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Thermodynamic Investigation of a Ternary Mixed Electrolyte ($CsCl/MgCl_2/H_2O$) System Using Electromotive Force Measurement at 298.15 K

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This work reports the results of a thermodynamic investigation of the ternary $CsCl-MgCl_2-H_2O$ mixed electrolyte system. The activity coefficients of this mixed aqueous electrolyte system have been studied with the electromotive force (EMF) measurement of the cell: Cs ion-selective electrode (ISE)|CsCl (m_A), $MgCl_2$ (m_B), H_2O|Ag/AgCl at 298.15 K and over total ionic strengths from (0.01 to 1.50) $mol \cdot kg^{-1}$ for different ionic strength fractions y_B of $MgCl_2$ with $y_B = 0$, 0.25, 0.50, and 0.75. The cesium ion-selective electrode (Cs-ISE) and the Ag/AgCl electrode used in this work were made in this laboratory and had a good Nernstian response. The experimental results obey the Harned rule, and the Pitzer model can be used to describe this aqueous system satisfactorily. The osmotic coefficients, excess Gibbs energies, and activities of water of the mixtures were also calculated.

Introduction

The measurement of thermodynamic properties such as activity coefficients, osmotic coefficients, and excess Gibbs energies for multicomponent electrolyte aqueous solutions plays an important role in the development of thermodynamic models and process simulation. However, they are also important in the design and operation of many chemical industrial processes, including extractive crystallization of salts, extractive distillation with salts, removal of acidic gases such as CO_2 and H_2S for ammonia manufacture and natural purification to mention a few.[1] In the salt lakes of western China, cesium and magnesium have been found in brine. To exploit these natural resources scientifically, preliminary investigation of cesium salt solution chemistry is necessary. Therefore, thermodynamic studies of the $CsCl + MgCl_2 + H_2O$ ternary system are very important. During the last few decades, many methods have been used to determine the activity coefficients of electrolytes in solutions, for example, isopiestic vapor pressure measurement,[3,4] solubility determination,[5] hygrometric methods,[6−8] electromotive force (EMF) measurement,[9−11] and so on. However, with the development of ion-selective electrodes (ISEs) in recent years, the measurement of EMF often tends to be chosen for the determination of activity coefficients of electrolytes in a solution. A considerable number of thermodynamic data by using EMF for CsCl in electrolyte aqueous solution or aqueous−organic mixtures have been reported.[12−16]

In the present article, EMF measurements were employed to determine the activity coefficients of a CsCl and $MgCl_2$ mixed electrolyte in aqueous solution, osmotic coefficients, activities of water, and excess Gibbs energies at $T = 298.15$ K and in (0.01 to 1.50) $mol \cdot kg^{-1}$ total ionic strength.

Experimental Section

Materials. CsCl (AR, purity > 99.5 %, Jiangxi) was recrystallized from a mixture (water + ethanol) and then dried overnight in an oven at 473.15 K to constant weight. Afterward, the salts were stored over silica gel in a desiccator before use. $MgCl_2 \cdot 6H_2O$ (AR, purity > 99.5 %, Shanghai) was used without further purification. Double-distilled deionized water was used in our experiments. Its specific conductance was approximately (1.0 to 1.2)$\cdot 10^{-4}$ $S \cdot m^{-1}$. Stock aqueous solutions of CsCl, $MgCl_2$, and different $CsCl/MgCl_2$ ionic strength ratios were prepared by weight.

Apparatus and Procedure. The Ag−AgCl electrode was the thermal-electrolytic type prepared by us according to the guidance described by Ives and Janz.[17] The Cs ion-selective electrode (Cs-ISE), the membrane of which has the following composition (mass %), 1.8 % valinomycin, 0.2 % potassium tetraphenylboron, 65.5 % di-*n*-octyl sebacate, and 32.5 % PVC, was prepared in our laboratory. The Cs-ISE was filled with 0.1 $mol \cdot L^{-1}$ CsCl as the internal liquid, and an Ag/AgCl wire was used as the internal reference electrode. The technique has been described by Wu et al.[18] Both electrodes were calibrated before use and showed good Nernstian response.

The cell arrangements in this work were as follows

$$\text{Cs-ISE}|\text{CsCl}(m_{A0})|\text{Ag/AgCl} \qquad (a)$$

$$\text{Cs-ISE}|\text{MgCl}_2(m_{B0})|\text{Ag/AgCl} \qquad (b)$$

$$\text{Cs-ISE}|\text{CsCl}(m_A), \text{MgCl}_2(m_B)|\text{Ag/AgCl} \qquad (c)$$

These galvanic cells contained a single liquid and are without liquid junction. Here m_{A0} and m_{B0} were the molalities of CsCl and $MgCl_2$ as the single salt in water, respectively. m_A and m_B were the molalities of CsCl and $MgCl_2$ in the mixtures, respectively. The molality of electrolyte in the galvanic cell was varied step by step using a standard addition method.[19,20] The EMF of the above three cells was measured at 298.15 K. To check the response of the Cs-ISE, the EMF readings on cell (a) were carried out first. Similarly, the cell (b) was used for the evaluation of the potentiometric selectivity coefficient. Finally, the EMF of cell (c) was measured in the sequence of the ionic strength fraction (y_B) of $MgCl_2$ in the solutions.

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Table 1. Values of the Pitzer Parameters for CsCl and $MgCl_2$ at 298.15 K[22]

electrolyte	$\beta^{(0)}$ / (kg·mol^{-1})	$\beta^{(1)}$ / (kg·mol^{-1})	C^{φ} / (kg^2·mol^{-2})	m_{max} / (mol·kg^{-1})	σ
CsCl	0.03643	−0.01169	−0.00096	11.000	0.00365
$MgCl_2$	0.35573	1.61738	0.00474	5.750	0.00360

Table 2. Electromotive Force, *E*, Mean Activity Coefficients, $\gamma_{\pm A}$ and $\gamma_{\pm B}$, Osmotic Coefficients, Φ, Activities of Water, a_W and Excess Gibbs Energies, G^E, at 298.15 K

I / mol·kg^{-1}	m_A / mol·kg^{-1}	m_B / mol·kg^{-1}	E_{exptl} / mV	$\gamma_{\pm A}$	$\gamma_{\pm B}$	Φ	a_W	G^E / J·mol^{-1}
				$y_B = 0.00$				
0.0100	0.0100	0	−112.2	0.9052	0.8061	0.9648	0.9997	−3.19
0.0200	0.0200	0	−78.9	0.8643	0.7466	0.9522	0.9993	−9.72
0.0300	0.0300	0	−59.7	0.8366	0.7069	0.9432	0.9990	−18.08
0.0400	0.0400	0	−46	0.8188	0.6768	0.9360	0.9987	−26.95
0.0500	0.0500	0	−35.5	0.8032	0.6526	0.9299	0.9983	−36.94
0.0800	0.0800	0	−13.8	0.7652	0.5995	0.9157	0.9974	−72.71
0.1000	0.1000	0	−3.6	0.7463	0.5736	0.9083	0.9967	−99.61
0.1500	0.1500	0	15.1	0.7155	0.5262	0.8937	0.9952	−169.98
0.2000	0.2000	0	27.5	0.6827	0.4927	0.8826	0.9937	−261.96
0.3000	0.3000	0	45.4	0.6444	0.4461	0.8656	0.9907	−453.70
0.5000	0.5000	0	67.7	0.5963	0.3897	0.8425	0.9849	−891.29
0.7000	0.7000	0	82.3	0.5656	0.3544	0.8261	0.9794	−1374.39
0.9000	0.9000	0	93.3	0.5447	0.3293	0.8132	0.9740	−1877.29
1.1000	1.1000	0	102	0.5277	0.3104	0.8023	0.9687	−2408.03
1.3000	1.3000	0	109.3	0.5146	0.2955	0.7929	0.9634	−2947.55
1.5000	1.5000	0	115.7	0.5050	0.2835	0.7843	0.9583	−3477.44
				$y_B = 0.25$				
0.0100	0.0075	0.0008	−121.8	0.9060	0.8095	0.9598	0.9993	−3.24
0.0300	0.0225	0.0025	−69.0	0.8423	0.7138	0.9359	0.9984	−17.08
0.0500	0.0375	0.0042	−44.8	0.8086	0.6619	0.9215	0.9975	−35.24
0.1000	0.0750	0.0083	−12.6	0.7557	0.5875	0.8982	0.9956	−92.93
0.2000	0.1500	0.0167	18.7	0.6942	0.5127	0.8702	0.9926	−241.66
0.3000	0.2250	0.0250	36.9	0.6589	0.4707	0.8514	0.9897	−412.01
0.5000	0.3750	0.0417	60.1	0.6204	0.4211	0.8244	0.9849	−774.59
0.7000	0.5250	0.0583	74.8	0.5896	0.3913	0.8044	0.9803	−1187.96
0.9000	0.6750	0.0750	85.8	0.5679	0.3710	0.7881	0.9758	−1619.59
1.1000	0.8250	0.0917	94.9	0.5544	0.3563	0.7744	0.9772	−2039.23
1.3000	0.9750	0.1083	102.4	0.5428	0.3454	0.7625	0.9734	−2471.04
1.5000	1.1250	0.1250	108.8	0.5325	0.3372	0.7522	0.9696	−2912.55
				$y_B = 0.50$				
0.0100	0.0050	0.0017	−134.6	0.9076	0.8124	0.9540	0.9990	−3.27
0.0300	0.0150	0.0050	−81.5	0.8487	0.7197	0.9279	0.9978	−16.39
0.0500	0.0250	0.0083	−57.5	0.8116	0.6702	0.9126	0.9967	−34.43
0.1000	0.0500	0.0167	−24.7	0.7674	0.6000	0.8887	0.9944	−87.57
0.2000	0.1000	0.0333	6.9	0.7089	0.5312	0.8611	0.9915	−224.06
0.3000	0.1500	0.0500	25.5	0.6779	0.4938	0.8428	0.9887	−376.08
0.5000	0.2500	0.0833	48.5	0.6358	0.4517	0.8169	0.9847	−713.34
0.7000	0.3500	0.1167	63.8	0.6115	0.4281	0.7977	0.9808	−1062.99
0.9000	0.4500	0.1500	75.0	0.5918	0.4133	0.7823	0.9770	−1427.30
1.1000	0.5500	0.1833	84.0	0.5768	0.4038	0.7695	0.9848	−1794.29
1.3000	0.6500	0.2167	91.7	0.5658	0.3979	0.7589	0.9821	−2154.70
1.5000	0.7500	0.2500	97.9	0.5536	0.3946	0.7501	0.9794	−2533.1
				$y_B = 0.75$				
0.0100	0.0025	0.0025	−155.1	0.9085	0.8148	0.9469	0.9986	−3.35256
0.0300	0.0075	0.0075	−101.7	0.8545	0.7247	0.9188	0.9973	−16.2504
0.0500	0.0125	0.0125	−77.6	0.8188	0.6772	0.9032	0.9959	−33.6271
0.1000	0.0250	0.0250	−44.4	0.7797	0.6109	0.8805	0.9933	−85.4333
0.2000	0.0500	0.0500	−12.4	0.7263	0.5479	0.8571	0.9904	−214.394
0.3000	0.0750	0.0750	6.1	0.6939	0.5152	0.8434	0.9875	−360.207
0.5000	0.1250	0.1250	29.9	0.6603	0.4809	0.8265	0.9841	−668.953
0.7000	0.1750	0.1750	45.3	0.6363	0.4641	0.8158	0.9807	−991.735
0.9000	0.2250	0.2250	57.0	0.6210	0.4555	0.8084	0.9773	−1313.09
1.1000	0.2750	0.2750	66.1	0.6068	0.4520	0.8036	0.9921	−1635.78
1.3000	0.3250	0.3250	73.8	0.5959	0.4518	0.8007	0.9907	−1951.52
1.5000	0.3750	0.3750	80.4	0.5873	0.4543	0.7995	0.9893	−2258.19

As usual, all measurements were performed under stirring conditions, and the temperature was kept constant at 298.15 K (± 0.02 K), employing a double-walled container enabling the circulation of the thermostatted water from a bath. Through the lid, preventing solvent evaporation, the electrodes were immersed in the solution. The EMF measure-

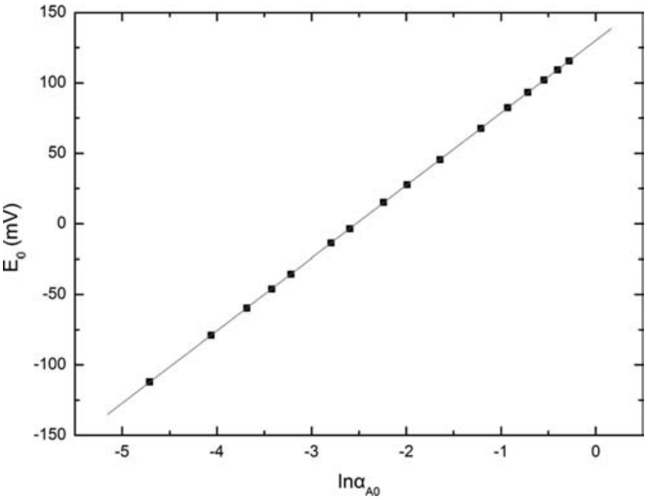

Figure 1. Response of Cs-ISE and Ag/AgCl electrode pairs in the mixtures.

ments were obtained on a pH/mV meter (Orion-868). Voltage readings were taken to be final when they were constant, within 0.1 mV, for at least five minutes. To prolong the life of the Cs-ISE, the entire experiment did not exceed 1.5 h.

Results and Discussion

Calibration of Ion-Selective Electrodes and Determination of Cs^+ ISE Potentiometric Selectivity Coefficient. The EMF of cell (a) can be expressed by the Nernst equation

$$E_a = E_0 + 2k \ln(m_{A0}\gamma_{\pm A0}) \qquad (1)$$

where $k = RT/F$ represents the theoretical Nernst slope. R, F, and T are the gas constant, Faraday constant, and absolute temperature, respectively. E_0 is the standard potential of cell (1) and $\gamma_{\pm A0}$ is the mean activity coefficients of pure CsCl at different m_{A0} values in water, and its values were estimated by the Pitzer equation,[21] in which the ionic interaction parameters of pure CsCl were taken from Kim and Frederick's data[22] and are listed in Table 1. The EMF values and molalities are listed in Table 2, and a series of sets of E_a was plotted versus $\ln \alpha_{A0}$ (the activity of pure CsCl in water) to check their linear relationship. Figure 1 shows that a good linear relationship really exists between E_a and $\ln \alpha_{A0}$. By way of this line, values of E_0 and k along with the standard deviation (rmsd) and the linear correlation coefficient (R_{LC}) can be evaluated using a linear regression method. They are 130.06 mV, (25.74 ± 0.03) mV, 0.15, and 0.99999, respectively. The obtained value of k is quite close to the theoretical value (25.69 mV) of the Nernst slope. Therefore, this provides an indication that the electrode pairs used here have a satisfactory Nernstian response and are well suited to our measurements.

The potentials of cell (b) for m_{B0} from 0.01 $mol \cdot kg^{-1}$ to 1.50 $mol \cdot kg^{-1}$ were determined. By combining the Nernst principle and reordering the relevant terms, we calculated the selective coefficient K^{Pot} according to the following equation

$$K^{Pot} = [\exp(E_b - E_0)/k]/[2(m_{B0}\gamma_{B0})^{3/2}] \qquad (2)$$

where K^{Pot} represents the potentiometric selectivity coefficient of the Cs^+ ISE toward the Mg^{2+} interfering ions and E_b is the EMF value of cell (b) at every measurement. $\gamma_{\pm B0}$ refers to the activity coefficient of pure $MgCl_2$ in water at $T = 298.15$ K, and its value was taken and calculated in a similar fashion to that of $\gamma_{\pm A0}$. The average value of K^{Pot} is found to be less than $1.0 \cdot 10^{-4}$.

Pitzer Equation. Using the galvanic cell (c), the EMF values (E_c) of the CsCl + $MgCl_2$ + H_2O ternary system were determined at 298.15 K and at different ionic strengths $I = m_A + m_B$ and mole fractions $y_B = 3m_B/(m_A + 3m_B)$. The Nernst equation of cell (c) can be written as follows

$$E_c = E_0 + k{\cdot}\ln[\gamma_{\pm A}^2{\cdot}m_A{\cdot}(m_A + 2m_B) + K^{Pot}{\cdot}\gamma_{\pm B}^{2/3}{\cdot}m_B^{1/2}{\cdot}(m_A + 2m_B)] \qquad (3)$$

in which, $\gamma_{\pm A}$ and $\gamma_{\pm B}$ are the mean activity coefficients of CsCl and $MgCl_2$, respectively, in cell (c). Because K^{Pot} is so small, the interfering effect of Mg^{2+} on the response of the Cs^+ ISE would be negligible, and the second term in eq 3 could be omitted without leading to an appreciable error. Therefore, eq 3 can be simplified to the Nernstian relation

$$E_c = E_0 + k{\cdot}\ln[\gamma_{\pm A}^2{\cdot}m_A{\cdot}(m_A + 2m_B)]$$
$$\text{or} \quad \ln \gamma_{\pm A} = (E_C - E_0)/(2{\cdot}k) - 1/2 \ln[m_A{\cdot}(m_A + 2{\cdot}m_B)] \qquad (4)$$

Through eq 4, the mean activity coefficients of CsCl in the mixture can be calculated, and the related results of cell (c) are collected in Table 2.

In this article, we chose the modified form of the Pitzer equation suggested by Harvie.[23] For the ternary system, the mean activity coefficients $\gamma_{\pm CsCl}$ and $\gamma_{\pm MgCl_2}$ and the osmotic coefficients, Φ, are given as follows

$$\ln \gamma_{\pm cscl} = 2(m_A + m_B)\beta^{(0)}_{cscl} + m_B\beta^{(0)}_{MgCl_2} + 2(m_A + m_B)g(2\sqrt{I})\beta^{(1)}_{cscl} + m_B g(2\sqrt{I})\beta^{(1)}_{MgCl_2} + (1.5m_A^2 + 4m_Am_B + 2m_B^2)C^{\varphi}_{cscl} + \sqrt{2}/2(m_Am_B + 2m_B^2)C^{\varphi}_{MgCl_2} + m_B\theta + m_B{}^{E}\theta + (1.5m_Am_B + m_B^2)\psi + F \qquad (5)$$

$$3 \ln \gamma_{\pm MgCl_2} = 4(m_A + 2m_B)(m_AC^{\varphi}_{cscl} + \sqrt{2}/2m_BC^{\varphi}_{MgCl_2}) + 4m_A\beta^{(0)}_{cscl} + (2m_A + 8m_B)\beta^{(0)}_{MgCl_2} + \sqrt{2}/2(m_A + 2m_B)^2C^{\varphi}_{MgCl_2} + 2m_A\theta + 2m_A{}^{E}\theta + (m_A^2 + 6m_Am_B)\psi + 6F \qquad (6)$$

$$F = -A_{\varphi}[\sqrt{I}/(1 + 1.2\sqrt{I}) + 2\ln(1 + 1.2\sqrt{I})/1.2] + (m_A + 2m_B)g'(2\sqrt{I})(m_A\beta^{(1)}_{cscl} + m_B\beta^{(1)}_{MgCl_2})/I + 2m_Am_B{}^{E}\theta' \qquad (7)$$

$$\Phi = [m_A(m_A + 2m_B)\beta^{(0)}_{cscl} + m_B(m_A + 2m_B)\beta^{(0)}_{MgCl_2} + m_A(m_A + 2m_B)\exp(-2\sqrt{I})\beta^{(1)}_{cscl} + m_B(m_A + 2m_B)\exp(-2\sqrt{I})\beta^{(1)}_{MgCl_2} + m_A(m_A + 2m_B)^2C^{\varphi}_{cscl} + \sqrt{2}/2m_B(m_A + 2m_B)^2C^{\varphi}_{MgCl_2} + 2m_Am_B({}^{E}\theta + \theta + {}^{E}\theta'I) + 2m_Am_B(m_A + 2m_B)\psi - A_{\varphi}I^{1.5}/(1 + 1.2\sqrt{I})]/(m_A + 1.5m_B) + 1 \qquad (8)$$

where, A_{φ} is the Debye−Hückel osmotic coefficient parameter and has the value of 0.39209 $(kg \cdot mol^{-1})^{1/2}$ [24] for water at 298.15 K, ${}^{E}\theta$ and ${}^{E}\theta'$ stand for the unsymmetrical higher-order electrostatic terms of the Pitzer equation, which can be calculated according to an empirical formula,[25] and all other symbols have their usual meanings. The ionic interaction parameters of pure $MgCl_2$ were taken from the data of Kim and Frederick.[22]

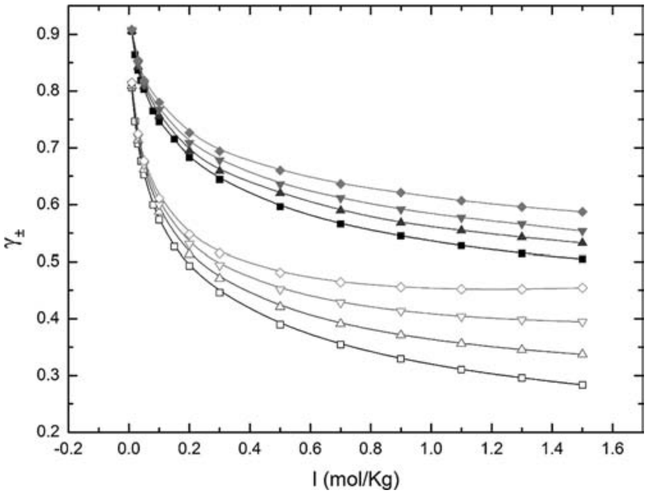

Figure 2. Plot of $\gamma_{\pm A}$ and $\gamma_{\pm B}$ against ionic strength, I, in the mixture ($\gamma_{\pm A}$: ■, $y_B = 0.00$; ▲, $y_B = 0.25$; ▼, $y_B = 0.50$; ◆, $y_B = 0.75$. $\gamma_{\pm B}$: □, $y_B = 0.00$; △, $y_B = 0.25$; ▽, $y_B = 0.50$; ◇, $y_B = 0.75$).

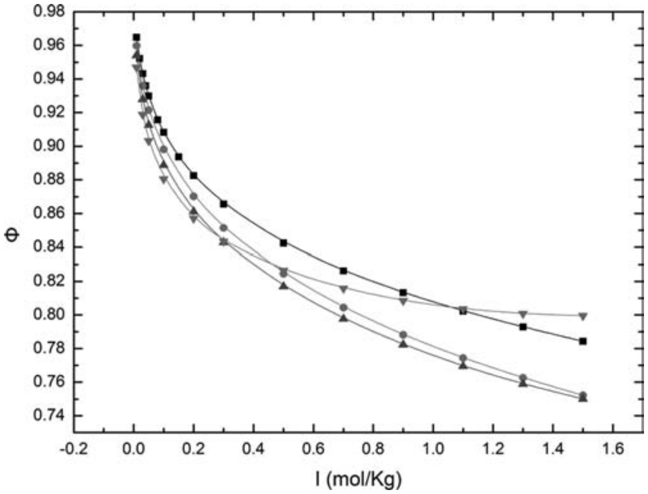

Figure 3. Osmotic coefficients, Φ, against ionic strength, I, in the mixtures (■, $y_B = 0.00$; ●, $y_B = 0.25$; ▲, $y_B = 0.50$; ▼, $y_B = 0.75$).

Through eq 5, we evaluated the mixing ionic parameters $\theta_{Cs,Mg} = -0.35048$ and $\Psi_{Cs,Mg,Cl} = 0.04577$ and the standard deviations rmsd = 0.00455 by using a multiple linear regression technique. The activity coefficients of $MgCl_2$ and the osmotic coefficients, Φ, for the ternary system at different ionic strengths were then calculated by eqs 6 and 8. These outcomes are also listed in Table 2. Figure 2 shows plots of $\gamma_{\pm A}$ and $\gamma_{\pm B}$ versus I. Obviously, the curves of variation of both $\gamma_{\pm A}$ and $\gamma_{\pm B}$ at different fractions y_B are quite similar in their dependence on the total ionic strength. For CsCl, $\gamma_{\pm A}$ decreases with increasing composition over the entire total concentration range. For $MgCl_2$, $\gamma_{\pm B}$ decreases with increasing composition in the concentrated region. Figure 3 is a plot of osmotic coefficients, Φ, versus the total ionic strength, I. As can be seen from these curves, the values of Φ decrease with increasing I.

Harned Rule. As is known, the Harned rule was one of the earliest treatments for strong electrolyte water mixtures. The form of Harned rule can be expressed by the experimental activity coefficients of CsCl in the mixtures

$$\ln \gamma_{\pm A} = \ln \gamma_{\pm A0} - \alpha_{AB} \cdot y_B - \beta_{AB} \cdot y_B^2 \qquad (9)$$

where α_{AB} and β_{AB} are adjustable parameters that depend only on the total ionic strength at a given pressure and temperature and $\gamma_{\pm A0}$ is the mean activity coefficients of CsCl in pure solutions at the same total ionic strength as that of the mixture. The values of α_{AB}, β_{AB}, and $\gamma_{\pm A0}$ are given in Table 3, together with the standard deviations of the fit, and the plots of ln $\gamma_{\pm A}$ versus y_B for each system are shown in Figure 4. The Figure shows that the results of $\gamma_{\pm A0}$ in eq 9 give fits of the experimental results very well.

Table 3. Adjustable Parameters of the Harned Equation

I (mol·kg^{-1})	ln $\gamma_{\pm A0}$	$-\alpha_{AB}$	$-\beta_{AB}$	10^3·rmsd
0.0100	−0.0997	0.0045	0.0008	0.313
0.0300	−0.1785	0.0279	0.0008	0.358
0.0500	−0.2187	0.0182	0.0084	1.810
0.1000	−0.2927	0.0485	0.0136	0.537
0.2000	−0.3817	0.0598	0.0304	0.268
0.3000	−0.4400	0.0972	0.0040	2.500
0.5000	−0.5156	0.1377	−0.0076	6.420
0.7000	−0.5695	0.1614	−0.0072	2.010
0.9000	−0.6072	0.1542	0.0260	1.590
1.1000	−0.6381	0.1792	0.0056	4.740
1.3000	−0.6634	0.1976	−0.0064	4.920
1.5000	−0.6815	0.1789	0.0236	7.710

Excess Gibbs Energy and Activity of Water. The values of excess Gibbs energies (G^E) and activities of water (a_w) were determined for all series of investigated mixed electrolyte solutions using eqs 10 and 11.

$$G^E = RT[\nu_A m_A(1 - \Phi + \ln \gamma_A) + \nu_B m_B(1 - \Phi + \ln \gamma_B)] \qquad (10)$$

$$a_W = \exp\left[\left(\frac{-M_W}{1000}\right)\left(\sum_i m_i\right)\Phi\right] \qquad (11)$$

where ν_A and ν_B are the total number of anions and cations of the electrolyte produced by dissociation of one molecule of CsCl and $MgCl_2$, respectively. M_W and m_i are the molecular mass of water (18.0153 g·mol^{-1}) and the molality of the solute species, respectively. The other symbols are as described above. The results of G^E and a_w are listed in Table 2. Figure 5 shows the excess Gibbs energies of the mixture G^E as a function of ionic strength. From this Figure, it can be seen that the values of G^E are always negative and increase with an increase in ionic strength fractions, y_B.

Conclusions

The mean activity coefficients of CsCl in the CsCl + $MgCl_2$ + H_2O ternary system were determined using the

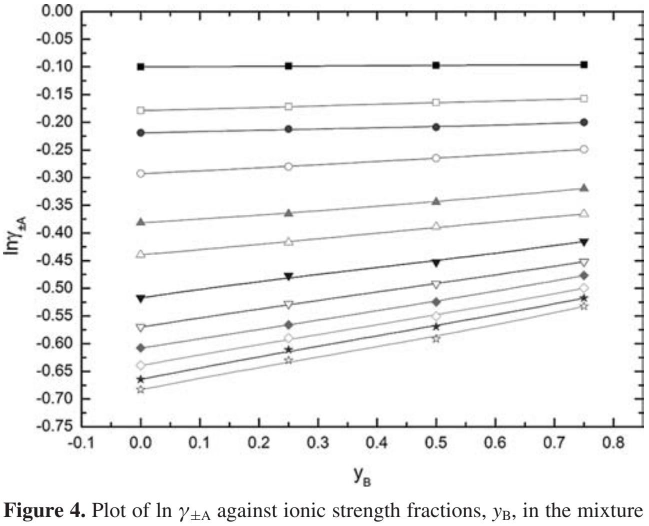

Figure 4. Plot of ln $\gamma_{\pm A}$ against ionic strength fractions, y_B, in the mixture (■, $I = 0.0100$; □, $I = 0.0300$; ●, $I = 0.0500$; ○, $I = 0.1000$; ▲, $I = 0.2000$; △, $I = 0.3000$; ▼, $I = 0.5000$; ▽, $I = 0.7000$; ◆, $I = 0.9000$; ◇, $I = 1.0000$; ★, $I = 1.3100$; ☆, $I = 1.5300$).

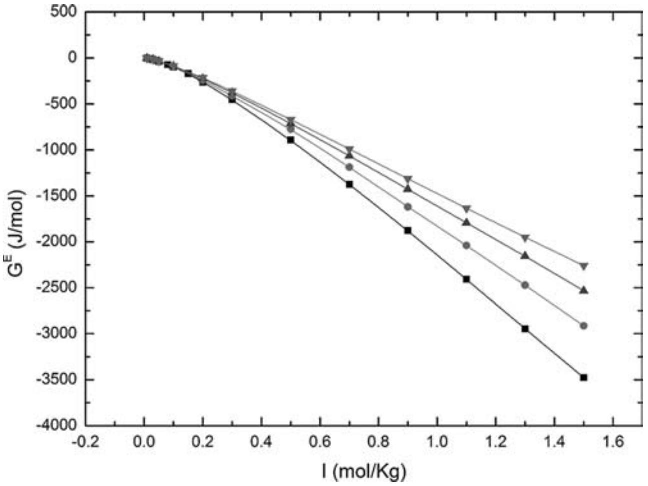

Figure 5. Plot of excess Gibbs energies, G^E, against ionic strength, I, in the mixtures (■, $y_B = 0.00$; ●, $y_B = 0.25$; ▲, $y_B = 0.50$; ▼, $y_B = 0.75$).

galvanic cell consisting of Cs-ISE|CsCl(m_A), $MgCl_2$(m_B), and H_2O|Ag/AgCl for different ionic strength fractions, y_B, of $MgCl_2$ with $y_B = 0$, 0.25, 0.5, and 0.75 at 298.15 K. In addition, mixing interaction parameters, $\theta_{Cs,Mg}$ and $\Psi_{Cs,Mg,Cl}$, activity coefficients of $MgCl_2$, osmotic coefficients, Φ, by the Pitzer equation, excess Gibbs energies, and activities of water were determined. The Harned rule was applied to the title system. In this article, the investigation indicated that both thermodynamic models could correlate the experimental data, and this study provided basic thermodynamic reference data for further research application.

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