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Activity coefficient measurements of the system $KCl + NiCl_2 + H_2O$ at 25, 35 and 45°C

S Sarada & J Ananthaswamy*
Department of Chemistry, Osmania University, Hyderabad 500 007

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EMFs of the cells consisting of potassium ion-selective electrode and Ag/AgCl reference electrode have been measured and the activity coefficients of KCl in the system $KCl + NiCl_2 + H_2O$ estimated at 25, 35 and 45°C and $I = 0.5$, 1.0, 2.0 and 3.0 *m*. The Harned coefficients have been calculated at 25, 35 and 45°C. The Pitzer parameters, excess free energies and osmotic coefficients have also been evaluated at 25°C.

Aqueous solutions of multicomponent electrolyte systems are analogous to the natural brines encountered in water pollution control, oceanography and petroleum drilling[1,2]. Although considerable information is available on the activity coefficients of single electrolyte solutions, such data are lacking on the mixed electrolyte solutions. We report here the activity coefficients of KCl in the system $KCl + NiCl_2 + H_2O$ at 25, 35 and 45°C and at total ionic strengths of 0.5, 1.0, 2.0 and 3.0 *m*.

Materials and Methods

Deionised, doubly distilled water was used for preparing all the solutions. KCl (AR, Glaxo) and $NiCl_2$ (GR, S Merck) were used as such. The stock solutions were standardised by estimation of chloride ion with $AgNO_3$, potentiometrically. Temperature was maintained constant by circulating water from a thermostat through the double walled glass cell in which the experimental solution was taken. A potassium ion-selective electrode (Elico, India) and an Ag/AgCl reference electrode[3] were used in all the measurements. The accuracy of the EMF measurements was ± 0.1 mV.

K ion-selective electrode	$KCl\,(m_A)$ + $NiCl_2\,(m_B)$	Ag/AgCl electrode

(I)

The K ion-selective electrode was calibrated by measuring the EMFs of the cell (I) with pure KCl solution at various dilutions. All dilutions were made using weight burettes and the concentrations of all the solutions were calculated in molalities. The method of estimating the activity coefficients and the experimental set up were the same as described earlier[4].

Results

The EMFs of the cell with aqueous $KCl + NiCl_2$ mixtures are given by the relation:

$$E_{KCl-NiCl_2} = E_0 + k \log(a_K a_{Cl} + K a_{Ni}^{1/2} a_{Cl}) \quad \dots (1)$$

where E_0 is the EMF of pure KCl solution at unit activity and $k = 2.303\ RT/nF$ is the Nernst slope. This equation could be rearranged as:

$$\gamma_\pm^2 = (1/m_K m_{Cl}).10^{(E_{KCl-NiCl_2} - E_0/k)} \quad \dots (2)$$

after setting $K = 0$ because the selectivity coefficient of *K* ion-selective electrode towards Ni^{2+} was negligible ($< 10^{-4}$). The activity coefficients of KCl in $KCl + NiCl_2 + H_2O$ mixtures were calculated at total ionic strengths of 0.5, 1.0, 2.0 and 3.0 *m* using Eq. (2) at different values of y_B, where

$$y_B = 3\,m_{NiCl_2}/(m_{KCl} + 3\,m_{NiCl_2}) \quad \dots (3)$$

These activity coefficient values are listed in Table 1.

Discussion

Variation of $\log \gamma_A$ vs y_B is shown in the Fig. 1, which shows that the plots are linear at all the temperatures studied. Therefore the Harned coefficients (α_{AB}) were calculated by fitting the data to the Harned equation[5]:

$$\log \gamma_A^0 = \log \gamma_A^0 - \alpha_{AB} y_B \quad \dots (4)$$

where γ_A^0 is the activity coefficient of pure KCl at the same ionic strength as the mixture. These α_{AB} values are listed in Table 2.

Table 1—Mean activity coefficients of KCl in KCl + $NiCl_2$-H_2O system

I = 0.5		I = 1.0		I = 2.0		I = 3.0	
y_B	$-\log \gamma_{KCl}$	y_B	$-\log \gamma_{KCl}$	y_B	$-\log \gamma_{KCl}$	y_B	$-\log \gamma_{KCl}$
			Temp. = 25°C				
0.1232	0.1919	0.1247	0.2225	0.1270	0.2443	0.1288	0.2466
0.2194	0.1931	0.2218	0.2233	0.2254	0.2531	0.2282	0.2465
0.2966	0.1897	0.2995	0.2282	0.3038	0.2575	0.3073	0.2505
0.3599	0.1979	0.3630	0.2277	0.3678	0.2567	0.4251	0.2595
0.4127	0.2002	0.4160	0.2298	0.4211	0.2586	0.4701	0.2549
0.4575	0.1961	0.4994	0.2315	0.4660	0.2626	0.5086	0.2605
0.5293	0.2013	0.5619	0.2308	0.4811	0.2638	0.5297	0.2576
0.5580	0.2020	0.5876	0.2323	0.5045	0.2600	0.5419	0.2593
0.6024	0.2004	0.6105	0.2347	0.5196	0.2607	0.5710	0.2594
0.6544	0.1990	0.5309	0.2315	0.5378	0.2673	0.5966	0.2606
0.7163	0.2011	0.5760	0.2309	0.5649	0.2690	0.6193	0.2629
0.7911	0.2034	0.6293	0.2307	0.5669	0.2675	0.6396	0.2576
0.8834	0.2028	0.6494	0.2336	0.6187	0.2693	0.6926	0.2603
		0.6936	0.2341	0.7644	0.2778	0.7717	0.2643
		0.7725	0.2379	0.8665	0.2796	0.8711	0.2654
		0.8717	0.2390				
			Temp. = 35°C				
0.1219	0.1911	0.1252	0.2280	0.1185	0.2430	0.1279	0.2479
0.2173	0.1997	0.2225	0.2358	0.2118	0.2534	0.2268	0.2550
0.2940	0.2039	0.3003	0.2395	0.2873	0.2591	0.3056	0.2663
0.3571	0.2030	0.3640	0.2463	0.3496	0.2675	0.3697	0.2727
0.4097	0.2046	0.4170	0.2475	0.4019	0.2701	0.4231	0.2736
0.4545	0.2082	0.4619	0.2508	0.4464	0.2663	0.4681	0.2767
0.4929	0.2136	0.5004	0.2559	0.4847	0.2724	0.5066	0.2816
0.5262	0.2123	0.8724	0.2843	0.8684	0.3030	0.8639	0.3118
0.8733	0.2283	0.7737	0.2796	0.7675	0.2977	0.7604	0.3059
0.7751	0.2237	0.6951	0.2701	0.6875	0.2877	0.6790	0.2953
0.6708	0.2144	0.6310	0.2684	0.6227	0.2856	0.6134	0.2927
0.6328	0.2128	0.5777	0.2617	0.5690	0.2785	0.5593	0.2851
0.5796	0.2143	0.5327	0.2549	0.5238	0.2796	0.5140	0.2858
0.5347	0.2076			0.4853	0.2753		
0.4962	0.2119						
			Temp. = 45°C				
0.1244	0.1981	0.1247	0.2269	0.1226	0.2456	0.1279	0.2516
0.2213	0.2048	0.2218	0.2335	0.2184	0.2527	0.2256	0.2656
0.2989	0.2076	0.2995	0.2441	0.2953	0.2637	0.3041	0.2678
0.3624	0.2135	0.3630	0.2500	0.3585	0.2699	0.3682	0.2812
0.4154	0.2140	0.4160	0.2505	0.4133	0.2706	0.4214	0.2814
0.4602	0.2166	0.4609	0.2531	0.4560	0.2734	0.4664	0.2917
0.4987	0.2210	0.4994	0.2575	0.4944	0.2780	0.5049	0.2959
0.8777	0.2434	0.8749	0.2933	0.5278	0.2840	0.8704	0.3348
0.7820	0.2358	0.7776	0.2854	0.8691	0.3138	0.7705	0.3263
0.7052	0.2375	0.6997	0.2788	0.7685	0.3056	0.6912	0.3191
0.6421	0.2301	0.6361	0.2711	0.6887	0.2977	0.6267	0.3108
0.5894	0.2251	0.5830	0.2658	0.5704	0.2835	0.5732	0.2972
0.5446	0.2278	0.5381	0.2603	0.5262	0.2854	0.5281	0.2993

Table 2—Harned coefficients of KCl + NiCl$_2$ + H$_2$O system

		T = 25°C			T = 35°C			T = 45°C		
S. No.	I	$\log \gamma_A^0$	α_{AB}	RMSD × 10^3	$\log \gamma_A^0$	α_{AB}	RMSD × 10^3	$\log \gamma_A^0$	α_{AB}	RMSD × 10^3
1	0.5	−0.1872	0.0220	3.38	−0.1874	0.0455	2.37	−0.1887	0.0647	2.11
2	1.0	−0.2184	0.0243	1.33	−0.2172	0.0771	1.72	−0.2175	0.0836	2.11
3	2.0	−0.2408	0.0458	2.17	−0.2370	0.0764	2.33	−0.2355	0.0892	2.00
4	3.0	−0.2438	0.0264	2.19	−0.2380	0.0867	1.88	−0.2351	0.1183	2.82

Table 3—$^s\theta$ and ψ values obtained from the activity coefficient data of KCl + NiCl$_2$ + H$_2$O system at 25°C

S. No.	I	$^s\theta_{KNi}$	ψ_{KNiCl}	RMSD × 10^3	RMSD for $^s\theta = -0.3783$ $\psi = 0.0978$
1	0.5	−0.2736	0.7205	2.122	5.720 × 10^{-3}
2	1.0	−0.2778	−0.0811	1.255	1.907 × 10^{-3}
3	2.0	−0.2909	−0.0055	2.095	6.713 × 10^{-3}
4	3.0	−0.1771	−0.0095	2.137	9.000 × 10^{-3}

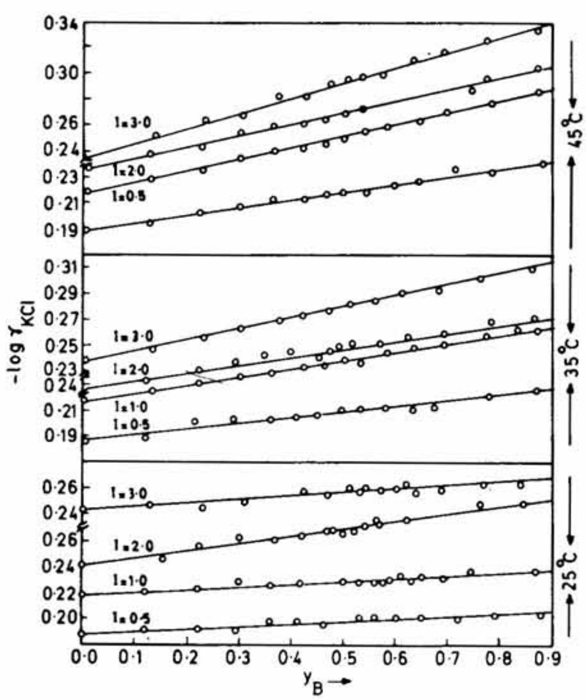

Fig. 1—Mean activity coefficients of KCl in KCl-NiCl$_2$-H$_2$O system.

Table 4—Osmotic coefficients in the mixtures KCl + NiCl$_2$ + H$_2$O at 25°C

S. No.	y_B	I = 0.5	I = 1.0	I = 2.0	I = 3.0
1	1.0	0.8607	0.8907	0.9770	1.081
2	0.9	0.8595	0.8771	0.9427	1.032
3	0.8	0.8603	0.8692	0.9200	0.9989
4	0.7	0.8627	0.8655	0.9057	0.9764
5	0.6	0.8661	0.8650	0.8977	0.9616
6	0.5	0.8705	0.8670	0.8943	0.9522
7	0.4	0.8756	0.8709	0.8943	0.9465
8	0.3	0.8813	0.8764	0.8969	0.9431
9	0.2	0.8874	0.8830	0.9014	0.9409
10	0.1	0.8939	0.8906	0.9071	0.9393
11	0.0	0.9007	0.8990	0.9136	0.9374

Table 5—Excess free energies of mixing ($\Delta_m G^E$) for the KCl + NiCl$_2$ + H$_2$O system at 25°C

S. No.	y_B	I = 0.5	I = 1.0	I = 2.0	I = 3.0
1	0.0	0.0	0.0	0.0	0.0
2	0.9	−11.92	−73.42	−484.0	−1193
3	0.8	−21.19	−130.5	−860.7	−2121
4	0.7	−27.82	−171.3	−1130	−2784
5	0.6	−31.79	−195.8	−1291	−3182
6	0.5	−33.12	−204.0	−1345	−3314

The activity coefficient data were also analysed using the Pitzer formalism[6-9]. The Pitzer coefficients for the pure electrolyte solutions[10,11] are given below.

$\beta^{(0)}_{KCl} = 0.04808$ $\quad \beta^{(1)}_{KCl} = 0.21875$ $\quad C^{\phi}_{KCl} = -0.00079$

$\beta^{(0)}_{NiCl_2} = 0.34991$ $\quad \beta^{(1)}_{NiCl_2} = 1.5300$ $\quad C^{\phi}_{NiCl_2} = -0.00471$

Then, the binary interaction coefficients ($^s\theta_{KNi}$) and the ternary interaction coefficients (ψ_{KNiCl}) were estimated at 25°C and at all the ionic strengths studied. The common $^s\theta$ and ψ values were obtained by fitting the data at all ionic strengths into a single least-squares programme. These values are listed in Table 3. Using these common

$^{s}\theta = -0.3783$ and $\psi = 0.0978$ values, we estimated the osmotic coefficients of the system at 25°C using the appropriate Pitzer equation and the values obtained are listed in Table 4. Also, the excess free energies of mixing ($\Delta_m G^E$) were calculated using the equation,

$$\Delta_m G^E = -2.3026\, y_A y_B\, RTI^2 (\alpha_{AB} + \alpha_{BA}) \quad \ldots (5)$$

where α_{BA} is the Harned coefficient for the variation of log γ_{NiCl_2} with y_A and other symbols have their usual significance[12]. These results are listed in Table 5.

Finally, using the $^{s}\theta$ and ψ values obtained in the present work, the activity coefficient of KCl was calculated at the concentrations ($m_{KCl} = 0.8637$; $m_{NiCl_2} = 4.655$) reported in the solubility data of the $KCl + NiCl_2 + H_2O$ system[13]. The activity coefficient value of 3.0112 thus evaluated is in satisfactory agreement with the value of 3.2920 calculated from the solubility data using the value[14] of $\Delta G_s^0 = -5178$ J/kg in the relation $\Delta G_s^0 = -RT \ln a_K a_{Cl}$. Thus, the Pitzer formalism is found to predict the thermodynamic properties in mixed electrolyte systems even upto the saturation limit.

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