Table V. X-Y Data for the 2,4-Dichloro Azo Cresol Compound in 75% Dioxane

[S], %	−log [S]	$-X$	$Y_{2,4\text{-dichloro}}$ $J = 1$	$J = 2$	$J = 3$	$J = 4$
55	0.2596	0.087				
60	0.2218	0.176	11.10	10.88	10.66	10.44
65	0.187	0.269	11.37	11.18	11.01	10.82
70	0.155	0.368	11.46	11.30	11.16	11.00
75	0.125	0.477	11.81	11.68	11.55	11.42

Table VI. Slopes of X-Y Relationship

substituent	slopes $J = 1$	$J = 2$	$J = 3$	$J = 4$
H	3.99	3.99	4.88	
p-CH_3		4.22	4.48	4.80
p-OCH_3		4.18	4.52	4.88
o-OCH_3		4.52	4.80	5.00
p-NO_2				4.52
p-Br	3.00	4.02	4.22	4.52
2,4-dichloro			4.12	

solvation is of minor importance. The obtained straight lines in most cases are the *J* values between 2 and 4.

Registry No. 2-Phenylazo-*p*-cresol, 952-47-6; 2-(*p*-nitrophenyl)azo-*p*-cresol, 1435-68-3; 2-(*p*-bromophenyl)azo-*p*-cresol, 26029-75-4; 2-(*p*-methylphenyl)azo-*p*-cresol, 17739-97-8; 2-(*p*-methoxyphenyl)azo-*p*-cresol, 15096-05-6; 2-(2,4-dichlorophenyl)azo-*p*-cresol, 19918-08-2; 2-(*o*-methoxyphenyl)azo-*p*-cresol, 15096-06-7.

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Densities of Aqueous NaCl, KCl, $MgCl_2$, and $CaCl_2$ Binary Solutions in the Concentration Range 0.5–6.1 *m* at 25, 30, 35, 40, and 45 °C

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The densities of the binary solutions NaCl–H_2O, KCl–H_2O, $MgCl_2$–H_2O, and $CaCl_2$–H_2O were measured at 1 atm, from 25 to 45 °C and from 0.5 to 6.1 *m*, by using a commercially available oscillating tube-type densitometer. The data sets were described by using least-squares polynomial regression analysis. Statistical evaluation of the experimental data indicates that uncertainties in the concentrations of the solutions due to adsorption of water by the salts during weighing is the major source of error in the density measurements. The magnitude of this error is greater for $MgCl_2$ and $CaCl_2$ solutions because of the hygroscopic nature of these salts. The measured densities of NaCl and KCl solutions have a standard deviation of 5.515×10^{-5} g/cm^3. Standard deviations for $MgCl_2$ and $CaCl_2$ solutions range from 2.329×10^{-4} to 2.334×10^{-4} g/cm^3 and from 2.796×10^{-4} to 2.839×10^{-4} g/cm^3, respectively. The experimental density data compare well with published values.

Introduction

Reliable experimental density data for aqueous binary salt solutions have important applications in geothermal energy and radioactive-waste-disposal research and technologies. The use of such data in fundamental thermodynamic calculations pertaining to the volumetric properties of brines is essential for accurate chemical modeling of complex geothermal brine systems. The Potter and Haas model (*1*) for calculating the density of a brine is one example of a predictive equation which requires precise experimental density data for binary systems. Raw experimental density data are available only for limited concentration ranges and temperature intervals. The diversity of experimental methods and the lack of a common system of units for reporting density data make meaningful comparisons between similar data sets somewhat difficult. This study has been undertaken to improve, as well as extend, the existing data base by providing internally consistent sets of density measurements at 1 atm, from 25 to 45 °C, for aqueous NaCl, KCl, $MgCl_2$, and $CaCl_2$ binary solutions with concentrations ranging from 0.5 to 6.1 *m*.

Experimental Method

We prepared the NaCl, KCl, and $CaCl_2$ solutions by weight using oven-dried (140 °C) reagent-grade chemicals and deionized water distilled with a Corning Mega-Pure automatic still. Because of particulate contamination, all $CaCl_2$ solutions were filtered after preparation. The $MgCl_2$ solutions were made by volumetrically diluting aliquots of a concentrated $MgCl_2$ stock solution. Formula weights used were 58.44, 74.55, 95.22, and 110.99 for NaCl, KCl, $MgCl_2$, and $CaCl_2$, respectively.

Table I. Results of Gravimetric Analyses of NaCl, $MgCl_2$, and $CaCl_2$ Solutions

soln no	wt. soln analyzed, g	wt. AgCl ppt, g	m
		NaCl	
1	3.08072	0.41481	0.99406
	3.07669	0.41572	0.99775
		$MgCl_2$	
1	2.79658	0.41304	0.5419
	2.79945	0.41204	0.5399
2	1.45871	0.41172	1.0866
	1.50903	0.42599	1.0868
3	0.98714	0.40016	1.6343
	0.98222	0.39679	1.6276
4	0.77302	0.40059	2.1838
	0.78070	0.40459	2.1840
5	0.68109	0.42551	2.7504
	0.69164	0.43209	2.7503
6	0.59808	0.43135	3.3089
	0.59936	0.43189	3.3051
		$CaCl_2$	
1	3.06539	0.38962	0.4630
	3.12432	0.39724	0.4631
2	1.62085	0.40002	0.9379
	1.53740	0.37578	0.9281
3	1.11396	0.37284	1.3138
	1.11144	0.37215	1.3143
4	0.88782	0.37706	1.7250
	0.93524	0.39674	1.7227
5	0.80665	0.40983	2.1324
	0.89964	0.45585	2.1256
6	0.67707	0.41506	2.6856
	0.67028	0.41103	2.6866
7	0.61891	0.41506	3.0103
	0.61158	0.41003	3.0092
8	0.62521	0.45205	3.3199
	0.61872	0.44714	3.3177
9	0.55960	0.43995	3.7123
	0.51015	0.40092	3.7104
10	0.52657	0.44254	4.0676
	0.49635	0.41732	4.0700
11	0.52756	0.47053	4.4216
	0.54946	0.48998	4.4206
12	0.40141	0.38057	4.8282
	0.41842	0.39680	4.8301
13	0.42387	0.41415	5.0468
	0.40044	0.39145	5.0504

The hygroscopic behavior of both $MgCl_2$ and $CaCl_2$ necessitated the precise determination of solute concentration. This was done gravimetrically by precipitation of chloride as silver chloride. A preliminary determination of the concentration of the 1.0 *m* NaCl solution verified the accuracy of this method. The results of the gravimetric analyses are given in Table I.

Density measurements were made with a Mettler/Paar DMA 55 digital readout calculating precision density meter, which operates on the basis of the oscillating-tube principle developed by Kratky et al. (*2*). The density, ρ, of a sample is calculated by the DMA according to the equation

$$\rho = (1/A)(T^2 - B) \tag{1}$$

where T = period of oscillation and A and B are apparatus constants which were determined for each experimental temperature by calibration with air and distilled-deionized water. The densities of pure water were taken from Kell (*3*).

A T-type (copper-constantan) thermocouple, calibrated against a platinum resistance thermometer, was used to monitor the temperature of the sample in the glass sample tube within the densitometer. The temperature within the sample tube was controlled to ±0.03 °C with a Neslab Exacal 300 bath circulator. This temperature variation corresponds to a density error of $\pm 1 \times 10^{-5}$ g/cm^3. To maintain experimental temperatures of 25, 30, and 35 °C, we used a Neslab Endocal 350 flow-through cooler in conjunction with the Exacal 300.

Results and Discussion

The measured densities of NaCl, KCl, $MgCl_2$, and $CaCl_2$ aqueous solutions are listed in Tables II–V, along with calcu-

Table II. Experimentally Determined NaCl Densities Compared with Those Calculated from Regression Equations

m	ρ expt. g/cm^3	ρ calc. g/cm^3	diff. (x10^{-5})	ρ expt. g/cm^3	ρ calc. g/cm^3	diff. (x10^{-5})	ρ expt. g/cm^3	ρ calc. g/cm^3	diff. (x10^{-5})
	25°C			30°C			35°C		
0.00	0.99700	0.99703	-3	0.99565	0.99567	-2	0.99403	0.99406	-3
1.00	1.03613	1.03605	+8	1.03441	1.03436	+5	1.03248	1.03243	+5
2.00	1.07211	1.07214	-3	1.07018	1.07018	0	1.06803	1.06801	+2
3.00	1.10557	1.10562	-5	1.10340	1.10346	-6	1.10101	1.10110	-9
4.00	1.13684	1.13685	-1	1.13453	1.13453	0	1.13202	1.13201	+1
5.00	1.16623	1.16617	+6	1.16376	1.16371	+5	1.16114	1.16106	+8
5.80	1.18848	1.18848	0	1.18594	1.18592	+2	1.18314	1.18316	-2
6.00	1.19390	1.19393	-3	1.19130	1.19133	-3	1.18850	1.18855	-5
6.10	1.19659	1.19663	-4	1.19401	1.19402	-1	1.19126	1.19123	+3
	40°C			45°C					
0.00	0.99220	0.99223	-3	0.99021	0.99024	-3			
1.00	1.03043	1.03035	+8	1.02824	1.02819	+5			
2.00	1.06572	1.06572	0	1.06342	1.06340	+2			
3.00	1.09857	1.09865	-8	1.09608	1.09617	-9			
4.00	1.12945	1.12945	0	1.12681	1.12682	-1			
5.00	1.15850	1.15841	+9	1.15578	1.15568	+10			
5.80	1.18042	1.18045	-3	1.17764	1.17768	-4			
6.00	1.18579	1.18583	-4	1.18298	1.18305	-7			
6.10	1.18854	1.18850	+4	1.18577	1.18572	+5			

Table III. Experimentally Determined KCl Densities Compared with Those Calculated from Regression Equations

m	ρ expt. g/cm^3	ρ calc. g/cm^3	diff. (x10^{-5})	ρ expt. g/cm^3	ρ calc. g/cm^3	diff. (x10^{-5})	ρ expt. g/cm^3	ρ calc. g/cm^3	diff. (x10^{-5})
	25°C			30°C			35°C		
0.00	0.99700	0.99704	-4	0.99565	0.99570	-5	0.99403	0.99407	-4
0.50	1.01977	1.01971	+6	1.01830	1.01823	+7	1.01653	1.01647	+6
1.00	1.04134	1.04131	+3	1.03972	1.03970	+2	1.03785	1.03782	+3
1.50	1.06189	1.06190	-1	1.06017	1.06018	-1	1.05820	1.05821	-1
2.00	1.08152	1.08156	-4	1.07970	1.07974	-4	1.07765	1.07768	-3
2.50	1.10031	1.10035	-4	1.09840	1.09844	-4	1.09627	1.09631	-4
3.00	1.11832	1.11833	-1	1.11633	1.11634	-1	1.11415	1.11416	-1
3.50	1.13562	1.13557	+5	1.13355	1.13351	+4	1.13132	1.13128	+4
4.00	1.15218	1.15215	+3	1.15007	1.15002	+5	1.14779	1.14775	+4
4.50	1.16808	1.16811	-3	1.16589	1.16593	-4	1.16358	1.16362	-4
	40°C			45°C					
0.00	0.99223	0.99228	-5	0.99022	0.99027	-5			
0.50	1.01466	1.01458	+8	1.01259	1.01250	+9			
1.00	1.03588	1.03586	+2	1.03372	1.03371	+1			
1.50	1.05614	1.05617	-3	1.05391	1.05396	-5			
2.00	1.07555	1.07557	-2	1.07330	1.07332	-2			
2.50	1.09410	1.09414	-4	1.09183	1.09184	-1			
3.00	1.11194	1.11193	+1	1.10959	1.10959	0			
3.50	1.12905	1.12901	+4	1.12665	1.12663	+2			
4.00	1.14547	1.14545	+2	1.14305	1.14303	+2			
4.50	1.16127	1.16130	-3	1.15883	1.15885	-2			

Table IV. Experimentally Determined $MgCl_2$ Densities Compared with Those Calculated from Regression Equations

m	ρ expt. g/cm^3	ρ calc. g/cm^3	diff. (x10^{-5})	ρ expt. g/cm^3	ρ calc. g/cm^3	diff. (x10^{-5})	ρ expt. g/cm^3	ρ calc. g/cm^3	diff. (x10^{-5})
	25°C			30°C			35°C		
0.00	0.99702	0.99709	-7	0.99565	0.99572	-7	0.99403	0.99410	-7
0.54	1.03795	1.03771	+24	1.03647	1.03623	+24	1.03477	1.03453	+24
1.09	1.07629	1.07657	-28	1.07473	1.07501	-28	1.07297	1.07325	-28
1.63	1.11249	1.11244	+5	1.11088	1.11082	+6	1.10909	1.10904	+5
2.18	1.14698	1.14685	+13	1.14531	1.14519	+12	1.14351	1.14340	+11
2.75	1.18039	1.18048	-9	1.17871	1.17879	-8	1.17691	1.17698	-7
3.31	1.21172	1.21170	+2	1.21002	1.21000	+2	1.20816	1.20815	+1
	40°C			45°C					
0.00	0.99223	0.99230	-7	0.99022	0.99029	-7			
0.54	1.03296	1.03272	+24	1.03097	1.03072	+25			
1.09	1.07116	1.07144	-28	1.06918	1.06945	-27			
1.63	1.10727	1.10722	+5	1.10529	1.10526	+3			
2.18	1.14169	1.14156	+13	1.13975	1.13964	+11			
2.75	1.17505	1.17513	-8	1.17317	1.17324	-7			
3.31	1.20632	1.20630	+2	1.20444	1.20444	0			

Table V. Experimentally Determined $CaCl_2$ Densities Compared with Those Calculated from Regression Equations

m	ρ expt. g/cm^3	ρ calc. g/cm^3	diff. (x10^{-5})	ρ expt. g/cm^3	ρ calc. g/cm^3	diff. (x10^{-5})	ρ expt. g/cm^3	ρ calc. g/cm^3	diff. (x10^{-5})
	25°C			30°C			35°C		
0.00	0.99702	0.99725	-23	0.99566	0.99587	-21	0.99403	0.99424	-21
0.46	1.03803	1.03775	+28	1.03647	1.03620	+27	1.03471	1.03442	+29
0.93	1.07742	1.07753	-11	1.07569	1.07581	-12	1.07376	1.07389	-13
1.31	1.10879	1.10855	+24	1.10691	1.10670	+21	1.10485	1.10466	+19
1.72	1.14122	1.14092	+30	1.13921	1.13893	+28	1.13706	1.13676	+30
2.13	1.17184	1.17220	-36	1.16974	1.17006	-32	1.16745	1.16778	-33
2.69	1.21288	1.21322	-34	1.21058	1.21090	-32	1.20813	1.20845	-32
3.01	1.23568	1.23582	-14	1.23327	1.23341	-14	1.23076	1.23086	-10
3.32	1.25706	1.25717	-11	1.25457	1.25465	-8	1.25193	1.25202	-9
3.71	1.28363	1.28327	+36	1.28094	1.28064	+30	1.27815	1.27789	+26
4.07	1.30697	1.30666	+31	1.30422	1.30392	+30	1.30138	1.30106	+32
4.42	1.32864	1.32879	-15	1.32578	1.32594	-16	1.32278	1.32296	-18
4.83	1.35419	1.35396	+23	1.35118	1.35099	+19	1.34808	1.34788	+20
5.05	1.36688	1.36715	-27	1.36386	1.36411	-25	1.36069	1.36094	-25
	40°C			45°C					
0.00	0.99223	0.99243	-20	0.99022	0.99040	-18			
0.46	1.03278	1.03251	+27	1.03069	1.03045	+24			
0.93	1.17175	1.07187	-12	1.06962	1.06976	-14			
1.31	1.10274	1.10256	+18	1.10059	1.10040	+19			
1.72	1.13486	1.13458	+28	1.13263	1.13235	+28			
2.13	1.16521	1.16552	-31	1.16292	1.16320	-28			
2.69	1.20577	1.20608	-31	1.20323	1.20362	-39			
3.01	1.22831	1.22842	-11	1.22587	1.22588	-1			
3.32	1.24943	1.24950	-7	1.24682	1.24688	-6			
3.71	1.27552	1.27527	+25	1.27276	1.27254	+22			
4.07	1.29863	1.29835	+28	1.29575	1.29551	+24			
4.42	1.31998	1.32016	-18	1.31707	1.31721	-14			
4.83	1.34521	1.34496	+25	1.34208	1.34188	+20			
5.05	1.35766	1.35795	-29	1.35454	1.35479	-25			

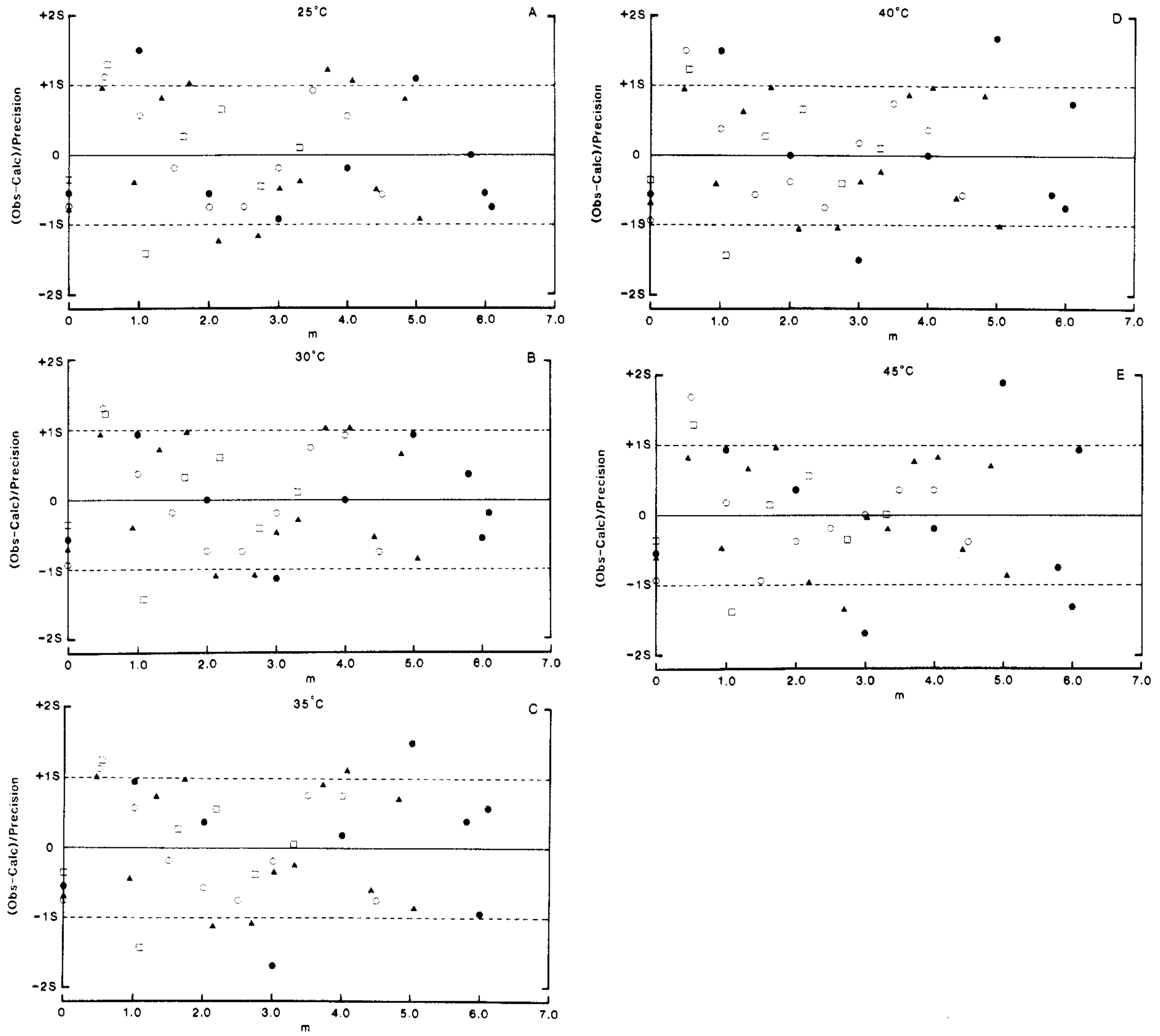

Figure 1. Error plots of (observed density - calculated density)/(precision of measurement) as a function of molality for each experimental temperature: NaCl (solid circles), KCl (open circles), $MgCl_2$ (open squares), $CaCl_2$ (solid triangles).

lated densities and deviations of measured values from calculated results. Each measured density value represents an average of several determinations. The calculated densities, d_{calcd} (g/cm^3), were obtained by a least-squares polynomial regression of experimental density values according to the equation

$$d_{\text{calcd}} = \sum_{0}^{i} a_i m^i \qquad (2)$$

where m is the molality of solution (mol of solute/kg of H_2O), a is a regression coefficient, and i is an integer. The regression coefficients are given in Table VI.

The measured densities of NaCl and KCl solutions have a standard deviation of 5.515×10^{-5} g/cm^3. This value was determined from replicate density measurements of 10 different 1.00 m NaCl solutions at 25 °C. Standard deviations for $MgCl_2$ and $CaCl_2$ solutions were calculated from the equation

$$\text{SD (g/cm}^3) = (A^2 + B^2)^{1/2} \qquad (3)$$

where A (g/cm^3) is the instrumental error and B (g/cm^3) is the estimated error in the density measurement due to uncertainty in the calculated molalities of $MgCl_2$ or $CaCl_2$ solutions. Standard deviations for $MgCl_2$ and $CaCl_2$ solutions range from 2.329×10^{-4} to 2.334×10^{-4} g/cm^3 and from 2.796×10^{-4} to 2.839×10^{-4} g/cm^3, respectively.

The instrumental error, A, was determined to be $\pm 1.4 \times 10^{-5}$ g/cm^3 for all solutions based on the reproducibility of density measurements of the 10 1.00 m NaCl solutions at 25 °C. The estimated concentration errors were found to be $\pm 3.6 \times 10^{-3}$ and $\pm 3.9 \times 10^{-3}$ m for $MgCl_2$ and $CaCl_2$ solutions, respectively. These numbers are the standard deviations of the differences in the duplicate gravimetric determinations of concentration (Table I). The value of B (in g/cm^3) is the product of the estimated error in concentration and the slope of the density/molality plot for a particular solution set at a given temperature. Errors in density values which may result from minor temperature fluctuations during measurement are included in the instrumental error. The instrumental error is assumed to remain constant in the temperature interval 25–45 °C and to be the same for all solutions studied in this experiment.

Error plots of the quantity (observed density - calculated density)/(precision of measurement) as a function of molality are presented in Figure 1 for each experimental temperature. Less than one-third of the points plot outside the bounds of one standard deviation ($\pm 1S$) and none exceed $\pm 2S$. This indicates that the magnitudes of the experimental errors are within the stated limits of experimental uncertainty and that the polynomial regression functions adequately describe the data.

The selection of the published data with which our experimental data were compared was based on the concentration ranges and temperatures examined. The annotated bibliography of Potter et al. (*4*) and the data compilation of Chapman and Newman (*5*) were extremely useful reference sources during the literature search. Our NaCl density data, from 1.0

Table VI. Regression Coefficients for Regression Equations

solutions	coefficients			
	a_0	a_1	a_2	a_3
NaCl (25°C)	0.9970305 (572)	0.0406103 (904)	-0.0016439 (369)	5.748×10^{-5} (401)
(30°C)	0.9956742 (449)	0.0402216 (694)	-0.0015931 (277)	5.408×10^{-5} (294)
(35°C)	0.9940550 (540)	0.0398756 (989)	-0.0015527 (394)	5.157×10^{-5} (420)
(40°C)	0.9922339 (718)	0.039591 (111)	-0.0015243 (442)	5.059×10^{-5} (470)
(45°C)	0.9902354 (758)	0.039435 (117)	-0.0015328 (467)	5.272×10^{-5} (497)
KCl (25°C)	0.9970434 (439)	0.0464489 (893)	-0.0022727 (477)	8.859×10^{-5} (696)
(30°C)	0.9956990 (479)	0.0461534 (975)	-0.0022407 (521)	8.685×10^{-5} (759)
(35°C)	0.9940742 (446)	0.0458643 (908)	-0.0021980 (485)	8.410×10^{-5} (708)
(40°C)	0.9922776 (441)	0.0456873 (898)	-0.0021906 (480)	8.545×10^{-5} (700)
(45°C)	0.9902688 (445)	0.0455295 (906)	-0.0021716 (484)	8.421×10^{-5} (705)
$MgCl_2$ (25°C)	0.997086 (226)	0.077625 (648)	-0.004540 (481)	2.046×10^{-4} (954)
(30°C)	0.995715 (223)	0.077403 (640)	-0.004491 (475)	2.010×10^{-4} (943)
(35°C)	0.994100 (224)	0.077180 (642)	-0.004389 (477)	1.840×10^{-4} (946)
(40°C)	0.992296 (225)	0.077190 (646)	-0.004408 (480)	1.875×10^{-4} (952)
(45°C)	0.990292 (221)	0.077181 (639)	-0.004380 (474)	1.838×10^{-4} (941)
$CaCl_2$ (25°C)	0.997245 (265)	0.089793 (461)	-0.003827 (213)	1.091×10^{-4} (273)
(30°C)	0.995869 (246)	0.089406 (427)	-0.003810 (197)	1.080×10^{-4} (253)
(35°C)	0.994241 (247)	0.089080 (430)	-0.003798 (199)	1.064×10^{-4} (254)
(40°C)	0.992431 (239)	0.088839 (415)	-0.003776 (192)	1.023×10^{-4} (246)
(45°C)	0.990398 (228)	0.088803 (397)	-0.003829 (184)	1.055×10^{-4} (235)

to 6.1 *m*, agree with the data of the International Critical Tables (*6*), Goncalves and Kestin (*7*), and Lengyel et al. (*8*) to within ±25 × 10^{-5}, ±41 × 10^{-5}, and ±34 × 10^{-5} g/cm^3, respectively. There is good agreement (to within ±16 × 10^{-5} g/cm^3) between our NaCl data and the pycnometric data of Fabuss and Korosi (*9*) (up to 2.0 *m*), Gucker et al. (*10*) (up to 1.0 *m*), and Stakhanova and Vasilev (*11*) (up to 3.0 *m*). Our data also agree well (to within ±19 × 10^{-5} g/cm^3) with the data of Potter and Brown (*12*), up to 4.0 *m*. However, at higher concentrations the data of Fabuss and Korosi (*9*) and Gucker et al. (*10*) deviate suddenly from our data in the direction of higher densities, whereas the data of Stakhanova and Vasilev (*11*) and Potter and Brown (*12*) diverge sharply in the direction of lower densities. It should be noted that the data of Potter and Brown (*12*) were obtained by a least-squares computer regression of experimental data rather than by experimentation.

Our KCl density data, from 0.5 to 4.5 *m*, agree with the data of the International Critical Tables (*6*), Lengyel et al. (*8*), Fabuss and Korosi (*9*), Gucker et al. (*10*), Kapustinskii (*13*), and Potter and Brown (*14*) to within ±26 × 10^{-5}, ±19 × 10^{-5}, ±32 × 10^{-5}, ±65 × 10^{-5}, ±29 × 10^{-5}, and ±36 × 10^{-5} g/cm^3, respectively. The data of Nickels and Allmand (*15*) are not in agreement (±462 × 10^{-5} g/cm^3) with our data. Our measured densities of KCl agree to within ±29 × 10^{-5} g/cm^3 with the data of Goncalves and Kestin except at 4.0 and 4.5 *m*; our values are 54 × 10^{-5} and 110 × 10^{-5} g/cm^3 higher, respectively. Our data for KCl agree to within ±25 × 10^{-5} g/cm^3 with the data of Firth and Tyrrell (*16*) at 35 °C, but at 45 °C agreement is limited (±105 × 10^{-5} g/cm^3). Representative density/molality plots for NaCl and KCl solutions are presented in Figures 2 and 3.

It is difficult to evaluate our experimental density values for $MgCl_2$ and $CaCl_2$ solutions because of the sparcity of published data, especially for concentrations above 1.0 *m*. Density/molality plots comparing our $MgCl_2$ and $CaCl_2$ density measurements with available literature values are presented in Figures 4–6. The $MgCl_2$ data of this investigation coincide with the data of the International Critical Tables (*6*), Phang and Stokes (*17*), Dunn (*18*), and Perron et al. (*19*) at lower concentrations (Figure 4) but diverge from published data (*6*, *17*) at higher concentrations in the directions of higher and lower densities, respectively. A similar trend is shown by our $CaCl_2$ density data. Our values agree with the data of Dunn (*18*), Perron et al. (*19*), Potter and Clynne (*20*), and Lyons and Riley (*21*) at low concentrations (Figure 5) but deviate from literature data (*20*, *21*) as molality increases. Our experimental density values for $CaCl_2$ at 30 °C are compared with the smoothed data of the International Critical Tables (*6*) and the aerometric data of Bogatykh and Evnovich (*22*) in Figure 6.

Impurities in the salts used, as well as the underestimation of the chloride in our concentrated $MgCl_2$ and $CaCl_2$ solutions, could account for the gradual deviation of our $MgCl_2$ and $CaCl_2$ density values from published data as molality increases. Because of high ionic strength of solution, the precipitation of silver chloride during the gravimetric analyses may have been incomplete. Insufficient accuracy in the density measurements of other workers might also explain the observed trend. However, the agreement between our $MgCl_2$ and $CaCl_2$ density data and published data at low concentrations, the consistency and comparability of our NaCl and KCl density data, and the ex-

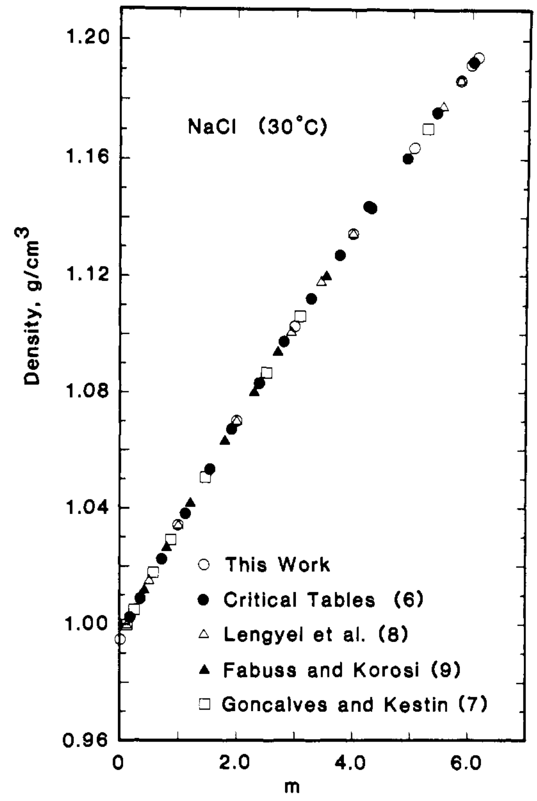

Figure 2. Comparison of density data for NaCl at 30 °C.

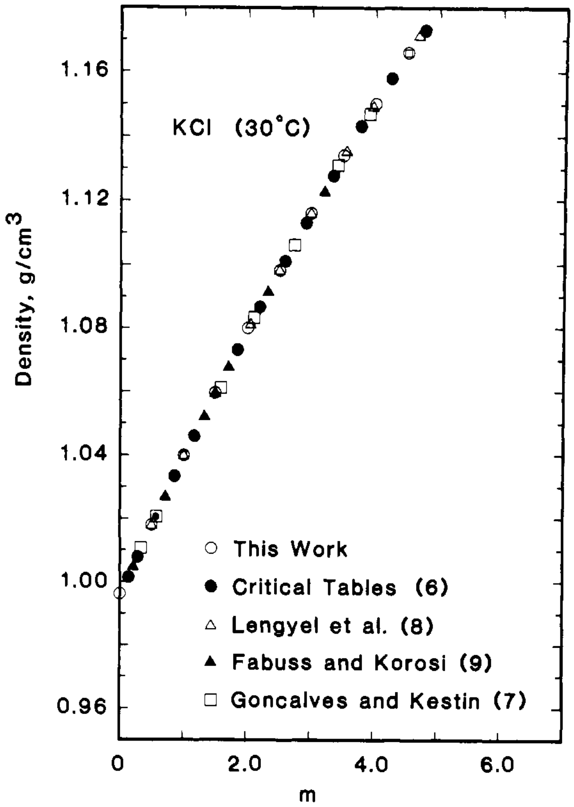

Figure 3. Comparison of density data for KCl at 30 °C.

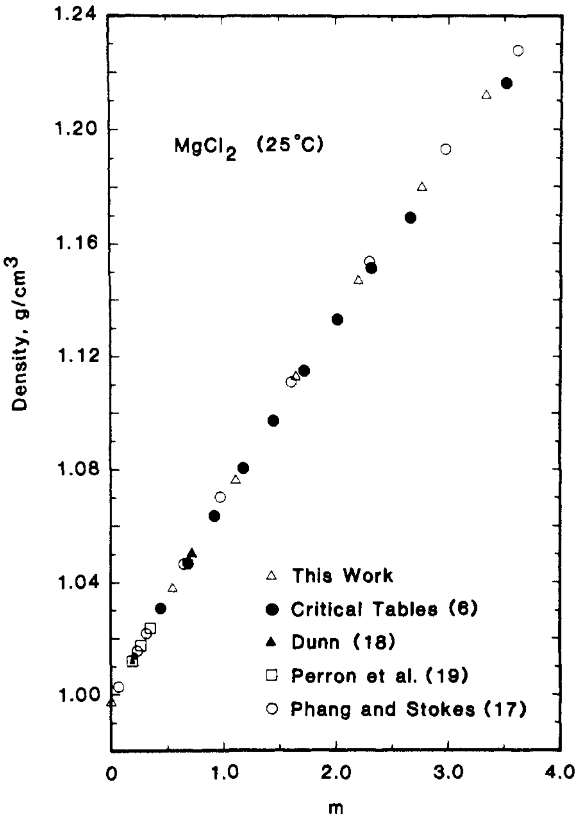

Figure 4. Comparison of density data for $MgCl_2$ at 25 °C.

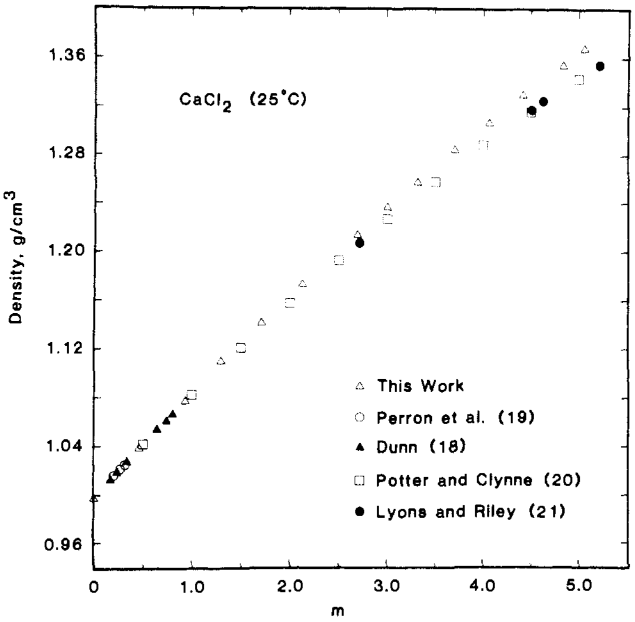

Figure 5. Comparison of density data for $CaCl_2$ at 25 °C. The data of the International Critical Tables (*6*), which are not shown, coincide with the data of Potter and Clynne (*20*).

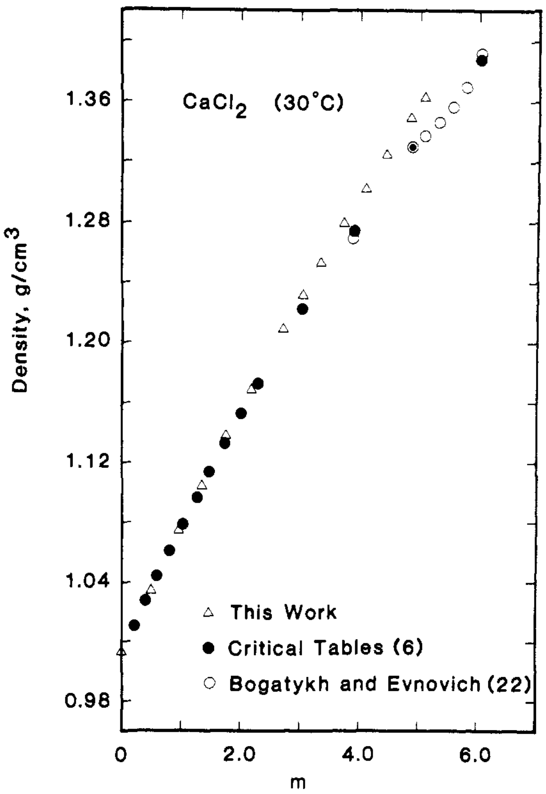

Figure 6. Comparison of density data for $CaCl_2$ at 30 °C.

cellent reproducibility of the gravimetric analyses suggest that our experimental method is accurate and that our density data are reliable.

Conclusions

The experimental density measurements for aqueous NaCl, KCl, $MgCl_2$, and $CaCl_2$ solutions reported in this paper supplement the available density data for binary salt solutions. Internally consistent sets of density data at 25, 30, 35, 40, and 45 °C are presented along with the results of least-squares regression analyses. It is important to note that the overall experimental precision is not determined solely by the instrumental error. The measured density of a given solution is also influenced by the accuracy to which the concentration of that solution can be determined. This is especially evident for $MgCl_2$ and $CaCl_2$ solutions. The addition of a remote cell to the densitometer in the near future will extend the range of possible density measurements to 150 °C and 6000 psi.

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Registry No. Sodium chloride, 7647-14-5; potassium chloride, 7447-40-7; magnesium chloride, 7786-30-3; calcium chloride, 10043-52-4.

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Densities, Viscosities, Refractive Indices, and Molar Refractions of the Binary System Tetraethylene Glycol Dimethyl Ether–Water at 25 °C

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Densities, viscosities, and refractive indices of tetraethylene glycol dimethyl ether and water solutions have been determined at 25.00 °C as part of a study of binary solvent systems. These data as well as the molar refractions and partial molal volumes are presented. The refractive indices of the solutions increase sharply, with increasing ether mole fraction, from the value of pure water to 0.20 mole fraction of ether and then they increase at a slower rate to the value for the pure ether. The partial molal volume of the ether passes through a minimum, which is about 8% less than the ideal molal volume, at 0.0075 mole fraction of ether. The viscosity exhibits a maximum at about 0.14 mole fraction of ether.

Introduction

As part of research designed to investigate physiochemical properties of binary solvent systems, the properties of density, viscosity, and refractive index have been determined for mixtures of tetraethylene glycol dimethyl ether and water at 25.00 °C. Also reported are the calculated molar refractions, partial molal volumes, and water–ether oxygen ratio.

Experimental Section

Technical-grade tetraethylene glycol dimethyl ether (Ansul Chemical Co., Ansul E-181) was distilled from sodium under a pressure of 6 mmHg at 115 °C. A controlled amount of nitrogen was bubbled through the boiling ether. Ether distilled under these conditions contains less than 0.01% water as measured by the Karl Fisher reagent and gave a negative peroxide test. At 25.00 °C the ether had a refractive index (n^{25}_D) of 1.4332 and a density (d^{25}_4) of 1.0047 compared with the respective values of 1.4320 and 1.0090 (*1*). Water used for the solutions was distilled from deionized water in a closed-system distilling apparatus. Solutions were prepared in 50-g samples by weighing the liquids to the nearest tenth of a milligram.

Densities were determined at 25.00 °C with an Ostwald pycnometer of 2.9404-mL capacity. Triplicate measurements were identical within ±0.0009 g/mL.

Table I. Densities, Viscosities, and Partial Molal Volumes of Water–Tetraethylene Glycol Dimethyl Ether at 25 °C

				partial molal vol, mL	
X_2[a]	W_2,[b] %	d^{25}_4-(obsd)[c]	viscosity, cP	V_2[d]	V_1[e]
0.0000	0.0000	0.9971	0.8937	203.94	18.09
0.0075	8.54	1.0033	1.323	203.41	18.09
0.0142	15.12	1.0090	1.533	203.61	18.08
0.0297	27.39	1.0190	2.433	205.33	18.04
0.0419	35.06	1.0253	3.198	206.98	17.98
0.0593	43.74	1.0323	4.289	209.27	17.86
0.0784	51.23	1.0359	5.240	211.42	17.70
0.1139	61.34	1.0368	6.253	214.38	17.39
0.1398	66.73	1.0360	6.469	215.88	17.18
0.1543	69.25	1.0351	6.411	216.58	17.05
0.1672	71.24	1.0350	6.408	217.08	16.96
0.1972	75.19	1.0309	6.200	218.05	16.74
0.2273	78.40	1.0301	5.915	218.77	16.55
0.3237	85.52	1.0243	5.112	220.09	16.06
0.4635	91.42	1.0169	4.334	220.86	15.58
0.5569	93.94	1.0151	4.179	221.08	15.36
0.6402	95.65	1.0119	3.780	221.19	15.20
0.7613	97.52	1.0078	3.495	221.27	15.02
0.8245	98.30	1.0073	3.443	221.29	14.93
1.0000	100.00	1.0047	3.295	221.31	14.76

[a] X_2 is the mole fraction of the ether. [b] W_2 is the weight percent of the ether. [c] d^{25}_4(obsd) is the observed density of the solution in g/mL. [d] For the ether. [e] For water.

Viscosities were determined at 25.00 °C with an Ubbelohde viscometer. Flow times were reproducible within ±0.0035 min for flow times ranging from 1.5 to 11 min.

Table I shows the densities, the viscosities, and the partial molal volumes with solution composition given both as mole fraction of ether (X_2) and as weight percent of the ether (W_2).

Refractive indices were measured with a separate set of solutions at 25.00 ± 0.01 °C with a Bausch and Lomb refractometer, Abbe type, using the sodium D line. Readings were reproducible within ±0.0002.

Table II shows refractive indices and molar refractions with solution composition given as mole fraction of tetraethylene glycol dimethyl ether (X_2). Also presented are the density data

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