Activity Coefficients of KCl in Several Mixed Electrolyte Solutions at 25°C

PETER G. CHRISTENSON[1] and JORIS M. GIESKES
Scripps Institution of Oceanography, La Jolla, Calif. 92037

The mean activity coefficients of KCl in aqueous $MgCl_2$, $CaCl_2$, $BaCl_2$, $MgSO_4$, and K_2SO_4 mixtures have been calculated from emf measurements at 25°C, all at a total ionic strength of 1. Results for the $CaCl_2$ and $BaCl_2$ systems agree with those reported using isopiestic measurements. The activity coefficients of KCl follow Harned's rule in $MgCl_2$, deviate very slightly from linearity in $CaCl_2$ and $BaCl_2$, and display large curvatures in $MgSO_4$ and K_2SO_4 solutions at this ionic strength.

This study was undertaken to determine the mean ionic activity coefficient behavior of KCl in several aqueous mixed electrolyte solutions using cationic glass and Ag–AgCl electrodes. Systems studied were $KCl–MgCl_2–H_2O$, $KCl–MgSO_4–H_2O$, $KCl–K_2SO_4–H_2O$, $KCl–CaCl_2–H_2O$, and $KCl–BaCl_2–H_2O$, all at a total ionic strength of 1 at 25° C. Other investigators have used the isopiestic method to study the systems containing $CaCl_2$ (*5*) and $BaCl_2$ (*4*).

EXPERIMENTAL

Reagents. Deionized, doubly distilled water was used in all solutions. KCl, $BaCl_2$, $CaCl_2$, and $MgCl_2$ were recrystallized from water after treating the aqueous solutions with chlorine gas to remove any trace impurities of Br^- and I^-. KCl solutions, 1*m*, were made up by weight and saturated with AgCl. The 0.3333*m* $MgCl_2$, $BaCl_2$, and $CaCl_2$ solutions were analyzed for Cl^- using $AgNO_3$ with dichlorofluorescein as an adsorption indicator. The 0.3333*m* K_2SO_4 solutions were made up by weight from reagent powder. The 0.2500*m* $MgSO_4$ solutions were analyzed with standardized Na_2EDTA using Erio Black T indicator. The three or four replicates of each analysis agreed to better than 0.1%. The pH of all solutions was greater than 5.2.

Method. Temperature was maintained at 25.000 ● 0.007°C. The procedure for obtaining potentials was very similar to the one used by Gieskes (*1*) in his study of NaCl in mixed electrolytes. Beckman No. 39137 cationic glass electrodes and Beckman Ag–AgCl electrodes were used in all measurements. Ag–AgCl electrodes were prepared electrolytically according to (*3*). Several different pairs of electrodes were used to collect data on each of the mixed electrolyte systems in order to get a true estimate of the precision of the method. The cell potentials were measured with a Leeds and Northrup K-5 potentiometer connected to a Keithley 640 electrometer and 370 recorder.

The Nernst slope, *S*, of each pair of electrodes was determined by making several successive dilutions of a 1*m* KCl solution with water. The slope was checked before and after a mixed electrolyte was run and agreement was always within 0.3%. Activity coefficients for these KCl solutions were taken from (*6*). Only electrodes which gave an average Nernst slope of 118.3 ± 1.0 mV were accepted, these slopes are listed in Table I.

Several successive dilutions of the 1*m* KCl solution with the other salt solution were then made. From these dilutions the mean ionic activity coefficient of KCl was calculated according to

$$\log [\gamma_1]_{i+1} = \Delta E/S - \frac{1}{2} \log \left(\frac{[m_K m_{Cl}]_{i+1}}{[m_K m_{Cl} \gamma_1^2]_i} \right) \quad (1)$$

Response time of the electrodes varied from 5 to 15 min, after which the drift became linear with time and less than 60 μV/hr. The true potential was obtained by extrapolating along the constant drift line to the time of the dilution. Overall precision of the emf measurements is about ±15 μV.

RESULTS AND DISCUSSION

Results are tabulated in Table I. Mean activity coefficients as a function of ionic strength contributions of both salts are plotted in Figures 1 and 2. These results are fitted to the "Harned's Rule" (*2, 6*) equation

$$\log \gamma_1 = \log \gamma_1^\circ - \alpha_{12}\mu_2 \quad (2)$$

and also to the second-order equation

$$\log \gamma_1 = \log \gamma_1^\circ - \alpha_{12}\mu_2 - \beta_{12}\mu_2^2 \quad (3)$$

by the method of least squares. The points are weighted according to their scatter by the weighting function

$$\omega_j = 10^{-5}/[0.0005 + 0.0015\, \mu_{1(j)}]^2 \quad (4)$$

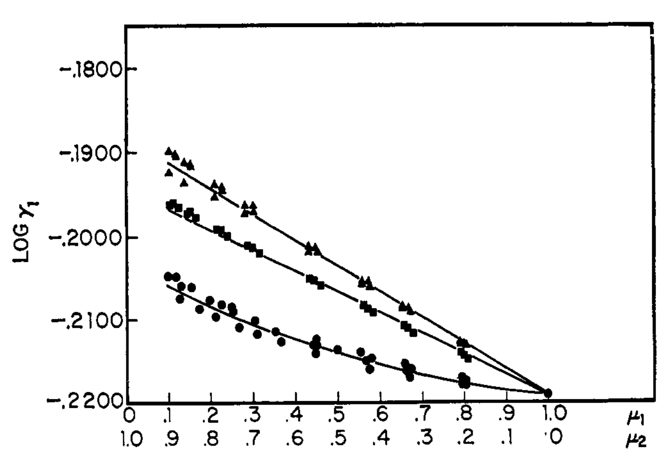

Figure 1. Mean activity coefficients of KCl

▲ $KCl–MgCl_2–H_2O$
■ $KCl–CaCl_2–H_2O$
● $KCl–MgSO_4–H_2O$

[1] To whom correspondence should be addressed.

Table I. Mean Activity Coefficients of KCl

$KCl-MgCl_2-H_2O$

Series 1, $S = 117.9$			Series 2, $S = 117.9$			Series 3, $S = 118.7$			Series 4, $S = 118.7$		
m_K	m_{Cl}	$-\log \gamma_1$	m_K	m_{Cl}	$-\log \gamma_1$	m_K	m_{Cl}	$-\log \gamma_1$	m_K	m_{Cl}	$-\log \gamma_1$
1.0000	1.0000	0.2190	1.0000	1.0000	0.2190	1.0000	1.0000	0.2190	1.0000	1.0000	0.2190
0.8018	0.9339	0.2129	0.7908	0.9303	0.2130	0.7910	0.9303	0.2127	0.8040	0.9347	0.2131
0.6692	0.8897	0.2087	0.6540	0.8847	0.2089	0.6542	0.8848	0.2085	0.6722	0.8908	0.2091
0.5742	0.8581	0.2055	0.5574	0.8526	0.2059	0.5578	0.8526	0.2054	0.5776	0.8592	0.2061
0.4473	0.8157	0.2013	0.4305	0.8102	0.2019	0.4308	0.8103	0.2013	0.4507	0.8169	0.2019
0.3023	0.7654	0.1964	0.2816	0.7605	0.1973	0.2819	0.7607	0.1964	0.3022	0.7674	0.1970
0.2283	0.7428	0.1941	0.2092	0.7390	0.1959	0.2095	0.7365	0.1938	0.2273	0.7425	0.1944
0.1545	0.7182	0.1917	0.1377	0.7143	0.1936	0.1385	0.7128	0.1912	0.1527	0.7176	0.1917
0.1167	0.7056	0.1905	0.1026	0.7021	0.1924	0.1035	0.7011	0.1899	0.1150	0.7050	0.1903

$KCl-CaCl_2-H_2O$

Series 1, $S = 118.8$			Series 2, $S = 118.8$			Series 3, $S = 118.7$		
m_K	m_{Cl}	$-\log \gamma_1$	m_K	m_{Cl}	$-\log \gamma_1$	m_K	m_{Cl}	$-\log \gamma_1$
1.0000	1.0000	0.2190	1.0000	1.0000	0.2190	1.0000	1.0000	0.2190
0.8000	0.9333	0.2143	0.8096	0.9365	0.2147	0.7935	0.9312	0.2141
0.6666	0.8889	0.2110	0.6801	0.8934	0.2115	0.6577	0.8859	0.2107
0.5714	0.8571	0.2086	0.5863	0.8621	0.2091	0.5616	0.8539	0.2083
0.4444	0.8148	0.2053	0.4595	0.8199	0.2059	0.4345	0.8115	0.2051
0.2987	0.7663	0.2013	0.3160	0.7720	0.2020	0.2883	0.7628	0.2011
0.2250	0.7417	0.1992	0.2407	0.7469	0.1999	0.2157	0.7386	0.1991
0.1515	0.7172	0.1970	0.1658	0.7219	0.1977	0.1435	0.7145	0.1971
0.1143	0.7048	0.1959	0.1265	0.7088	0.1965	0.1075	0.7025	0.1961

$KCl-BaCl_2-H_2O$

Series 1, $S = 118.9$			Series 2, $S = 118.9$			Series 3, $S = 118.9$		
m_K	m_{Cl}	$-\log \gamma_1$	m_K	m_{Cl}	$-\log \gamma_1$	m_K	m_{Cl}	$-\log \gamma_1$
1.0000	1.0000	0.2190	1.0000	1.0000	0.2190	1.0000	1.0000	0.2190
0.7943	0.9314	0.2169	0.8001	0.9333	0.2170	0.8014	0.9338	0.2171
0.6588	0.8863	0.2155	0.6667	0.8889	0.2157	0.6686	0.8895	0.2156
0.5628	0.8542	0.2143	0.5715	0.8571	0.2147	0.5736	0.8578	0.2146
0.4358	0.8119	0.2128	0.4445	0.8148	0.2133	0.4466	0.8155	0.2132
0.2887	0.7629	0.2109	0.2993	0.7665	0.2113	0.3004	0.7668	0.2112
0.2158	0.7386	0.2099	0.2256	0.7419	0.2103	0.2263	0.7421	0.2103
0.1499	0.7166	0.2087	0.1569	0.7189	0.2092	0.1525	0.7175	0.2092
0.1148	0.7049	0.2082	0.1202	0.7067	0.2087	0.1150	0.7050	0.2086

$KCl-K_2SO_4-H_2O$

Series 1, $S = 117.5$			Series 2, $S = 117.4$			Series 3, $S = 118.8$		
m_K	m_{Cl}	$-\log \gamma_1$	m_K	m_{Cl}	$-\log \gamma_1$	m_K	m_{Cl}	$-\log \gamma_1$
1.0000	1.0000	0.2190	1.0000	1.0000	0.2190	1.0000	1.0000	0.2190
0.9361	0.8083	0.2231	0.9364	0.8091	0.2235	0.9364	0.8093	0.2237
0.8928	0.6783	0.2264	0.8931	0.6795	0.2268	0.8932	0.6797	0.2274
0.8614	0.5844	0.2291	0.8619	0.5856	0.2296	0.8619	0.5859	0.2303
0.8192	0.4576	0.2333	0.8196	0.4589	0.2341	0.8197	0.4591	0.2344
0.7711	0.3135	0.2384	0.7695	0.3086	0.2398	0.7707	0.3121	0.2394
0.7461	0.2385	0.2413	0.7441	0.2324	0.2429	0.7455	0.2365	0.2421
0.7211	0.1635	0.2445	0.7187	0.1563	0.2463	0.7203	0.1610	0.2450
0.7081	0.1245	0.2464	0.7059	0.1178	0.2481	0.7073	0.1220	0.2465

$KCl-MgSO_4-H_2O$

Series 1, $S = 118.8$			Series 2, $S = 118.9$			Series 3, $S = 118.9$		
m_K	m_{Cl}	$-\log \gamma_1$	m_K	m_{Cl}	$-\log \gamma_1$	m_K	m_{Cl}	$-\log \gamma_1$
1.0000	1.0000	0.2190	1.0000	1.0000	0.2190	1.0000	1.0000	0.2190
0.8013	0.8013	0.2181	0.7983	0.7983	0.2175	0.7969	0.7969	0.2178
0.6685	0.6685	0.2171	0.6643	0.6643	0.2161	0.6624	0.6624	0.2162
0.5734	0.5734	0.2160	0.4973	0.4973	0.2136	0.5667	0.5667	0.2150
0.4465	0.4465	0.2142	0.2489	0.2489	0.2087	0.4397	0.4397	0.2130
0.3649	0.3649	0.2127				0.3523	0.3523	0.2116
0.3086	0.3086	0.2118				0.2521	0.2521	0.2091
0.2673	0.2673	0.2110				0.1962	0.1962	0.2076
0.2109	0.2109	0.2097				0.1320	0.1320	0.2059
0.1726	0.1726	0.2088				0.0994	0.0994	0.2047
0.1267	0.1267	0.2075						

(*Continued on next page*)

Table I. (*Continued*)

KCl–$MgSO_4$–H_2O (*Continued*)

Series 4, S = 118.8			Series 5, S = 117.9		
m_K	m_{Cl}	$-\log \gamma_1$	m_K	m_{Cl}	$-\log \gamma_1$
1.0000	1.0000	0.2190	1.0000	1.0000	0.2190
0.8035	0.8035	0.2175	0.7941	0.7941	0.2171
0.6715	0.6715	0.2160	0.6584	0.6584	0.2153
0.5767	0.5767	0.2148	0.5624	0.5624	0.2140
0.4498	0.4498	0.2131	0.4467	0.4467	0.2125
0.3035	0.3035	0.2100			
0.2290	0.2290	0.2082			
0.1539	0.1539	0.2061			
0.1159	0.1159	0.2048			

Table II. Parameters for Equations 2 and 3

System	Parameters for Eq. 2			Parameters for Eq. 3				
	α_{12}	$\sigma_{\alpha_{12}}$	$\Sigma\omega_j R_j^2$	α_{12}	$\sigma_{\alpha_{12}}$	β_{12}	$\sigma_{\beta_{12}}$	$\Sigma\omega_j R_j^2$
KCl–$MgCl_2$–H_2O	−0.0312	0.0002	7.0×10^{-5}	−0.0297	0.0006	−0.0022	0.0009	5.8×10^{-5}
KCl–$CaCl_2$–H_2O	−0.0250 (−0.0251)[a]	0.0002	2.5×10^{-5}	−0.0225	0.0002	−0.0037	0.0002	1.8×10^{-6}
KCl–$MgSO_4$–H_2O	−0.0117	0.0005	4.1×10^{-4}	−0.0044	0.0007	−0.0114	0.0011	9.9×10^{-5}
KCl–$BaCl_2$–H_2O	−0.0111 (−0.008)[b]	0.0002	2.1×10^{-5}	−0.0089	0.0002	−0.0033	0.0002	2.2×10^{-6}
KCl–K_2SO_4–H_2O	0.0290	0.0006	3.2×10^{-4}	0.0205	0.0007	0.0129	0.0010	3.5×10^{-5}

[a] From Robinson and Covington (*5*). [b] From Robinson and Bower (*4*).

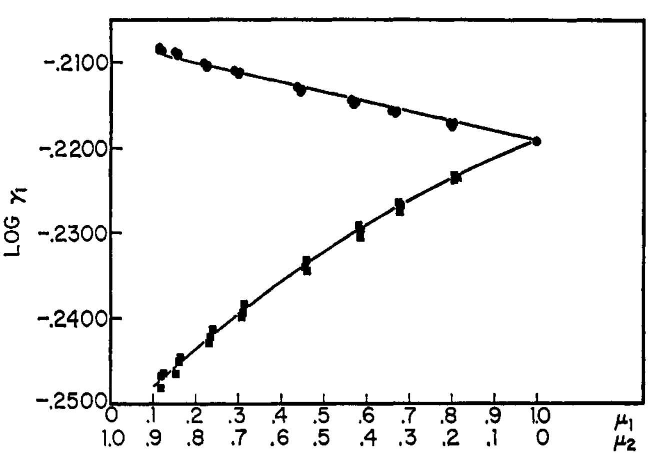

Figure 2. Mean activity coefficients of KCl

● KCl–$BaCl_2$–H_2O
■ KCl–K_2SO_4–H_2O

where the denominator represents an estimate of the variance of the jth point, and the numerator normalizes the weights to values near unity. Thus the quantity to be minimized in the least squares procedure is $\Sigma_j\omega_j R_j^2$. Values of the parameters for Equations 2 and 3 are given in Table II, together with sums of weighted residuals, standard deviations, and available published values obtained by the isopiestic method.

As can be seen from Figures 1 and 2, the activity coefficients of KCl in $MgCl_2$ follow Harned's Rule at $\mu = 1$. Slight curvatures in the $BaCl_2$ and $CaCl_2$ systems suggest real, but very small deviations from Harned's Rule. In these two systems, the first-order fit is probably sufficient for most uses.

Large curvatures in the $MgSO_4$ and K_2SO_4 systems show that in these the activity coefficient of KCl does not follow Harned's Rule at $\mu = 1$. Part of the curvatures in these plots may be due to formation of $MgSO_4^{\circ}$ and KSO_4^- ion pairs.

NOMENCLATURE

ΔE = change in potential in millivolts resulting from changing $[m_K m_{Cl}]_i$ to $[m_K m_{Cl}]_{i+1}$
γ_1 = mean activity coefficient of KCl
γ_1° = mean activity coefficient of KCl in pure KCl solution
m = molality, moles solute per kilogram H_2O
μ = total ionic strength
μ_1 = ionic strength contribution of KCl
μ_2 = ionic strength contribution of the other salt
R_j = residual of the jth point
S = Nernst slope of the electrode pair, in millivolts
σ = standard deviation of a parameter computed by least squares
ω_j = weight assigned to the jth point

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