Densities of Binary and Ternary Aqueous Solutions of NaCl, $NaSO_4$, and $MgSO_4$, of Sea Waters, and Sea Water Concentrates

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Densities of binary and ternary aqueous solutions of NaCl, Na_2SO_4, and $MgSO_4$ have been determined from 25° to 175°. The solutions contained these compounds at concentrations corresponding to sea water and its concentrates up to fivefold concentration. A simple method of determining the densities of binary and ternary solutions is based on apparent molal volumes of these compounds over a wide temperature range. Literature data on densities of sea water and its concentrates have been critically correlated. The method for estimating sea water densities uses the apparent molal volumes of the salt components of the sea water and a single interaction constant. A table of selected sea water density values gives the best values for the 25° to 150° C. temperature range for normal sea water and its concentrates.

KNOWLEDGE of the densities of sea water brines, which contain primarily NaCl, Na_2SO_4, and $MgSO_4$, is important in the development and operation of an economic desalination process. Density measurements were made on aqueous solutions of these salts individually and in pairs at concentrations varying from approximately those of sea water to a maximum fivefold increase, at temperatures of 25° to 175° C.

Several correlation techniques were used for evaluation of the experimental data. The empirical or semi-empirical techniques suggested by Mikulin (*14*), Zdanovskii (*20*), and Lengyel (*11*) were found to be complex and tedious, and that by Ezrokhi (*3*) was insufficiently sensitive. The data were satisfactorily correlated to the temperature and composition of the solutions by a method based on the apparent molal volumes of the dissolved salts.

The literature contains precise density data on sea water only at or near room temperature. The reliability of the data, however, seems to diminish with increasing concentration and temperature. Only sporadic density information is available above the atmospheric boiling point of sea water.

A critical review of density data and the development of a computational method for the estimation of sea water densities in the entire range of interest were the further objects of this study. The correlations developed on the binary systems investigated were combined to yield a method for accurate calculation of sea water densities. The calculation method, and the comparison of experimental and calculated data along with selected values of sea water densities, are presented in this paper.

EXPERIMENTAL METHOD

Densities were determined from a measurement of the volume of a known mass of solution using Lipkin pycnometers in the 25° to 75° C. temperature range (*12*) and dilatometer tubes from 75° to 175° C.

The dilatometer tubes consisted of a heavy-walled bulb section (19-mm. o.d.) with a capacity of 7 cc., attached to a 420-mm. long, precision-bore, 2-mm. diameter capillary stem. The capillary stem contained a fused fiducial mark 12 mm. above its junction with the bulb and a constriction 360 mm. above the bulb. The volume of solution within the tubes was determined by measuring with a cathetometer the height of liquid in the capillary stem above the fiducial mark. In the calculation of densities, corrections were made for air buoyancy, meniscus, and glass thermal expansion.

The volume calibration of the dilatometers was made by measuring the mass of mercury necessary to fill the tubes to different heights in the capillary stem. In filling the tubes with mercury, it was necessary to ensure that no air bubbles were entrapped at the liquid-glass interface and that no liquid droplets adhered to the glass walls above the liquid level. Air bubbles and free liquid droplets were eliminated by evacuating the tubes and filling them through a thin-walled 1-mm. diameter Teflon tubing passed through the wall of a thick rubber vacuum tube connected to the top of the capillary stem through a rubber septum. This allowed movement of the tubing during filling of the dilatometer. The dilatometer was evacuated, while mercury or other liquid was allowed to flow in from a reservoir through the Teflon line. The line was gradually withdrawn as the filling progressed, to maintain the end of the Teflon line immediately above the liquid level in the dilatometer.

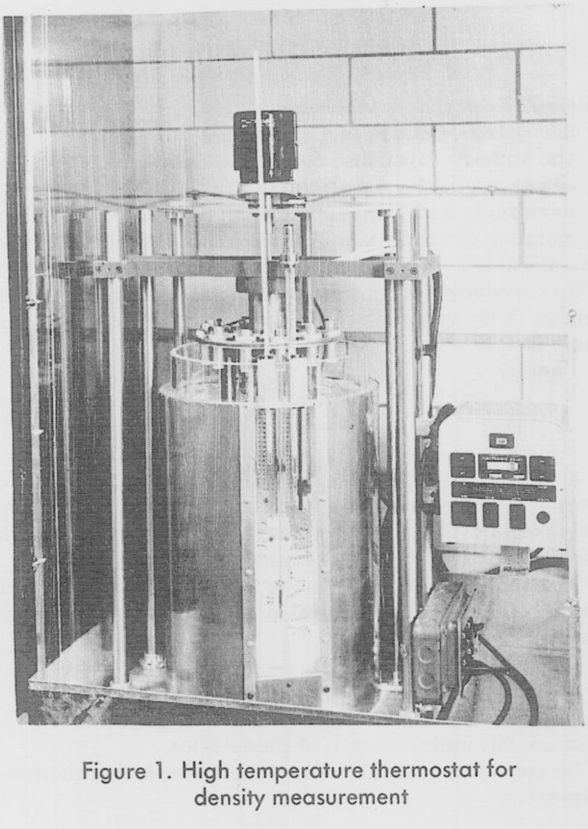

Figure 1. High temperature thermostat for density measurement

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Volume calibration data were taken at several liquid levels in the capillary stem of the dilatometer tubes. These calibrations were checked by filling the dilatometers with spectro quality benzene and distilled water, respectively. Densities calculated from the weight and volume of the benzene and water measured in the dilatometer tubes were less than ±0.01% in error compared to true values. Repeated calibrations of a series of dilatometers with water over the entire temperature range did not show any significant elastic after effects.

In regular tests, following the introduction of the salt solutions, the tubes were sealed at the constriction in the capillary stem and weighed. Twelve sealed dilatometers were placed in a special thermostat, shown in Figure 1, where the required 75°, 100°, 125°, 150°, and 175° C. temperatures were maintained with ±0.05° C. accuracy. The tubes were mounted in Teflon-lined cylindrical adjustable holders on a horizontal disk (head plate) connected to a mechanically driven rotor. By leveling the head plate and with the help of guide rods, the plummbed vertical positioning of the tubes was achieved.

The thermostat was filled with polyphenyl ether (Monsanto OS-124). This oil retained its transparency even after prolonged high-temperature exposure. Since the oil has a low vapor pressure and is easily soluble in organic solvents, it had some advantages over silicon oils. The addition of 1 gram per liter of triphenylbismuth to the fluid further enhanced the stability of the oil.

The measurements of the high temperature range were carried out in sealed glass tubes under the combined pressure of the air trapped in the dilatometer and the water that evaporated from the solution. Under the most severe conditions, at 175° C., the partial pressure of air was calculated to be about 3 atm. and resulted in a compression of about 0.01% of the liquid volume. Similarly, the water evaporation in the sealed tube resulted in a concentration increase of about 0.03% and a decrease in the liquid volume of the same order. At 150° C. these values were reduced by a factor of 2, and at 125° C. they become insignificant. The experimental data at 150° and 175° C. were adjusted for these effects and the tables give the final corrected values.

EVALUATION OF EXPERIMENTAL DATA

Binary Systems. The experimental data are compared with our calculated densities and published data (*7*) in Table I for the binary systems containing NaCl, Na_2SO_4, and $MgSO_4$, respectively. To obtain densities at the given molal concentrations and temperatures, the published data were interpolated by the technique given in the International Critical Tables.

The correlation technique was based on apparent molal volumes. The apparent molal volume of a dissolved component is

$$\phi = \frac{V - V_o}{m} \qquad (1)$$

where V is the volume of a solution containing 1000 grams of water and m moles of solute and V_o is the volume of 1000 grams of water at the given temperature.

The apparent molal volume, ϕ, was expressed as a function of concentration in terms of ionic strength according to Masson's rule (*13*):

$$\phi = \phi_o + b\mu^{1/2} \qquad (2)$$

where μ is the ionic strength of the solution.

The constants ϕ_o and b were expressed as a function of temperature:

$$\phi_o = A + Bt + Ct^2 \qquad (3)$$

$$b = D + Et + Ft^2 \qquad (4)$$

where t is the temperature in ° C.

The values of these constants, calculated by the method of least squares, are given in the first three lines of Table II. The density data at low concentrations were either omitted or were considered with smaller weight because of the large effect of the experimental error on the calculated apparent molal volume value.

Using these constants, the calculated densities in Table I were determined from the following expression:

$$\mathrm{d} = \frac{1000 + mM}{V_o + m\phi} \qquad (5)$$

where M is the molecular weight of the solute and d is the density.

Although more exact density measurements have been carried out at or near room temperature, no consistent series of density measurements has been published covering the entire temperature and concentration range investigated in the author's work. The precision of our experimental data as established by parallel measurements was 0.9×10^{-4} unit. The standard deviation of corresponding previously published data is given in Table III. The larger standard deviation between our measured and calculated data can be attributed to the much wider temperature range (25° to 175° C.) as compared to the narrower temperature range for the published data (25° to 100° C. for NaCl and Na_2SO_4, and 25° to 75° C. for $MgSO_4$).

The present results on apparent molal volumes of sodium chloride agree well with the data given by Redlich and Meyer (*15*), which were based on the measurements of Kruis (*10*). The present data can be expressed by the equation:

$$\phi = 16.522 + 2.049\mu^{0.5}$$

and Redlich and Meyer gave the equation:

$$\phi = 16.61 + 1.86\mu^{0.5}$$

The difference between the densities of a molal NaCl solution calculated by these equations is 1×10^{-4} unit.

Equation 2 was expressed in a slightly different form by Redlich and Meyer (*15*) as:

$$\phi = \phi_o + s\omega^{1.5}m^{0.5} \qquad (6)$$

where $\omega = 0.5 \sum \nu_i z_i^2$, ν_i is the number of ions of species i formed by one molecule of the electrolyte, and z_i is the valence of ion species i. For a single solute, $\mu = \omega m$ and

$$b = s\omega. \qquad (7)$$

The s value is a temperature-dependent constant that can be expressed by means of the gas constant, the charge of a univalent ion, the compressibility of the solvent, and the pressure dependence of the dielectric constant. Figure 2 shows the theoretically calculated slopes (s values) in the 0° to 70° C. temperature range, as well as the slopes calculated from the b values given in Table IV. Although the theoretical slopes increase consistently with temperature, each experimental curve shows a negative slope at low temperatures and a minimum in the 40° to 64° C. temperature range. The same negative slope was obtained in earlier work by Redlich (*16*) based on the data of Baxter and Wallace (*1*) on alkali halides. Dilatometric measurements of Halasey (*4*) on solutions of potassium nitrate also indicate a decrease in the s value between 5° and 30° C. Although the present data cannot be considered conclusive

Table I. Comparison of Measured and Calculated Densities of NaCl Solutions

(Grams per cc.)

Temp., °C.	Source	NaCl, Molality 0.1	1.0	2.0	2.5
25	Exptl.	1.0011	1.0361	1.0721	1.0892
	Calcd.	1.0011	1.0361	1.0720	1.0890
	ICT[a]	1.00114	1.03610	1.07222	1.08925
45	Exptl.	0.9941	1.0280	1.0632	1.0799
	Calcd.	0.9941	1.0281	1.0633	1.0800
	ICT	0.99419	1.02794	1.06338	1.08005
65	Exptl.	0.9845	1.0178	1.0526	1.0692
	Calcd.	0.9845	1.0179	1.0527	1.0693
	ICT	0.9845	1.0175	1.0528	1.0693
75	Exptl.	0.9789	1.0123	1.0470	1.0633
	Calcd.	0.9788	1.0121	1.0468	1.0633
	ICT	0.9788	1.0116	1.0469	1.0633
100	Exptl.	0.9627	0.9963	1.0313	1.0477
	Calcd.	0.9623	0.9960	1.0308	1.0473
	ICT	0.9623	0.9961	1.0307	1.0472
125	Exptl.	0.9436	0.9781	1.0133	1.0299
	Calcd.	0.9434	0.9781	1.0133	1.0299
	ICT	...	...	...	...
150	Exptl.	0.9221	0.9576	0.9937	1.0105
	Calcd.	0.9217	0.9580	0.9941	1.0108
	ICT	...	...	...	...
175	Exptl.	0.8979	0.9353	0.9723	0.9895
	Calcd.	0.8967	0.9350	0.9722	0.9892
	ICT	...	...	...	...

Temp., °C.	Source	Na_2SO_4, Molality 0.01	0.05	0.10	0.15
25	Exptl.	0.9981	1.0034	1.0096	1.0158
	Calcd.	0.9983	1.0033	1.0096	1.0159
	ICT	0.9984	1.0034	1.0097	1.0159
45	Exptl.	0.9913	0.9964	1.0023	1.0083
	Calcd.	0.9914	0.9963	1.0025	1.0086
	ICT	0.9915	0.9965	1.0026	1.0086
65	Exptl.	0.9818	0.9867	0.9926	0.9985
	Calcd.	0.9818	0.9867	0.9927	0.9987
	ICT	0.9818	0.9867	0.9928	0.9988
75	Exptl.	0.9761	0.9811	0.9870	0.9929
	Calcd.	0.9761	0.9810	0.9870	0.9930
	ICT	0.9761	0.9810	0.9870	0.9931
100	Exptl.	0.9599	0.9652	0.9710	0.9767
	Calcd.	0.9597	0.9646	0.9708	0.9769
	ICT	0.9596	0.9645	0.9706	0.9766
125	Exptl.	0.9408	0.9460	0.9520	0.9577
	Calcd.	0.9406	0.9458	0.9522	0.9585
	ICT	...	...	...	...
150	Exptl.	0.9189	0.9244	0.9305	0.9363
	Calcd.	0.9187	0.9242	0.9310	0.9377
	ICT	...	...	...	...
175	Exptl.	0.8948	0.9003	0.9064	0.9125
	Calcd.	0.8935	0.8994	0.9067	0.9138
	ICT	...	...	...	...

Temp., °C.	Source	$MgSO_4$, Molality 0.00972	0.09722	0.19444	0.29165
25	Exptl.	0.9982	1.0086	1.0201	1.0315
	Calcd.	0.9982	1.0087	1.0201	1.0315
	ICT	0.9983	1.0088	1.0202	1.0315
45	Exptl.	0.9912	1.0016	1.0129	1.0242
	Calcd.	0.9913	1.0016	1.0130	1.0242
	ICT	0.9915	1.0018	1.0131	1.0242
65	Exptl.	0.9817	0.9920	1.0032	1.0145
	Calcd.	0.9817	0.9919	1.0032	1.0145
	ICT	0.9818	0.9922	1.0034	1.0145
75	Exptl.	0.9762	0.9864	0.9976	1.0089
	Calcd.	0.9760	0.9863	0.9975	1.0087
	ICT	0.9761	0.9864	0.9976	1.0088
100	Exptl.	0.9598	0.9702	0.9816	0.9927
	Calcd.	0.9596	0.9698	0.9821	0.9924
	ICT	...	...	...	...
125	Exptl.	0.9405	0.9510	0.9624	0.9737
	Calcd.	0.9405	0.9512	0.9626	0.9738
	ICT	...	...	...	...
150	Exptl.	0.9186	0.9294	0.9411	0.9523
	Calcd.	0.9186	0.9297	0.9408	0.9524
	ICT	...	...	...	...
175	Exptl.	0.8945	0.9053	0.9170	0.9282
	Calcd.	0.8934	0.9050	0.9169	0.9279
	ICT	...	...	...	...

[a] (7).

Table II. Constants of Equations 3 and 4 for Calculating Apparent Molal Volumes

Component	Temp. Range, °C.	Concn. Range, *m*	Constants *A*	*B*	*C* $\times 10^{-3}$	*D*	*E* $\times 10^{-2}$	*F* $\times 10^{-4}$	S.D.[a] $\times 10^{-4}$
NaCl	25–175	0.02–2.5	13.083	0.16936	−1.2720	3.252	−5.985	4.688	2.9
KCl	25–175	0.01–0.05	29.123	0.26785	−3.5699	0	0	0	3.5
Na_2SO_4	25–175	0.01–0.15	6.423	0.49865	−3.6063	4.035	−19.211	12.577	5.3
$MgSO_4$	25–175	0.01–0.3	−10.969	0.42140	−3.7702	19.514	−56.061	45.740	2.9
NaBr	25–100	0.098–0.62	18.81	0.167	−1.030	4.04	−5.30	3.15	0.9
$MgCl_2$	25–100	0.21–0.91	12.34	0.175	−1.977	8.18	−10.81	9.15	0.9
Na_2CO_3	25–100	0.095–0.60	−17.685	0.571	−4.570	19.077	−36.90	28.73	1.3
$CaCl_2$	25–140	0.18–0.78	17.08	0.087	−10.004	5.54	−31.50	0.212	4.5

[a] Standard deviation = $\sqrt{(\Sigma\Delta^2)/(\text{D.F.})}$ where D.F. are degrees of freedom.

Table III. Standard Deviations of Data

	NaCl	Na_2SO_4	$MgSO_4$
Measured *vs.* calculated	$\pm 2.9 \times 10^{-4}$	$\pm 5.3 \times 10^{-4}$	$\pm 2.9 \times 10^{-4}$
Measured *vs.* ICT[a]	$\pm 3.0 \times 10^{-4}$	$\pm 2.7 \times 10^{-4}$	$\pm 1.6 \times 10^{-4}$
Calculated *vs.* ICT	$\pm 1.9 \times 10^{-4}$	$\pm 1.3 \times 10^{-4}$	$\pm 1.5 \times 10^{-4}$

[a] (7).

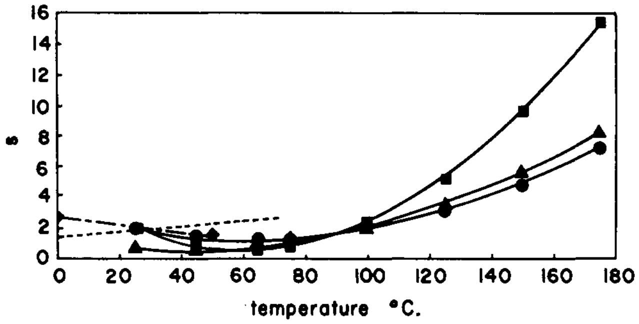

Figure 2. Slopes of apparent molal volume equations as functions of temperature

● NaCl
▲ Na_2SO_4
■ $MgSO_4$
---- Theoretical values (*14*)
● Alkali halides (*1*)

evidence concerning the limiting slopes, because of their limited precision and the high concentrations of the solutions, the consistency of this trend could not escape attention.

Ternary Systems. The experimental data are compared with the calculated densities in Tables IV, V, and VI.

The method of estimating densities of ternary systems was based on an equation proposed by Young and Smith (*19*).

$$V = V_o + m_1\phi_1 + m_2\phi_2 + m_1m_2k \tag{8}$$

where m_1 and m_2 are the molalities of the components, ϕ_1 and ϕ_2 are the apparent molal volumes of the components in binary solutions at the total ionic strength of the ternary solution, and k is an interaction constant.

In our correlation the ϕ_1 and ϕ_2 values were taken at their own ionic strength to avoid an extrapolation above the concentration limit of measurements to concentrations

Table IV. Densities of Solutions Containing NaCl and $NaSO_4$
(Grams per cc.)

		NaCl, Molality								
		0.1			1.0			2.5		
		Na_2SO_4, Molality								
Temp., °C.		0.01	0.05	0.15	0.01	0.05	0.15	0.01	0.05	0.15
25	Exptl.	1.0024	1.0072	1.0196	1.0372	1.0419	1.0532	1.0894	1.0942	1.1046
	Calcd.	1.0024	1.0074	1.0199	1.0372	1.0419	1.0533	1.0900	1.0940	1.1038
45	Exptl.	0.9954	1.0000	1.0120	1.0292	1.0337	1.0449	1.0801	1.0849	1.0950
	Calcd.	0.9954	1.0002	1.0124	1.0292	1.0338	1.0450	1.0810	1.0850	1.0947
65	Exptl.	0.9856	0.9904	1.0024	1.0193	1.0236	1.0347	1.0695	1.0742	1.0843
	Calcd.	0.9857	0.9905	1.0025	1.0190	1.0235	1.0346	1.0702	1.0742	1.0839
75	Exptl.	0.9802	0.9848	0.9968	1.0136	1.0180	1.0292	1.0638	1.0684	1.0786
	Calcd.	0.9800	0.9848	0.9968	1.0132	1.0177	1.0287	1.0643	1.0682	1.0777
100	Exptl.	0.9641	0.9686	0.9803	0.9977	1.0021	1.0134	1.0478	1.0524	1.0627
	Calcd.	0.9636	0.9685	0.9807	0.9972	1.0017	1.0129	1.0483	1.0522	1.0617
125	Exptl.	0.9450	0.9496	0.9613	0.9791	0.9836	0.9949	1.0300	1.0344	1.0448
	Calcd.	0.9447	0.9499	0.9625	0.9793	0.9840	0.9955	1.0309	1.0348	1.0443
150	Exptl.	0.9237	0.9284	0.9402	0.9588	0.9633	0.9746	1.0107	1.0153	1.0257
	Calcd.	0.9231	0.9285	0.9419	0.9592	0.9641	0.9760	1.0117	1.0156	1.0250
175	Exptl.	0.8995	0.9045	0.9167	0.9363	0.9408	0.9522	0.9898	0.9944	1.0049
	Calcd.	0.8982	0.9041	0.9182	0.9364	0.9417	0.9539	0.9901	0.9940	1.0032

Table V. Densities of Solutions Containing NaCl and $MgSO_4$
(Grams per cc.)

		NaCl, Molality								
		0.1			1.0			2.5		
		$MgSO_4$, Molality								
Temp., °C.		0.00972	0.09722	0.29165	0.00972	0.09722	0.29165	0.00972	0.09722	0.29165
25	Exptl.	1.0022	1.0129	1.0360	1.0372	1.0474	1.0690	1.0901	1.0993	1.1195
	Calcd.	1.0023	1.0128	1.0354	1.0372	1.0473	1.0690	1.0901	1.0994	1.1195
45	Exptl.	0.9951	1.0058	1.0286	1.0290	1.0392	1.0608	1.0809	1.0900	1.1102
	Calcd.	0.9953	1.0056	1.0281	1.0292	1.0390	1.0606	1.0811	1.0902	1.1102
65	Exptl.	0.9855	0.9962	1.0189	1.0192	1.0291	1.0506	1.0702	1.0794	1.0995
	Calcd.	0.9856	0.9958	1.0182	1.0190	1.0287	1.0502	1.0703	1.0793	1.0993
75	Exptl.	0.9801	0.9906	1.0133	1.0136	1.0235	1.0450	1.0645	1.0737	1.0938
	Calcd.	0.9800	0.9905	1.0137	1.0133	1.0234	1.0457	1.0644	1.0738	1.0946
100	Exptl.	0.9639	0.9745	0.9975	0.9978	1.0078	1.0293	1.0488	1.0583	1.0778
	Calcd.	0.9635	0.9736	0.9964	0.9972	1.0069	1.0287	1.0483	1.0573	1.0776
125	Exptl.	0.9447	0.9554	0.9785	0.9792	0.9893	1.0110	1.0309	1.0405	1.0602
	Calcd.	0.9447	0.9553	0.9777	0.9793	0.9895	1.0110	1.0310	1.0405	1.0602
150	Exptl.	0.9233	0.9340	0.9572	0.9588	0.9690	0.9908	1.0116	1.0214	1.0412
	Calcd.	0.9230	0.9341	0.9567	0.9593	0.9699	0.9914	1.0119	1.0217	1.0413
175	Exptl.	0.8992	0.9101	0.9334	0.9363	0.9467	0.9686	0.9908	1.0007	1.0207
	Calcd.	0.8981	0.9097	0.9325	0.9364	0.9475	0.9691	0.9904	1.0006	1.0201

Table VI. Densities of Solutions Containing Na_2SO_4 and $MgSO_4$

(Grams per cc.)

		Na_2SO_4, Molality								
		0.01			0.05			0.15		
		$MgSO_4$, Molality								
Temp., °C.		0.01	0.10	0.30	0.01	0.10	0.30	0.01	0.10	0.30
25	Exptl.	0.9994	1.0101	1.0336	1.0046	1.0150	1.0382	1.0170	1.0273	1.0500
	Calcd.	0.9999	1.0104	1.0332	1.0050	1.0154	1.0379	1.0176	1.0277	1.0496
45	Exptl.	0.9924	1.0031	1.0262	0.9975	1.0079	1.0307	1.0096	1.0199	1.0423
	Calcd.	0.9931	1.0033	1.0260	0.9980	1.0082	1.0306	1.0102	1.0202	1.0421
65	Exptl.	0.9829	0.9935	1.0164	0.9878	0.9982	1.0210	1.0000	1.0101	1.0322
	Calcd.	0.9834	0.9936	1.0161	0.9883	0.9984	1.0207	1.0003	1.0102	1.0321
75	Exptl.	0.9774	0.9880	1.0110	0.9821	0.9926	1.0154	0.9942	1.0043	1.0268
	Calcd.	0.9777	0.9879	1.0104	0.9826	0.9927	1.0150	0.9946	1.0045	1.0263
100	Exptl.	0.9611	0.9720	0.9949	0.9660	0.9767	0.9994	0.9782	0.9883	1.0106
	Calcd.	0.9613	0.9716	0.9940	0.9662	0.9764	0.9986	0.9785	0.9884	1.0098
125	Exptl.	0.9419	0.9528	0.9759	0.9467	0.9574	0.9802	0.9592	0.9693	0.9915
	Calcd.	0.9423	0.9529	0.9754	0.9474	0.9579	0.9800	0.9602	0.9702	0.9911
150	Exptl.	0.9203	0.9312	0.9544	0.9253	0.9360	0.9588	0.9379	0.9478	0.9703
	Calcd.	0.9204	0.9315	0.9541	0.9259	0.9367	0.9587	0.9393	0.9495	0.9699
175	Exptl.	0.8963	0.9071	0.9304	0.9011	0.9119	0.9348	0.9140	0.9241	0.9468
	Calcd.	0.8953	0.9069	0.9296	0.9012	0.9124	0.9343	0.9155	0.9258	0.9455

that may even exceed the solubility of certain electrolytes. For this reason the interaction coefficients cannot be compared with previously determined data.

The interaction coefficients were expressed as functions of temperature by the following equations:

$NaCl$-Na_2SO_4 System.

$$k = 10.69 - 0.1468t + 1.2248 \times 10^{-3}t^2$$

$NaCl$-$MgSO_4$ System

$$k = 3.60 - 0.0290t + 0.2658 \times 10^{-3}t^2$$

Na_2SO_4-$MgSO_4$ System.

$$k = 42.95 - 0.863t + 7.7242 \times 10^{-3}t^2$$

The standard deviations of the calculated and experimental data given in Tables IV, V, and VI are $\pm 6.1 \times 10^{-4}$, $\pm 4.3 \times 10^{-4}$, and $\pm 6.2 \times 10^{-4}$, respectively.

The interaction coefficient curves show a minimum in the 55° to 75° C. temperature range, similar to the previously mentioned s value minima. This minimum, occurring in about the same temperature range (which probably varies only because of the limited precision of data and the mathematical smoothing operation involved in their derivation), may have certain theoretical significance.

DENSITIES OF SEA WATER AND ITS CONCENTRATES

Table VII gives the data on density of sea water used in our evaluation (*2, 5, 6, 8, 9, 18*) and shows the concentration and temperature range of the measurements.

A simple empirical approach was taken to correlate the density data on sea water solutions. It utilized an additivity rule involving the apparent molal volumes of individual salts and a single interaction coefficient for all the ions present. Thus, at a given temperature, the volume of a sea water solution containing 1000 grams of water is given by

$$V = V_o + \sum \phi_i m_i + k\mu \tag{9}$$

where k is an interaction coefficient of the sea water and μ is the ionic strength of the solution.

This equation is based on Equation 8 derived by Young and Smith (*19*) for ternary systems.

Their equation could not be expanded for use on sea water for two reasons: The partial molal volumes of certain components of the sea water must be extrapolated well above their solubility limits, and the multicomponent sea water yields an excessive number of interaction terms. For these reasons this relationship was used in the simple form of Equation 9, using the partial molal volume of the component at its concentration and only a single interaction coefficient. This equation can be applied only to sea water and similar solutions and cannot be used to yield accurate results for very dilute (belwo 0.01 molal) system.

The constants used to calculate the apparent molal volume of each sea water component according to Equations 2, 3, and 4 are given in Table II. The table also gives the standard deviation of the calculated densities from the observed densities in these binary solutions over the entire concentration and temperature range. To calculate these constants densities of solutions of the other components of sea water—namely, $NaBr$, $MgCl_2$, Na_2CO_3, and $CaCl_2$—were taken from the International Critical Tables and KCl densities were measured.

The interaction coefficient was expressed as a function of concentration and temperature in a way similar to the apparent molal volumes

$$k = k_o + \alpha\mu^{1/2} \tag{10}$$

where

$$k_o = 0.744 - 4.366 \times 10^{-2}t + 3.620 \times 10^{-4}t^2 \tag{11}$$

$$\alpha = 0.145 + 1.778 \times 10^{-2}t - 1.360 \times 10^{-4}t^2 \tag{12}$$

Table VII. Concentration (as Ionic Strength) and Temperature Range of Sea Water Density Data

Concn., Range, μ^a	Temp., Range, °C.	No. of Concn. Levels	No. of Temp. Levels	Ref.
0.59–0.87	15– 35	3	3	(*8*)
0.05–0.87	20– 40	6	3	(*2*)
0.66–3.22	25– 90	6	4	(*5*)
0.60–6.78	25–175	4	7	(*6*)
0.01–0.31	0– 25	36	2	(*18*)^b

^{a} μ = total strength. ^{b} Water of Azov Sea.

The calculated and experimental data are compared in Table VIII.

In developing the constants of Equation 10, the data of each investigator were taken separately at each temperature level. The k_o and α values of Knudsen (*8, 9*), Bein, Hirsenkorn, and Moller (*2*), and Tsurikova (*18*) showed good agreement; those of Hampel (*5*) and Hara, Nakamura, and Higashi (*6*) showed a systematic deviation. The final values of the k_o and α constants, given in Equations 11 and 12, were obtained by smoothing all experimental results by a least squares method using weighted averages. The change of density caused by the interaction coefficient is very small; for standard sea water (Table IX) at 25° C. the last term of Equation 9 decreases the calculated density by only 2×10^{-4} unit.

Although there is a tendency toward greater deviations at higher temperatures (above 100° C.), perhaps because of increased experimental difficulties in measurements at these temperatures, the results of various authors show characteristic deviations of their own, which are good indications of their relative experimental accuracy. According to this criterion the order of decreasing accuracy of reported data is: Knudsen > Bein *et al.* > Hampel > Hara *et al.* The data of Tsurikova are very exact, but they were not included in this series since they pertain to sea water of low salt content. The data of Hara *et al.*, which cover a wide concentration range (normal sea water to tenfold concentration), show large deviations not only at higher temperatures but also near room temperature. Hampel's data, which cover a more restricted concentration range (normal sea water to about fivefold concentration) and temperature range (22° to 86° C.), show deviations smaller than those of Hara *et al.*, but yet large enough to be considered barely satisfactory.

CONCLUSIONS

Experimental data are given on densities of binary and ternary solutions of NaCl, Na_2SO_4, and $MgSO_4$ in the 25° to 175° C. temperature range. Based on apparent molal volumes of these electrolytes, and on interaction coefficients in the ternary system, the density values can be calculated with a deviation of 1 to 3×10^{-4} in binary systems and 4 to 6×10^{-4} in ternary systems, over the range investigated.

This correlation technique has been extended to estimate densities of sea water solutions and their concentrates from the composition of sea water.

Table IX gives selected normal sea water densities as a function of concentration (expressed as concentration factor and chlorinity) for normal sea water and its concentrates up to fivefold concentration, from 25° to 150° C. This table was calculated with the presented correlation based on available experimental evidence. It can be considered highly reliable (about 1×10^{-4} density unit) at low concentrations and temperatures but major inaccuracies (as much at 1×10^{-3}) may be expected at high concentrations.

Table VIII. Comparison of Calculated and Experimental Density Data on Sea Water and Its Concentrates

			Standard Deviation × 10^{-4}				
Temp., °C.	k_o	α	Knudsen (3)[a]	Bein (6)[a]	Hampel (6)[a]	Hara (4)[a]	Tsurikova (36)[a]
0	0.744	0.145					±0.03
15	0.171	0.381	±0.39				
20	0.016	0.446		±0.08			
25	−0.121	0.504	±0.26		±9.0	±14.2	±0.02
30	−0.240	0.556		±1.3			
35	−0.340	0.600	±0.27				
40	−0.423	0.638		±0.51			
50	−0.534	0.694			±8.5	±16.4	
75	−0.494	0.713			±7.6	±17.7	
90	−0.253	0.643			±8.0		
100	−0.002	0.563				±18.0	
125	0.943	0.242				±16.9	
150	2.340	−0.248				±11.0	
175	4.190	−0.908				±34.9	

[a] No. of experiments at each temperature level.

Table IX. Selected Densities of Normal Sea Water Concentrates at Different Temperatures[a]

		Temperature, ° C.					
Concn. Factor	Cl‰	25	50	75	100	125	150
		Density, Grams per Cc.					
1	19.381[a]	1.0234	1.0123	1.0003	0.9840	0.9656	0.9447
2	38.762	1.0501	1.0391	1.0261	1.0101	0.9924	0.9724
3	58.143	1.0792	1.0659	1.0527	1.0369	1.0198	1.0008
4	77.524	1.1058	1.0935	1.0802	1.0646	1.0480	1.0298
5	96.905	1.1348	1.1219	1.1084	1.0930	1.0769	1.0596

Ionic Concn. of Sea Water (*5, 17*)

Ion	Concn., grams/kg. sea water	Ion	Concn., grams/kg. sea water
Na	10.812	Cl	19.381[a]
Mg	1.287	SO_4	2.711
Ca	0.426	CO_3[b]	0.137
K	0.388	Br	0.066

[a] 1937 International value of chlorinity (Cl ‰) of "normal water" (*17*, p. 51). [b] Combined CO_2.

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Vapor-Liquid Equilibria of Methanol–Methyl Ethyl Ketone in the Presence of Diethyl Ketone

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Vapor-liquid equilibrium data are reported for the binary system methanol-methyl ethyl ketone at 760 mm. of Hg total pressure. The effect of various concentrations of diethyl ketone on the relative volatilities of methanol with respect to methyl ethyl ketone in normal binary azeotropic mixtures (84.7 mole % methanol) are shown. Vapor-liquid equilibrium data are also reported on a solvent (diethyl ketone) free basis for this binary system in the presence of 70 mole % diethyl ketone which breaks the binary azeotrope.

THE BINARY system methanol-methyl ethyl ketone forms an azeotrope at 760 mm. of Hg total pressure. Because of commercial interest, there was incentive to devise a technique to separate various mixtures of these materials into pure components. Sufficient data were obtained to illustrate that this can be done by extractive distillation using diethyl ketone as the extractive agent. These data were: the vapor-liquid equilibria of the binary system methanol–methyl ethyl ketone, the variation of the relative volatility of methanol with respect to methyl ethyl ketone at the binary azeotropic composition in the presence of various concentrations of diethyl ketone, the vapor-liquid equilibria of the system methanol–methyl ethyl ketone with 70 mole % diethyl ketone in the liquid phase, and a normal distillation of the binary systems methanol–diethyl ketone and methyl ethyl ketone–diethyl ketone into pure components to show that they could be separated. The equilibria data of the first three items are presented here.

EXPERIMENTAL

The vapor-liquid equilibrium data were determined on a Gillespie equilibrium still as modified by Foster (*2*). Temperatures were measured in the still by a calibrated thermistor while pressures were controlled at 760.0 ± 0.1 mm. of Hg by a Wallace and Tiernan Aneroid Manostat and measured by a Wallace and Tiernan Precision Mercurial Manometer. Reagent grade materials whose boiling points and refractive indices compared favorably with literature values were used as pure materials. The binary samples were analyzed by refractive index determinations using a Bausch and Lomb precision refractometer with a sodium lamp and a temperature controlled prism. The ternary samples obtained from the binary system in the presence of solvent (diethyl ketone) were analyzed for relative methanol–methyl ethyl ketone concentrations on a solvent-free basis. These data were determined by gas chromatography methods using a Perkin-Elmer Vapor Fractometer with a standard Perkin-Elmer "B" column. Peak areas were used in the chromatographic calibration. Total experimental errors were estimated to be less than ±0.5 mole % methanol.

RESULTS AND DISCUSSION

Even though at least two sources of vapor-liquid equilibrium data for the binary system methanol–methyl ethyl ketone can be found in the literature (*1, 4*), an experimental investigation was conducted to ascertain these data since some discrepancy exists among those reported. Table I

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