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Activity Coefficients of CsCl in 1,2-Propanediol + Water or 1,3-Propanediol + Water Mixed Solvents at 298.15 K

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ABSTRACT: The mean activity coefficients of the CsCl + propylene glycol + water system were determined at 298.15 K using potentiometric measurements. The range of CsCl molality (m) is (0.01 to 1.20) $\text{mol}\cdot\text{kg}^{-1}$, and the mass fraction of propylene glycol (w) in mixed solvent is 0.10 to 0.40. The Pitzer, the modified Pitzer, and the extended Debye−Hückel equations are used to describe the nonideal behavior of the electrolyte. The activity coefficients and the osmotic coefficients of CsCl were calculated by the Pitzer equation. We also obtained the Gibbs energy of transfer of CsCl from water to propylene glycol + water mixtures.

INTRODUCTION

The study of the activity coefficients of electrolyte solutions and other related thermodynamic properties, such as osmotic coefficients and the standard Gibbs energy of transfer, is required for the investigation of the phase equilibria and separation techniques. Moreover, electrolyte systems have applications in many chemical industries, as geochemistry, biological, and environmental systems, to solve environmental problems and optimize industrial processes.[1,2] Consequently, in recent years there have been a growing number of studies providing experimental data on electrolyte in aqueous solutions or aqueous + organic mixtures. For example, Lopes et al. investigated the activity coefficients of NaCl in ethanol + water mixtures.[3] Hernandez-Luis et al. determined the activity coefficients of alkali metal salts in mixed solvent systems (NaCl + formamide or ethylene carbonate + water, LiCl or KCl + PEG 4000 + water).[4−7] Moreover, the activity coefficients of NH_4Cl in ROH + water mixed solvents (R = Me, Et, 1-Pr, and 2-Pr) and HCl + 2-propanol + water systems have been obtained by the Deyhimi group.[8−11] Zhuo et al. determined the activity coefficients for the $CaCl_2$ + amino acid + water system at $T = 298.15$ K.[12]

In previous work, our group has obtained the activity coefficients of CsCl or RbCl in methanol + water, ethanol + water, and *N*,*N*-dimethylformamide (DMF) + water mixtures.[13−15] The present study, we report the activity coefficients for CsCl in different mass fractions of propylene glycol $w = 0.10$, 0.20, 0.30, and 0.40 in mixed solvents. In addition the results of some thermodynamic correlation concerning the calculated osmotic coefficients and the standard Gibbs energy of transfer for this electrolyte in 1,2-propanediol or 1,3-propanediol + water are presented.

EXPERIMENTAL SECTION

Cesium chloride (analytical reagent (A.R.) purity > 0.9950) was purchased from Sichuan China Lithium Industrial Co., Ltd. and dried under vacuum to constant weight before use. It was used without further purification. Analytical grade 1,2-propanediol and 1,3-propanediol (A.R. purity > 0.9950) used in this study were purchased from Shanghai China Lithium Industrial Co., Ltd. Double-distilled water was used in all of the experiments whose specific conductance was approximately $(1.0 \text{ to } 1.2)\cdot 10^{-4}\ \text{S}\cdot\text{m}^{-1}$.

The Cs ion-selective electrode (Cs-ISE) was a PVC membrane type based on valinomycin and was filled with $0.10\ \text{mol}\cdot\text{L}^{-1}$ CsCl as the internal liquid. Both Cs-ISE and Ag−AgCl electrodes were conditioned overnight in the appropriate propylene glycol + water mixture before each series of measurements. Electrodes were calibrated before use and showed good Nernstian response and selectivity. The cells we used were as follows:

$$\text{Cs-ISE}|\text{CsCl}(m), \text{propylene glycol}(w), \text{water}(1-w)|\text{Ag}|\text{AgCl} \quad (1)$$

In the cells, m is the molality of CsCl in different 1,2-propanediol or 1,3-propanediol + water mixed solvents, and w was the mass fraction of propylene glycol. The uncertainties in the electrolyte molality, potential, and mass fraction of propylene glycol are ± 0.0001, ± 0.1, and ± 0.01, respectively.

As usual, electrodes, cells, apparatus, and temperature control system, as well as the measurement procedure employed in the present study, have been described in detail in our previous work.[13,14]

A BI-870 dielectric constant meter of Brookhaven Instruments Corporation was used to measure the dielectric constant of the different mass fraction of propylene glycol. The temperature was controlled with a precision of ± 0.02 K. The dielectric constant meter was calibrated with pure water ($\varepsilon = 78.4$ at 298.15 K).

RESULTS

The potential of the cell can be expressed by the Nernst equation:

$$E = E^0 + 2k\ln(m\gamma_\pm) \quad (2)$$

where E^0 represents the standard potential of the cell (1), the $\gamma_\pm$ is the mean activity coefficient of CsCl, and $k = RT/F$ is the

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Table 1. Values of the Molality m, Potential E, Mean Activity Coefficients $\gamma_{\pm}$, and Osmotic Coefficients Φ for CsCl in the Different (1,2-Propanediol or 1,3-Propanediol + Water) Mixtures at 298.15 K

m	E			m	E		
mol·kg^{-1}	mV	$\gamma_{\pm}$	Φ	mol·kg^{-1}	mV	$\gamma_{\pm}$	Φ
CsCl + Pure Water							
0.0041	−154.7	0.9317	0.9771	0.1797	24.7	0.6990	0.8995
0.0082	−120.7	0.9065	0.9686	0.2525	39.9	0.6680	0.8898
0.0123	−100.8	0.8885	0.9625	0.3661	56.3	0.6335	0.8797
0.0207	−75.7	0.8615	0.9534	0.4774	68.0	0.6089	0.8730
0.0331	−53.4	0.8329	0.9437	0.6219	79.5	0.5849	0.8671
0.0504	−33.6	0.8039	0.9340	0.7198	85.7	0.5719	0.8643
0.0716	−17.2	0.7773	0.9251	0.8814	94.5	0.5545	0.8612
0.1009	−1.5	0.7494	0.9158	1.0427	101.9	0.5406	0.8593
0.1393	13.4	0.7218	0.9068	1.2210	108.8	0.5282	0.8584
CsCl + 1,2-Propanediol (w) + Water ($1 - w$)							
$w = 0.10$							
0.0036	−147.1	0.9296	0.9763	0.1473	28.2	0.6982	0.8984
0.0067	−117.0	0.9074	0.9688	0.1998	41.7	0.6700	0.8895
0.0102	−96.8	0.8888	0.9625	0.2837	57.2	0.6370	0.8795
0.0131	−84.5	0.8762	0.9582	0.3551	66.9	0.6159	0.8736
0.0195	−65.4	0.8541	0.9507	0.4818	80.1	0.5876	0.8662
0.0289	−46.9	0.8293	0.9422	0.6007	89.8	0.5676	0.8616
0.0412	−30.1	0.8045	0.9338	0.7017	96.4	0.5538	0.8589
0.0568	−15.3	0.7800	0.9255	0.8623	105.4	0.5361	0.8558
0.0779	−0.7	0.7542	0.9168	1.0619	114.4	0.5190	0.8535
0.1084	14.5	0.7258	0.9074	1.2327	120.9	0.5071	0.8523
$w = 0.20$							
0.0025	−151.3	0.9350	0.9781	0.2039	55.5	0.6431	0.8787
0.0048	−119.0	0.9129	0.9706	0.2616	66.5	0.6186	0.8710
0.0071	−99.4	0.8960	0.9648	0.3315	76.9	0.5954	0.8642
0.0118	−75.2	0.8711	0.9562	0.4418	89.1	0.5677	0.8566
0.0188	−52.8	0.8434	0.9467	0.5432	97.9	0.5482	0.8519
0.0285	−33.3	0.8154	0.9370	0.6566	105.7	0.5309	0.8482
0.0411	−16.3	0.7880	0.9275	0.7875	113.6	0.5148	0.8453
0.0797	13.8	0.7321	0.9083	0.9632	122.1	0.4978	0.8430
0.1169	31.3	0.6969	0.8963	1.1173	128.8	0.4858	0.8420
0.1549	43.4	0.6699	0.8873	1.2573	133.7	0.4765	0.8415
$w = 0.30$							
0.0027	−133.9	0.9258	0.9750	0.1161	43.5	0.6725	0.8868
0.0050	−103.4	0.9022	0.9669	0.1523	55.4	0.6453	0.8775
0.0072	−85.0	0.8846	0.9608	0.2516	76.9	0.5943	0.8609
0.0096	−71.5	0.8698	0.9557	0.3232	87.2	0.5690	0.8531
0.0167	−45.2	0.8362	0.9440	0.4121	97.6	0.5448	0.8462
0.0237	−28.7	0.8116	0.9354	0.6242	115.4	0.5051	0.8366
0.0331	−13.3	0.7861	0.9264	0.7974	125.5	0.4831	0.8325
0.0449	1.2	0.7607	0.9175	0.9696	133.7	0.4664	0.8303
0.0609	14.7	0.7340	0.9081	1.1352	140.3	0.4536	0.8293
0.0818	28.2	0.7065	0.8986	1.2550	144.7	0.4458	0.8291
$w = 0.40$							
0.0027	−118.0	0.9194	0.9727	0.1480	67.6	0.6239	0.8666
0.0047	−91.0	0.8974	0.9651	0.1843	76.7	0.6001	0.8580
0.0068	−72.7	0.8792	0.9588	0.2428	88.4	0.5700	0.8471
0.0111	−49.6	0.8514	0.9490	0.3200	99.8	0.5397	0.8363

Table 1. Continued

m / mol·kg^{-1}	E / mV	$\gamma_{\pm}$	Φ	m / mol·kg^{-1}	E / mV	$\gamma_{\pm}$	Φ
0.0177	−27.3	0.8200	0.9379	0.4042	109.3	0.5143	0.8274
0.0284	−5.7	0.7838	0.9249	0.5348	120.6	0.4843	0.8171
0.0461	16.8	0.7416	0.9097	0.6296	127.2	0.4672	0.8113
0.0655	32.4	0.7082	0.8975	0.8204	137.5	0.4400	0.8024
0.0895	45.9	0.6769	0.8860	0.9979	145.6	0.4203	0.7961
0.1143	56.5	0.6514	0.8767	1.1697	151.5	0.4047	0.7911
$CsCl + 1,3$-Propanediol (w) + Water $(1 - w)$							
$w = 0.10$							
0.0031	−156.4	0.9350	0.9781	0.2697	54.1	0.6401	0.8795
0.0108	−94.4	0.8864	0.9616	0.3603	66.9	0.6124	0.8714
0.0160	−75.4	0.8655	0.9545	0.4176	73.2	0.5984	0.8675
0.0220	−60.4	0.8469	0.9482	0.4949	80.6	0.5825	0.8634
0.0433	−28.4	0.8006	0.9323	0.5785	87.4	0.5681	0.8600
0.0657	−9.1	0.7680	0.9212	0.6804	94.3	0.5536	0.8570
0.0847	2.4	0.7468	0.9141	0.7835	100.1	0.5413	0.8548
0.1144	16.0	0.7204	0.9052	0.8866	105.3	0.5308	0.8534
0.1620	31.5	0.6885	0.8947	1.0313	112.2	0.5186	0.8523
0.2023	41.4	0.6675	0.8880	1.2026	119.1	0.5068	0.8520
$w = 0.20$							
0.0025	−152.7	0.9362	0.9785	0.1216	32.0	0.6974	0.8972
0.0050	−117.4	0.9118	0.9703	0.2097	56.4	0.6456	0.8807
0.0079	−95.6	0.8924	0.9636	0.2837	69.5	0.6165	0.8720
0.0106	−81.2	0.8778	0.9586	0.3647	80.4	0.5925	0.8653
0.0162	−60.8	0.8543	0.9506	0.5522	98.3	0.5540	0.8560
0.0229	−44.3	0.8325	0.9431	0.7920	113.6	0.5223	0.8502
0.0323	−28.3	0.8087	0.9349	0.8874	118.5	0.5128	0.8489
0.0428	−15.3	0.7874	0.9276	0.9922	123.3	0.5037	0.8479
0.0686	6.3	0.7487	0.9144	1.1154	128.4	0.4944	0.8471
0.0934	20.4	0.7215	0.9052	1.2011	131.8	0.4887	0.8468
$w = 0.30$							
0.0022	−143.6	0.9336	0.9776	0.1256	46.3	0.6702	0.8859
0.0042	−112.7	0.9116	0.9701	0.1570	56.1	0.6480	0.8784
0.0066	−90.4	0.8921	0.9633	0.2561	77.0	0.5986	0.8626
0.0087	−77.0	0.8780	0.9585	0.3220	86.4	0.5757	0.8558
0.0200	−37.6	0.8281	0.9411	0.4249	98.4	0.5487	0.8487
0.0277	−22.2	0.8045	0.9328	0.5244	107.3	0.5289	0.8443
0.0376	−7.9	0.7805	0.9243	0.6474	116.6	0.5099	0.8410
0.0504	5.7	0.7559	0.9157	0.8809	129.8	0.4841	0.8385
0.0681	19.0	0.7290	0.9062	1.0401	136.8	0.4714	0.8386
0.0979	35.4	0.6946	0.8942	1.1731	141.8	0.4626	0.8393
$w = 0.40$							
0.0025	−122.8	0.9241	0.9743	0.1658	72.3	0.6128	0.8624
0.0045	−93.7	0.9006	0.9662	0.2090	82.3	0.5876	0.8533
0.0074	−68.9	0.8755	0.9574	0.2820	94.7	0.5549	0.8418
0.0102	−53.5	0.8576	0.9511	0.3630	105.1	0.5276	0.8324
0.0172	−28.9	0.8234	0.9390	0.4692	115.4	0.5003	0.8235
0.0250	−11.5	0.7952	0.9289	0.5716	123.6	0.4799	0.8172
0.0355	4.9	0.7661	0.9184	0.6894	130.9	0.4609	0.8117
0.0582	26.8	0.7210	0.9020	0.8554	139.8	0.4398	0.8061
0.0874	44.9	0.6805	0.8871	1.0296	147.1	0.4224	0.8019
0.1205	58.9	0.6470	0.8749	1.1865	152.9	0.4094	0.7991

Table 2. Values of Average Molecular Mass M, Dielectric Constant ε, Density ρ, Debye−Hückel Constants A and B, and Pitzer Constants A_φ for (1,2-Propanediol + Water and 1,3-Propanediol + Water) Mixtures at 298.15 K

	M		ρ	A	B	A_φ
w	$g \cdot mol^{-1}$	ε	$g \cdot cm^{-3}$	$kg^{1/2} \cdot mol^{-1/2}$	$kg^{1/2} \cdot mol^{-1/2} \cdot Å^{-1}$	$kg^{1/2} \cdot mol^{-1/2}$
			1,2-Propanediol + Water			
0.00	18.02	78.3	0.9970	0.5108	0.3286	0.3921
0.10	19.50	74.2	1.0043	0.5557	0.3388	0.4266
0.20	21.26	69.9	1.0127	0.6103	0.3506	0.4685
0.30	23.36	65.2	1.0211	0.6803	0.3645	0.5222
0.40	25.93	62.2	1.0287	0.7328	0.3746	0.5625
			1,3-Propanediol + Water			
0.10	19.50	74.3	1.0033	0.5543	0.3385	0.4255
0.20	21.26	70.5	1.0105	0.6019	0.3487	0.4640
0.30	23.36	66.6	1.0183	0.6580	0.3601	0.5051
0.40	25.93	62.6	1.0260	0.7249	0.3729	0.5564

Table 3. Values of E^0 and the Debye−Hückel Parameters for CsCl in the Different (1,2-Propanediol or 1,3-Propanediol + Water) Mixtures at 298.15 K

	a	c	d	E^0		a	c	d	E^0	
w	Å	$kg \cdot mol^{-1}$	$kg^2 \cdot mol^{-2}$	mV	SD	Å	$kg \cdot mol^{-1}$	$kg^2 \cdot mol^{-2}$	mV	SD
		CsCl + 1,2-Propanediol + Water					CsCl + 1,3-Propanediol + Water			
0.00	2.72	0.0234	−0.00230	131.3	0.14					
	2.79	0.0177	-	131.3	0.14					
0.10	2.75	0.0237	−0.00044	145.0	0.10	2.76	0.0167	0.00363	144.4	0.15
	2.77	0.0227	-	145.0	0.10	2.65	0.0255	-	144.4	0.15
0.20	2.69	0.0267	0.00012	160.0	0.16	2.70	0.0319	−0.00188	159.0	0.11
	2.68	0.0270	-	160.0	0.16	2.74	0.0261	-	158.6	0.11
0.30	2.75	0.0251	0.00114	174.5	0.15	2.56	0.0370	0.00139	173.4	0.17
	2.72	0.0278	-	174.5	0.15	2.53	0.0372	-	173.4	0.17
0.40	2.71	0.0081	0.00073	190.0	0.18	2.58	0.0195	0.00069	190.0	0.11
	2.70	0.0097	-	190.0	0.18	2.56	0.0161	-	190.0	0.11

Nernst slope. R, T, and F are the universal gas constant, thermodynamic temperature, and Faraday constant, respectively.

The values of E for CsCl in pure water are shown in Table 1 and allow for carrying out a calibration of the electrode system using eq 2. The typical value of k obtained from the linear regression analysis of the experimental points is 25.70 ± 0.04 mV with a standard deviation of the fit 0.14 mV and a linear correlation coefficient of 0.9999. Reasonable agreement between the experimental and the theoretical values (25.69 mV at T = 298.15 K) were found. So it can be concluded that the electrode pair used here has a good Nernst response and is satisfactory enough for our study.

In this work, we use the extended Debye−Hückel,[16,17] Pitzer,[18,19] and modified Pitzer[20] equations to determine the standard potential (E^0) in mixed solvents.

For 1−1 type electrolyte CsCl, the extended Debye−Hückel equation was written as:[16,17]

$$\log \gamma_\pm = -Am^{1/2}/(1 + Bam^{1/2}) + cm + dm^2 - \log(1 + 0.002mM) + \text{Ext} \qquad (3)$$

where a is the ion size parameter, c and d are the ion-interaction parameters, M is the average molecular mass of mixed solvent, and Ext is the contribution of the extended terms. The fitting parameters are a, c, and d. A and B are the Debye− Hückel constants, which are given by:

$$A = 1.8247 \cdot 10^6 \rho^{1/2}/(\varepsilon T)^{3/2} \text{ kg}^{1/2} \cdot \text{mol}^{-1/2} \qquad (3a)$$

$$B = 50.2901 \rho^{1/2}/(\varepsilon T)^{1/2} \text{ kg}^{1/2} \cdot \text{mol}^{-1/2} \cdot \text{Å}^{-1} \qquad (3b)$$

In these equations, ρ, ε, and T are the density, dielectric constant of the mixed solvents, and the thermodynamic temperature, respectively.

The Pitzer equations for the mean activity coefficient ($\gamma_\pm$) is:[18,19]

$$\ln \gamma_\pm = f^\gamma + mB^\gamma + m^2 C^\gamma \qquad (4)$$

with

$$f^\gamma = -A_\varphi[I^{1/2}/(1 + bI^{1/2}) + (2/b)\ln(1 + bI^{1/2})] \qquad (4a)$$

Table 4. Values of E^0 and the Pitzer and Modified Pitzer Parameters of CsCl in the Different (1,2-Propanediol or 1,3-Propanediol + Water) Mixtures at 298.15 K

	Pitzer					modified Pitzer				
	$\beta^{(0)}$	$\beta^{(1)}$	C^{φ}	E^0		b_{MX}	B_{MX}	C_{MX}	E^0	
w	kg·mol^{-1}	kg·mol^{-1}	kg^2·mol^{-2}	mV	SD	kg$^{1/2}$·mol$^{-1/2}$	kg·mol^{-1}	kg^2·mol^{-2}	mV	SD
				CsCl + 1,2-Propanediol + Water						
0.00	0.0300	0.0558	0.00038	131.3	0.14	1.2769	0.0426	−0.0052	131.3	0.14
0.10	0.0483	0.0513	−0.00730	145.0	0.10	1.3422	0.0445	−0.0041	145.0	0.11
0.20	0.0543	0.0616	−0.00697	160.0	0.16	1.3577	0.0493	−0.0039	160.0	0.16
0.30	0.0601	0.1050	−0.00690	174.5	0.15	1.4542	0.0504	−0.0037	174.5	0.15
0.40	0.0442	0.1218	−0.00891	190.0	0.18	1.4778	0.0325	−0.0047	190.0	0.18
				CsCl + 1,3-Propanediol + Water						
0.10	0.0394	0.0526	−0.00068	144.4	0.15	1.3913	0.0284	0.0010	144.4	0.15
0.20	0.0571	0.0738	−0.00837	159.0	0.11	1.3880	0.0520	−0.0049	159.0	0.11
0.30	0.0694	0.0465	−0.00760	173.4	0.17	1.3316	0.0611	−0.0030	173.4	0.16
0.40	0.0519	0.0847	−0.00788	190.0	0.11	1.4232	0.0365	−0.0024	190.0	0.11

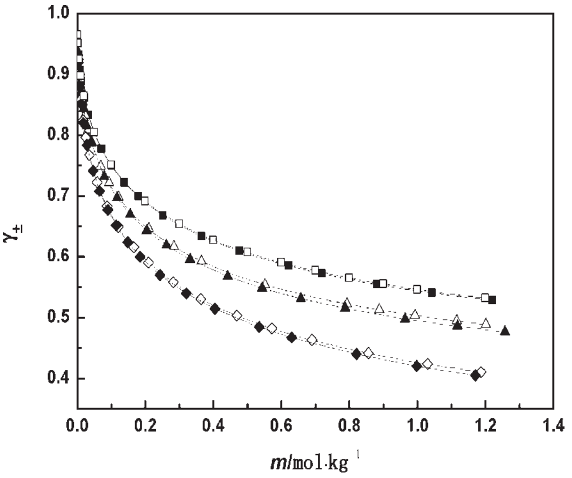

Figure 1. Comparison of $\gamma_{\pm}$ versus CsCl molality in mass fraction of 1,2-propanediol + water and 1,3-propanediol + water mixtures at 298.15 K. ■, w = 0.00; △, 1,3-propanediol (w = 0.20); ▲, 1,2-propanediol (w = 0.20); ◇, 1,3-propanediol (w = 0.40); ◆, 1,2-propanediol (w = 0.40); □, referred literature data in pure water.[22]

$$B^{\gamma} = 2\beta^{(0)} + 2\beta^{(1)}\{[1 - \exp(-\alpha I^{1/2})(1 + \alpha I^{1/2} - 1/2\alpha^2 I)]/(\alpha^2 I)\} \qquad (4b)$$

$$C^{\gamma} = 1.5C^{\varphi} \qquad (4c)$$

the osmotic coefficient (Φ) is:

$$\Phi - 1 = f^{\varphi} + mB^{\varphi} + m^2C^{\varphi} \qquad (5)$$

with

$$f^{\varphi} = -A_{\varphi}(I^{1/2}/(1 + bI^{1/2})) \qquad (5a)$$

$$B^{\varphi} = \beta^{(0)} + \beta^{(1)}\exp(-\alpha I^{1/2}) \qquad (5b)$$

In eqs 4 to 5b, I is the summation of ionic strength, and α and b are empirical parameters with values of (2.0 and 1.2) kg$^{1/2}$·mol$^{-1/2}$, respectively. $\beta^{(0)}$, $\beta^{(1)}$, and C^{φ} are solute-specific interaction parameters, and the three parameters can be found by regressing the potential data. Table 1 shows the experimental results, including E values, the activity coefficients, and osmotic coefficients of CsCl in mixed solvent, for the Pitzer equation.

The modified Pitzer equation is given by[20]

$$\ln \gamma_{\pm} = -A_{\varphi}[I^{1/2}/(1 + b_{MX}I^{1/2}) + (2/b_{MX})\ln(1 + b_{MX}I^{1/2})] + 2mB_{MX} + 3m^2C_{MX} \qquad (6)$$

In eq 6, the fitting parameters are b_{MX}, B_{MX}, and C_{MX}. Equation 6 has been applied here to further verify and ratify the values of E^0 obtained by the other two methods.

A_{φ} is the Debye−Hückel constant for the osmotic coefficient defined by:

$$A_{\varphi} = (1/3)[(2\pi N_0\rho)/1000]^{1/2}\cdot[e^2/(\varepsilon KT)]^{3/2} \qquad (7)$$

where N_0 and K are Avogadro's number and Boltzmann's constant, respectively. After the values of the fundamental physical constants are introduced to eq 7, it becomes

$$A_{\varphi} = 1.4006\cdot 10^6\rho^{1/2}(\varepsilon T)^{3/2} \qquad (7a)$$

The values of density were measured using a densimeter (DMA4500) and dielectric constant for the mixed solvents were measured by us, and they are shown in Table 2, together with those for M, A, B, and A_{φ}.

By combining eqs 2 and 3, 2 and 4, or 2 and 6 the values of E^0, according to the different models used, can be optimized, as well as the characteristic interaction parameters of each model. These values are presented in Tables 3 and 4, as well as the corresponding standard deviation of the fit.

■ DISCUSSION

It can be seen from Tables 3 and 4 that the E^0 values obtained from the extended Debye−Hückel equation, the Pitzer equation, and modified Pitzer equation are in good agreement with each other.

Table 5. Average Values of Standard Potential E^{0*} in Three Equations, Standard Gibbs Energy of Transfer ΔG_t^0 of CsCl from Water to 1,2-Propanediol + Water and 1,3-Propanediol + Water Mixtures at 298.15 K

	E^{0*}	ΔG_t^0		E^0	ΔG_t^0
w	mV	$\text{kJ}\cdot\text{mol}^{-1}$	w	mV	$\text{kJ}\cdot\text{mol}^{-1}$
CsCl + 1,2-Propanediol + Water			CsCl + 1,3-Propanediol + Water		
0.00	131.3	0.00	0.00	131.3	0.00
0.10	145.0	1.29	0.10	144.4	1.23
0.20	160.0	2.69	0.20	159.0	2.61
0.30	174.5	4.05	0.30	173.4	3.95
0.40	190.0	5.51	0.40	190.0	5.52

For the extended Debye−Hückel equation, the results obtained by three-parameter (a, c, and d) fitting have no appreciable changes when we consider those by two-parameter ($d = 0$) fitting (see Table 3), indicating that the parameter d can be ignored at low concentrations. The values of parameter a (related to the size of the ion) were obtained, and in all cases, the values of a were less than the sum of the crystallographic radii (3.4 Å),[21] which can be related to possible ionic association or other phenomena.[4−7]

Figure 1 show that the mean activity coefficients of CsCl versus the electrolyte molality in pure water and in mixed solvents (with different mass fraction of 1,2-propanediol or 1,3-propanediol in water). For comparison, the available data concerning those of Hamer and Wu[22]at 298.15 K in pure water were also included in Figure 1. As it can be seen, the obtained mean activity coefficient values for CsCl in pure water, as well as the corresponding Pitzer ion-interaction parameters, generated with the used Cs^+ ion-selective electrode compare well with those previously reported in pure water. The $\gamma_\pm$ decreases with an increase of propylene glycol content (decrease in dielectric constant) in mixed solvents and with an increase in the molality of CsCl. This phenomenon can be interpreted as ion−solvent and ion−ion interactions in the mixture.

It is necessary to note that the mean activity coefficients of CsCl in the 1,2-propanediol + water and 1,3-propanediol + water have no appreciable changes in the trend, which is due to the two alcohols being isomerides. The mean activity coefficient of CsCl in 1,3-propanediol + water mixed solvent is a little greater than that in 1,2-propanediol + water mixtures. This is probably due to the fact that the dielectric constant for 1,2-propanediol + water mixtures is a little smaller than that of 1,3-propanediol + water mixtures.

Using the obtained Pitzer ion−interaction parameters for CsCl in different mixed alcohol + water solvent systems, the corresponding osmotic coefficients were calculated by Pitzer eq 5. The osmotic coefficients (Φ) of the CsCl + 1,2-propanediol + water or 1,3-propanediol + water system show a similar variation as $\gamma_\pm$.

The standard Gibbs energy of transfer, (ΔG_t^0), is one of the most useful thermodynamic properties of solution. It can be calculated from E^0 values according to the following equation[23]

$$\Delta G_t^0 = F(E_m^0 - E_w^0) + 2RT \ln(d_w/d_m) \qquad (8)$$

where E_w^0 and E_m^0 are the standard of electromotive force of CsCl in pure water and in mixed solvents, respectively. d_w and d_m are the relative density of water and mixed solvent, respectively. The values of ΔG_t^0 are given in Table 5.

If the electrostatic component of is ΔG_t^0 assumed to be well-described by the Born model of ion solvation, then for CsCl it should be expressed by the following equation:[24]

$$\Delta G_t^0 = Ne^2(1/\varepsilon_m - 1/\varepsilon_w)(1/r_+ + 1/r_-)/2 \qquad (9)$$

where N is the Avogadro constant, e is the electron charge, and ε_m and ε_w are the dielectric constant of the mixed solvent and water. r_+ and $r_-$are the crystal radii of the cation and anion.

It can be observed from Table 5 that ΔG_t^0 are all positive, which indicates that the transfer of CsCl from water to the propylene glycol + water mixed solvents is not spontaneous. On the other hand, ΔG_t^0 becomes more positive with an increase of propylene glycol content, indicating that the thermodynamic stabilization of the CsCl decreases in the mixed solvent. By comparison, it is found that the values of ΔG_t^0 for 1,2-propanediol + water are consistent basically with those from 1,3-propanediol + water system. This is due to the dielectric constant of two systems is close to each other.

■ CONCLUSION

In this work, the determination of the activity coefficients for CsCl in 1,2-propanediol + water or 1,3-propanediol + water mixed solvents along with the osmotic coefficients and the standard Gibbs energy of transfer from the water to the propylene glycol + water mixtures is presented. The Pitzer, the modified Pitzer, and the extended Debye−Hückel equations are reported based on experimental potentiometric data. The three equations could correlate the experimental data well. The various Pitzer ($\beta^{(0)}$, $\beta^{(1)}$, and C^φ) parameters, the modified Pitzer (b_{MX}, B_{MX}, and C_{MX}) parameters, and extended Debye−Hückel (a, c, and d) parameters were determined for each series of measurement in the corresponding mixed solvents. The thermodynamic data of the 1,2-propanediol + water system have no appreciable changes with those of the 1,3-propanediol + water system because of their closely related structures. These data may be useful for further research applications.

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