Table I. Comparison of K'_p/K'_1 As Calculated by MARFRA and SMARME Equations with Those Tabulated by Millero (8) at 0 and 25 °C for Sea Water

press., bar	Millero (0 °C)[a]	MARFRA or SMARME[a]	Millero (25 °C)[b]	MARFRA or SMARME[b]
1	1.00	1.00	1.00	1.00
200	1.19	1.19	1.15	1.15_5
400	1.40	1.42	1.33	1.34
600	1.63	1.66	1.51	1.54
800	1.88	1.91	1.72	1.75_5
1000	2.16	2.20	1.95	1.99

[a] Average difference = 0.024. [b] Average difference = 0.024.

Marshall and Franck (3) have published a generalized equation (MARFRA) for estimating the ion product of water, and proposed its applicability up to 1000 °C and 10 000 bar. This equation has been found to be in good agreement with the reported values (1, 5, 6). The equation is

$$\log K_w^0(\text{MARFRA}) = -4.098 - 3.2452 \times 10^3 T^{-1} + 2.2362 \times 10^5 T^{-2} - 3.9840 \times 10^7 T^{-3} + (13.937 - 1.2623 \times 10^3 T^{-1} + 8.5641 \times 10^5 T^{-2}) \log \rho_w \quad (4)$$

where ρ_w is the density of pure water.

In order to use eq 2 (SMARME) and eq 4 (MARFRA) for estimating the ion product of water in sea water, we substitute the density of pure water by the density of sea water. The remaining portions of the equations do not change. We use a prime for sea water in order to distinguish it from that for pure water. Densities of sea water can be taken from UNESCO tables (7).

Results and Discussion

According to Millero (8), the directly measured experimental values of the ion product of water in sea water are not available at high pressures. He obtained them by using ΔV and Δk values which are the experimentally determined values of volume and compressibility changes. He also listed the values of K'_p/K'_1 at different pressures at 0 and 25 °C.

In Table I, we list the values of K'_p/K'_1 obtained from the uses of eq 2 and 4, along with those obtained by Millero (8) at both 0 and 25 °C for ready comparison. The values of log K'_w used in these calculations were −14.386 and −13.776 at 0 and 25 °C, respectively, and at 1 bar pressure.

An inspection of Table I shows that both SMARME and MARFRA yield the same predictions of log K'_w. The average difference between the calculated values and those obtained by Millero are 0.02 and 0.007 units for K'_p/K'_1 and log K'_w, respectively.

The log K'_w values thus obtained from either equation, when differentiated with respect to pressure and temperature, yield the change in molar volume (ΔV^*) and enthalpy (ΔH^*), respectively, upon ionization. The ΔV^* thus obtained is −18.07 cm^3 mol^{-1}, which agrees closely with that of Millero (−18.10 cm^3 mol^{-1}). The ΔH^* is 13.63 kcal mol^{-1}, which is nearly 0.30 kcal mol^{-1} higher than that of pure water.

Thus, it is clear that by introduction of the density of sea water at a given pressure, the equation of Marshall and Franck describes some reliably calculated values of the ion product of water in sea water. The equation of Sweeton, Mesmer, and Baes with an added density relationship based on the Marshall and Franck equation also provides these values.

Acknowledgment

I thank Professors E. U. Franck and Loren G. Hepler for many suggestions to improve the quality of the manuscript. I also thank an anonymous reviewer for pointing out errors in the manuscript through his excellent reviews.

Registry No. Water, 7732-18-5.

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Received for review September 30, 1985. Revised manuscript received June 1, 1987. Accepted August 18, 1987.

Densities of Binary Aqueous Solutions of 306 Inorganic Substances

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Constants of equations expressing the density of binary aqueous solutions as a function of concentration, and where possible also of temperature, are given for 306 inorganic substances. The goodness of fit and limits of the equation validity are indicated for each system.

Introduction

The density of aqueous solutions of inorganic substances and its dependence on solution concentration and/or temperature represents important information for chemical engineering and physical chemistry. A comparatively large volume of relevant data for a wide variety of systems is available in the periodical literature and the existing monographs. However, the presentation of density data, even in the recent monographs (1, 2), is not very suitable for direct use as they are given for particular concentrations and temperatures, which rarely cover the whole interval required. Moreover, different sources present mutually inconsistent sets of data for most systems.

We have, therefore, critically evaluated the existing density data for binary aqueous solutions of inorganic substances and those regarded as reliable, correlated in a consistent manner.

0021-9568/88/1733-0049$01.50/0

Table I. Constants of Eq 1 Expressing the Density of Aqueous Solutions of 167 Substances as a Function of Solution Concentration and Temperature

substance	$A \times 10^{-2}$	$-B \times 10$	$C \times 10^{3}$	$-D$	$E \times 10^{2}$	$-F \times 10^{4}$	$s_r \times 10^{2}$	t	c_{max}	ref
$AgClO_4$	1.727	2.858	2.138	4.015	7.604	4.963	18.7	0–100	satd	27–31
$AgNO_3$	1.473	3.442	2.869	4.298	11.74	9.798	29.5	0–100	satd	5–7
$Al(ClO_4)_3$	2.255	1.644	0	6.674	0	0	3.2	10–40	50	32
$Al(NO_3)_3$	1.785	18.85	84.24	25.78	408.4	1806	20.0	10–35	38	6, 7
$Al_2(SO_4)_3$	3.699	6.816	5.346	55.22	39.07	33.00	10.1	0–100	satd	6, 33, 34
$BaBr_2$	2.569	4.798	1.387	3.546	24.33	−2.784	37.9	0–100	satd	5, 6, 22
$BaCl_2$	1.878	1.535	−3.400	7.075	−84.98	−47.04	36.1	0–100	satd	6
$Ba(ClO_3)_2$	2.368	8.322	19.68	−0.1765	−2.594	84.22	20.0	0–60	satd	5, 6
BaI_2	3.379	5.313	3.887	8.130	23.12	16.67	7.6	0–100	satd	5
$Ba(NO_3)_2$	2.738	28.04	5.422	123.8	625.2	424.1	6.0	0–70	satd	5–7, 22
$CaBr_2$	1.740	2.575	2.359	8.300	7.635	7.212	4.8	0–100	satd	5
$CaCl_2$	1.012	61.56	1.028	9.749	96.94	3.165	14.7	0–100	satd	5, 6, 22
CaI_2	2.696	12.66	10.85	25.46	99.78	86.93	29.0	0–100	40	5, 6, 22
$Ca(NO_3)_2$	1.298	2.052	1.023	8.426	0.776	−4.225	18.2	0–70	satd	5, 35–38
$CdBr_2$	2.376	3.817	2.510	6.035	16.42	11.83	14.9	0–100	satd	5, 39
$CdCl_2$	1.637	2.355	1.325	6.428	6.973	3.648	8.9	0–100	satd	5, 6, 22
CdI_2	3.073	2.411	1.364	4.539	4.843	2.609	7.2	0–100	satd	5, 6, 22
$Cd(NO_3)_2$	1.948	−0.09302	−0.03925	5.591	−6.808	−5.439	9.7	0–100	satd	6, 40–42
$CdSO_4$	3.706	1.409	286.6	102.4	775.1	1579	34.3	0–25	satd	6, 22
$Co(NO_3)_2$	1.527	−0.2613	−0.4448	8.247	−2.591	−2.866	11.7	0–100	satd	43, 5, 6, 22, 41
$CoSO_4$	1.714	−16.29	−99.52	16.32	−194.3	−973.2	17.2	5–40	satd	5, 6, 22
CsBr	1.693	1.123	0.9765	2.066	0	0	2.1	0–100	45	5
CsCl	1.327	1.511	1.251	3.113	4.181	3.319	5.5	0–100	satd	5, 6
CsF	1.352	1.535	1.837	3.569	3.856	4.391	2.8	0–70	70	44, 45
CsI	2.051	1.521	1.193	1.306	0	0	1.8	0–100	satd	5
$CsNO_3$	1.503	2.602	1.872	4.299	8.322	5.842	4.8	0–100	satd	5, 6, 46
Cs_2SO_4	3.071	4.340	7.308	11.67	17.54	32.15	5.7	0–100	satd	5, 7
$CuCl_2$	1.291	3.214	2.704	9.100	15.50	18.21	29.1	0–100	satd	47–53
$Cu(NO_3)_2$	1.470	−21.33	−68.82	0.4527	−126.0	−376.3	11.3	10–45	satd	5, 6
$CuSO_4$	1.943	9.174	6.138	39.37	83.51	53.81	36.5	0–100	satd	5, 6, 22
$DyCl_3$	2.589	1.001	1.376	13.32	0	0	2.5	0–100	40	18
$ErCl_3$	2.655	0.9711	1.314	13.60	0	0	2.6	0–100	50	18
$FeCl_3$	1.356	−7.891	−9.754	7.320	−51.82	−54.24	38.6	10–50	satd	5, 54
$FeSO_4$	1.992	21.20	−40.35	63.49	305.3	22.43	15.4	10–60	satd	5, 6
$GdCl_3$	2.538	1.149	1.386	13.06	0	0	3.4	0–100	40	18
H_3BO_3	0.5092	10.35	8.291	28.20	95.20	75.11	10.6	0–100	satd	5, 22, 55
HBr	0.5998	1.300	1.061	1.263	2.160	1.647	13.5	0–70	60	5, 56
HCl	0.2046	0.9435	1.090	1.227	1.269	1.980	5.4	0–80	36	57
$HClO_4$	0.5985	3.334	3.190	−0.05668	8.249	9.076	10.2	0–50	60	58
HI	0.9397	2.176	2.343	0.08738	5.792	7.778	12.9	0–70	66	5, 6, 19, 45
HNO_3	0.4063	1.554	1.096	2.798	2.478	2.761	14.8	0–100	0–50	5, 59
	0.4984	1.092	0.1525	5.557	0.9001	−0.1289	11.3	0–100	51–100	
H_3PO_4	0.5574	5.606	0.2366	2.050	0.3387	−0.5906	23.7	0–80	95	7
H_2SO_4	0.7060	2.367	1.676	4.903	5.698	3.985	7.8	0–100	0–70	5, 59, 60
	0.7433	1.500	2.191	5.852	2.766	5.012	15.2	0–100	71–90	
	1.318	0.8177	−0.3053	19.91	0.6813	−1.321	17.4	0–100	91–100	
$HgCl_2$	1.793	−22.07	−42.70	−124.1	−569.1	−839.1	8.2	5–50	satd	5–7, 22
$Hg(CN)_2$	1.811	−6.178	−5.559	−26.25	−111.8	−79.22	3.2	0–50	satd	5, 7, 22
$KAg(CN)_2$	1.362	3.401	1.754	6.495	9.481	−4.920	5.6	0–80	10	61
$KAl(SO_4)_2$	2.839	17.49	3.178	83.17	433.4	257.6	6.7	0–80	satd	6, 22, 41
KBr	0.9057	1.876	1.425	4.019	5.985	4.092	14.0	0–100	satd	5, 6
$KBrO_3$	1.256	1.322	1.648	2.519	0	0	3.5	0–100	satd	5, 22
KTart[a]	1.479	−1.819	−2.369	7.129	−28.01	−30.26	25.8	0–80	satd	6, 62
K_2CO_3	1.358	2.628	1.986	16.36	8.768	5.385	22.5	0–100	satd	5, 6, 22
KCl	0.4971	0.7150	0.6506	2.376	0	0	3.6	0–100	satd	5
$KClO_3$	0.8222	1.214	1.374	6.223	7.488	7.211	8.4	0–100	satd	5, 22, 64, 67
$KClO_4$	0.8620	9.970	18.48	−60.10	−92.15	45.09	5.1	10–90	satd	5, 7
$K_3Co(CN)_6$	2.310	21.62	24.29	93.16	405.9	478.8	3.0	10–70	13	61, 65
K_2CrO_4	1.706	14.52	14.71	17.18	86.86	89.26	48.2	0–100	satd	5, 6, 35
$K_2Cr_2O_7$	2.441	16.79	13.60	58.17	177.5	136.3	13.4	0–100	satd	5–7, 66
KF	0.5364	1.208	1.317	3.790	3.121	3.399	9.4	0–60	45	5, 6, 44, 45, 91
$K_3Fe(CN)_6$	1.847	0.2936	−0.9857	13.43	−27.84	−42.71	17.2	0–100	satd	5, 6, 61, 41, 64
$K_4Fe(CN)_6$	2.616	7.400	8.012	23.51	21.60	31.37	7.6	0–100	satd	5, 6, 55, 67
$KHCO_3$	0.6315	−0.5602	1.991	0.2904	−11.27	0.2195	17.2	0–70	satd	5, 6, 22
KH_2PO_4	1.001	5.870	7.083	7.676	38.06	45.61	13.7	0–100	satd	5, 55, 68
$KHSO_4$	0.9981	−1.777	−17.01	3.911	−49.49	−197.7	4.9	0–60	satd	5–7
KI	1.256	2.125	1.515	3.022	5.980	4.090	3.6	0–100	satd	5, 6
KIO_3	1.735	−4.609	−0.4706	0	−45.37	0	3.8	0–100	satd	5, 6, 22
$KMnO_4$	1.223	1.029	8.093	14.85	90.79	75.66	8.9	0–100	satd	5, 22, 41
$K_4Mo(CN)_8$	3.038	8.047	12.71	37.05	68.93	209.4	1.0	10–70	9	61
KN_3	0.4896	1.020	0.8214	2.594	0	0	5.1	0–100	34	5
KNO_2	0.5586	2.176	1.369	2.729	4.447	2.163	39.7	0–90	satd	6, 55
KNO_3	0.6553	1.477	0.9596	2.323	2.364	1.500	12.2	0–100	satd	5, 6, 22
KOH	0.5459	1.156	1.009	4.383	2.343	1.865	7.6	0–100	satd	22, 69, 70
KSCN	0.5792	3.997	2.914	5.116	12.67	9.190	23.2	0–100	satd	6, 55, 67
K_2SO_4	1.619	7.181	5.994	34.81	77.97	61.85	10.0	0–100	satd	5, 6, 71, 89

Table I (Continued)

substance	$A \times 10^{-2}$	$-B \times 10$	$C \times 10^{3}$	$-D$	$E \times 10^{2}$	$-F \times 10^{4}$	$s_r \times 10^{2}$	t	c_{max}	ref
$LaCl_3$	2.319	0.8064	1.110	13.20	0	0	2.1	0–100	satd	72
LiBr	0.6032	0.00444	0.2329	0.6188	−2.448	−1.773	17.6	0–80	satd	5, 6, 22
LiCl	0.2446	0.5505	0.8671	0.7927	1.169	1.761	9.2	0–100	satd	5, 6
$LiClO_4$	0.6957	3.280	2.913	3.409	12.42	12.88	5.9	0–100	satd	6, 73
LiI	0.9992	1.486	1.304	0.5602	3.721	3.197	5.1	0–100	satd	5
$LiNO_3$	0.4303	1.242	1.002	1.389	2.096	1.810	9.5	0–100	satd	5, 6, 74
LiOH	0.3016	−0.4827	−0.6976	2.786	−4.538	−5.916	8.1	0–100	satd	5, 7, 75, 76
Li_2SO_4	1.008	1.058	1.329	10.07	0	0	3.9	0–100	satd	5, 6
$MgBr_2$	1.585	1.676	1.987	7.343	5.026	5.966	11.6	0–100	satd	5, 6, 22
$Mg(BrO_3)_2$	3.224	51.20	15.01	64.78	338.5	179.2	6.4	0–40	satd	5, 6
$MgCl_2$	0.8099	1.887	2.315	6.029	7.449	8.305	15.7	0–100	satd	5, 6, 22, 89
$Mg(ClO_4)_2$	1.694	3.138	1.278	9.611	8.639	0	2.4	0–100	satd	41
MgI_2	2.357	3.178	2.723	6.551	12.35	9.773	4.7	0–100	satd	5, 6, 22
$Mg(NO_3)_2$	1.190	1.440	0.1877	8.257	−7.177	−16.99	6.2	0–80	30	5, 6, 22, 18
$MgSO_4$	1.437	6.531	5.263	23.28	39.11	27.83	26.3	0–100	satd	5, 22, 77–79
MnCl	1.022	−4.966	−13.07	3.659	−16.31	−47.74	25.9	0–70	satd	5, 54, 80
$MnSO_4$	1.551	1.258	−0.5341	13.64	6.703	−3.531	19.3	0–100	satd	5, 55, 81
NH_3	−0.0688	0.1989	0.09711	−0.1843	−0.4392	0.01126	12.7	0–75	40	5, 59
$NH_4Al(SO_4)_2$	2.111	−3.694	−5.642	15.42	−34.35	−42.53	6.5	0–100	satd	6, 19, 41
NH_4Ac^a	0.2328	2.948	2.644	4.013	11.01	10.79	6.7	0–100	40	5, 41
NH_4Ox^a	0.6697	0.3180	−0.05828	13.05	0.7378	−12.31	2.3	0–100	satd	5, 41
NH_4Cl	0.2061	1.577	1.553	2.556	5.670	5.082	3.9	0–100	satd	5, 22
NH_4ClO_4	0.6375	5.744	13.22	2.497	10.09	46.34	10.0	0–50	satd	5, 6
$NH_4Fe(SO_4)_2$	2.483	2.470	1.462	39.48	14.73	0	2.9	0–100	satd	19
$NH_4H_2PO_4$	0.7666	3.191	2.382	13.39	23.41	15.34	15.5	0–100	satd	22, 55, 68, 62, 82
NH_4HSO_4	0.7754	2.064	2.135	11.05	7.436	7.135	3.1	0–100	50	5
NH_4I	0.963	−0.8591	−3.218	−0.4009	−19.70	−30.20	21.8	10–60	50	5, 85
NH_4NO_3	0.3614	1.446	1.009	1.898	2.918	1.870	10.6	0–100	satd	83, 84
$(NH_4)_2Ni(SO_4)_2$	2.917	18.18	18.07	125.4	378.4	362.5	6.1	10–80	7	55, 85, 86
$(NH_4)_2SO_4$	0.8878	2.258	2.241	13.43	8.457	7.462	6.3	0–100	satd	5, 6, 22
$Na_2B_4O_7$	2.577	19.73	12.12	192.1	517.9	365.6	11.4	0–100	satd	5, 22, 55
NaBr	0.8362	1.872	1.353	2.847	4.791	3.413	5.0	0–100	satd	5, 6
$NaBrO_3$	1.231	2.778	1.726	5.168	12.05	7.415	4.9	0–100	satd	5, 22
$NaAc^a$	0.4364	0.6740	0.6482	2.113	−0.9843	0	4.9	0–100	satd	5, 6
$NaTart^a$	1.466	3.657	2.732	15.98	15.10	10.76	4.0	0–100	32	5, 6
NaCl	0.4485	0.9634	0.6136	2.712	1.009	0	4.2	0–100	satd	5
$NaClO_3$	0.7725	3.607	4.286	4.040	10.16	12.59	10.1	0–90	satd	5–7, 22
$NaClO_4$	0.8462	3.788	3.966	3.025	9.968	11.13	19.1	0–100	satd	5, 6, 87
Na_2CO_3	1.241	6.213	6.124	18.36	31.78	36.72	16.8	0–100	satd	5, 6, 22
$NaOx^a$	1.178	5.450	5.997	7.073	45.83	77.51	3.6	0–100	satd	5, 7
Na_2CrO_4	1.541	3.173	3.623	15.53	13.08	15.21	22.4	0–100	satd	5, 6, 66, 88
$Na_2Cr_2O_7$	2.029	13.15	10.16	22.81	59.66	45.67	22.2	0–100	satd	6, 66
NaF	0.4940	2.985	3.365	4.752	16.22	18.72	6.1	0–70	satd	5, 7, 89–92
$NaForm^a$	0.4520	0	−1.950	2.761	0	−3.695	3.8	0–60	satd	5–7
NaH_2PO_4	0.7649	−5.207	−6.142	−1.086	−26.60	−24.97	51.8	0–100	satd	62, 93, 94
Na_2HPO_4	1.255	−7.321	−5.656	−2.343	−52.46	−41.66	14.5	0–100	satd	7, 41, 93
$Na_5P_3O_7$	3.505	3.627	2.354	53.23	1.838	1.210	6.1	20–80	12	85
$NaHSO_4$	1.022	3.093	3.084	9.324	0	0	3.5	0–50	22	5
NaI	1.196	2.120	1.396	2.502	5.095	3.346	3.9	0–100	satd	5, 6
$NaIO_3$	1.785	10.80	29.84	−10.59	−7.927	170.5	11.8	0–60	satd	5, 7, 22, 95
$NaKTart^a$	1.490	2.323	1.944	13.45	4.364	2.506	4.2	0–80	satd	5
$NaMnO_4$	1.096	0.4598	−3.979	5.206	−18.29	61.06	8.7	0–40	26	96
Na_2MoO_4	1.923	6.168	5.791	−21.30	47.48	42.86	7.1	15–100	satd	5, 41
NaN_3	0.4116	1.560	1.025	1.188	2.594	1.536	4.2	0–100	30	5
$NaNO_2$	0.5142	3.362	4.079	3.242	7.155	9.671	11.2	0–80	satd	5–7, 97
$NaNO_3$	0.6298	2.382	1.520	4.138	6.626	4.208	7.4	0–100	satd	5, 6, 22
NaOH	0.4916	0.9064	0.6308	4.907	1.633	1.041	13.3	0–100	satd	5, 98–100
Na_3PO_4	1.473	−13.06	−10.43	−11.76	111.3	−86.91	6.5	0–100	satd	5; 41
$Na_4P_2O_7$	3.030	9.731	5.524	113.8	203.8	119.1	4.4	0–100	satd	5, 7, 41
Na_2S	0.8653	0.4961	−40.69	9.759	−3.120	−5.370	10.5	0–100	satd	5–7
NaSCN	0.4840	2.752	1.735	3.530	7.631	5.247	4.7	0–70	satd	6, 87
Na_2SO_3	1.651	22.90	22.80	45.90	177.1	176.2	18.1	0–100	satd	5–7, 41
Na_2SO_4	1.412	4.535	3.766	17.51	21.11	17.73	4.8	0–100	satd	5, 6, 22, 89
$N_2S_2O_3$	1.409	3.063	2.082	16.05	12.45	8.138	5.5	0–100	satd	6, 41
Na_2WO_4	2.554	−2.885	−2.066	1.756	−26.65	−21.07	16.9	0–100	satd	5, 6, 41
$NdCl_3$	2.446	1.140	1.211	14.57	0	0	3.0	0–100	satd	72
$NiCl_2$	1.187	−5.607	−5.650	2.635	−37.42	−34.53	23.2	0–100	satd	5–7, 22, 101
$Ni(NO_3)_2$	1.527	−12.09	−46.48	4.919	−67.71	−233.5	17.2	10–50	satd	5, 6, 43
$NiSO_4$	1.772	2.278	0.2337	22.04	6.476	−5.069	32.7	0–100	satd	5–7, 22
$Pb(NO_3)_2$	2.649	−9.459	−6.758	−19.60	−139.3	−91.02	28.3	0–100	satd	5–7, 102
$PrCl_3$	2.399	1.066	1.180	14.40	0	0	3.0	0–100	satd	72
RbBr	1.303	1.609	1.190	2.820	2.544	0	3.7	0–80	satd	5
RbF	0.9859	1.589	1.940	3.972	4.153	4.878	2.6	0–70	55	45
RbCl	0.9251	1.051	0.3060	3.330	2.809	0	4.3	0–100	satd	5
RbI	1.665	0.8912	−0.7021	2.708	−3.551	−12.94	14.7	0–80	satd	5
$RbNO_3$	1.044	1.294	1.640	0.7562	−0.1728	2.592	21.8	0–100	satd	5
Rb_2SO_4	2.324	6.489	8.260	17.22	37.98	47.91	5.8	0–100	satd	5

Table I (Continued)

substance	$A \times 10^{-2}$	$-B \times 10$	$C \times 10^{3}$	$-D$	$E \times 10^{2}$	$-F \times 10^{4}$	$s_r \times 10^{2}$	t	c_{max}	ref
$SmCl_3$	2.501	1.309	1.351	13.99	0	0	3.5	0–100	satd	18
$SrBr_2$	2.200	2.770	2.119	8.825	7.717	4.571	7.8	0–100	satd	5, 6, 22
$Sr(BrO_3)_2$	2.853	−2.778	0.2361	5.434	−24.18	−11.06	10.9	0–100	satd	5, 22
$Sr(Ac)_2$[a]	−1.134	−236.4	−521.3	−82.93	−780.2	−1426	2.5	20–35	26	5, 6
$SrCl_2$	1.536	4.157	3.586	14.63	23.11	18.94	8.1	0–100	satd	5, 6, 22
SrI_2	3.012	6.103	3.874	11.72	28.70	17.04	5.1	0–100	satd	5, 6
$Sr(NO_3)_2$	1.800	4.794	3.631	12.14	18.35	14.25	4.8	0–100	satd	5, 6
$TlNO_3$	2.470	15.82	13.66	−3.533	58.72	67.73	17.1	0–100	satd	5, 6, 103
Tl_2SO_4	5.062	−4.033	−6.553	195.3	−78.83	−126.7	4.7	0–100	satd	5
$UO_2(NO_3)_2$	3.182	0.6041	2.092	−5.374	−16.83	−1.337	18.2	0–100	satd	104, 105
UO_2SO_4	3.189	−21.21	−36.17	13.28	−215.6	−337.6	40.6	10–95	36	6
$YbCl_3$	2.737	1.041	1.352	13.88	0	0	2.8	0–100	50	18
$ZnBr_2$	1.990	2.767	1.040	9.900	7.184	1.730	20.9	0–100	satd	5, 6
$ZnCl_2$	1.211	3.632	1.954	8.380	12.00	6.587	24.3	0–100	satd	5–7
ZnI_2	2.762	3.293	1.959	10.82	9.385	6.576	20.8	0–100	satd	5, 22
$Zn(NO_3)_2$	1.687	5.047	4.492	13.56	28.31	26.11	8.3	0–80	50	5, 6, 85, 106
$ZnSO_4$	1.758	3.895	3.402	15.83	19.79	16.43	8.0	0–100	satd	5, 6, 22

[a] Ac = acetate, Form = formate, Ox = oxalate, Tart = tartrate; c_{max} in wt % or up to a saturated solution (satd).

Table II. Constants of Eq 3 Expressing the Density of Aqueous Solutions of 139 Substances as a Function of Solution Concentration at a Constant Temperature

substance	t, °C	$G \times 10^{-2}$	$-H \times 10^{-1}$	c_{max}, wt %	$s_r \times 10^{2}$	ref
AgF	18	1.217	0.1421	62	50.0	5
$AlBr_3$	20	2.086	1.128	22	13.7	6
$AlCl_3$	0	1.144	1.278	30	4.0	6
	15	9.642	0.5767	31	1.1	6
	25	1.183	0.8182	31	2.8	8
$Ba(Ac)_2$[a]	17.5	1.786	0.8983	40	29.9	6
$Ba(ClO_4)_2$	25	2.621	0.8486	60	0.6	6
$Ba(Form)_2$[a]	18	1.888	1.044	22	2.1	5
$Ba(OH)_2$	80	1.536	1.077	38	42.9	6
$Ba(SCN)_2$	25	1.807	0.4414	58	12.3	6
$BeCl_2$	25	0.5861	0.5002	30	12.6	5, 9
$Be(IO_3)_2$	15	3.105	−0.07855	22	20.0	6
$Be(NO_3)_2$	18	0.8092	0.1028	30	0.6	5
$BeSO_4$	25	0.9893	0.8743	28	2.1	5, 6, 10
$Ca(Ac)_2$[a]	17.5	0.8711	0.9909	25	2.3	6
$Ca(ClO_3)_2$	18	1.582	0.9327	64	4.2	5
$Ca(ClO_4)_2$	25	1.720	1.047	37	5.4	11
$CaCr_2O_7$	30	2.029	0.9380	54	5.6	6
$Ca_2Fe(CN)_6$	0	2.604	3.758	32	2.7	5
$Cd(ClO_3)_2$	18	2.240	0.6579	40	1.3	5
$CeCl_3$	25	2.305	1.105	44	10.2	6
$Ce(NO_3)_3$	15	3.256	2.256	24	2.5	6
$CoBr_2$	18	1.939	0.4898	30	0.4	5
$CoCl_2$	20	1.179	0.4724	20	0.9	12, 63
	25	1.183	0.5939	34	0.9	
$Co(ClO_3)_2$	18	1.787	0.7321	40	0.8	5
CsForm[a]	50.5	1.304	0.0887	75	22.6	14
CsOH	25	1.303	0.0900	17	1.5	15
$CuBr_2$	25	2.112	0.8487	44	1.6	16
$Cu(ClO_3)_2$	18	1.888	0.8423	30	0.9	5
$Cu(ClO_4)_2$	20	2.137	1.365	58	14.1	6
$Dy(ClO_4)_3$	25	3.708	1.283	67	0.9	17
$Er(ClO_4)_3$	25	3.795	1.442	68	2.2	17
$EuCl_3$	25	2.465	1.272	48	2.5	18
$Eu(ClO_4)_3$	25	3.639	1.495	67	4.1	17
$FeBr_2$	18	1.894	0.4664	35	1.5	5
$FeCl_2$	15.5	1.137	0.4805	37	7.8	5
$Fe(ClO_4)_3$	15	3.272	3.151	50	0.8	6
$Fe(NO_3)_2$	15	1.429	0.5318	44	1.5	5, 6
	20	1.470	0.8229	45	0.9	
$Fe(NO_3)_3$	18	1.896	0.7949	25	1.4	5
$Fe_2(SO_4)_3$	17.5	3.341	21.82	60	25.1	19
	25	3.743	29.68	15	18.3	7
$Gd(ClO_4)_3$	25	3.684	1.442	67	4.3	17
H_3AsO_4	15	9.112	0.0675	70	4.7	5
	25	9.298	0.1830	14	1.2	
H_2CrO_4	25	0.7942	0.5619	44	17.4	6
$H_2Cr_2O_7$	0	1.420	0.4853	57	5.5	6
HF	20	0.1081	0.09743	44	28.8	19
HIO_3	0	1.565	0.7194	27	4.7	6
	25	1.486	0.3374	14	3.9	
HIO_4	17	1.688	0.04977	32	2.8	19
$H_2S_2O_8$	14	1.101	0.003379	35	5.6	19
H_2SeO_4	25	1.111	0.4238	97	46.6	19

Table II (Continued)

substance	t, °C	$G \times 10^{-2}$	$-H \times 10^{-1}$	c_{max}, wt %	$s_r \times 10^2$	ref
$Hg(ClO_4)_2$	25	1.343	6.388	81	16.5	6
$HoCl_3$	25	2.598	1.305	50	1.4	20
$Ho(ClO_4)_3$	25	3.762	1.433	68	2.2	17
$InBr_3$	18	1.862	0.4001	32	1.8	5
$InCl_3$	25	1.700	0.3083	30	9.6	21
K_2CdI_4	18	5.360	1.281	45	1.6	5
KAc[a]	18	0.5156	0.3510	60	3.8	5, 22
	25	0.5101	0.3385	60	3.8	
KCitr[a]	18	2.127	2.274	34	0.9	5
	25	2.126	2.354	60	2.2	
KOx[a]	18	1.293	1.438	21	7.5	5, 6
	25	1.266	1.120	14	0.7	
KCN	20	0.3637	0.3068	35	7.5	5, 59
KCNO	15	0.5085	0.3484	34	1.7	5
K_2CS_3	15	1.293	1.221	68	18.7	6
$KFe(SO_4)_2$	15	2.483	1.358	20	1.9	5
KForm[a]	21	0.5249	0.3987	28	9.5	6
K_2HPO_4	18	1.541	1.528	27	7.4	6
KHS	18	0.4499	0.3408	50	1.9	5
K_2MoO_4	15	1.665	0.8992	16	0.9	5
K_3PO_4	25	1.116	1.839	23	12.2	23
K_2S	18	0.9401	0.8344	45	8.4	19
K_2SO_3	15	1.331	1.019	26	2.2	5
$K_2S_2O_7$	15	1.989	2.471	22	1.3	5
K_2SeO_4	15	1.845	1.489	14	0.3	5
	20	1.829	1.267	50	0.6	
K_2SiO_3	20	1.439	1.304	28	2.7	19
K_2WO_4	15	2.787	0.9494	18	0.4	5
$La(ClO_4)_3$	25	3.497	1.814	67	3.3	17
$La(NO_3)_3$	18	2.960	2.020	32	1.1	5
LiAc[a]	18	0.2587	0.08703	24	0.3	5
$LiClO_3$	25	0.5583	0.07032	75	7.5	5, 6
LiCNS	18	0.2576	0.09595	18	0.3	5
Li_2CrO_4	18	1.144	0.9888	22	0.4	5
$Li_2Cr_2O_7$	18	1.603	0.6688	20	0.7	5, 6
	30	1.454	0.3448	60	4.0	
LiForm[a]	18	0.2901	0.2367	27	4.1	5, 6
$LiIO_3$	18	1.626	0.7212	44	13.4	5
$LuCl_3$	25	2.744	1.377	53	2.2	20
$Lu(ClO_4)_3$	25	3.904	1.482	68	2.6	17
$Mg(Ac)_2$[a]	15	0.5508	0.3506	50	8.0	5, 7
	25	0.8617	0.8502	43	8.7	
$Mg(ClO_3)_2$	18	1.476	1.149	56	7.4	5
$MgCrO_4$	18	1.421	1.180	48	1.8	6
$MnBr_2$	18	1.807	0.4588	32	0.8	19
$Mn(Ac)_2$[a]	20	0.8827	0.3699	30	2.9	5
$Mn(NO_3)_2$	18	1.411	0.7527	55	5.4	5
NH_4Br	18	0.5528	0.1046	34	1.1	7
	25	0.5498	0.1038	40	0.9	
$(NH_4)_2CO_3$	15	0.3652	0.3932	40	6.1	19
$(NH_4)_2Cr_2O_7$	12	1.392	0.2687	20	0.5	5, 7
	23	1.439	0.5519	26	11.8	
NH_4F	18	0.2144	0.3659	14	2.6	5, 6
$NH_4Fe(SO_4)_2$	15	2.380	3.764	40	10.1	19
NH_4Form[a]	15	0.1951	0.2015	55	3.6	5
	25	0.1910	0.1940	55	2.7	
NH_4HF_2	25	0.2510	0.4214	30	21.3	24
$(NH_4)_2MoO_4$	20	1.076	1.567	30	8.2	6
NH_4OCl	17	0.3186	0.1755	40	2.8	6, 25
	25	0.3242	0.2846	22	2.7	
NH_4SCN	18	0.1792	0.06591	28	0.4	5
	25	0.1634	0.02594	58	5.4	
$(NH_4)_2SiF_6$	20	0.7899	0.1992	17	0.6	6
Na_3AsO_4	17	2.331	2.714	12	0.9	5
NaBenz[a]	25	0.6117	0.4306	36	0.7	5
$NaClO_2$	20	0.5140	0.05241	33	14.2	7
$Na_4Fe(CN)_6$	20	2.218	1.493	15	1.0	63
NaH_2AsO_4	25	1.320	0.8006	14	0.8	5
Na_2HAsO_4	14	1.674	0.2870	18	8.0	6
Na_2HPO_3	15	0.9160	0.9022	60	12.7	6
	25	0.8916	0.8060	60	21.0	
$NaHSO_3$	15	1.254	2.492	38	12.5	19
Na_2SeO_4	15	1.730	1.432	14	0.8	6
Na_2SiO_3	18	1.383	1.416	26	3.0	19
Na_2SnO_3	20	1.873	1.721	20	2.4	19
$Nd(ClO_4)_3$	25	3.601	1.839	67	4.1	17
$NiBr_2$	18	1.999	0.5654	30	1.1	5
	25	1.947	0.3823	44	2.2	26

Table II (Continued)

substance	t, °C	$G \times 10^{-2}$	$-H \times 10^{-1}$	c_{max}, wt %	$s_r \times 10^2$	ref
$Ni(ClO_3)_2$	18	1.844	0.7610	30	1.3	5
$Pb(Ac)_2$[a]	14	2.403	0.7703	25	1.5	6
$Pr(ClO_4)_3$	25	3.564	1.867	67	4.1	17
Rb_2Tart[a]	20	2.123	1.138	64	7.2	6
RbOH	18	0.9807	0.4443	28	2.1	5
$Sm(ClO_4)_3$	25	3.652	1.670	67	5.0	17
$SnCl_2$	15	1.434	0.3705	70	11.8	5
$SnCl_4$	15	1.963	0.5578	70	10.4	5
$Sr(ClO_3)_2$	18	2.044	0.9238	36	3.0	5, 6
$Sr(ClO_4)_2$	25	2.192	0.9658	60	6.0	6
$Sr_2Fe(CN)_6$		3.509	3.566	20	1.1	5
$TbCl_3$	25	2.519	1.238	48	0.8	20
$Tb(ClO_4)_3$	25	3.677	1.328	67	2.1	17
$ThCl_4$	18	3.556	1.766	28	1.5	5
$Th(NO_3)_4$	15	4.175	1.181	18	1.0	5
TlF	18	2.176	0.7726	30	3.3	5
TlOH	15	2.105	0.5925	26	22.4	6
$TmCl_3$	25	2.664	1.345	51	2.2	20
$Tm(ClO_4)_3$	25	3.822	1.443	68	1.8	17
UO_2Cl_2	25	2.962	0.5491	57	0.7	6
UO_2F_2	25	2.812	0.5722	61	2.1	6
YCl_3	0	1.887	1.539	41	1.0	20
	25	1.827	1.285	43	1.3	
$Yb(ClO_4)_3$	25	3.912	1.638	68	2.4	17
$Zn(BrO_3)_2$	18	2.792	1.041	35	1.9	5
$Zn(Ac)_2$[a]	23.5	1.396	2.398	22	0.4	6
$Zn(ClO_3)_2$	18	1.814	0.4548	65	5.9	5

[a] Ac = acetate, Form = formate, Ox = oxalate, Tart = tartrate, Citr = citrate, Benz = benzoate.

The resulting "best" estimates of densities for every system treated have been tabulated in ref *3* for solution concentration, and where possible also temperature, increasing in specific increments. The present paper summarizes the constants of the correlation expression for 306 inorganic substances.

Processing of Experimental Data

The density of aqueous solutions as a function of their temperature and concentration can be expressed as (*3*)

$$\rho = \rho_w + Ac + Bct + Cct^2 + Dc^{3/2} + Ec^{3/2}t + Fc^{3/2}t^2 \quad (1)$$

where A through F are adjustable constants, c is the solute concentration in mol·dm^{-3}, t is the temperature in °C, and ρ is the density of solution in kg·m^{-3}. Equation 1, which is theoretically substantiated (see ref *3*), can be used for evaluating the densities of ternary aqueous solutions, if the constants of the respective binary solutions are known (*4*).

The density of water, ρ_w, is calculated according to the empirical equation

$$\rho_w = 999.65 + 2.0438 \times 10^{-1}t - 6.174 \times 10^{-2}t^{3/2} \quad (2)$$

which results from the correlation of the appropriate data given in ref *5*.

The density of aqueous solutions as a function of concentration at constant temperature can be expressed as (*3*)

$$\rho = \rho_w + Gc + Hc^{3/2} \quad (3)$$

where G and H are adjustable constants.

The goodness of fit of eq 1 and 3 to experimental data is given by the relative standard deviation

$$s_r = 100(\sum(\rho_{expt} - \rho_{calcd})^2/(N - i))^{-1/2}/\bar{\rho} \quad (4)$$

where ρ_{expt} and ρ_{calcd} represent the experimental and calculated value of the solution density, respectively, $\bar{\rho}$ is the average density, and N and i are the number of experimental data and the number of the correlation equation constants, respectively.

Results

The constants of eq 1 for binary aqueous solutions of 167 substances, the relative standard deviation, the ranges of temperature in °C and concentration in wt % at which the correlation is applicable, and the references to the source of used experimental data are given in Table I.

For several systems the number of density values calculated from eq 1 deviating from the respective experimental data by more than 1 kg.m^{-3} did not exceed 5% of the total number of experimental data. In this case, the constant in eq 1 of the least statistical significance was dropped and the correlation was repeated. This procedure was continued until omitting the next constant increased the number of deviating points above 5% of their total number.

The constants of eq 3 are given in Table II for 139 substances. The relative standard deviation, the temperature at which the correlation holds, the concentration limit of its validity, and the reference to the source of experimental data are also indicated.

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Received for review May 21, 1986. Accepted August 3, 1987.

Excess Molar Volumes of Binary Mixtures of Diols and Water

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The excess molar volumes of binary mixtures of water and 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,3-propanediol, and 1,5-pentanediol have been determined at 293.15, 303.15, and 313.15 K.

Introduction

In a previous paper (*1*) we reported the excess molar volumes V_m^E measured in binary mixtures of dipolar compounds with nonpolar solvents. Here we report the results of measurements of the V_m^E carried out for binary mixtures of the strongly self-associated hydroxylic compounds: diols + water.

Table I. Densities ρ (g·cm^{-3}) of Pure Diols

	ρ		
diol	T = 293.15 K	T = 303.15 K	T = 313.15 K
1,2-Bu(OH)$_2$	1.003 47	0.995 44	0.987 87
1,3-Bu(OH)$_2$	1.005 79	0.999 04	0.992 39
1,4-Bu(OH)$_2$	1.016 22	1.010 11	1.004 15
1,3-Pr(OH)$_2$	1.053 70	1.047 44	1.041 10
1,5-Pen(OH)$_2$	0.992 79	0.986 73	0.981 25

0021-9568/88/1733-0055$01.50/0