
70.0	1.0	-9.85	-4.69	-3.29	-1.64	-0.50	0.18	0.69	1.10
80.0	1.0	-11.22	-5.50	-3.98	-2.23	-1.10	-0.44	0.04	0.42
90.0	1.0	-12.81	-6.51	-4.85	-3.00	-1.86	-1.22	-0.77	-0.41
100.0	1.0	-14.64	-7.71	-5.91	-3.95	-2.78	-2.16	-1.73	-1.39
110.0	1.5	-16.75	-9.12	-7.16	-5.06	-3.87	-3.26	-2.85	-2.53
120.0	2.0	-19.21	-10.77	-8.62	-6.36	-5.12	-4.53	-4.14	-3.84
130.0	2.7	-22.13	-12.70	-10.32	-7.85	-6.56	-5.97	-5.59	-5.32
140.0	3.6	-25.62	-14.95	-12.28	-9.55	-8.18	-7.58	-7.22	-6.96
150.0	4.8	-29.83	-17.56	-14.51	-11.45	-9.97	-9.36	-9.01	-8.76
160.0	6.2	-34.89	-20.58	-17.05	-13.54	-11.92	-11.28	-10.93	-10.69
170.0	7.9	-40.98	-24.04	-19.88	-15.81	-13.99	-13.30	-12.93	-12.69
180.0	10.0	-48.27	-27.98	-23.01	-18.22	-16.12	-15.35	-14.94	-14.68
190.0	12.6	-56.96	-32.41	-26.42	-20.69	-18.23	-17.33	-16.86	-16.56
200.0	15.6	-67.25	-37.36	-30.06	-23.14	-20.19	-19.11	-18.53	-18.15

B

		m/mol·kg^{-1}							
t/°C	P/bar	0.00	0.01	0.02	0.05	0.10	0.15	0.20	0.25
0.0	100.0	-13.85	-9.00	-7.55	-5.63	-3.99	-2.84	-1.92	-1.14
10.0	100.0	-10.41	-5.87	-4.53	-2.75	-1.26	-0.22	0.60	1.29
20.0	100.0	-8.44	-3.91	-2.59	-0.89	0.49	1.43	2.17	2.79
25.0	100.0	-7.87	-3.26	-1.94	-0.26	1.08	1.98	2.68	3.27
30.0	100.0	-7.54	-2.80	-1.45	0.22	1.52	2.38	3.05	3.61
40.0	100.0	-7.43	-2.31	-0.89	0.80	2.04	2.83	3.45	3.96
50.0	100.0	-7.87	-2.28	-0.76	0.98	2.17	2.92	3.48	3.95
60.0	100.0	-8.72	-2.58	-0.95	0.86	2.03	2.73	3.25	3.68
70.0	100.0	-9.85	-3.14	-1.39	0.50	1.66	2.32	2.81	3.21
80.0	100.0	-11.22	-3.92	-2.03	-0.05	1.10	1.73	2.19	2.56
90.0	100.0	-12.81	-4.89	-2.87	-0.79	0.37	0.98	1.40	1.74
100.0	100.0	-14.64	-6.06	-3.90	-1.70	-0.53	0.05	0.45	0.76
110.0	100.0	-16.75	-7.45	-5.13	-2.80	-1.61	-1.05	-0.68	-0.40
120.0	100.0	-19.21	-9.09	-6.58	-4.09	-2.88	-2.34	-2.00	-1.74
130.0	100.0	-22.13	-11.02	-8.27	-5.60	4.35	-3.82	-3.51	-3.28
140.0	100.0	-25.62	-13.28	-10.24	-7.33	-6.02	-5.51	-5.22	-5.02
150.0	100.0	-29.83	-15.91	-12.51	-9.28	-7.90	-7.39	-7.12	-6.94
160.0	100.0	-34.89	-18.97	-15.10	-11.46	-9.97	-9.45	-9.20	-9.04
170.0	100.0	-40.98	-22.49	-18.01	-13.85	-12.20	-11.66	-11.41	-11.27
180.0	100.0	-48.27	-26.51	-21.25	-16.42	-14.54	-13.95	-13.70	-13.56
190.0	100.0	-56.96	-31.05	-24.81	-19.11	-16.92	-16.25	-15.97	-15.82
200.0	100.0	-67.25	-36.14	-28.64	-21.84	-19.24	-18.43	-18.08	-17.89

Review of Equations

We have the dual objectives of representation in simple equations of the present measurements and the expression of the resulting pressure dependency of various thermodynamic properties. Both of these objectives are met by use of the same form of equations used for the other thermodynamic properties (*1*). These are the virial-series-plus-Debye–Hückel (Pitzer) equations as developed by Pitzer (*19*, *20*) and Pitzer and Mayorga (*21*). The general set of equations for various properties are given in several papers (*1*, *2*, *4*, *20*) and will not be duplicated here. The excess Gibbs energy is related to the total Gibbs energy in the molality system by the equation

$$G = n_1G^\circ_1 + n_2\bar{G}^\circ_2 + G^{EX} + n_2\nu RT(\ln m - 1) \qquad (7)$$

where n_1 and n_2 are the numbers of moles of water and salt of standard molar Gibbs energies G°_1 and $\bar{G}^\circ_2$. The composition dependence of G^{EX} is then given by the following equation

$$1000G^{EX}/n_1M_wRT = -A_\phi(4I/b)\ln(1 + bI^{1/2}) + 2\nu_M\nu_X[m^2B_{MX}(I) + m^3\nu_MZ_MC_{MX}] \qquad (8a)$$

$$B_{MX}(I) = \beta_{MX}^{(0)} + \beta_{MX}^{(1)}g(\alpha_1I^{1/2}) + \beta_{MX}^{(2)}g(\alpha_2I^{1/2}) \qquad (8b)$$

$$g(x) = 2[1 - (1 + x)\exp(-x)]/x^2 \qquad (8c)$$

where the electrolyte MX contains ν_M and ν_X ions of charge Z_M and Z_X, and $\nu = \nu_M + \nu_X$. In some papers the quantity $C^\phi = 2|Z_MZ_X|^{1/2}C$ is used instead of C. I is the ionic strength

$$I = \frac{1}{2}\sum_i m_iZ_i^2 \qquad (9)$$

and A_ϕ is the Debye–Hückel slope for the osmotic coefficient for which values are given by Bradley and Pitzer (*22*):

$$A_\phi = (1/3)(2\pi N_0d_w/1000)^{1/2}(e^2/DkT)^{3/2} \qquad (10)$$

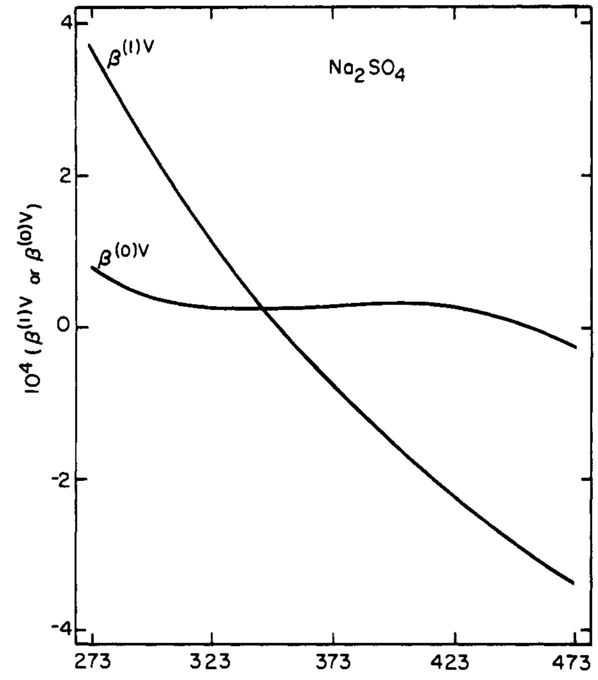

Figure 2. Temperature dependence of the fitting parameters $\beta^{(0)V}$ and $\beta^{(1)V}$ for Na_2SO_4.

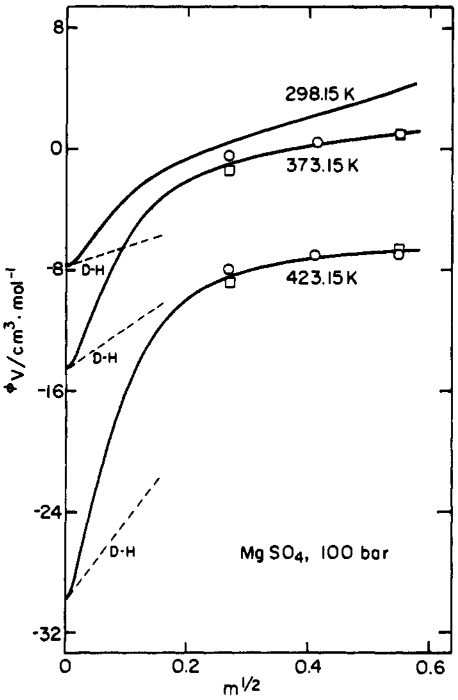

Figure 3. The apparent molar volume, $^{\phi}V$, for $MgSO_4$ at 100 bar: ○, rising temperature; □, falling temperature. Solid curves are calculated from the fit (eq 20); dashed lines are the Debye–Hückel slopes.

Here d_w is the density and D the dielectric constant of pure water.

The parameter b has a fixed value of 1.2 $kg^{1/2}\cdot mol^{-1/2}$ and α_1 and α_2 have values of 1.4 and 12.0 $kg^{1/2}\cdot mol^{-1/2}$ for a 2:2 electrolyte. For a 2:1 or a 1:1 electrolyte α_1 = 2.0 $kg^{1/2}\cdot mol^{-1/2}$, and the term in $\beta^{(2)}$ is omitted. The only quantities fitted for a particular electrolyte are those with the MX subscript in eq 8.

The total volume of the solution, V, is given by the pressure derivative of the total Gibbs energy of the solution

$$V = (\partial G/\partial P)_T \qquad (11)$$

$$V = n_1V_1^0 + n_2\bar{V}_2^0 + (\partial G^{EX}/\partial P)_T \qquad (12)$$

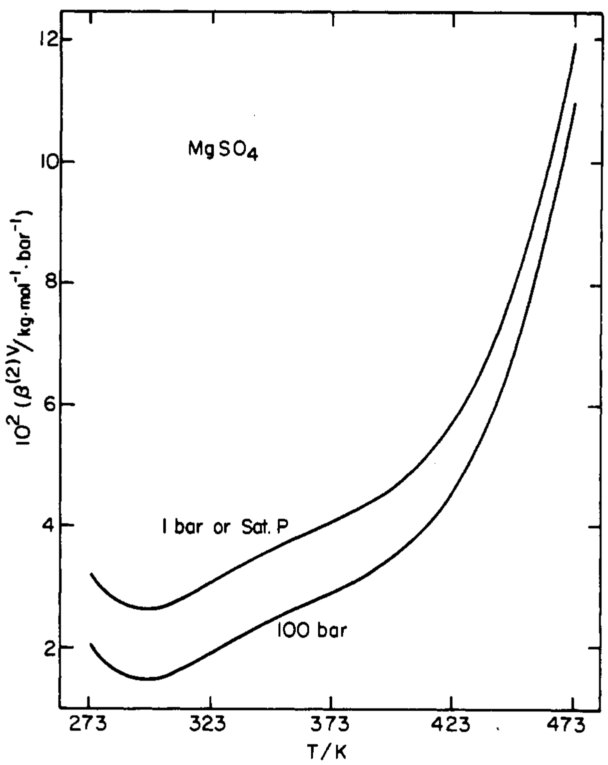

Figure 4. Temperature dependence of the fitting parameter $\beta^{(2)V}$ for $MgSO_4$.

The apparent molar volume is defined by

$$^{\phi}V = (V - n_1V_1^0)/n_2 \qquad (13)$$

By using eq 12 in the above equation

$$^{\phi}V = \bar{V}_2^0 + (1/n_2)(\partial G^{EX}/\partial P)_T \qquad (14)$$

$\bar{V}_2^0$ is the partial molar volume of the solute at infinite dilution. Substitution of eq 8 into the above equation yields the parametric form of the equation for the apparent molar volume

$$^{\phi}V = \bar{V}_2^0 + \nu|Z_MZ_X|A_Vh(I) + 2\nu_M\nu_XRT[mB_{MX}^V(I) + m^2(\nu_MZ_M)C_{MX}^V] \qquad (15a)$$

where

$$h(I) = \ln(1 + bI^{1/2})/2b \qquad (15b)$$

$$B_{MX}^V(I) = (\partial B_{MX}(I)/\partial P)_{T,I} \qquad (16a)$$

$$C_{MX}^V = (\partial C_{MX}/\partial P)_T \qquad (16b)$$

Also

$$A_V = -4RT(\partial A_{\phi}/\partial P)_T \qquad (17)$$

There is some theoretical basis for making the parameter α_2 proportional to the Debye-Hückel slope A_{ϕ} rather than a constant. This is discussed in detail elsewhere (*1*, *21*). The alternate basis yields an improved fit to some measurements at very low molality and improved agreement with treatments based on an ion-pairing reaction equilibrium, but there is no difference above molality 0.1 $mol\cdot kg^{-1}$ for a 2-2 electrolyte. Thus, for most practical purposes the assumption α_2 = 12 $kg^{1/2}\cdot mol^{-1/2}$ is adequate and avoids many complications. The resulting $\beta^{(2)V}$ from this paper gives the correct pressure dependency for $\beta^{(2)}$ on the constant α_2 basis in ref *1*.

The equations on the basis α_2 proportional to A_{ϕ} are complicated by the pressure and temperature dependencies of A_{ϕ}. While this can all be handled without real difficulty, the advantages are so limited that it does not seem worthwhile to treat the present data on that basis. The present $\beta^{(2)V}$ values will give the correct pressure dependency of the quantity $\beta^{(2)*}$, defined for use with variable α_2, through the equation

$$(\partial\beta^{(2)*}/\partial P)_T = \partial/\partial P\,[\beta^{(2)}A_\phi{}^2(30.6_5/12\ \mathrm{kg}^{1/2}\cdot\mathrm{mol}^{-1/2})^2] = [\beta^{(2)V}A_\phi{}^2 - \beta^{(2)}A_\phi A_V/2RT](30.6_5/12\ \mathrm{kg}^{1/2}\cdot\mathrm{mol}^{-1/2})^2 \quad (18)$$

The second term in the brackets will be very small and can, probably, be neglected in comparison with the first term.

Sodium Sulfate

Our results for the apparent molar volumes of sodium sulfate extend up to 0.33 *m*, to 473 K, and to 100 bar. We used our results along with the literature values up to 1 *m* and 100 bar in order to get an equation for the apparent molar volumes up to 473 K. These data were fitted to eq 15. The fitting parameters $\bar{V}_2{}^0$, $\beta^{(0)V}$, and $\beta^{(1)V}$ in eq 15 were assumed to be temperature- and pressure-dependent and the triple interaction parameter $C_{MX}{}^V$ was assumed zero since our data extend only to 1 mol·kg^{-1}. The parameter $\beta^{(2)V}$ was also zero in this case—it is needed only for 2:2 electrolytes where there is a significant tendency toward ion pairing. Several different functional forms of the three fitting parameters were tried and the following parameters were found to be necessary to fit all the data within uncertainties.

$$\bar{V}_2{}^0 = p_1/T + p_2 + p_3T + p_4T^2 + p_5T^3 + p_6P \quad (19a)$$

$$\beta^{(0)V} = p_7/T + p_8 + p_9T + p_{10}T^2 \quad (19b)$$

$$\beta^{(1)V} = p_{11}/T + p_{12} \quad (19c)$$

Here the p_i's are the fitting parameters, T is the temperature in kelvin, and P is the pressure in bar.

The uncertainties in the data were given as quoted by the authors or as judged by us. In general, the uncertainties in the data were increased with increasing temperature. Also a few values from the literature at very low molalities showed larger deviations and therefore were assigned larger uncertainties. The data of Fabuss et al. (*6*) showed substantial deviations from the fit and from other literature values and were not used in the final fit. The overall standard deviation of the fit was 0.28 cm^3·mol^{-1}.

Magnesium Sulfate

Our results for magnesium sulfate extend up to 0.25 *m*, to 473 K, and to 100 bar. Again we used our results along with the literature values up to 0.25 *m* and 100 bar in order to get an equation for the apparent molar volumes up to 473 K. These data were fitted to eq 15.

Because of the rapid change of ion association at low molalities in $MgSO_4$, it is not possible to obtain an accurate value of $\bar{V}_2{}^0$ by extrapolation. Therefore this quantity was obtained indirectly as follows

$$\bar{V}_2{}^0(\mathrm{MgSO_4}) = \bar{V}_2{}^0(\mathrm{MgCl_2}) + \bar{V}_2{}^0(\mathrm{Na_2SO_4}) - 2\bar{V}_2{}^0(\mathrm{NaCl})$$

where the equation for NaCl is available from literature (*3*, *4*), for Na_2SO_4 is described in this paper, and for $MgCl_2$ has been developed recently from the results of Saluja (*15*) and others in literature and is being prepared for publication separately (*16*). $\bar{V}_2{}^0$ for $MgSO_4$ was assumed pressure-independent because the pressure effect for the sum of $MgCl_2$ and Na_2SO_4 is roughly the same as twice that for NaCl and therefore cancels out. The values of $\bar{V}_2{}^0$ for $MgSO_4$ thus obtained from 273 to 473 K were fitted to a temperature-dependent equation. The parameters $\beta^{(0)V}$ and $C_{MX}{}^V$ were not needed in our concentration range and therefore the fitting parameters of eq 15 were only $\beta^{(1)V}$ and $\beta^{(2)V}$. The following equations were found necessary to fit the array of data.

$$\bar{V}_2{}^0 = q_1/T + q_2 + q_3T + q_4T^2 + q_5T^3 \quad (20a)$$

$$\beta^{(1)V} = q_6/T + q_7 + q_8T + q_9T^2 \quad (20b)$$

$$\beta^{(2)V} = q_{10}/T + q_{11} + q_{12}T + q_{13}T^2 + q_{14}T^3 + q_{15}P \quad (20c)$$

where q_i's are the fitting parameters.

The pattern of uncertainties for $MgSO_4$ was the same as that for Na_2SO_4 and the data of Fabuss et al. (*6*) were ignored in this case also. The overall standard deviation of the fit was 0.29 cm^3·mol^{-1}.

Results

Table III gives the parameters for the eq 19 and 20 for the apparent molar volume of Na_2SO_4 and $MgSO_4$.

Sections A and B of Table IV give the values of the apparent molar volume of Na_2SO_4 at rounded molalities, temperatures, and pressures. Table IVa gives the values at 1 atm or saturation pressure up to 1 mol·kg^{-1}. Table IVb gives the values at 100 bar up to 0.4 mol·kg^{-1}. Our equation for Na_2SO_4 is valid only up to 0.33 mol·kg^{-1} to 100 bar, and up to 1 mol·kg^{-1} to 20 bar.

Sections A and B of Table V give the values of the apparent molar volume of $MgSO_4$ at rounded molalities, temperatures, and pressures.

Discussion

Figure 1 shows experimental values at 373 and 423 K for Na_2SO_4 and the curves from the equations adopted as well as the limiting Debye–Hückel slopes. The curve for 298 K is also shown for comparison. Even at 423 K the extrapolation to zero molality is straightforward while the curves at lower temperatures are nearly linear. Figure 2 shows the two ion-interaction parameters as a function of temperature. There is no indication of ion pairing since that would yield a positive $\beta^{(1)V}$ whereas the actual trend of $\beta^{(1)V}$ is to negative values at higher temperature.

Figure 3 shows the experimental points, calculated curves, and Debye–Hückel limiting slopes for $MgSO_4$ at 373 and 423 K with the 298 K curve for comparison. Here the large positive departures from the Debye–Hückel slopes are a clear indication of ion-pairing. This effect is also apparent in Figure 4 which shows a large, positive $\beta^{(2)V}$ which also increases rapidly above 423 K. The $\beta^{(1)}V$ parameter for $MgSO_4$ is relatively small and shows a negative slope with T.

The large, positive value of $\beta^{(2)V}$ indicates that ion-pairing decreases with increase in pressure, which is the expected effect.

Registry No. Na_2SO_4, 7757-82-6; $MgSO_4$, 7487-88-9.

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Ultrasonic Velocities in, and Adiabatic Compressibilities for, Binary Liquid Mixtures of 1,2-Dichloroethane with Benzene, Toluene, *p*-Xylene, Quinoline, and Cyclohexane

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Measurements of ultrasonic velocities (u) and adiabatic compressibilities (k_s) have been made for mixtures of 1,2-dichloroethane (CH_2ClCH_2Cl) with benzene, toluene, and quinoline at 303.15 and 313.15 K, for mixtures of CH_2ClCH_2Cl with *p*-xylene at 303.15 and 318.15 K, and for mixtures of CH_2ClCH_2Cl with cyclohexane at 308.15 K. The values of the quantity Δk_s, which refers to the deviations of the experimental values of k_s for mixtures from the mole fraction mixture law values, have been found to be positive for CH_2ClCH_2Cl–benzene, CH_2ClCH_2Cl–toluene, CH_2ClCH_2Cl–*p*-xylene, and CH_2ClCH_2Cl–cyclohexane, and negative for CH_2ClCH_2Cl–quinoline.

Introduction

Quite recently, Nath and Singh (*1*) made measurements of excess volumes for binary liquid mixtures of 1,2-dichloroethane (CH_2ClCH_2Cl) with benzene, toluene, *p*-xylene, quinoline, and cyclohexane at different temperatures, and the results obtained have been discussed from the viewpoint of the existence of specific interaction between the components of the various mixtures. It has been indicated (*1*) that there exists specific interaction leading to the formation of molecular complexes of CH_2ClCH_2Cl with the aromatic hydrocarbons and quinoline in the liquid state. Since the adiabatic compressibilities as obtained from ultrasonic velocities in binary liquid mixtures are known (*2*–*5*) to shed light on the existence of specific interaction between the components, it was thought worthwhile to get further information concerning the formation of adducts between the components of the binary mixtures of CH_2ClCH_2Cl with the aromatic hydrocarbons, and quinoline, from measurements of ultrasonic velocities. Hence, in the present program, we have made measurements of ultrasonic velocities in, and adiabatic compressibilities for, the binary liquid mixtures of CH_2ClCH_2Cl with benzene, toluene, *p*-xylene, quinoline, and cyclohexane and the results obtained have been interpreted in this paper.

Table I. Values of Ultrasonic Velocities in, and Adiabatic Compressibilities[a] for, Various Pure Liquids at 303.15 K

	u, m s^{-1}			$10^{12}k_s$, Pa^{-1}		
liquid	this work	lit.	ref	this work	lit.	ref
benzene	1278	1278	*8*	705	705	*8*
toluene	1284	1284.5	*8*	707	706.6	*8*
p-xylene	1289	1288	*3*	706	707	*3*
1,2-dichloroethane	1175	1175[b]	*5*	585	585	*5*

[a] Values of k_s calculated from eq 1, by using densities obtained from the data reported in ref 7. [b] Value obtained by interpolation.

Experimental Section

Materials. The methods of purifying the various components and checking their purity have been described earlier (*1*).

Method. The ultrasonic velocities, u, in pure liquids and their binary mixtures were measured with a single-crystal interferometer (supplied by Mittal Enterprises, New Delhi) at a frequency of 2 MHz s^{-1}. The accuracy in the values of u is of the order of ±1.0 m s^{-1}. The adiabatic compressibilities, k_s, were calculated from the relation (*3*–*6*)

$$k_s = u^{-2}\rho^{-1} \qquad (1)$$

where ρ refers to the density. The densities used to calculate k_s for pure liquids at various temperatures were obtained from the data reported by Timmermans (*7*), whereas the densities used to calculate k_s for mixtures were estimated from the densities of pure liquids, and the data on excess volumes for the various mixtures, as reported earlier (*1*). The accuracy in the values of $10^{12}k_s$ is of the order of ±1.0 Pa^{-1}.

The working of the interferometer was tested by making measurements for pure liquids benzene, toluene, *p*-xylene, and 1,2-dichloroethane at 303.15 K. Table I shows that present values of u and k_s for these liquids are in good agreement with the data available in literature (*3*, *5*, *8*).

Results and Discussion

The experimental values of ultrasonic velocities in, and adi-

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