# Viscosities of Aqueous Solutions of Several Electrolytes Present in Sea Water

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Experimental viscosity and density measurements are reported on ternary solutions of several electrolytes present in sea water, and on a synthetic sea water over the range of ionic strength levels from 0.7 to 3.5 and for sea water up to a concentration factor of 3 and the temperature range from 25° to 150°C. The experimental viscosity data were correlated with a precision of 0.2 to 0.3%, assuming an additivity of the constants of the Othmer rule. Literature data were reviewed and compared with the correlation. Recommended sea water viscosity data are given as a function of temperature and concentration.

 $\mathbf{K}$ NOWLEDGE of viscosities of sea water and brackish water brines, which contain primarily NaCl, KCl, Na<sub>2</sub>SO<sub>4</sub>, and MgSO<sub>4</sub>, is important in the development and design of economic desalination processes. In a previous paper (7) the viscosities of the binary mixtures were evaluated on the basis of the Othmer rule or relation based on the properties of a reference substance under a similar condition. The reference substance was water and the single similar condition was temperature.

This paper presents viscosity measurements on ternary aqueous solutions and on calcium-free synthetic sea waters from  $25^{\circ}$  to  $150^{\circ}$  C., covering ionic strength concentration levels from 0.7 to 3.5. The experimental data were correlated with satisfactory precision, assuming an additivity of the constants of the Othmer rule.

The experimental apparatus, method, and calculation techniques have been given (6, 7).

# EVALUATION OF EXPERIMENTAL DATA

**Ternary Systems.** The viscosity of a solution of a single salt was expressed by the Othmer rule (11):

$$\log \eta_{Si} = C_i + m_i \log \eta_w \tag{1a}$$

Similarly, the relative viscosity, which has some advantages and is more frequently used, can be given as:

$$\log \eta_{Ri} = A_{0i} + B_{0i} \log \eta_w \tag{1b}$$

where

 $\eta_{Ri}$  is the relative viscosity of the solution,  $\eta_{Si}/\eta_{w}$ 

 $\eta_{Si}$  is the viscosity of the solution, cp.

 $\eta_w$  is the viscosity of water at the same temperature, cp.

 $B_{0i} = m_i - 1$  and  $A_{0i} = C_i$ 

 $A_{0i}$  and  $B_{0i}$  are temperature-independent Othmer constants for compound *i* for the linear equation. These constants were expressed as functions of ionic strength in molal units in the forms

$$A_{0i} = A_{1i}I + A_{2i}I^2 + A_{3i}I^3$$
<sup>(2)</sup>

$$B_{0i} = B_{1i}I + B_{2i}I^2 + B_{3i}I^3 \tag{3}$$

To correlate the measured viscosities of two salts containing the Othmer constants of the mixture,  $A_M$  and  $B_M$ were calculated for each solution at three constant ionic

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strength levels over the entire test temperature range. Since the concentration of the solutions under our test conditions increased somewhat at high temperatures (this was caused by water evaporation into the vapor space of the closed viscometer system), the measured data were adjusted to constant ionic strength by graphical interpolation. Then, an attempt was made to plot the obtained  $A_M$  and  $B_M$ constants as a function of the mixture composition at each constant ionic strength level. The composition of the mixture was expressed as ionic strength fraction with respect to the salt components. Figures 1, 2, and 3 show the  $A_M$  and  $B_M$  values plotted against the ionic strength fraction of NaCl  $(X_{NaCl})$  for the NaCl-KCl, NaCl-Na<sub>2</sub>SO<sub>4</sub>, and NaCl-MgSO<sub>4</sub> systems. The experimental data fell on the line connecting the  $A_0$  and  $B_0$  values of the pure compounds for the first two systems, thus confirming the additivity of these values. The  $A_M$  and  $B_M$  values, therefore, can be calculated from:

$$A_{M} = A_{01} \frac{I_{1}}{I_{T}} + A_{02} \frac{I_{2}}{I_{T}}$$
(4)

$$B_{M} = B_{01} \frac{I_{1}}{I_{T}} + B_{02} \frac{I_{2}}{I_{T}}$$
(5)

where

 $A_{01}$  and  $B_{01}$  are the Othmer constants of compound 1

 $A_{02}$  and  $B_{02}$  are the Othmer constants of compound 2

 $I_1$  and  $I_2$  are the ionic strengths of the compounds

 $I_{\rm T}$  is the total ionic strength of the solution

The constant values derived from measurements in binary systems are given in Table I. In the NaCl-MgSO<sub>4</sub> system the experimental  $A_M$  and  $B_M$  values fell below the linear relationship, which is most apparent at high ionic strength. Thus, these mixtures seem to behave like mixtures containing more NaCl and less MgSO<sub>4</sub> than was actually the case. This behavior was attributed to the partial dissociation of MgSO<sub>4</sub> into its ions, which reduces the ionic strength of MgSO<sub>4</sub>. To compensate for this, the dissociation constants given by Marshall (9) over the 0° to 200°C. temperature range were used. This calculation is rather lengthy. The activity coefficients must be used and the results can be obtained only by an iterative technique. Therefore, the results of the exact calculation were expressed in a simplified

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Figure 1.  $A_M$  and  $B_M$  values

for the NaCI-KCI system



Figure 2.  $A_M$  and  $B_M$  values for the NaCl-Na<sub>2</sub>SO<sub>4</sub> system

form, to yield the corrected MgSO4 ionic strength. The calculated degrees of dissociation of MgSO4 in simulated sea water at concentration factors of 1 and 3 and at 25° and 150°C., respectively, ranged from 72.7 to 73.0%; an average value of 0.728 was used in the concentration adjustment. The corrected ionic strength fractions of NaCl and  $MgSO_4$  were expressed as:

$$X_{\text{NaCl}} = \frac{I_{\text{NaCl}}}{I_T - I_{\text{MgSO}_*} (1 - \alpha)}$$
(6)

and

$$X_{\rm MgSO_4} = 1 - X_{\rm NaCl} \tag{7}$$

where

#### $\alpha = 0.728$ , degree of dissociation

The average deviations of the calculated  $A_M$  and  $B_M$ constants, from the experimentally determined values were:

> For additivity.  $\pm 0.30\%$ For the exact method.  $\pm 0.10\%$ For the approximate method.  $\pm 0.10\%$

The deviations in the constants usually compensate one another.

The experimental data and calculated results are summarized in Tables II, III, and IV for the three systems investigated. The standard deviations of the calculated and experimental viscosity values for these systems are:

NaCl-KCl system. 0.27% NaCl-Na<sub>2</sub>SO<sub>4</sub> system. 0.27% NaCl-MgSO<sub>4</sub> system. 0.38%

0.2

0.24

0.20

0.16

Am 17 = 1.42

0.71

0,6

0.4

Figure 3.  $A_M$  and  $B_M$  values

in the NaCl-MgSO4 system

×Na Cl

IONIC STRENGTH FRACTION

0.8

1.0

N B 0.12

٦

₹ 0.08

0,04

-0.04

n

0

The simplified technique used to take into consideration the dissociation of magnesium sulfate with a fixed degree of dissociation (72.8%) can be applied only to sea water, its concentrates, and sea water-like solutions. For solutions of entirely different concentration and composition, the exact calculation must be used.

Calcium-Free Sea Water. The ionic composition of normal sea water as reported by Spiegler (14) is listed at the left of Table V. The ionic composition converted into salt composition is given at the right with two minor changes. The bicarbonate content was replaced by equivalent sulfate ions, and the potassium content was slightly reduced to balance the anions.

To avoid experimental difficulties caused by CaSO<sub>4</sub> precipitation at higher temperatures, MgCl<sub>2</sub> was substituted for CaCl<sub>2</sub>. This calcium-free synthetic sea water with the given composition and four of its concentrates were prepared for the viscosity measurements. In calculating the sea water viscosities the ions were grouped as shown in the last column of Table V. Here it was assumed that all  $SO_4^{2-}$  was present as  $MgSO_4$ , and the small quantity of KBr was added to the NaCl content. In this way the synthetic sea water was reduced to a mixture of only four components: NaCl, MgCl<sub>2</sub>, MgSO<sub>4</sub>, and KCl.

The constant values used in the calculation are given in Table I. The constants for MgCl<sub>2</sub> and CaCl<sub>2</sub> solutions

	Table I. Consto	ints for Correlation	n of Viscosity by th	e Othmer Rule (Eq	uations 2 and 3)	
Compound	$A_1$	$A_2$	$A_3$	$B_1$	$B_2$	$B_3$
NaCl	0.03550	0.00231	-0.00003	-0.04753	0.01598	-0.00194
KCl	-0.00522	0.00175	0.00016	-0.09677	0.03215	-0.00547
Na₂SO₄	0.06672	-0.00721	0.00176	-0.01547	0.01356	-0.00189
MgSO₄	0.07341	-0.00278	0.00063	-0.01104	0.03467	-0.00740
$MgCl_2$	0.05508	-0.00045	0.00050	-0.00682	0.01614	-0.00217
$CaCl_2$	0.04241	-0.00051		-0.01450		

Table II. Relative Viscosities and Densities of Ternary Aqueous NaCl–KCl Soluti	ions
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Temp.,	Mol	ality	Ionic Strength NaCl			7	1 R	. Temp.,	Mol	ality	Ionic Strength NaCl			<u>r</u> ,	IR
°C.	NaCl	KCl	+ KCl	Density	ν, Cs.	Exptl.	Calcd.	°C.	NaCl	KCl	+KCl	Density	ν, Cs.	Exptl.	Calcd.
25	$\begin{array}{c} 0.6362\\ 1.2724\\ 3.1810\\ 0.5655\\ 1.1310\\ 2.8275\\ 0.4807\\ 0.9614\\ 2.4034 \end{array}$	$\begin{array}{c} 0.0707\\ 0.1414\\ 0.3535\\ 0.1414\\ 0.2828\\ 0.7070\\ 0.2262\\ 0.4524\\ 1.1311\end{array}$	$\begin{array}{c} 0.7069 \\ 1.4138 \\ 3.5345 \\ 0.7069 \\ 1.4138 \\ 3.5345 \\ 0.7069 \\ 1.4138 \\ 3.5345 \\ 3.5345 \end{array}$	$\begin{array}{c} 1.0257\\ 1.0521\\ 1.1243\\ 1.0259\\ 1.0529\\ 1.1255\\ 1.0262\\ 1.0538\\ 1.1274\end{array}$	$\begin{array}{c} 0.9178\\ 0.9493\\ 1.0967\\ 0.9115\\ 0.9362\\ 1.0587\\ 0.9036\\ 0.9209\\ 1.0158\end{array}$	$\begin{array}{c} 1.057\\ 1.122\\ 1.385\\ 1.050\\ 1.107\\ 1.338\\ 1.042\\ 1.090\\ 1.286\end{array}$	$\begin{array}{c} 1.059\\ 1.125\\ 1.387\\ 1.052\\ 1.111\\ 1.344\\ 1.044\\ 1.094\\ 1.295\end{array}$	100	$\begin{array}{c} 0.6393\\ 1.2787\\ 3.1957\\ 0.5683\\ 1.1366\\ 2.8408\\ 0.4830\\ 0.9660\\ 2.4144 \end{array}$	$\begin{array}{c} 0.0710\\ 0.1421\\ 0.3551\\ 0.1421\\ 0.2842\\ 0.7102\\ 0.2273\\ 0.4546\\ 1.1363\end{array}$	$\begin{array}{c} 0.7103 \\ 1.4208 \\ 3.5508 \\ 0.7104 \\ 1.4207 \\ 3.5510 \\ 0.7104 \\ 1.4206 \\ 3.5507 \end{array}$	$\begin{array}{c} 0.9865\\ 1.0126\\ 1.0827\\ 0.9867\\ 1.0132\\ 1.0843\\ 0.9873\\ 1.0139\\ 1.0859\end{array}$	$\begin{array}{c} 0.3130\\ 0.3311\\ 0.3904\\ 0.3116\\ 0.3283\\ 0.3824\\ 0.3101\\ 0.3254\\ 0.3748 \end{array}$	$1.095 \\ 1.189 \\ 1.499 \\ 1.090 \\ 1.179 \\ 1.470 \\ 1.086 \\ 1.170 \\ 1.443 \\$	$\begin{array}{c} 1.095\\ 1.186\\ 1.501\\ 1.092\\ 1.178\\ 1.476\\ 1.088\\ 1.167\\ 1.447\end{array}$
40	$\begin{array}{c} 0.6362 \\ 1.2724 \\ 3.1810 \\ 0.5655 \\ 1.1310 \\ 2.8275 \\ 0.4807 \\ 0.9614 \\ 2.4034 \end{array}$	$\begin{array}{c} 0.0707\\ 0.1414\\ 0.3535\\ 0.1414\\ 0.2828\\ 0.7070\\ 0.2262\\ 0.4524\\ 1.1311 \end{array}$	$\begin{array}{c} 0.7069 \\ 1.4138 \\ 3.5345 \\ 0.7069 \\ 1.4138 \\ 3.5345 \\ 0.7069 \\ 1.4138 \\ 3.5345 \end{array}$	$\begin{array}{c} 1.0202\\ 1.0460\\ 1.1171\\ 1.0204\\ 1.0468\\ 1.1184\\ 1.0207\\ 1.0477\\ 1.1202 \end{array}$	$\begin{array}{c} 0.6837\\ 0.7124\\ 0.8274\\ 0.6796\\ 0.7039\\ 0.8029\\ 0.6746\\ 0.6939\\ 0.7750\\ \end{array}$	$\begin{array}{c} 1.069\\ 1.142\\ 1.416\\ 1.062\\ 1.129\\ 1.376\\ 1.055\\ 1.114\\ 1.330\end{array}$	$1.068 \\ 1.141 \\ 1.416 \\ 1.062 \\ 1.128 \\ 1.378 \\ 1.056 \\ 1.113 \\ 1.333$	125	$\begin{array}{c} 0.6429\\ 1.2862\\ 3.2130\\ 0.5715\\ 1.1431\\ 2.8563\\ 0.4858\\ 0.9714\\ 2.4274 \end{array}$	$\begin{array}{c} 0.0714\\ 0.1429\\ 0.3570\\ 0.1429\\ 0.2858\\ 0.7141\\ 0.2286\\ 0.4572\\ 1.1424 \end{array}$	$\begin{array}{c} 0.7144\\ 1.4291\\ 3.5700\\ 0.7144\\ 1.4289\\ 3.5704\\ 0.7145\\ 1.4286\\ 3.5698 \end{array}$	$\begin{array}{c} 0.9682\\ 0.9947\\ 1.0661\\ 0.9684\\ 1.0677\\ 0.9690\\ 0.9962\\ 1.0692\\ \end{array}$	$\begin{array}{c} 0.2528\\ 0.2679\\ 0.3173\\ 0.2515\\ 0.2659\\ 0.3118\\ 0.2505\\ 0.2639\\ 0.3063 \end{array}$	$\begin{array}{c} 1.103 \\ 1.201 \\ 1.525 \\ 1.097 \\ 1.193 \\ 1.500 \\ 1.094 \\ 1.185 \\ 1.476 \end{array}$	$\begin{array}{c} 1.103\\ 1.201\\ 1.529\\ 1.101\\ 1.193\\ 1.509\\ 1.097\\ 1.184\\ 1.484\end{array}$
60	$\begin{array}{c} 0.6362 \\ 1.2724 \\ 3.1810 \\ 0.5655 \\ 1.1310 \\ 2.8275 \\ 0.4807 \\ 0.9614 \\ 2.4034 \end{array}$	$\begin{array}{c} 0.0707\\ 0.1414\\ 0.3535\\ 0.1414\\ 0.2828\\ 0.7070\\ 0.2262\\ 0.4524\\ 1.1311 \end{array}$	0.7069 1.4138 3.5345 0.7069 1.4138 3.5345 0.7069 1.4138 3.5345	$\begin{array}{c} 1.0108\\ 1.0363\\ 1.1064\\ 1.0111\\ 1.0372\\ 1.1078\\ 1.0114\\ 1.0380\\ 1.1097 \end{array}$	0.4980 0.5222 0.6103 0.4955 0.5170 0.5952 0.4924 0.5108 0.5778	$1.079 \\ 1.160 \\ 1.447 \\ 1.074 \\ 1.149 \\ 1.413 \\ 1.068 \\ 1.137 \\ 1.375 \\$	$1.079 \\ 1.159 \\ 1.448 \\ 1.074 \\ 1.147 \\ 1.415 \\ 1.068 \\ 1.134 \\ 1.377$	150	$\begin{array}{c} 0.6495\\ 1.2996\\ 3.2448\\ 0.5774\\ 1.1549\\ 2.8848\\ 0.4909\\ 0.9813\\ 2.4512 \end{array}$	$\begin{array}{c} 0.0722\\ 0.1444\\ 0.3606\\ 0.1444\\ 0.2888\\ 0.7212\\ 0.2310\\ 0.4618\\ 1.1536\end{array}$	0.7217 1.4440 3.6054 0.7218 1.4437 3.6060 0.7219 1.4431 3.6048	0.9477 0.9750 1.0485 0.9480 0.9757 1.0502 0.9484 0.9766 1.0517	$\begin{array}{c} 0.2135\\ 0.2261\\ 0.2684\\ 0.2119\\ 0.2247\\ 0.2648\\ 0.2112\\ 0.2231\\ 0.2606\\ \end{array}$	$\begin{array}{c} 1.115\\ 1.214\\ 1.550\\ 1.107\\ 1.208\\ 1.532\\ 1.104\\ 1.200\\ 1.510\\ \mathrm{S.D.}=\end{array}$	$\begin{array}{c} 1.111\\ 1.214\\ 1.557\\ 1.109\\ 1.207\\ 1.541\\ 1.106\\ 1.199\\ 1.521\\ 0.27\%\end{array}$
75	$\begin{array}{c} 0.6375\\ 1.2749\\ 3.1869\\ 0.5666\\ 1.1333\\ 2.8329\\ 0.4816\\ 0.9632\\ 2.4078 \end{array}$	$\begin{array}{c} 0.0708\\ 0.1417\\ 0.3541\\ 0.1417\\ 0.2833\\ 0.7083\\ 0.2267\\ 0.4533\\ 1.1332 \end{array}$	$\begin{array}{c} 0.7083\\ 1.4166\\ 3.5411\\ 0.7083\\ 1.4166\\ 3.5412\\ 0.7083\\ 1.4165\\ 3.5410\\ \end{array}$	$\begin{array}{c} 1.0024 \\ 1.0285 \\ 1.0983 \\ 1.0028 \\ 1.0291 \\ 1.0998 \\ 1.0033 \\ 1.0298 \\ 1.1014 \end{array}$	$\begin{array}{c} 0.4097\\ 0.4316\\ 0.5060\\ 0.4079\\ 0.4273\\ 0.4940\\ 0.4053\\ 0.4226\\ 0.4819 \end{array}$	$\begin{array}{c} 1.085\\ 1.173\\ 1.469\\ 1.081\\ 1.162\\ 1.436\\ 1.075\\ 1.150\\ 1.403\end{array}$	$\begin{array}{c} 1.086\\ 1.170\\ 1.470\\ 1.081\\ 1.160\\ 1.440\\ 1.076\\ 1.148\\ 1.405\end{array}$								

Molality (m) = g. moles salt/1000 g. H<sub>2</sub>O. Ionic strength  $(I_T) = m_{NaCl} + m_{KCl}$ . Density = g./cc.  $\nu$  = Kinematic viscosity, centistokes.  $\eta_R = \eta_{soln} / \eta_{H_2O}$ .

Table III. Relative Viscosities and Densities of Ternary Aqueous NaCl–Na<sub>2</sub>SO<sub>4</sub> Solutions

Temp	Mol	ality	Ionic Strength			η	R	Temp	Mol	lality	Ionic Strength NaCl +			η	R
°C.	NaCl	$Na_2SO_4$	$Na_2SO_4$	Density	ν, Cs.	Exptl.	Calcd.	°C.	NaCl	$Na_2SO_4$	Na <sub>2</sub> SO <sub>4</sub>	Density	ν, Cs.	Exptl.	Calcd.
25	$\begin{array}{c} 0.6716\\ 1.3431\\ 3.3578\\ 0.6362\\ 1.2724\\ 3.1810\\ 0.5514\\ 1.1028\\ 2.7569 \end{array}$	$\begin{array}{c} 0.0118\\ 0.0235\\ 0.0589\\ 0.0236\\ 0.0471\\ 0.1178\\ 0.0518\\ 0.1036\\ 0.2591 \end{array}$	0.7069 1.4138 3.5344 0.7069 1.4138 3.5344 0.7068 1.4137 3.5343	$\begin{array}{c} 1.0250\\ 1.0515\\ 1.1230\\ 1.0252\\ 1.0516\\ 1.1234\\ 1.0253\\ 1.0520\\ 1.1239\end{array}$	0.9258 0.9657 1.1426 0.9276 0.9688 1.1501 0.9313 0.9761 1.1688	$1.066 \\ 1.141 \\ 1.441 \\ 1.068 \\ 1.144 \\ 1.451 \\ 1.073 \\ 1.153 \\ 1.476$	$\begin{array}{c} 1.068\\ 1.143\\ 1.442\\ 1.070\\ 1.147\\ 1.453\\ 1.075\\ 1.154\\ 1.480\end{array}$	60	$\begin{array}{c} 0.6716\\ 1.3431\\ 3.3578\\ 0.6362\\ 1.2724\\ 3.1810\\ 0.5514\\ 1.1028\\ 2.7569\end{array}$	$\begin{array}{c} 0.0118\\ 0.0235\\ 0.0589\\ 0.0236\\ 0.0471\\ 0.1178\\ 0.0518\\ 0.1036\\ 0.2591 \end{array}$	$\begin{array}{c} 0.7069 \\ 1.4138 \\ 3.5344 \\ 0.7069 \\ 1.4138 \\ 3.5344 \\ 0.7068 \\ 1.4137 \\ 3.5343 \end{array}$	$\begin{array}{c} 1.0102\\ 1.0356\\ 1.1050\\ 1.0103\\ 1.0358\\ 1.1054\\ 1.0104\\ 1.0362\\ 1.1061 \end{array}$	$\begin{array}{c} 0.5012\\ 0.5285\\ 0.6277\\ 0.5016\\ 0.5295\\ 0.6299\\ 0.5029\\ 0.5029\\ 0.5318\\ 0.6357\end{array}$	1.085 1.173 1.487 1.086 1.176 1.493 1.089 1.181 1.507	1.085 1.172 1.489 1.086 1.175 1.497 1.090 1.178 1.514
40	$\begin{array}{c} 0.6716 \\ 1.3431 \\ 3.3578 \\ 0.6362 \\ 1.2724 \\ 3.1810 \\ 0.5514 \\ 1.1028 \\ 2.7569 \end{array}$	$\begin{array}{c} 0.0118\\ 0.0235\\ 0.0589\\ 0.0236\\ 0.0471\\ 0.1178\\ 0.0518\\ 0.1036\\ 0.2591 \end{array}$	$\begin{array}{c} 0.7069\\ 1.4138\\ 3.5344\\ 0.7069\\ 1.4138\\ 3.5344\\ 0.7068\\ 1.4137\\ 3.5343\end{array}$	$\begin{array}{c} 1.0196\\ 1.0455\\ 1.1157\\ 1.0197\\ 1.0456\\ 1.1161\\ 1.0198\\ 1.0459\\ 1.0459\\ 1.1167\end{array}$	$\begin{array}{c} 0.6889\\ 0.7228\\ 0.8566\\ 0.6898\\ 0.7247\\ 0.8608\\ 0.6922\\ 0.7288\\ 0.8717\end{array}$	$1.076 \\ 1.158 \\ 1.464 \\ 1.078 \\ 1.161 \\ 1.472 \\ 1.081 \\ 1.168 \\ 1.491$	$\begin{array}{c} 1.076\\ 1.157\\ 1.465\\ 1.078\\ 1.160\\ 1.474\\ 1.082\\ 1.166\\ 1.496\end{array}$	75	0.6729 1.3456 3.3637 0.6375 1.2749 3.1870 0.5524 1.1049 2.7621	0.0118 0.0236 0.0590 0.0236 0.0472 0.1180 0.0519 0.1038 0.2596	0.7083 1.4164 3.5407 0.7083 1.4165 3.5410 0.7082 1.4164 3.5409	1.0022 1.0276 1.0970 1.0022 1.0277 1.0974 1.0023 1.0280 1.0980	0.4116 0.4358 0.5185 0.4125 0.4361 0.5204 0.4132 0.4371 0.5229	1.090 1.183 1.503 1.092 1.184 1.509 1.095 1.187 1.517	1.091 1.182 1.506 1.092 1.184 1.512 1.095 1.186 1.527

(Continued)

	Table III. Continued														
Temp., _	Molality		Ionic Strength NaCl +			η	R	Temp.,	Mol	ality	Ionic Strength NaCl +		_	<u>η</u> R	
°C.	NaCl	Na <sub>2</sub> SO <sub>4</sub>	$Na_2SO_4$	Density	ν, Cs.	Exptl.	Calcd.	°C.	NaCl	Na₂SO₄	Na <sub>2</sub> SO <sub>4</sub>	Density	ν, Cs.	Exptl.	Calcd.
100	0.6748 1.3494 3.3726 0.6395 1.2785 3.1960 0.5540 1.1080 2.7698	$\begin{array}{c} 0.0118\\ 0.0236\\ 0.0592\\ 0.0237\\ 0.0473\\ 0.1183\\ 0.0521\\ 0.1041\\ 0.2603 \end{array}$	$\begin{array}{c} 0.7103 \\ 1.4204 \\ 3.5500 \\ 0.7105 \\ 1.4206 \\ 3.5510 \\ 0.7103 \\ 1.4204 \\ 3.5508 \end{array}$	$\begin{array}{c} 0.9861 \\ 1.0116 \\ 1.0813 \\ 0.9860 \\ 1.0116 \\ 1.0816 \\ 0.9862 \\ 1.0119 \\ 1.0822 \end{array}$	$\begin{array}{c} 0.3140\\ 0.3335\\ 0.3981\\ 0.3144\\ 0.3337\\ 0.3989\\ 0.3151\\ 0.3342\\ 0.4000\\ \end{array}$	$\begin{array}{c} 1.098\\ 1.196\\ 1.527\\ 1.099\\ 1.197\\ 1.530\\ 1.102\\ 1.199\\ 1.535\end{array}$	$\begin{array}{c} 1.099\\ 1.196\\ 1.530\\ 1.100\\ 1.197\\ 1.535\\ 1.102\\ 1.198\\ 1.545\end{array}$	150	$\begin{array}{c} 0.6857\\ 1.3704\\ 3.4219\\ 0.6504\\ 1.2989\\ 3.2457\\ 0.5628\\ 1.1253\\ 2.8126\end{array}$	$\begin{array}{c} 0.0120\\ 0.0240\\ 0.0600\\ 0.0241\\ 0.0481\\ 0.1202\\ 0.0529\\ 0.1058\\ 0.2644 \end{array}$	$\begin{array}{c} 0.7218 \\ 1.4424 \\ 3.6020 \\ 0.7227 \\ 1.4432 \\ 3.6062 \\ 0.7215 \\ 1.4426 \\ 3.6057 \end{array}$	$\begin{array}{c} 0.9472\\ 0.9740\\ 1.0467\\ 0.9471\\ 0.9740\\ 1.0471\\ 0.9473\\ 0.9742\\ 1.0476\end{array}$	$\begin{array}{c} 0.2133\\ 0.2271\\ 0.2727\\ 0.2130\\ 0.2271\\ 0.2721\\ 0.2135\\ 0.2272\\ 0.2719\\ \end{array}$	1.113 1.219 1.572 1.111 1.219 1.570 1.114 1.219 1.569 S.D. =	$\begin{array}{c} 1.114\\ 1.220\\ 1.575\\ 1.114\\ 1.220\\ 1.578\\ 1.114\\ 1.218\\ 1.581\\ 0.27\%\end{array}$
125	$\begin{array}{c} 0.6787\\ 1.3569\\ 3.3900\\ 0.6434\\ 1.2857\\ 3.2135\\ 0.5572\\ 1.1141\\ 2.7849 \end{array}$	$\begin{array}{c} 0.0119\\ 0.0238\\ 0.0594\\ 0.0238\\ 0.0476\\ 0.1190\\ 0.0524\\ 0.1047\\ 0.2618 \end{array}$	$\begin{array}{c} 0.7114\\ 1.4282\\ 3.5683\\ 0.7148\\ 1.4285\\ 3.5740\\ 0.7142\\ 1.4283\\ 3.5702 \end{array}$	0.9677 0.9937 1.0645 0.9676 0.9937 1.0649 0.9678 0.9939 1.0654	0.2532 0.2695 0.3225 0.2533 0.2695 0.3228 0.2538 0.2696 0.3229	$\begin{array}{c} 1.104\\ 1.207\\ 1.547\\ 1.105\\ 1.207\\ 1.549\\ 1.107\\ 1.208\\ 1.550\end{array}$	$\begin{array}{c} 1.107\\ 1.209\\ 1.552\\ 1.107\\ 1.209\\ 1.555\\ 1.108\\ 1.208\\ 1.562\end{array}$							5.12	0.2170
Molality centistok	Molality $(m) = g$ . moles salt/1000 g. H <sub>2</sub> O. Ionic strength $(I_T) = m_{NaCl} + 3m_{Na_2SO_4}$ . Density = g./cc. $\nu$ = kinematic viscosity, centistokes. $\eta_R = \eta_{soln} / \eta_{H_2O}$ .														

Table IV. Relative Viscosities and Densities of Terno	ary Aqueous NaCl—MgSO4 Solutions
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	Mol	ality	Ionic Strength						Mol	ality	Ionic Strength			-	_
Temp.,	NaCl	Maso	NaCl +	Donaitu	Ca	Erre tl	Calad	Temp.,	NaCl	M-SO	NaCl +	Demoiter	C.	 From th	Calad
С.	NaCI	IvigoU4	WIg504	Density	$\nu$ , Cs.	Expti.	Calcu.	-0.	INACI	Ivig50₄	Mg50₄	Density	ν, Cs.	Expu.	Calca.
25	0.6370	0.0177	0.7078	1.0246	0.9290	1.069	1.070	100	0.6400	0.0178	0.7111	0.9854	0.3147	1.100	1.100
	2 1 95 9	0.0304	1.4100	1.0502	0.9714	1.146	1.149		1.2802	0.0356	1.4225	1.0109	0.3344	1.199	1.197
	0.5662	0.0865	0.7079	1.1204	1,1040	1.400	1.420		0.1997	0.0009	3.0002 0.7112	0.0840	0.4000	1.001	1.030
	1 1 3 2 5	0.0708	1 4156	1.0200	0.9812	1.074	1.070		1 1380	0.0330	1 4994	1 0098	0.3151	1 200	1.102
	2.8312	0.1770	3.5390	1.1180	1.1746	1.475	1.475		2.8443	0.1778	3 5554	1.0000	0.0002	1.200 1.537	1.130 1.543
	0.4813	0.0566	0.7078	1.0229	0.9401	1.080	1.083		0.4836	0.0569	0.7111	0.9841	0.3155	1.101	1.104
	0.9626	0.1132	1.4156	1.0476	0.9921	1.167	1.171		0.9673	0.1138	1.4225	1.0086	0.3363	1.203	1.199
	2.4065	0.2831	3.5390	1.1151	1.2012	1.504	1.506		2.4177	0.2844	3.5554	1.0743	0.4056	1.545	1.555
40	0.6370	0.0177	0.7078	1.0191	0.6907	1.078	1.076	125	0.6435	0.0179	0.7150	0.9670	0.2533	1.104	1.107
	1.2740	0.0354	1.4156	1.0442	0.7262	1.162	1.162		1.2875	0.0358	1.4306	0.9929	0.2699	1.208	1.208
	3.1852	0.0885	3.5390	1.1133	0.8640	1.474	1.473		3.2170	0.0893	3.5743	1.0621	0.3233	1.547	1.556
	0.5662	0.0354	0.7078	1.0184	0.6938	1.083	1.083		0.5722	0.0358	0.7152	0.9665	0.2535	1.104	1.108
	1.1325	0.0708	1.4156	1.0430	0.7319	1.170	1.169		1.1444	0.0715	1.4305	0.9918	0.2702	1.208	1.207
	2.8312	0.1770	3.5390	1.1110	0.8766	1.492	1.492		2.8598	0.1787	3.5748	1.0602	0.3244	1.550	1.562
	0.4813	0.0566	0.7078	1.0175	0.6972	1.087	1.088		0.4862	0.0572	0.7150	0.9656	0.2537	1.104	1.108
	0.9626	0.1132	1.4100	1.0417	0.7384	1.178	1.179		0.9728	0.1144	1.4306	0.9906	0.2706	1.208	1.206
	2.4000	0.2001	3.0590	1.1082	0.8926	1.919	1.918		2.4308	0.2860	3.5747	1.0074	0.3259	1.553	1.569
60	0.6370	0.0177	0.7078	1.0097	0.5020	1.086	1.082	150	0.6499	0.0180	0.7221	0.9464	0.2129	1.110	1.113
	1.2740	0.0354	1.4156	1.0344	0.5304	1.176	1.175		1.3009	0.0361	1.4454	0.9732	0.2271	1.218	1.218
	3.1852	0.0880	3.5390	1.1027	0.6320	1.494	1.496		3.2484	0.0902	3.6093	1.0445	0.2724	1.568	1.578
	0.0002	0.0304	1.4156	1.0092	0.5030	1.090	1.090		0.0781	0.0361	0.7226	0.9459	0.2130	1.110	1.113
	2 8319	0.0708	3 5390	1 1006	0.0000	1.102	1.100		2 8881	0.0722	3 6109	1.0423	0.2272	1.217	1.210
	0.4813	0.0566	0.7078	1.1000	0.5054	1.000	1.011		0.4911	0.1803	0 7222	0.9450	0.2729	1 1 1 9	1.119
	0.9626	0.1132	1.4156	1.0321	0.5369	1.188	1.186		0.9828	0.0010	1 4453	0.9705	0.2120 0.2271	1 214	1 213
	2.4065	0.2831	3.5390	1.0980	0.6483	1.526	1.531		2.4548	0.2888	3.6100	1.0395	0.2732	1.565	1.587
														S.D. =	0.38%
75	0.6382	0.0177	0.7091	1.0015	0.4130	1.093	1.093								
	1.2765	0.0355	1.4184	1.0266	0.4375	1.187	1.184								
	3.1910	0.0886	3.5455	1.0946	0.5216	1.509	1.512								
	0.5673	0.0355	0.7092	1.0009	0.4138	1.095	1.095								
	1.1347	0.0709	1.4184	1.0257	0.4391	1.190	1.188								
	2.8365	0.1773	3.5456	1.0925	0.5265	1.520	1.524								
	0.4822	0.0567	0.7091	1.0002	0.4147	1.096	1.098								
	0.9640	0.1135	1.4184 2.5456	1.0245	U.4415 0.5296	1.195	1.192								
	2.4110	0.2000	3.3430	1.0090	0.0320	1.034	1.941		-						

Molality (m) = g. moles salt/1000 g. H<sub>2</sub>O. Ionic strength  $(I_T) = m_{\text{NaCl}} + 4m_{\text{MgSO}_{\star}}$ . Density = g./cc.  $\nu$  = kinematic viscosity, centistokes.  $\eta_R = \eta_{\text{soin}} / \eta_{\text{H_2O}}$ .

were calculated from literature data (2, 5, 12, 15). The ionic strength fractions of NaCl, MgCl<sub>2</sub>, and KCl were calculated using Equation 6 and

$$X_{\rm MgSO_4} = 1 - X_{\rm NaCl} - X_{\rm MgCl_2} - X_{\rm KCl}$$

The Othmer constants of the mixture were calculated from:

$$A_M = \Sigma A_{0i} \cdot X_i \tag{8}$$

$$B_M = \Sigma B_{0i} \cdot X_i \tag{9}$$

and the viscosity was determined from Equation 1.

Thus the relative viscosity of the calcium-free sea water was calculated with the equation

$$\log \eta_R = 0.04280I + 0.00123I^2 + 0.000131I^3 +$$

$$(-0.03724I + 0.01859I^2 - 0.00271I^3) \log \eta_w \qquad (10a)$$

for standard calcium-free sea water (I = 0.70989)

Com-

ponent

NaCl

Na₂SO₄

 $MgCl_2$ 

MgSO₄

CaCl<sub>2</sub>

KCI

KBr

Ionic Composition

Sodium

Calcium

Potassium

Bicarbonate

Chloride

Sulfate

Bromide

Magnesium

P.p.m.

10,561

1.272

400

480

18,980

Total ionic strength  $(I_T)$ 

2,649

142

65

$$\log \eta_R = 0.03103 - 0.01803 \log \eta_w \tag{10b}$$

and for the absolute viscosity of calcium-free standard sea water

$$\log \eta_{s.w.} = 0.03103 + 0.98197 \log \eta_w \tag{10c}$$

# Table V. Composition of Sea Water

Carbonate-

free sea

water

molality

0.41674

0.02979

0.05423

0.01034

0.00923

0.00084

0.70989

0.70989

The experimental and calculated data are compared in Table VI. The concentration factor used in this table is the salt content per 1000 grams of water in the given solution divided by the salt content per 1000 grams of water in standard sea water. The slight increase of concentration factors with temperature was caused by water evaporation inside of the viscometer. The standard deviation of the experimental and calculated viscosities is 0.28% up to a concentration factor of 2, 0.45% up to a concentration factor of 2.5, and 0.63% up to a concentration factor of 3.

Table V	11.	Relative	Viscosity	of	Sea	Water	at	25°	C.

	5	10	20	30	40
Krümmel (8) Calculated	$\begin{array}{c} 1.010\\ 1.010\end{array}$	$\begin{array}{c} 1.022 \\ 1.021 \end{array}$	$\begin{array}{c} 1.044 \\ 1.043 \end{array}$	$1.069 \\ 1.066$	$1.093 \\ 1.090$
	5	10	15	20	
Miyake (10) Calculated	$1.026 \\ 1.019$	$\begin{array}{c} 1.041 \\ 1.039 \end{array}$	$1.059 \\ 1.059$	$\begin{array}{c} 1.079 \\ 1.081 \end{array}$	

# Table VIII. Relative Viscosity of Sea Water

Sal	t Composit	tion	Chlorinity <sup>a</sup>	25° C.	50° C.	75° C.	100° C.	125° C.	150° C.	Salinitv
te- a	Calcium- free sea	Regrouped composi-	5.0 10.0	1.019 1.039	1.022 1.044	1.024 1.049	1.026 1.052	$1.028 \\ 1.055$	1.029 1.057	9.05 18.11
у	water molality	tion molality	15.0 20.0	1.059 1.081	$1.067 \\ 1.090$	1.073 1.098	$1.078 \\ 1.104$	$1.082 \\ 1.109$	$1.085 \\ 1.113$	27.16 36.21
1	0.41674	0.47716	25.0	1.103	1.114	1.123	1.130	1.136	1.140	45.27
) 3	$0.02979 \\ 0.06457$	0.03478	30.0 35.0	1.127 1.152	1.139 1.165	$1.149 \\ 1.175$	1.156 1.183	1.162	1.167	$54.32 \\ 63.37$
4	• • •	0.02979	40.0 45.0	$1.178 \\ 1.206$	$1.191 \\ 1.219$	1.202 1.229	$1.210 \\ 1.238$	1.216	1.222 1.250	72.43 81.48
± 3	0.00923	0.00923	50.0	1.235	1.248	1.259	1.267	1.273	1.279	90.53
1	0.00084	•••	$\begin{array}{c} 55.0 \\ 60.0 \end{array}$	$\begin{array}{c} 1.266 \\ 1.300 \end{array}$	$\begin{array}{c} 1.279 \\ 1.312 \end{array}$	$\begin{array}{c} 1.289 \\ 1.322 \end{array}$	$\begin{array}{c} 1.297 \\ 1.330 \end{array}$	$\begin{array}{c} 1.304 \\ 1.336 \end{array}$	$\begin{array}{c} 1.309 \\ 1.341 \end{array}$	$99.60 \\ 108.66$
			<sup>a</sup> Grams abl	orino or	d brom	ino (orr	more of	o o o o o o o o o o o o o o o o o o o	alont ab	lorino) ir

Grams chlorine and bromine (expressed as equivalent chlorine) in kg. sea water. <sup>b</sup>Grams salt per kg. sea water.

# Table VI. Relative Viscosities and Densities of Calcium-Free Synthetic Sea Waters

0.70989

	Concn	Total Ionic			η	R	<b>T</b>	Comm	Total			η	R
°C.	Concn. Factor	Strength	Density	v, Cs.	Exptl.	Calcd.	°C.	Factor	Strength	Density	v, Cs.	Exptl.	Calcd.
25	$1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ 3.0$	0.7099 1.0648 1.4198 1.7747 2.1297	$\begin{array}{c} 1.0227 \\ 1.0350 \\ 1.0470 \\ 1.0590 \\ 1.0704 \end{array}$	$\begin{array}{c} 0.9367 \\ 0.9600 \\ 0.9851 \\ 1.0120 \\ 1.0416 \end{array}$	$1.076 \\ 1.116 \\ 1.159 \\ 1.204 \\ 1.252$	1.076 1.117 1.161 1.207 1.256	100	$\begin{array}{c} 1.0048 \\ 1.5072 \\ 2.0096 \\ 2.5120 \\ 3.0144 \end{array}$	0.7133 1.0699 1.4266 1.7832 2.1399	$\begin{array}{c} 0.9834 \\ 0.9954 \\ 1.0071 \\ 1.0186 \\ 1.0299 \end{array}$	$\begin{array}{c} 0.3151 \\ 0.3252 \\ 0.3357 \\ 0.3462 \\ 0.3572 \end{array}$	$1.099 \\ 1.148 \\ 1.199 \\ 1.250 \\ 1.305$	$\begin{array}{c} 1.099 \\ 1.145 \\ 1.193 \\ 1.240 \\ 1.289 \end{array}$
40	$1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ 3.0$	0.7099 1.0648 1.4198 1.7747 2.1297	$\begin{array}{c} 1.0174 \\ 1.0294 \\ 1.0411 \\ 1.0529 \\ 1.0641 \end{array}$	$0.6954 \\ 0.7144 \\ 0.7343 \\ 0.7556 \\ 0.7782$	$1.084 \\ 1.127 \\ 1.171 \\ 1.219 \\ 1.269$	$1.082 \\ 1.125 \\ 1.169 \\ 1.216 \\ 1.265$	125	$\begin{array}{c} 1.0104 \\ 1.5156 \\ 2.0208 \\ 2.5260 \\ 3.0312 \end{array}$	0.7173 1.0759 1.4345 1.7932 2.1518	$\begin{array}{c} 0.9652 \\ 0.9776 \\ 0.9897 \\ 1.0016 \\ 1.0132 \end{array}$	$\begin{array}{c} 0.2535 \\ 0.2618 \\ 0.2704 \\ 0.2789 \\ 0.2880 \end{array}$	$1.103 \\ 1.153 \\ 1.206 \\ 1.259 \\ 1.315$	$1.105 \\ 1.153 \\ 1.201 \\ 1.248 \\ 1.297$
60	$1.0 \\ 1.5 \\ 2.0 \\ 2.5 \\ 3.0$	0.7099 1.0648 1.4198 1.7747 2.1297	$\begin{array}{c} 1.0081 \\ 1.0201 \\ 1.0317 \\ 1.0433 \\ 1.0543 \end{array}$	$\begin{array}{c} 0.5046 \\ 0.5194 \\ 0.5348 \\ 0.5509 \\ 0.5677 \end{array}$	$1.090 \\ 1.136 \\ 1.183 \\ 1.232 \\ 1.283$	$1.089 \\ 1.133 \\ 1.179 \\ 1.225 \\ 1.274$	150	$\begin{array}{c} 1.0207 \\ 1.5310 \\ 2.0414 \\ 2.5518 \\ 3.0621 \end{array}$	0.7246 1.0869 1.4492 1.8115 2.1738	0.9445 0.9575 0.9702 0.9826 0.9948	$\begin{array}{c} 0.2130 \\ 0.2200 \\ 0.2274 \\ 0.2346 \\ 0.2421 \end{array}$	1.108 1.160 1.215 1.270 1.327 S.D. =	$1.110 \\ 1.160 \\ 1.208 \\ 1.256 \\ 1.306 \\ 0.63\%$
75 Density =	1.0019 1.5029 2.0039 2.5048 3.0058 = g./cc. v	0.7113 1.0669 1.4225 1.7782 2.1338 = kinemati	1.0001 1.0119 1.0234 1.0352 1.0460 c viscosity	0.4145 0.4268 0.4401 0.4535 0.4675 7, centistol	1.096 1.141 1.190 1.241 1.292 kes. $\eta_{R} = \eta_{R}$	1.093 1.139 1.185 1.231 1.280							

# LITERATURE DATA

The experimental technique developed to calculate viscosities of ternary mixtures was used to check the only other available data on ternary systems. Ruby and Kawai (13) measured viscosities in the ternary NaCl-KCl-H<sub>2</sub>O system at 25°C., and Ezrokhi (3) published data on this system at 25°, 40°, and 60° C. The data given by Ruby and Kawai were correlated with an average deviation of  $\pm 0.19\%$  and those of Ezrokhi with an average deviation of  $\pm 0.55\%$ up to an ionic strength of 3.0.

Unfortunately, available data on sea water viscosity cover only a narrow temperature and concentration range. Dorsey (1) summarized Krümmel's (8) data over the  $0^{\circ}$  to  $30^{\circ}$  C. temperature range for salinities from 5 to 40, and Myake and Koizumi (10) gave new results over the same temperature and concentration range. Their data are compared with the calculated results for the synthetic sea water in Table VII. The average deviation between the given and calculated data is  $\pm 0.21\%$ .

# CONCLUSIONS

Since all other data on the viscosity of sea water and its concentrates are estimated data, based on sodium chloride solutions of equivalent chloride content or on some other assumption, it is felt that the present measurements on calcium-free sea water represent the best available information, and Equations 10 can be used for the calculation of sea water viscosities. Deviations between calculated viscosities of the calcium-free sea water and calciumcontaining sea water were within the precision of the method. Table VIII gives the interpolated data on sea water and its concentrates as a function of chlorinity and salinity.

Additional tables on salt and sea water solutions containing density, vapor pressure, and viscosity data were prepared for the Office of Saline water (4).

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# **Thermal Properties of Propane**

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This contribution summarizes the results of an experimental investigation of the thermal properties of propane as part of a continuing effort to determine such properties for materials that are gases under normal conditions, light hydrocarbons, and their mixtures. New data on the isobaric heat capacity are presented. These data are compared with previously published experimental data in regions where such comparisons are possible. Published data on propane, including PVT determinations, isobaric heat capacity, latent heat, isothermal throttling coefficient, and Joule-Thomson data, were used together with the new data to determine values of enthalpy in the liquid, critical, super-critical, gaseous, and two-phase regions in the temperature range from  $-280^{\circ}$  to  $+300^{\circ}$  F., at pressures up to 2000 p.s.i.a. These results were checked for thermodynamic consistency and are believed to be accurate to better than 0.5%. The BWR equation of state was used, together with published data on isothermal enthalpy departures, to extend the upper limit of the tabulation of thermal properties to  $+500^{\circ}$  F. A table of enthalpy values is presented.

 $T_{ABLES}$  and charts of thermodynamic properties of propane have been published (2, 3, 4, 6, 18, 28, 32, 34, 38). The ranges in temperature and pressure covered by these published tables are indicated in Figure 1. The values of the thermal properties, enthalpy and entropy, presented in these tables were calculated using heat capacity data at low pressure and volumetric (PVT) data. This general procedure has been followed as there are few calorimetric data for propane at elevated pressures, with the exception of data on the latent heat of vaporization (6, 13, 30) and results of Joule-Thomson experiments (31).

Recently, results of direct experimental determinations of the effect of both pressure and temperature on the thermal properties of propane have been published (9, 12, 35, 37). These data extend over a considerable range of temperatures (-250° to +400° F.) at pressures up to 2000 p.s.i.a. However, information was sketchy in the regions near the critical point and in the vicinity of the two-phase regioni.e., where rapid changes in properties are encountered. Therefore, the purposes of this contribution are to present the results of experimental determinations in these regions and to summarize all published experimental data on the