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Activity Coefficients of Cesium Chloride and Cesium Sulfate in Aqueous Mixtures Using an Electromotive Force Method at 298.15 K

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Activity coefficients for the $CsCl + Cs_2SO_4 + H_2O$ ternary system were determined at 298.15 K by electromotive force (EMF) measurements of the cell: Cs ion-selective electrode (ISE)|$CsCl(m_A)$, $Cs_2SO_4(m_B)$, H_2O|Ag|AgCl. 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 Nernst response. The experimental data were interpreted using Harned's rule and the Pitzer model. The corresponding parameters required in the Pitzer model have been evaluated for this system. Osmotic coefficients of this system and activity coefficients of the second salt Cs_2SO_4 were also calculated in the same molality range.

Introduction

Activity coefficients of the electrolytes in a mixed-electrolyte solution are one of the important thermodynamic properties. In the past decade, several methods have been used to determine the activity coefficients of electrolytes in solutions, such as solubility determination, static vapor pressure measurement, electromotive force (EMF) measurement, and so on.[1] With the development of ion-selective electrodes and the simplicity, high speed, and accuracy of the electromotive force measurement, such a method is widely used to determine the activity coefficient of electrolytes in solution in comparison with other techniques.[2]

Actually, in many previous works, people have used EMF measurement to determine the activity coefficients of electrolytes. For example, Yang and Pitzer[3] and Koh et al.[4] have used this method to obtain the activity coefficients of 1−1 type electrolytes in mixed solvents. Lopes et al.[5,6] have reported the activity coefficients of alkali metal chlorides (KCl and NaCl) in water−ethanol mixtures.

Since the beginning of the 20th century, the activities of alkali metals in aqueous or aqueous−organic mixtures have been studied.[7−17] The study of the thermodynamic properties of aqueous mixed-electrolyte solutions has received considerable attention. Yao et al.[18] have reported the studies of the ternary system $LiCl + Li_2SO_4 + H_2O$ at different temperatures. Sarada et al.[19] have studied the activity coefficients for aqueous mixtures of $NaCl + Na_2SO_4 + H_2O$ using a cell consisting of a sodium ion-selective electrode and an Ag|AgCl electrode. The thermodynamic property data for $KCl + K_2SO_4 + H_2O$[20] and $RbCl + Rb_2SO_4 + H_2O$[21] have also been published.

In this work, we have carried out the investigation of $CsCl + Cs_2SO_4 + H_2O$ at 298.15 K to enrich the thermodynamic data of alkali chlorides. The data could be used to predict the solute activity coefficients in the mixture at high ionic strength. The experimental data were fitted using the Pitzer model and Harned's rule. Moreover, the osmotic coefficients and the activity coefficient of the second salt Cs_2SO_4 were also calculated.

Experimental Section

Materials. Cesium chloride (CsCl), analytical grade (purity > 99.5 %, Jiangxi), and cesium sulfate (Cs_2SO_4), analytical grade (purity > 99.5 %, Jiangxi), were dried overnight in a muffle furnace ($T = 500$ °C). Subsequently, the salts were stored over silica gel in a desiccator before use. Double distilled deionized water was used in our experiments. Its specific conductance was approximately (1.0 to 1.2)$\cdot 10^{-4}$ $S \cdot m^{-1}$.

Apparatus and Procedure. The cesium ion-selective electrode, which was a PVC membrane type based on valinomycin, was filled with 0.1 $mol \cdot L^{-1}$ of CsCl as an internal liquid (the related technique was exactly described by Wu[22]). The Ag|AgCl electrode was a thermal-electrolytic type prepared in our laboratory. Both the electrodes were standardized before use and showed good Nernstian response.

The cell arrangements in this work were as follows

(a) Cs-ISE|$CsCl(m_{A0})$|Ag|AgCl

(b) Cs-ISE|$CsCl(m_A)$, $Cs_2SO_4(m_B)$|Ag|AgCl

The above galvanic cells without liquid junction used one fluid. Here m_{A0} was the molality of CsCl as the single salt in water. m_A and m_B were the molalities of CsCl and Cs_2SO_4 in the mixtures, respectively. The electromotive force of cell (a) and cell (b) was measured at 298.15 K. To check the response of the Cs-ISE, the EMF readings on cell (a) were carried out first.

All measurements were performed under stirring conditions, and the temperature was kept constant at 298.15 K (± 0.02 K), employing a double-walled glass bottle enabling the circulation of the thermostated water from a bath. The ion analyzer used was an Orion-868 (USA), with a precision of ± 0.1 mV. Each concentration of the solutions was prepared by directly weighing the materials, using a Sartorius electronic balance (Germany), with a precision of 0.1 mg. Cell equilibrium was deemed to have been attained when voltage readings were stable within 0.1 mV for at least 5 min. To prolong the life of the Cs-ISE, the entire experiment did not exceed 1.5 h.

Results and Discussion

The cell (a) was employed to determine the EMF values E_{exp} of CsCl in the aqueous solutions at 298.15 K. The experimental

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Table 1. Electromotive Force E, the Mean Activity Coefficients $\gamma_{\pm\mathrm{CsCl}}$ and $\gamma_{\pm\mathrm{Cs_2SO_4}}$, and the Osmotic Coefficients Φ at 298.15 K[a]

I / mol·kg^{-1}	m_{CsCl} / mol·kg^{-1}	$m_{\mathrm{Cs_2SO_4}}$ / mol·kg^{-1}	E_{exp} / mV	$\gamma_{\pm\mathrm{CsCl}}$	$\gamma_{\pm\mathrm{Cs_2SO_4}}$	Φ	I / mol·kg^{-1}	m_{CsCl} / mol·kg^{-1}	$m_{\mathrm{Cs_2SO_4}}$ / mol·kg^{-1}	E_{exp} / mV	$\gamma_{\pm\mathrm{CsCl}}$	$\gamma_{\pm\mathrm{Cs_2SO_4}}$	Φ
$y_B = 0.00$													
0.0009	0.0009	0.0000	−241.0	0.9695	0.9325	0.9887	0.1330	0.1330	0.0000	1.0	0.7213	0.5130	0.9047
0.0035	0.0035	0.0000	−173.9	0.9177	0.8737	0.9785	0.1755	0.1755	0.0000	13.6	0.6982	0.4765	0.8963
0.0075	0.0075	0.0000	−135.4	0.9045	0.8241	0.9695	0.2288	0.2288	0.0000	25.7	0.6774	0.4416	0.8883
0.0146	0.0146	0.0000	−103.1	0.8701	0.7688	0.9591	0.2934	0.2934	0.0000	36.6	0.6528	0.4093	0.8809
0.0251	0.0251	0.0000	−76.9	0.8418	0.7153	0.9486	0.3841	0.3841	0.0000	48.3	0.6258	0.3748	0.8734
0.0388	0.0388	0.0000	−56.3	0.8125	0.6672	0.9387	0.5050	0.5050	0.0000	60.1	0.5986	0.3407	0.8665
0.0552	0.0552	0.0000	−39.8	0.7868	0.6253	0.9298	0.6551	0.6551	0.0000	71.5	0.5758	0.3092	0.8611
0.0767	0.0767	0.0000	−24.5	0.7622	0.5843	0.9209	0.8356	0.8356	0.0000	81.5	0.5482	0.2807	0.8574
0.1019	0.1019	0.0000	−10.9	0.7471	0.5478	0.9127	1.0445	1.0445	0.0000	90.5	0.5223	0.2554	0.8556
$y_B = 0.25$													
0.0050	0.0037	0.0004	−163.8	0.9455	0.8540	0.9704	0.4000	0.3000	0.0333	40.1	0.6181	0.3837	0.8426
0.0100	0.0075	0.0008	−130.2	0.9024	0.8041	0.9596	0.5999	0.4500	0.0500	58.0	0.5834	0.3352	0.8250
0.0500	0.0375	0.0042	−52.6	0.8171	0.6438	0.9210	0.7999	0.6000	0.0667	70.3	0.5556	0.3022	0.8124
0.1000	0.0750	0.0083	−20.9	0.7562	0.5590	0.8980	1.0000	0.7500	0.0833	79.1	0.5273	0.2776	0.8024
0.2000	0.1500	0.0167	9.9	0.6876	0.4706	0.8716							
$y_B = 0.50$													
0.0050	0.0025	0.0008	−175.7	0.9583	0.8550	0.9654	0.3999	0.2000	0.0666	27.2	0.6180	0.3959	0.8157
0.0100	0.0050	0.0017	−143.3	0.9038	0.8067	0.9530	0.5999	0.3000	0.1000	44.2	0.5732	0.3491	0.7928
0.0500	0.0250	0.0083	−66.6	0.7994	0.6492	0.9084	0.7999	0.4000	0.1333	56.2	0.5427	0.3174	0.7752
0.1000	0.0501	0.0166	−34.4	0.7468	0.5664	0.8818	0.9998	0.5000	0.1666	65.3	0.5181	0.2937	0.7604
0.1999	0.1000	0.0333	−3.3	0.6836	0.4803	0.8509							
$y_B = 0.75$													
0.0050	0.0013	0.0012	−196.1	0.9584	0.8563	0.9593	0.4000	0.1000	0.1000	6.0	0.6103	0.4063	0.7930
0.0100	0.0025	0.0025	−163.3	0.9050	0.8078	0.9445	0.6000	0.1500	0.1500	23.0	0.5660	0.3611	0.7692
0.0500	0.0125	0.0125	−87.5	0.7937	0.6532	0.8935	0.8001	0.2000	0.2000	34.5	0.5308	0.3308	0.7512
0.1000	0.0250	0.0250	−55.6	0.7377	0.5722	0.8639	1.0001	0.2500	0.2500	43.1	0.5018	0.3083	0.7363
0.2000	0.0500	0.0500	−24.5	0.6750	0.4882	0.8302							

[a] $y_B = 0.00$; $\gamma_{\pm\mathrm{Cs_2SO_4}}$ means the activity coefficients of Cs_2SO_4 in trace.

mean activity coefficients of CsCl in the mixtures were calculated from the following Nernst equation or

$$E_{\mathrm{exp}} = E^0 + k \ln \alpha_{A0} \tag{1}$$

$$E_{\mathrm{exp}} = E^0 + 2k \ln(m_{A0}\gamma_{\pm A0}) \tag{2}$$

where $k = RT/F$; R, T, and F are the universal gas constant, absolute temperature, and Faraday constant, respectively; E^0 is the standard potential of the cell (a); α_{A0} is the activity of CsCl in the system; and $\gamma_{\pm A0}$ is the mean activity coefficients of pure CsCl at different m_{A0} values in the aqueous solution.

The activity coefficients of CsCl were calculated using the Pitzer equations. For 1−1 type electrolytes, the Pitzer equations[23] for mean activity coefficients can be written as follows

$$\ln \gamma_{\pm} = f^{\gamma} + mB^{\gamma} + m^2C^{\gamma} \tag{3}$$

where

$$f^{\gamma} = -A_{\varphi}x \tag{3-1}$$

$$B^{\gamma} = 2\beta^{(0)} + 2\beta^{(1)}y \tag{3-2}$$

$$C^{\gamma} = (3/2)C^{\varphi} \tag{3-3}$$

$$x = I^{1/2}/(1 + bI^{1/2}) + (2/b)\ln(1 + bI^{1/2}) \tag{3-4}$$

$$y = [1 - \exp(-\alpha I^{1/2})(1 + \alpha I^{1/2} - 1/2\alpha^2 I)]/(\alpha^2 I) \tag{3-5}$$

In these equations, $\beta^{(0)}$, $\beta^{(1)}$, and C^{φ} are the parameters of the Pitzer equations, which were given by Kim and Frederich;[24] α and b are assumed to be fixed parameters whose values are (2.0 and 1.2) kg$^{1/2}$·mol$^{-1/2}$. A_{φ} is the Debye−Hückel constant for the osmotic coefficient defined by

$$A_{\varphi} = \frac{1}{3}\left(\frac{2\pi N_0 d_N}{1000}\right)^{1/2} \cdot \left(\frac{e^2}{DKT}\right)^{3/2} \tag{4}$$

where N_0, d_N, D, and K are Avogadro's number, the density of solvent mixtures, the dielectric constant, and Boltzmann's constant, respectively. After the values of the fundamental physical constants are introduced into eq 4, it becomes

$$A_{\varphi} = 1.4006 \cdot 10^6 [d_N/(DT)^3]^{1/2} \tag{5}$$

The A_{φ} value in water is 0.39209.[4]

The EMF values and molarities are listed in Table 1 and depicted in Figure 1. A plot of E_{exp} against $\ln \alpha_{A0}$ produced a straight line. The value of E^0 for cell (a) was 121.7 mV, and the value of k was 25.49 mV. They were evaluated by a linear regression method, and the linear correlation coefficient was 0.99998. It was clear that the value of k was close to the theoretical one (25.69 mV) of the Nernst slope, so it was concluded that the electrode pairs we used had good Nernstian response and were satisfactory enough for our research.

The cell (b) was used to obtain the EMF values (E_{exp}) of CsCl in admixture with Cs_2SO_4 at 298.15 K for the different ionic strengths, $I = m_A + 3m_B$, and the mole fraction, $y_B = 3m_B/(m_A + 3m_B)$. The Nernst equation of cell (b) is written as

$$E_{\mathrm{exp}} = E^0 + k \ln\{\gamma_{\pm A}{}^2 \cdot m_A(m_A + 2m_B) + K^{\mathrm{pot}}\gamma_{\pm B}{}^{2/3} \cdot m_A{}^{1/2}(m_A + 2m_B)\} \tag{6}$$

where $\gamma_{\pm A}$ and $\gamma_{\pm B}$ refer to the mean activity coefficients of CsCl and Cs_2SO_4 in cell (b). The selective coefficient of the Ag|AgCl electrode for the $SO_4{}^{2-}$ ion was found to be less than

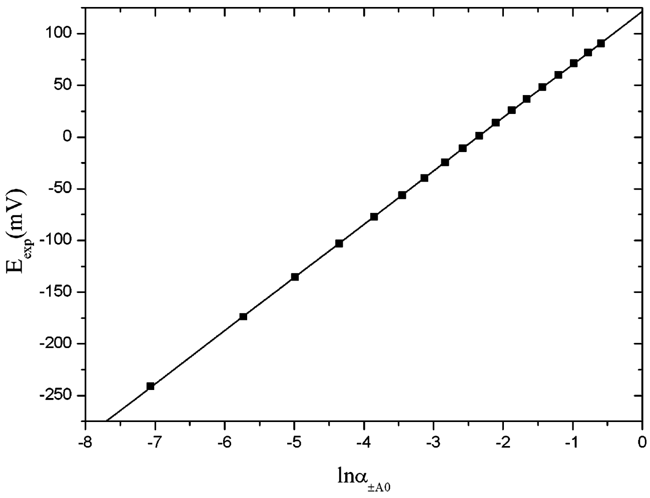

Figure 1. Response of Cs-ISE and Ag|AgCl electrode pairs in the mixtures.

$1.0{\cdot}10^{-4}$. Equation 6 can be neglected without leading to an appreciable, and the simplified form is

$$E_{\mathrm{exp}} = E^0 + k\ln\{\gamma_{\pm\mathrm{A}}{}^2{\cdot}m_\mathrm{A}(m_\mathrm{A} + 2m_\mathrm{B})\} \tag{7}$$

Pitzer equations for the activity coefficients of the 1:1 electrolyte A (CsCl) and 1:2 electrolyte B (Cs_2SO_4) and the osmotic coefficients Φ are given by eqs 8 to 11,[25] respectively.

$$\begin{aligned}\ln\gamma_{\pm\mathrm{CsCl}} = {}& 2(m_\mathrm{A} + m_\mathrm{B})\beta^{(0)}_{\mathrm{CsCl}} + m_\mathrm{B}\beta^{(0)}_{\mathrm{Cs_2SO_4}} + \\ & 2(m_\mathrm{A} + m_\mathrm{B})g(2\sqrt{I})\beta^{(1)}_{\mathrm{CsCl}} + m_\mathrm{B}g(2\sqrt{I})\beta^{(1)}_{\mathrm{Cs_2SO_4}} + \\ & (1.5m_\mathrm{A}{}^2 + 4m_\mathrm{A}m_\mathrm{B} + 2m_\mathrm{B}{}^2)C^{\varphi}_{\mathrm{CsCl}} + \\ & \sqrt{2}/2(m_\mathrm{A}m_\mathrm{B} + 2m_\mathrm{B}{}^2)C^{\varphi}_{\mathrm{Cs_2SO_4}} + m_\mathrm{B}\theta + \\ & m_\mathrm{B}{}^{\mathrm{E}}\theta + (1.5m_\mathrm{A}m_\mathrm{B} + m_\mathrm{B}{}^2)\psi + F\end{aligned} \tag{8}$$

$$\begin{aligned}3\ln\gamma_{\pm\mathrm{Cs_2SO_4}} = {}& 4(m_\mathrm{A} + 2m_\mathrm{B})(m_\mathrm{A}C^{\varphi}_{\mathrm{CsCl}} + \\ & \sqrt{2}/2m_\mathrm{B}C^{\varphi}_{\mathrm{Cs_2SO_4}}) + 4m_\mathrm{A}\beta^{(0)}_{\mathrm{CsCl}} + (2m_\mathrm{A} + 8m_\mathrm{B})\beta^{(0)}_{\mathrm{Cs_2SO_4}} + \\ & \sqrt{2}/2(m_\mathrm{A} + 2m_\mathrm{B})^2C^{\varphi}_{\mathrm{Cs_2SO_4}} + 4m_\mathrm{A}g(2\sqrt{I})\beta^{(1)}_{\mathrm{CsCl}} + \\ & (2m_\mathrm{A} + 8m_\mathrm{B})g(2\sqrt{I})\beta^{(1)}_{\mathrm{Cs_2SO_4}} + 2m_\mathrm{A}\theta + \\ & 2m_\mathrm{A}{}^{\mathrm{E}}\theta + (m_\mathrm{A}{}^2 + 6m_\mathrm{A}m_\mathrm{B})\psi + 6F\end{aligned} \tag{9}$$

$$\begin{aligned}F = {}& -A_{\varphi}\{\sqrt{I}/(1 + 1.2\sqrt{I}) + 2\ln(1 + 1.2\sqrt{I})/1.2\} + \\ & (m_\mathrm{A} + 2m_\mathrm{B})g'(2\sqrt{I})(m_\mathrm{A}\beta^{(1)}_{\mathrm{CsCl}} + m_\mathrm{B}\beta^{(1)}_{\mathrm{Cs_2SO_4}})/I + 2m_\mathrm{A}m_\mathrm{B}{}^{\mathrm{E}}\theta'\end{aligned} \tag{10}$$

$$\begin{aligned}\Phi = {}& \{m_\mathrm{A}(m_\mathrm{A} + 2m_\mathrm{B})\beta^{(0)}_{\mathrm{CsCl}} + m_\mathrm{B}(m_\mathrm{A} + 2m_\mathrm{B})\beta^{(0)}_{\mathrm{Cs_2SO_4}} + \\ & m_\mathrm{A}(m_\mathrm{A} + 2m_\mathrm{B})\exp(-2\sqrt{I})\beta^{(1)}_{\mathrm{CsCl}} + \\ & m_\mathrm{B}(m_\mathrm{A} + 2m_\mathrm{B})\exp(-2\sqrt{I})\beta^{(1)}_{\mathrm{Cs_2SO_4}} + \\ & m_\mathrm{A}(m_\mathrm{A} + 2m_\mathrm{B})^2C^{\varphi}_{\mathrm{CsCl}} + \\ & \sqrt{2}/2m_\mathrm{B}(m_\mathrm{A} + 2m_\mathrm{B})^2C^{\varphi}_{\mathrm{Cs_2SO_4}} + \\ & 2m_\mathrm{A}m_\mathrm{B}({}^{\mathrm{E}}\theta + \theta + {}^{\mathrm{E}}\theta' I) + \\ & 2m_\mathrm{A}m_\mathrm{B}(m_\mathrm{A} + 2m_\mathrm{B})\psi - \\ & A_{\varphi}I^{1.5}/(1 + 1.2\sqrt{I})\}/(m_\mathrm{A} + 1.5m_\mathrm{B}) + 1\end{aligned} \tag{11}$$

where the two higher-order electrostatic terms ${}^{\mathrm{E}}\theta_{\mathrm{Cl,SO_4}}$ and ${}^{\mathrm{E}}\theta'_{\mathrm{Cl,SO_4}}$ of the Pitzer equation can be calculated by an empirical formula.[26] Here, in eqs 8 to 11, the pure electrolyte parameters of the Pitzer model were given by Kim and Frederich.[24] The Pitzer mixing interaction parameters were evaluated by using a multiple linear regression technique. The calculated mixing parameters ($\theta_{\mathrm{Cl,SO_4}}$, $\psi_{\mathrm{Cl,SO_4,Cs}}$) and the pure electrolyte parameters are listed in Table 2. The relationship between the osmotic coefficients Φ for the mixtures and the total ionic strength I is shown in Figure 2. It can be seen that there is a decrease in Φ with an increase in I and a decrease of Φ for a given I value with increasing y_B in the system.

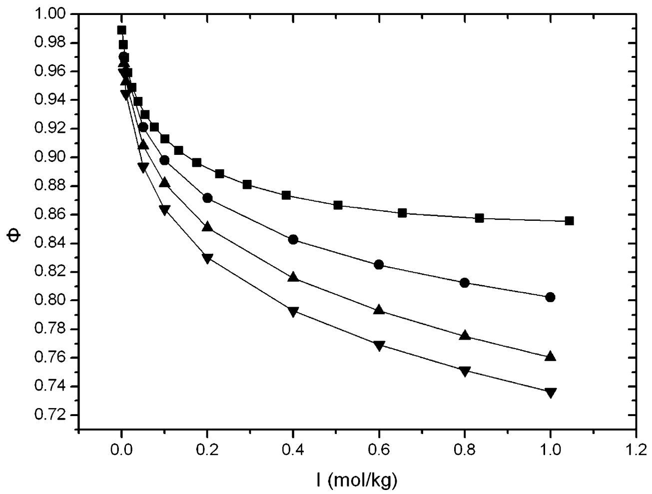

Figure 2. Plot of the osmotic coefficient Φ of CsCl + Cs_2SO_4(aq) against ionic strength I in the mixture (■, $y_\mathrm{B} = 0.00$; ●, $y_\mathrm{B} = 0.25$; ▲, $y_\mathrm{B} = 0.50$; ▼, $y_\mathrm{B} = 0.75$).

Table 2. Pitzer Parameters for CsCl + Cs_2SO_4 + H_2O at 298.15 K

	single electrolytes	
	CsCl[24]	Cs_2SO_4[24]
$\beta^{(0)}$	0.03643	0.14174
$\beta^{(1)}$	−0.01169	0.69456
C^{φ}	−0.00096	−0.02686
m(max)/mol·kg^{-1}	11.00	1.831
σ	0.00365	0.00113

	mixtures
θ	−0.20127
Ψ	−0.00381
m(max)/mol·kg^{-1}	1.0445
σ	0.00869

Table 3. Parameter Values of the Harned Equation and the rmsd

I/mol·kg^{-1}	$\ln\gamma_{\pm\mathrm{A0}}$	α_{AB}	β_{AB}	10^3·rmsd
0.0050	−0.0787	−0.1155	0.0892	0.453
0.0100	−0.1083	−0.0245	0.0179	0.416
0.0500	−0.2188	−0.0601	0.1071	6.311
0.1000	−0.2928	−0.0639	0.1078	3.075
0.2000	−0.3822	−0.0474	0.0829	0.801
0.4000	−0.4849	−0.0367	0.0639	0.982
0.6000	−0.5463	−0.0324	0.0865	3.552
0.8000	−0.5915	−0.0250	0.1105	3.331
1.0000	−0.6276	0.0245	0.0766	1.095

Harned's rule gives a good description of the variation found for the studied electrolytic system and can be written as follows

$$\ln\gamma_{\pm\mathrm{A}} = \ln\gamma_{\pm\mathrm{A0}} - \alpha_{\mathrm{AB}}{\cdot}y_\mathrm{B} - \beta_{\mathrm{AB}}{\cdot}y_\mathrm{B}{}^2 \tag{12}$$

where α_{AB} and β_{AB} represent the Harned interaction parameters, which are dependent on both ionic strength and temperature, and $\gamma_{\pm\mathrm{A0}}$ is the mean activity coefficient of CsCl in pure solution. The outcomes are listed in Table 3, and the plot of $\ln\gamma_{\pm\mathrm{A}}$ vs y_B for each system is shown in Figure 3, which indicate that $\ln\gamma_{\pm\mathrm{CsCl}}$ is a linear function at each constant ionic strength studied, thus obeying Harned's rule. It is obvious that the mean

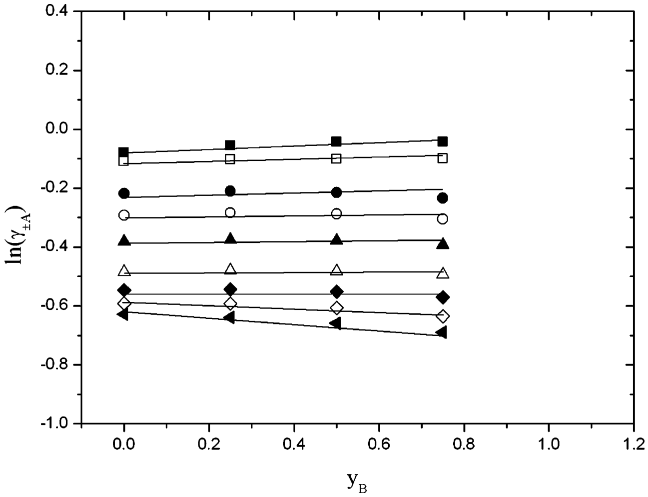

Figure 3. Harned's rule lines for CsCl ln($\gamma_{\pm A}$) against y_B (■, $I = 0.0050$; □, $I = 0.0100$; ●, $I = 0.0500$; ○, $I = 0.1000$; ▲, $I = 0.2000$; △, $I = 0.4000$; ◆, $I = 0.6000$; ◇, $I = 0.8000$; solid arrow pointing left, $I = 1.0000$).

activity coefficients of CsCl give good fits of the experimental results in the Harned equation.

Conclusion

The galvanic cell consisting of a Cs-ISE and Ag|AgCl electrode can be used to study the thermodynamic properties of $CsCl + Cs_2SO_4 + H_2O$ with great precision. In this work, we have obtained the results concerning the mean activity coefficients for CsCl in water, the osmotic coefficients, the corresponding Pitzer and Harned parameters, and the activity coefficients of Cs_2SO_4 by the former model. The results showed us that both thermodynamic models could correlate the experimental data very well, which also indicated that the electrode pairs and the experimental measurement we used were proper and satisfactory for our studies.

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