Thermodynamic Study of the Aqueous (KCl + K_2SO_4) Electrolyte Based on Potassium Amalgam Electrode Cells

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The thermodynamic behavior of the aqueous KCl + K_2SO_4 electrolyte has been studied on the basis of potential difference measurements on the reversible cell K-amalgam|KCl (m_{KCl}) + K_2SO_4 ($m_{K_2SO_4}$) |AgCl|Ag|Pt. The mean molal activity coefficients γ_{KCl} of KCl at molalities m_{KCl} and $\gamma_{K_2SO_4}$ of K_2SO_4 at $m_{K_2SO_4}$ in (KCl + K_2SO_4) mixtures have been determined at various constant values of total ionic strengths I of the mixed electrolyte studied. It has been found that log(γ_{KCl}) is a linear function of m_{KCl} at each constant ionic strength studied, thus obeying Harned's rule. The corresponding trace activity coefficients, $\gamma_{(0)KCl}$, vary linearly with log I. Using Pitzer's scheme of equations has allowed fair reproduction of the experimental activity coefficients γ_{KCl} for I values ≥ 0.5 mol·kg^{-1} and the evaluation of $\gamma_{K_2SO_4}$ in the same range.

Introduction

As outlined by Robinson and Stokes,[1] one very accurate method of studying the thermodynamics of mixed electrolytes uses reversible cells of the type

$$\mathrm{Pt}|\mathrm{H_2}|\mathrm{HX}\ (m_1) + \mathrm{MX}\ (m_2)|\mathrm{AgX}|\mathrm{Ag}|\mathrm{Pt} \qquad (1)$$

where X = halide anion, M = alkali cation, and the silver halide electrode may be replaced by the mercurous halide or the thallous halide electrode. By the cell in (1), a great deal of (hydrohalic acid + alkali halide) binary mixtures have been studied by various schools. When the system studied consists of a binary mixture MX + MY of the same cation M with different halide anions X and Y, an M-amalgam electrode cells replaces (1)

$$\mathrm{Pt}|\mathrm{M\text{-}amalgam}|\mathrm{MX}\ (m_1) + \mathrm{MY}\ (m_2)|\mathrm{AgX}|\mathrm{Ag}|\mathrm{Pt} \qquad (2)$$

However, the complicated operation of an amalgam electrode cell has somewhat discouraged the use of cells of type (2), and some electroanalysts have instead used the following nonreversible variant of the cell in (2) where a M^+-selective membrane electrode (ISE) replaces the M-amalgam electrode

$$\mathrm{Pt}|\mathrm{M^+\text{-}ISE}|\mathrm{MX}\,(m_1) + \mathrm{MY}\ (m_2)|\mathrm{AgX}|\mathrm{Ag}|\mathrm{Pt} \qquad (3)$$

Of course, using a nonthermodynamic half cell as the M^+-ISE one (definitionally characterized by the irreversible diffusional process originating the membrane potential) is conceptually at variance with the purpose of the thermodynamic functions being investigated, even if in recent times good results have been obtained working with appropriately calibrated membrane electrodes. Therefore, for the conceptual thermodynamic correctness and quality of results, the use of reversible electrodes should definitely be recommended and, whenever the appropriate M-amalgam electrodes are available, these should be preferred to the M^+-ISEs.

The system investigated in the present study is the KCl + K_2SO_4 mixture, composed by one symmetrical and one unsymmetrical valence electrolyte, using the reversible cell (4)

$$\mathrm{Pt}|\mathrm{K}_x\mathrm{Hg}_{1-x}|\mathrm{KCl}\ (m_{\mathrm{KCl}}) + \mathrm{K_2SO_4}\ (m_{\mathrm{K_2SO_4}})|\mathrm{AgCl}|\mathrm{Ag}|\mathrm{Pt} \qquad (4)$$

comprising a flowing dilute potassium-amalgam electrode and a silver chloride electrode. The KCl + K_2SO_4 system has already been considered by Christenson and Gieskes[2] and, more recently, by Chen and Yang,[3] using a nonreversible cell where the K-amalgam electrode was replaced by a K^+-ISE.

The potential difference E of the key cell in (4) is a function of the molalities m_{K+} of K^+ cation and m_{Cl}- of Cl^- anion according to the Nernstian expression

$$E = E°\{\mathrm{Ag}|\mathrm{AgCl}|\mathrm{Cl^-}\} - E°\{\mathrm{K^+}|\mathrm{K(Hg)}\} + k\ \log(xf)_{\mathrm{K}} - k\ \log(m_{\mathrm{Cl^-}}\gamma_{\mathrm{Cl^-}}\, m_{\mathrm{K^+}}\gamma_{\mathrm{K^+}}) = E° + k\ \log(xf)_{\mathrm{K}} - k\ \log[m_{\mathrm{KCl}}(m_{\mathrm{KCl}} + 2m\, m_{\mathrm{K_2SO_4}})(\gamma_{\mathrm{KCl}})^2]$$

$$= \Phi° - k\ \log[m_{\mathrm{KCl}}\,(m_{\mathrm{KCl}} + 2m_{\mathrm{K_2SO_4}})\ (\gamma_{\mathrm{KCl}})^2] \qquad (5)$$

where $\gamma_{KCl} = (\gamma_{K^+}\,\gamma_{Cl^-})^{1/2}$ = mean molal activity coefficient of KCl in admixture with K_2SO_4, k = (ln10)RT/F, R = molar gas constant, F = Faraday's constant, T = thermodynamic temperature, $E° = E°\{\mathrm{Ag}|\mathrm{AgCl}|\mathrm{Cl^-}\} - E°\{\mathrm{K^+}|\mathrm{K(Hg)}\}$ = standard potential difference of cell, $m_{K+} = m_{KCl} + 2m_{K_2SO_4}$, m_{Cl}- = m_{KCl}, and f = rational activity coefficient of K metal in amalgam at mole fraction x and activity a, based on the standard state implying $f = a/x \rightarrow 1$ as $x \rightarrow 0$ (Henry's law). For dilute amalgams such as those used in the K^+/K-amalgams used here, the following relation holds:

$$\log f = Qx \qquad (6)$$

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where Q is a constant, specific for each alkali metal and alkaline-earth metal in dilute amalgam, independent of x and T, whose values were determined critically by Mussini et al.[4] The standard potential difference $E°$ can be determined from separate measurements (using the same electrode pair as that of the cell in (4)) of the potential difference E_7 of the cell in (7)

$$\mathrm{Pt}|\mathrm{K}_x\mathrm{Hg}_{1-x}|\mathrm{KCl}\ (m°)|\mathrm{AgCl}|\mathrm{Ag}|\mathrm{Pt} \tag{7}$$

whose Nernstian expression is

$$E_7 = E°\{\mathrm{Ag}|\mathrm{AgCl}|\mathrm{Cl}^-\} - E°\{\mathrm{K}^+|\mathrm{K(Hg)}\} + k\log(xf)_{\mathrm{K}} - 2k\log(m°\gamma°)_{\mathrm{KCl}} =$$

$$= E° + k\,[\log x + Qx]_{\mathrm{K}} - 2k\log(m°\gamma°)_{\mathrm{KCl}} = \Phi° - 2k\log(m°\gamma°)_{\mathrm{KCl}} \tag{8}$$

However, to practically and accurately standardize the cell in (4), it would not be strictly required to perform the time-consuming double-extrapolation procedure described earlier[3] aimed at obtaining $E°$, but rather the indirect method introduced by Bates et al.[5,6] and recently applied to other amalgam electrodes[7] can be used advantageously. This is based on using known accurate values of the $\gamma°_{\mathrm{KCl}}$ activity coefficients as a function of $m°_{\mathrm{KCl}}$[8] and is aimed to obtaining the equally well-behaved function $\Phi°$ (which includes the function of the potassium mole fraction x in amalgam) for each pair of freshly prepared such electrodes. Thus, measuring E_7 at a selected $m°_{\mathrm{KCl}}$ (and at the same mole fraction x used in the cell in (4)) gives $\Phi°$. Subsequently $\Phi°$ is introduced into eq 5, and $(\gamma_{\mathrm{KCl}})^2$ for KCl *in the admixture* with K_2SO_4 is obtained therefrom.

If in the cell in (4) the silver chloride electrode is replaced by the lead-amalgam|lead-sulfate electrode recently reassessed critically,[7] the resulting reversible cell in (9)

$$\mathrm{Pt}|\mathrm{K}_x\mathrm{Hg}_{1-x}|\mathrm{KCl}\ (m_{\mathrm{KCl}}) + \mathrm{K_2SO_4}\ (m_{\mathrm{K_2SO_4}})|\mathrm{PbSO_4}|\mathrm{Pb\text{-}amalgam}|\mathrm{Pt} \tag{9}$$

would conceptually allow the symmetrical determination of the activity coefficients $\gamma_{\mathrm{K_2SO_4}}$ of K_2SO_4 *in the admixture* with KCl. This second goal is, however, impaired by the factors outlined in the section Results and Discussion.

Experimental Section

The potassium amalgam electrodes for the cell in (4) were prepared and operated in the dilute flowing amalgam mode by means of the all-glass apparatus described earlier.[8] The mole fraction x of potassium was lower than 0.007. The silver/silver chloride electrodes were prepared according to the bielectrolytic type.[9] The cell in (4) resulting from the combination of potassium amalgam electrode with silver/silver chloride electrode was standardized using (8) by the procedure introduced by Bates et al.[5,6] relying on accurate activity coefficients of the supporting electrolyte of the cell. Here the relevant cell is (7), and its supporting electrolyte is KCl, for which critically assessed activity coefficients are available as a function of molality m.[8] The potential differences of the cells involved were measured at (25 ± 0.05) °C by a high-input-impedance Mod.619 Keithley differential electrometer and were accurate to within ±0.1 mV. The thermostatic apparatus was described earlier.[10] All solutions were prepared by mass from redistilled deionized water and reagent-grade chemicals.

Results and Discussion

The potential differences E of the cell in (4), measured as a function of the molality m_{KCl} of KCl in admixture with K_2SO_4 of molality $m_{\mathrm{K_2SO_4}}$ for various constant values of the total ionic strengths $I = m_{\mathrm{KCl}} + 3m_{\mathrm{K_2SO_4}}$, are quoted in Table 1, together with the corresponding values of the mean molal activity coefficients γ_{KCl} pertinent to each molality m_{KCl} in admixture with K_2SO_4 and other thermodynamic functions, including Harned's coefficients α^*_{KCl}, with the respective standard deviations. In Table 1, the superscripts ^{a} and ^{b} refer to two distinct series of E and E_7 measurements obtained working with two distinct x mole fractions of K in the amalgam electrodes used, leading to two corresponding distinct $\Phi°$ standardization parameters but to the same derived activity coefficients. The relevant values of the parameter $\Phi°$, indispensable for the calculation of γ_{KCl}, were determined experimentally from the potential difference E_7 of the cell in (7) on KCl solutions at selected molalities $m°_{\mathrm{KCl}}$ of accurately known activity coefficients $\gamma°_{\mathrm{KCl}}$.[8] The pertinent $\gamma°_{\mathrm{KCl}}$ values have been taken from the recent critically redetermined data by Archer.[8] In keeping with Robinson and Stokes' notation,[1] the added subscript (0) *after* KCl is henceforth used to denote total absence of K_2SO_4, namely, $\gamma_{\mathrm{KCl(0)}}$ will be the activity coefficient of pure aqueous KCl, whereas a subscript (0) *before* KCl means total replacement of KCl by K_2SO_4, namely, $\gamma_{\mathrm{(0)KCl}}$ is the *trace activity coefficient* of KCl. At each constant ionic strength investigated, the system studied satisfies Harned's rule: in fact, the relation of γ_{KCl} vs m_{KCl} is linear and is described by

$$\log\gamma_{\mathrm{KCl}} = \log\gamma_{\mathrm{(0)KCl}} + \alpha^*_{\mathrm{KCl}}m_{\mathrm{KCl}} = \log\gamma_{\mathrm{KCl(0)}} - \alpha^*_{\mathrm{KCl}}\mu_{\mathrm{K_2SO_4}}I \tag{10}$$

where, of course, both $\gamma_{\mathrm{(0)KCl}}$ and α^*_{KCl} are independent of m_{KCl} but depending on the ionic strength of the mixture studied. In eq 10, $\mu_{\mathrm{K_2SO_4}}$ is the ionic strength fraction of K_2SO_4. The value, $\alpha^*_{\mathrm{KCl}} = 0.021 \pm 0.004$, of Harned's coefficient at $I = 1.0\ \mathrm{mol\cdot kg^{-1}}$, substantiates the value, $\alpha^*_{\mathrm{KCl}} = 0.029$, obtained by Christenson and Gieskes,[2] who worked with a nonreversible cell of the type in (3).

Figure 1 summarizes the thermodynamic behavior of the mixtures studied here. The dotted curve connecting the right-hand ends of the various Harned's lines represents the experimentally determined variation of the activity coefficient $\gamma_{\mathrm{KCl(0)}}$ when K_2SO_4 is absent. These $\gamma_{\mathrm{KCl(0)}}$ values are in excellent agreement with the critically established γ_{KCl} data in the literature.[8] The intercept of each line at $m_{\mathrm{KCl}} = 0$ in Figure 1 gives the trace activity coefficient $\gamma_{\mathrm{(0)KCl}}$, the values of which could be reproduced by the following equation as a function of the total ionic strength I:

$$\log\gamma_{\mathrm{(0)KCl}} = -(0.1506 \pm 0.0042)\log I - (0.2404 \pm 0.0024) \tag{11}$$

($r^2 = 0.998$). Figure 2 shows the regular $\log\gamma_{\mathrm{KCl}}$ versus $\sqrt{m_{\mathrm{KCl}}}$ variation upon varying the ionic strength of the mixed electrolyte.

The structure of the cell in (9) suggests that it could, in principle, be used to symmetrically obtain the values of $\gamma_{\mathrm{K_2SO_4}}$ for $_{\mathrm{K_2SO_4}}$ *in the admixture* with KCl, at the same constant ionic strengths studied above. However, at molalities $m_{\mathrm{K_2SO_4}}$ higher than about 0.03, K_2SO_4 in the presence of the electrode material $PbSO_4$ gives rise to the double salt $PbSO_4{\cdot}K_2SO_4$,[7,11] and the Pb-amalgam|$PbSO_4$ electrode does no longer respond in a Nernstian manner [7] to variations in $\log(m_{\mathrm{K_2SO_4}}\gamma_{\mathrm{K_2SO_4}})$. This is in accord with the findings of Mellon and Henderson,[11] who assessed the formation of the double salt $PbSO_4{\cdot}K_2SO_4$ although exclud-

Table 1. Potential Differences *E* at 298.15 K for the Cell in (4) as a Function of KCl Molality m_{KCl} and Ionic Strength Fraction μ_{KCl} in Aqueous (KCl + K_2SO_4) Mixtures of Different Constant Ionic Strengths *I*, with the Corresponding Smoothed Activity Coefficients γ_{KCl}, and the Parallel $(\gamma_{\mathrm{KCl}})_P$ and $(\gamma_{K_2SO_4})$ Values Calculated from Pitzer's Equations,[12,13] Together with Harned's Coefficients α_{KCl}, and the Trace Activity Coefficients $\gamma_{(0)\mathrm{KCl}}$ with Respective Standard Deviations[†]

m_{KCl} / mol·kg^{-1}	μ_{KCl}	$m_{K_2SO_4}$ / mol·kg^{-1}	*E* / V	γ_{KCl}[‡]	$(\gamma_{\mathrm{KCl}})_P$[§]	$(\gamma_{\mathrm{KCl}})_P$[&]	$(\gamma_{K_2SO_4})_P$[§]	$(\gamma_{K_2SO_4})_P$[&]
				I/(mol·kg^{-1}) = 0.1000				
0.0050	0.05	0.03167	2.2928	(0.814 ± 0.002)	0.757	0.754	0.571	0.570
0.0100	0.1	0.03000	2.2740	(0.812 ± 0.002)	0.757	0.755	0.571	0.570
0.0300	0.3	0.02333	2.2446	(0.803 ± 0.002)	0.760	0.758	0.571	0.569
0.0300	0.3	0.02333	2.2441	(0.803 ± 0.002)	0.760	0.758	0.571	0.569
0.0500	0.5	0.01667	2.2288	(0.795 ± 0.003)	0.762	0.761	0.571	0.569
0.0700	0.7	0.01000	2.2195	(0.786 ± 0.003)	0.764	0.764	0.571	0.568
0.0900	0.9	0.00333	2.2114	(0.778 ± 0.004)	0.766	0.766	0.571	0.568
0.1000	1.0	0.00000	2.2088	(0.767 ± 0.004)	0.767	0.767	0.571	0.567
α^*_{KCl}/(kg·mol^{-1})	−(0.234 ± 0.037)							
$\gamma_{(0)\mathrm{KCl}}$	(0.816 ± 0.004)							
E_7/V	(2.2088 ± 0.0001)							
$m°_{\mathrm{KCl}}$/(mol·kg^{-1})	0.1000							
$\gamma°_{\mathrm{KCl}}$	0.7670							
$\Phi°$/V	(2.0768 ± 0.0001)							
				I/(mol·kg^{-1}) = 0.2000				
0.0100	0.05	0.06333	2.2624	(0.732 ± 0.003)	0.713	0.709	0.493	0.491
0.0200	0.1	0.06000	2.2447	(0.731 ± 0.003)	0.713	0.710	0.494	0.492
0.0600	0.3	0.04667	2.2140	(0.728 ± 0.003)	0.714	0.711	0.498	0.495
0.1000	0.5	0.03333	2.1990	(0.725 ± 0.003)	0.714	0.712	0.501	0.498
0.1400	0.7	0.02000	2.1881	(0.722 ± 0.004)	0.715	0.714	0.504	0.500
0.2000	1.0	0.00000	2.1771	(0.716 ± 0.004)	0.716	0.716	0.507	0.501
α^*_{KCl}/(kg·mol−^{1})	−(0.042 ± 0.016)							
$\gamma_{(0)\mathrm{KCl}}$	(0.732 ± 0.004)							
E_7/V	(2.1771 ± 0.0001)							
$m°_{\mathrm{KCl}}$/(mol·kg^{-1})	0.2000							
$\gamma°_{\mathrm{KCl}}$	0.7156							
$\Phi°$/V	(2.0772 ± 0.0001)							
				I/(mol·kg^{-1}) = 0.5000				
0.0250	0.05	0.15833	2.2240	(0.629 ± 0.002)	0.624	0.616	0.378	0.375
0.0500	0.1	0.15000	2.2045	(0.630 ± 0.002)	0.626	0.618	0.380	0.376
0.0500	0.1	0.15000	2.2046	(0.630 ± 0.002)	0.626	0.618	0.380	0.376
0.1500	0.3	0.11667	2.1745	(0.634 ± 0.002)	0.632	0.626	0.386	0.381
0.2500	0.5	0.08333	2.1588	(0.638 ± 0.002)	0.637	0.633	0.388	0.383
0.3500	0.7	0.05000	2.1473	(0.642 ± 0.003)	0.642	0.640	0.388	0.381
0.4500	0.9	0.01667	2.1389	(0.646 ± 0.003)	0.646	0.645	0.385	0.377
0.4750	0.95	0.00833	2.1371	(0.647 ± 0.003)	0.647	0.647	0.384	0.376
0.5000	1.0	0.00000	2.1352	(0.648 ± 0.003)	0.648	0.648	0.383	0.374
α^*_{KCl}/(kg·mol^{-1})	(0.027 ± 0.006)							
$\gamma_{(0)\mathrm{KCl}}$	(0.628 ± 0.003)							
E_7/V	(2.1352 ± 0.0001)							
$m°_{\mathrm{KCl}}$	0.5000							
$\gamma°_{\mathrm{KCl}}$	0.6481							
$\Phi°$/V	(2.0773 ± 0.0001)							
				I/(mol·kg^{-1}) = 1.0000				
0.0500	0.05	0.31667	2.1921	(0.572 ± 0.002)	0.568	0.554	0.305	0.301
0.1000	0.1	0.30000	2.1739	(0.574 ± 0.002)	0.570	0.557	0.310	0.306
0.3000	0.3	0.23333	2.1431	(0.579 ± 0.002)	0.578	0.569	0.327	0.322
0.5000	0.5	0.16667	2.1269	(0.585 ± 0.003)	0.586	0.579	0.334	0.328
0.7000	0.7	0.10000	2.1163	(0.590 ± 0.003)	0.593	0.589	0.331	0.324
0.9500	0.95	0.01667	2.1049	(0.598 ± 0.004)	0.601	0.601	0.313	0.305
1.0000	1	0.00000	2.1030	(0.603 ± 0.004)	0.603	0.603	0.308	0.300
α^*_{KCl}/(kg·mol^{-1})	(0.021 ± 0.004)							
$\gamma_{(0)\mathrm{KCl}}$	(0.571 ± 0.003)							
E_7/V	(2.1030 ± 0.0001)							
$m°_{\mathrm{KCl}}$/(mol·kg^{-1})	0.5000							
$\gamma°_{\mathrm{KCl}}$	0.6027							
$\Phi°$/V	(2.0770 ± 0.0001)							
				I/(mol·kg^{-1}) = 2.0000				
1.0000	0.5	0.33333	2.0695[a]	(0.549 ± 0.002)	0.544	0.536	0.343	0.343
1.0000	0.5	0.33333	2.0698[a]	(0.549 ± 0.002)	0.544	0.536	0.343	0.343
1.4000	0.7	0.20000	2.0582[a]	(0.559 ± 0.002)	0.555	0.551	0.323	0.325
1.4000	0.7	0.20000	2.0580[a]	(0.559 ± 0.002)	0.555	0.551	0.323	0.325

Table 1. (Continued)

m_{KCl}		$m_{K_2SO_4}$	E					
mol·kg^{-1}	μ_{KCl}	mol·kg^{-1}	V	γ_{KCl}[‡]	$(\gamma_{KCl})_P$[§]	$(\gamma_{KCl})_P$[&]	$(\gamma_{K_2SO_4})_P$[§]	$(\gamma_{K_2SO_4})_P$[&]
			I/(mol·kg^{-1}) = 2.0000 (Continued)					
1.8000	0.9	0.06667	2.0492^a	(0.570 ± 0.003)	0.566	0.565	0.269	0.272
1.9000	0.95	0.03333	2.0474^a	(0.573 ± 0.003)	0.569	0.569	0.251	0.255
1.9000	0.95	0.03333	2.0471^a	(0.573 ± 0.003)	0.569	0.569	0.251	0.255
2.0000	1.0	0.00000	2.0450^a	(0.575 ± 0.003)	0.572	0.572	0.233	0.237
0.1000	0.05	0.63333	2.1643^b	(0.525 ± 0.002)	0.519	0.498	0.247	0.245
0.2000	0.1	0.60000	2.1447^b	(0.528 ± 0.002)	0.522	0.502	0.265	0.262
0.6000	0.3	0.46667	2.1132^b	(0.538 ± 0.002)	0.533	0.519	0.321	0.319
1.0000	0.5	0.33333	2.0968^b	(0.549 ± 0.002)	0.544	0.536	0.343	0.343
1.4000	0.7	0.20000	2.0852^b	(0.559 ± 0.002)	0.555	0.551	0.323	0.325
1.8000	0.9	0.06667	2.0756^b	(0.570 ± 0.003)	0.566	0.565	0.269	0.272
1.9000	0.95	0.03333	2.0740^b	(0.573 ± 0.003)	0.569	0.569	0.251	0.255
2.0000	1.0	0.00000	2.0722^b	(0.576 ± 0.003)	0.572	0.572	0.233	0.237
α^*_{KCl}/(kg·mol$-^1$)	(0.021 ± 0.001)							
$\gamma_{(0)KCl}$	(0.523 ± 0.002)							
E_7/V^a	(2.0450 ± 0.0001)							
E_7/V^b	(2.0722 ± 0.0001)							
$m°_{KCl}$/(mol·kg^{-1})	2.0000							
$\gamma°_{KCl}$	0.5745							
$\Phi°$/V^a	(2.0521 ± 0.0001)							
$\Phi°$/V^b	(2.0793 ± 0.0001)							

[†] Also quoted the potential differences E_7 of the cell in (7) measured at selected $m°_{KCl}$ and $\gamma°_{KCl}$,[8] which leads to the function $\Phi°$ used to standardize the cell in (4). E and E_7 were measured at the same mole fraction x of potassium in amalgam electrode. The superscripts a and b refer to two distinct series of E and E_7 measurements based on two distinct x mole fractions of K in the amalgam electrode used, together with the corresponding two distinct $\Phi°$ calibration parameters (cf. eq 8).

[‡] This work. [§] With Pitzer's parameters generated in this work. [&] With Pitzer's parameters from ref 13.

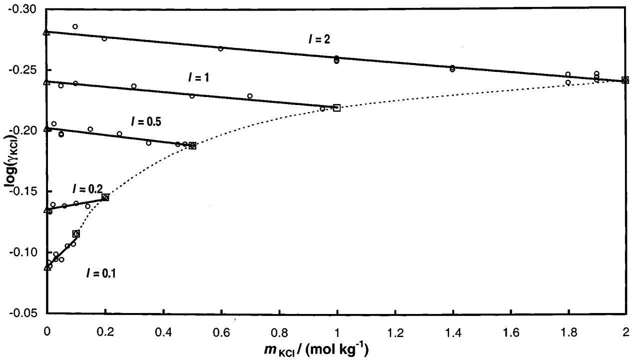

Figure 1. Harned's rule lines for KCl at various molalities m_{KCl} in aqueous (KCl + K_2SO_4) mixtures of various ionic strengths I. Dotted curve represents variation of the activity coefficients $\gamma_{KCl(0)}$ of KCl when K_2SO_4 is absent. The intercepts of straight lines at $m = 0$ give the respective values of the trace activity coefficient $\gamma_{(0)KCl}$.

ing it in the cases of Li_2SO_4 and Na_2SO_4. Therefore, the cell in (9) is not applicable in the present case. Replacement of the Pb-amalgam|$PbSO_4$ electrode by the Hg|Hg_2SO_4 electrode would be equally ineffective because of the too high solubility of Hg_2SO_4 in aqueous solution. In these circumstances, an insight into the behavior of the K_2SO_4 component must be sought in the thermodynamic relations linking the latter to KCl. To this purpose, the treatment based on Pitzer' scheme of equations[12-16] is appropriate. Accordingly, the mean molal activity coefficients γ_{KCl} in the (KCl + K_2SO_4 + H_2O) system above-mentioned are given by

$$\begin{aligned}\ln \gamma_{KCl} = f^{\gamma} + (m_K + m_{Cl})\,(B_{K,Cl} + m_K\, C_{K,Cl}) + \\ m_{SO4}\,(B_{K,SO4} + m_K\, C_{K,SO4} + {}^{S}\theta_{Cl,SO4} + {}^{E}\theta_{Cl,SO4}) + \\ m_K m_{Cl}(B'_{K,Cl} + C_{K,Cl}) + m_K m_{SO4}(B'_{K,SO4} + C_{K,SO4} + \\ 0.5\,\Psi_{K,Cl,SO4}) + m_{Cl}\, m_{SO4}\,({}^{S}\theta'_{Cl,SO4} + {}^{E}\theta'_{Cl,SO4} + \\ 0.5\Psi_{K,Cl,SO4}) \quad (12)\end{aligned}$$

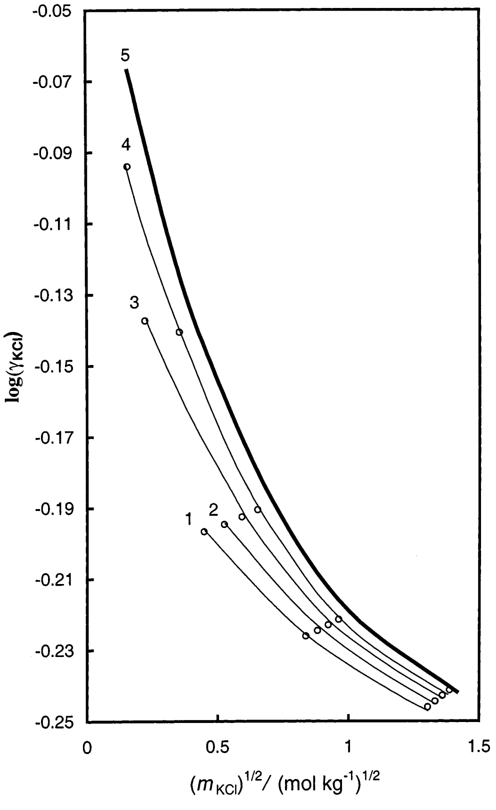

Figure 2. Debye–Hückel plot of log γ_{KCl} versus $\sqrt{m_{KCl}}$ for aqueous (KCl + K_2SO_4) mixtures at various molalities $m_{K_2SO_4}$ of K_2SO_4, at 298.15 K: 1, $m_{K_2SO_4} = 0.1$; 2, $m_{K_2SO_4} = 0.075$; 3, $m_{K_2SO_4} = 0.05$; 4, $m_{K_2SO_4} = 0.025$; 5, $m_{K_2SO_4} = 0$ mol·kg^{-1}.

where: m = molality of the subscripted ionic species (with no indication of charge numbers, for convenience); f^{γ} = Debye–Hückel function for the activity coefficient $= -A_{\phi}\,[I^{1/2}/(1 + bI^{1/2}) + (2/b)\ln(1 + bI^{1/2})]$; $B_{I,J}$ = second virial coefficient $= \beta^{(0)}{}_{I,J} + [(2\beta^{(1)}{}_{I,J})/(\alpha^2 I)]\,[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})]$; $B'_{I,J} = [(2\beta^{(1)}{}_{I,J})/(\alpha^2 I^2)][-1 + (1 + \alpha I^{1/2} + 0.5\alpha^2 I)$

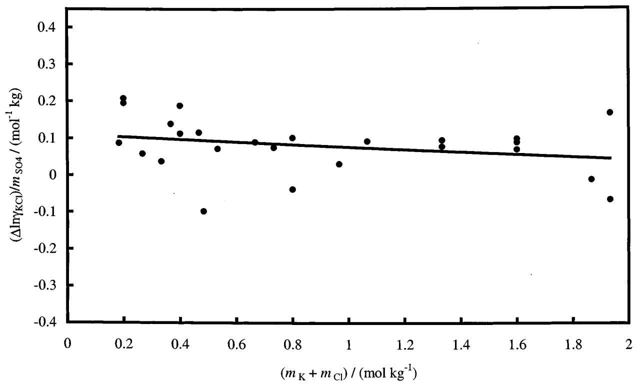

Figure 3. Concentration dependence of $((\Delta \ln \gamma_{KCl})/m_{SO4})$ vs $(m_K + m_{Cl})$ at 298.15 K from eq 15.

$\exp(-\alpha I^{1/2})]$; $C_{I,J}$ = third virial coefficient = $C^{\phi}_{I,J}/[2|z_I z_J|^{1/2}]$. Furthermore, in the present case (i.e., in water medium at 298.15 K), we have $A_\phi = 0.39211$ and, as shown by Pitzer,[12-16] $\alpha = 2$, $b = 1.2$; $\beta^{(0)}_{I,J}$, $\beta^{(1)}_{I,J}$ and $C^{\phi}_{I,J}$ are tabulated.[12,14]

The two higher-order electrostatic terms ${}^{E}\theta_{Cl,SO4}$ and ${}^{E}\theta'_{Cl,SO4}$, which may be important for 1−2 mixing[13] are calculated using the following respective equations:

$$ {}^{E}\theta_{Cl,SO4} = (z_{Cl}z_{SO4}/4I)[J(x_{Cl,SO4}) - 0.5J(x_{Cl,Cl}) - 0.5J(x_{SO4,SO4})] \quad (13)$$

$$ {}^{E}\theta'_{Cl,SO4} = -({}^{E}\theta_{Cl,SO4}/I) + (z_{Cl}z_{SO4}/8I^2)[x_{Cl,SO4}J'(x_{Cl,SO4}) - 0.5x_{Cl.Cl}J'(x_{Cl,Cl}) - 0.5x_{SO4,SO4}J'(x_{SO4,SO4})] \quad (14)$$

where the variable $x_{I,J}$ is defined by $x_{I,J} = 6z_I z_J A_\phi I^{1/2}$, and the values of J and J' are appropriately interpolated using the values suggested by Pitzer.[12]

The mixing parameters ${}^{S}\theta_{Cl,SO4}$ and $\Psi_{K,Cl,SO4}$ are then calculated using the following equation:

$$(\Delta \ln \gamma_{\pm KCl})/m_{SO4} = {}^{S}\theta_{Cl,SO4} + 0.5(m_K + m_{Cl})\Psi_{K,Cl,SO4} \quad (15)$$

where $(\Delta \ln \gamma_{\pm KCl})$ is the difference between the experimentally determined activity coefficients and those calculated with eq 12 with all pure electrolyte terms and assuming the values of ${}^{S}\theta_{Cl,SO4}$ and $\Psi_{K,Cl,SO4}$ to be equal to zero. Figure 3 shows the $(\Delta \ln \gamma_{\pm KCl})/m_{SO4}$ vs $0.5(m_K + m_{Cl})$ linear relation.

In the calculation of the mixing parameters, because of the large uncertainties and negative deviations, data for $(m_K + m_{Cl})/2 < 0.2$ mol kg^{-1} are not included, as already done by other authors[12,15] in similar Pitzer's treatments of unsymmetrical mixed electrolytes. The calculated mixing parameters with the corresponding standard deviations are ${}^{S}\theta_{Cl,SO4} = (0.111 \pm 0.026)$ and $\Psi_{K,Cl,SO4} = (-0.034 \pm 0.024)$. Earlier, Pitzer[13,16] suggested the use of the following values: ${}^{S}\theta_{Cl,SO4} = 0.020$ and $\Psi_{K,Cl,SO4} = 0.000$, based on the osmotic coefficients obtained by Robinson et al.[17] by the isopiestic method. Then the activity coefficients of both KCl and K_2SO_4 at different ionic strengths, and molalities have here been calculated using either of the two above pairs of mixing parameters and are quoted in Table 1.

(1) Looking over the calculations carried out within the framework of Pitzer's equations (cf. Table 1, 6th and 7th columns), a good agreement turns out for the $(\gamma_{KCl})_P$ values with the experimental γ_{KCl} data (5th column) at total ionic strength $I \geq 0.5$ and $m_{K_2SO_4} \geq 0.13$ mol·kg^{-1}, a feature which is consistent with findings in the literature.[15,18] It is regrettable that the low solubility of K_2SO_4 (<0.7 mol·kg^{-1} at 298.15 K) has here prevented investigations of higher molalities and ionic strength to get a wider verification of this behavior pattern. Consequently, in the absence of direct pd-based results with SO_4^{2-}-reversible electrode cells, we consider the parallel $(\gamma_{K_2SO_4})_P$ values calculated from Pitzer's equation (8th and 9th columns) to be reasonably dependable.

(2) The logarithm of the experimental γ_{KCl} at $m_{KCl} \leq 0.2$ mol·kg^{-1} decreases linearly with increasing m_{KCl} in the ($KCl + K_2SO_4$) mixture at constant ionic strength. Such a feature is however not reproduced by the $(\gamma_{KCl})_P$ data calculated from Pitzer's model, which only approaching the upper m_{KCl}s become satisfactory.

(3) Using for Pitzer's mixing parameters the values generated from our results, or those suggested in the literature,[13,16] causes very little deviations, as shown by Table 1 (last four columns): evidently the values of the above mixing parameters are here not critical.

(4) The calculated $(\gamma_{K_2SO_4})_P$ at ionic strengths as low as $I \leq 0.2$ mol·kg^{-1} are unreliable. However, the $(\gamma_{K_2SO_4})_P$ at $I \geq 0.5$ are reliable and show parabolic dependence on $m_{K_2SO_4}$; therefore, they point to their noncompliance with Harned's rule, a result previously found by Christenson and Gieskes[2] working with ISE cells of the type in (3).

Conclusions

In the present work, the thermodynamics of the aqueous ($KCl + K_2SO_4$) mixed electrolyte at various ionic strengths has been investigated by the method of the reversible potential of the potassium amalgam electrode cell $Pt|K_xHg_{1-x}|KCl\ (m_{KCl}) + K_2SO_4\ (m_{K_2SO_4})|AgCl|Ag|Pt$. It turns out that this mixed electrolyte system is characterized by dissymmetrical behavior with respect to compliance with Harned's rule. In fact, the component KCl obeys Harned's rule, whereas K_2SO_4 does not. In this context, the trace activity coefficients $\gamma_{(0)KCl}$ of KCl vary with the total ionic strength I of the mixture according to the linear relation $\log \gamma_{(0)KCl} = -(0.1506 \pm 0.0042) \log I - (0.2404 \pm 0.0024)$. Using Pitzer's scheme of equations with generation of the relevant parameters has allowed the estimation of the activity coefficients of the component K_2SO_4 even in the absence of pd data measured with SO_4^{2-}-reversible electrode cells. Total ionic strengths $I > 2$ mol·kg^{-1} for the ($KCl + K_2SO_4$) mixtures could not be explored because of the low solubilities of the components. Better perspectives would be expected when working with the parallel ($RbCl + Rb_2SO_4$) and ($CsCl + Cs_2SO_4$) systems, for which the solubility limits are about three times as great. The present method of the M-amalgam electrode cell could also be extended to a variety of MX + MY systems in nonaqueous or aqueous−organic systems where the (M-amalgam + silver halide) electrode pair is generally well behaved and particularly suited to systematic studies covering wide ranges of solvent compositions and temperatures, as are being carried out in these laboratories.

Literature Cited

(1) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd rev. ed.; Butterworth: London, 1965; pp 432−454.

(2) Christenson, P. G.; Gieskes, J. M. Activity coefficients of KCl in several mixed electrolyte solutions at 25 °C. *J. Chem. Eng. Data* **1971**, *16*, 398−400.

(3) Chen, G.; Yang, L. Determination of the activity coefficients of potassium chloride-potassium sulfate solutions at constant ionic strength. *Shandong Haiyang Xueyuan Xuebao* **1987**, *17* (2), 55−61.

(4) Mussini, T.; Longhi, P.; Rondinini, S. Standard potentials of amalgam electrodes in aqueous solutions, temperature coefficients

and activity coefficients of metals in mercury. *Pure Appl. Chem.* **1985**, *57*, 169−179.
(5) Bates, R. G.; Guggenheim, E. A.; Harned, H. S.; Ives, D. J. G.; Janz, G. J.; Monk, C. B.; Prue, J. E.; Robinson, R. A.; Stokes, R. H.; Wynne-Jones, W. F. K Standard electrode potential of the silver−silver chloride electrode. *J. Chem. Phys.* **1956**, *25*, 361.
(6) Dickson, A. G. Standardization of the (AgCl + 1/2 H_2 = Ag + HCl) cell from 273.15 to 318.15 K. *J. Chem. Thermodyn.* **1987**, *19*, 993−1000.
(7) Fusi, P.; Mussini, P. R. The lead amalgam/lead sulfate electrode redesigned and reassessed. *J. Solution Chem.* **1997**, *26*, 337−353.
(8) Archer, D. G. Thermodynamic properties of the KCl+H_2O system. *J. Phys. Chem. Ref. Data* **1972**, *1*, 1047−1099.
(9) Mussini, T.; Pagella, A. Standard potentials of the calcium amalgam electrode at various temperatures, with related thermodynamic functions. *J. Chem. Eng. Data* **1971**, *16*, 49−52.
(10) Ives, D. J. G.; Janz, G. J. *Reference Electrodes*−*Theory and Practice*; Academic Press: New York, 1961; pp 203−207.
(11) Mellon, M. G.; Henderson, W. E. Further studies on a lead standard cell. *J. Am. Chem. Soc.* **1920**, *42*, 676−689.
(12) Pitzer, K. S. *Activity Coefficients in Electrolyte Solutions*, 2nd ed.; CRC Press: Boca Raton, FL, 1991.
(13) Pitzer, K. S. Thermodynamics of Electrolytes. V. Effects of Higher-Order Electrostatic Terms. *J. Solution Chem.* **1975**, *4*, 249−265.
(14) Pitzer, K. S.; Mayorga, G. Thermodynamics of Electrolytes. II. Activity Coefficients for Strong Electrolytes with One or Both Ions Univalent. *J. Phys. Chem.* **1973**, *77*, 2300−2308.
(15) Roy, R. N.; Gibbons, J. J.; Roy, L. N.; Greene, M. A. Thermodynamics of the Unsymmetrical Mixed Electrolyte HCl−$SrCl_2$. Application of Pitzer Equations. *J. Phys. Chem.* **1986**, *90*, 6242−6247.
(16) Pitzer, K. S.; Kim, J. J. Thermodynamics of Electrolytes. IV. Activity and Osmotic Coefficients for Mixed Electrolytes. *J. Am. Chem. Soc.* **1974**, *96*, 5701−5707.
(17) Robinson, R. A.; Platford, R. F.; Childs, C. W. Thermodynamics of Aqueous Mixtures of Sodium Chloride, Potassium Chloride, Sodium Sulfate and Potassium Sulfate at 25 °C. *J. Solution Chem.* **1972**, *1*, 167−172.
(18) Tishchenko, P. Ya.; Bychkov, A. S.; Hrabéczy-Páll, A.; Tóth, K.; Pungor, E. Activity Coefficients for the System NaCl + Na_2SO_4 + H_2O at Various Temperatures. Application of Pitzer's Equations. *J. Solution Chem.* **1992**, *21*, 261−273.

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