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Activity Coefficients of RbF or CsF in the Ethene Glycol + Water System by Potentiometric Measurements at 298.15 K

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ABSTRACT: In this work, we report the measurements of the thermodynamic properties of RbF or CsF in the ethene glycol + water system at 298.15 K in the range of w = 0.10 to 0.40 ethene glycol. The experimental data were calculated by Pitzer model. Standard cell potentials and Pitzer parameters were obtained. From these, mean activity coefficients of RbF or CsF, osmotic coefficients of the mixtures, and standard Gibbs energies of transfer of RbF or CsF from water to ethene glycol + water mixtures were calculated.

INTRODUCTION

Aqueous electrolyte solutions are involved in many industrial processes, such as extractive distillation, solution crystallization, ion exchange, membrane separation, wastewater treatment, absorption refrigeration, and so forth. The properties of electrolyte in mixed water−organic solvents are of particular interest in many industrial and environmental applications, particularly, for separation processes.

Recent years, many aqueous electrolyte solutions or electrolyte in mixture solvents were investigated by potentiometric measurements. This measurement is one of the commonly used methods to determine the mean activity coefficients because of its simplicity, high speed, and accuracy.

So far, there are a lot of studies of alkali metal chlorides in mixtures and obtained various thermodynamic data for MCl (M = H, Li, Na, K, Rb, and Cs) in mixed solvents.[1−6] For example, Lopes et al. investigated the activity coefficients of KCl or NaCl in ethanol + water mixtures.[7,8] Deyhimi et al. measured the activity coefficient of HCl in *N*,*N*-dimethylformamide and water mixed solvent systems and the 2-propanol + water system.[9,10]But, only a few studies are cited in the literature that describe the thermodynamic properties of fluorine compound MF (M = H, Li, Na, K, Rb, and Cs) in organic solvents. Hernández-Luis et al. determined the activity coefficients of NaF in methanol + water, ethanol + water, fructose + water, and formamide + water mixtures.[11−13]

As a continuation of our previous investigations in the field of the thermodynamic properties of rare alkali metal salts in mixture systems (RbCl or CsCl + methanol/ethanol + water, CsCl + Cs_2SO_4 + H_2O, and CsCl + $MgCl_2$ + H_2O),[14−17] in this work, we determined the mean activity coefficients of RbF or CsF in the ethene glycol + water system by potentiometric measurements at 298.15 K. The mass fraction of ethene glycol is from 0.10 to 0.40. The Pitzer model was applied to describe the behavior of the system.

EXPERIMENTAL SECTION

The materials used were analytical grade rubidium fluoride and cesium fluoride (purity > 0.9950 mass fraction, Shanghai China Lithium Industrial Co., Ltd.) and ethene glycol of analytical grade high purity (purity > 0.9950 mass fraction, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China). These materials were used without further purification. All primary stock solutions were prepared by weight using doubly distilled water or the ethene glycol + water mixed solvent.

The Rb or Cs ion-selective electrode (Rb or Cs-ISE) was a poly(vinyl chloride) (PVC) membrane type based on valinomycin and was filled with 0.1 mol·L^{-1} RbF or CsF as the internal liquid. The F^- ion-selective electrode used was taken by Jiangsu Jiangfen Electroanalytical Instrument Co. The electrode was calibrated before experiment and showed good Nernstian response. The cells used in this work belong to the type of galvanic cell without a liquid junction with only one fluid, as follows:

$$\text{Rb-ISE}|\text{RbF}(m), \text{ethene glycol}(w), \text{H}_2\text{O}|\text{F-ISE} \quad \text{(I)}$$

$$\text{Cs-ISE}|\text{CsF}(m), \text{ethene glycol}(w), \text{H}_2\text{O}|\text{F-ISE} \quad \text{(II)}$$

The cells were carried out at different molalities of RbF or CsF in mixtures containing (w = 0.00, 0.10, 0.20, 0.30, and 0.40) weight percent of ethene glycol at 298.15 K. In the cells, w is the mass fraction of ethene glycol, m is the molality of RbF or CsF, and a rubidium or cesium ion-selective electrode (Rb-ISE or Cs-ISE) was employed. The uncertainties in the electrolyte molality and mass fraction of ethene glycol are ± 0.0001 and ± 0.01, respectively. As usual, all of the measurements were performed under stirring conditions, and the temperature in the cells was maintained to a constant within T = 298.15 K (± 0.02 K) by employing a double-wall container enabling the circulation of water from a thermostat. The EMF readings were obtained on a pH/mV meter (Orion 868, U.S. with precision ± 0.1 mV). Voltage readings were taken as final when they were constant, within 0.1 mV, for at least 5 min.

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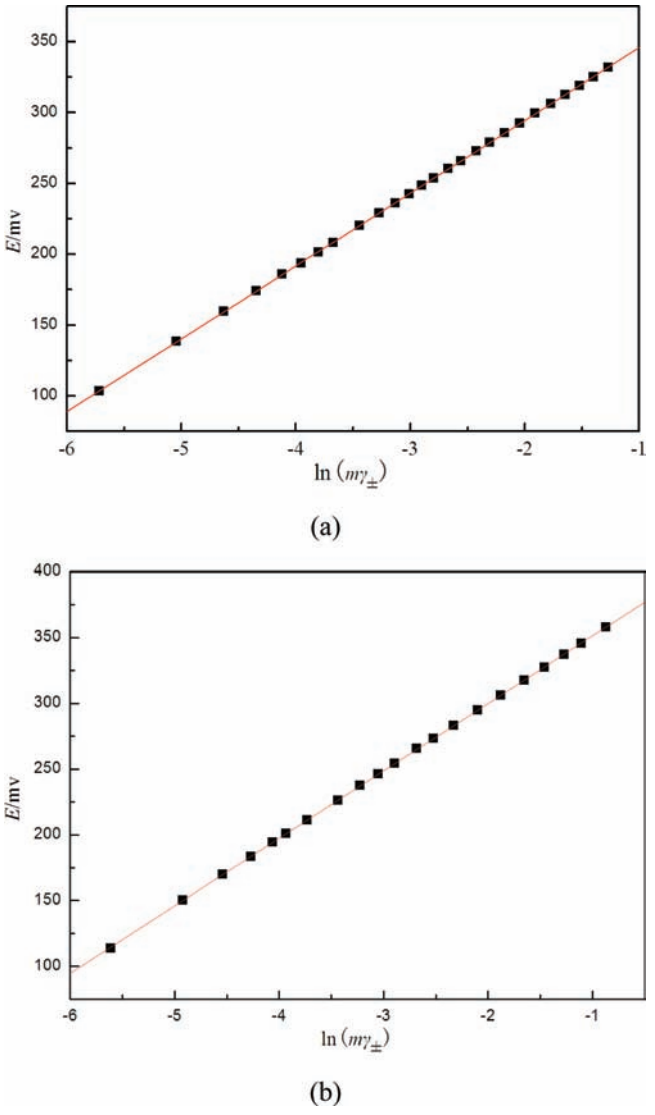

Figure 1. Response of the Rb-ISE (a) or Cs-ISE (b) and F-ISE electrode pair in the mixture at 298.15 K. The linear regression line in the figure has an equation of the form $y = a + bx$, a is 398.5 and 420.9 mV, and b is 51.42 and 51.21 for the Rb-ISE (a) or Cs-ISE (b) and F-ISE electrode, respectively.

DATA PROCESSING AND RESULTS AND DISCUSSION

The experimental mean activity coefficients of RbF or CsF in the mixtures were calculated by combined Nernstian equation and Pitzer equation. The Nernstian equation can be written as:

$$E = E^0 + 2k \ln(m\gamma_{\pm}) \quad (1)$$

where $\gamma_{\pm}$ are the mean activity coefficients of RbF or CsF; $k = (RT/F)$ is the theoretical Nernstian slope in which the symbols (R, T, and F) have their usual meanings. E^0 is the fitted potential of the cells I and II.

The cells' calibration of the electrode should be done before the determination. Combining the Nernst eq 1 with the single 1−1 electrolyte Pitzer equation, we obtained the mean activity coefficient of RbF or CsF in the pure water form experiment.

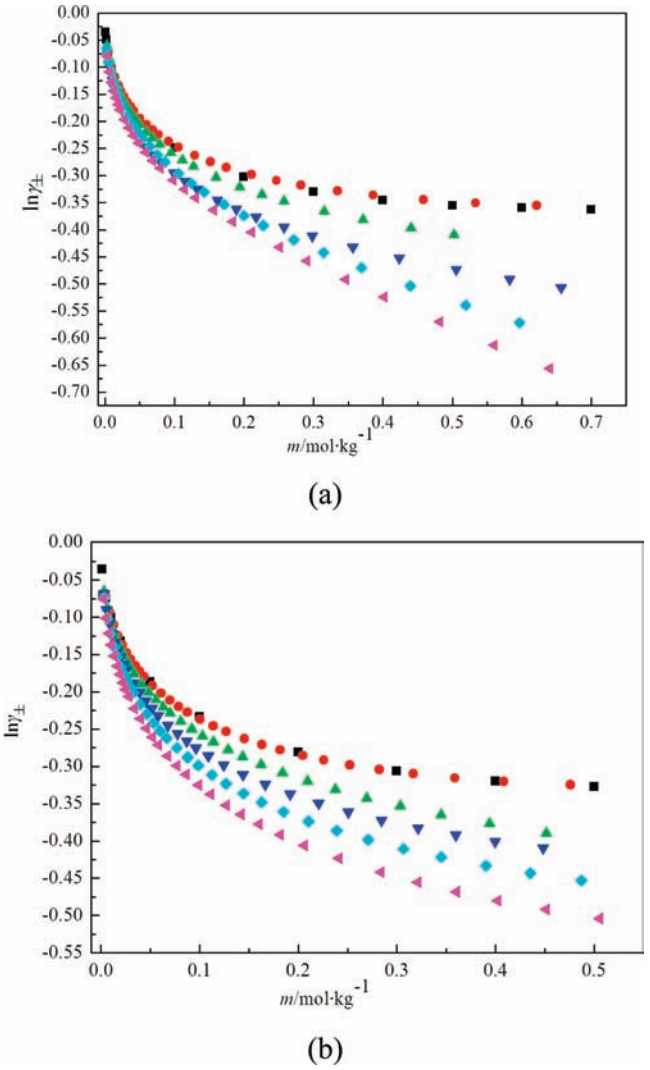

Figure 2. Plot of ln $\gamma_{\pm}$ (RbF) (a) and ln $\gamma_{\pm}$ (CsF) (b) vs m of RbF or CsF in ethene glycol + water at 298.15 K for different mass fractions of ethene glycol. ■, 0.00 ethene glycol, ref 18; ●, 0.00 ethene glycol, this work; ▲, 0.10 ethene glycol; ▼, 0.20 ethene glycol; ◆, 0.30 ethene glycol; left-pointing triangle, 0.40 ethene glycol.

Table 1. Values of the Density ρ, Permittivity ε, and Debye−Huckel Osmotic Coefficient Parameter A_φ for the Ethene Glycol + Water Mixtures at 298.15 K[19]

w (ethene glycol)	ρ/g·cm^{-3}	ε	A_φ
0.00	0.9970	78.3	0.3921
0.10	1.0096	75.6	0.4159
0.20	1.0228	72.8	0.4430
0.30	1.0361	69.8	0.4749
0.40	1.0494	66.6	0.5128

As shown in Figure 1, a plot of E against ln($m\gamma_{\pm}$) produced a straight line, with a linear correlation of 0.9999. In Figure 1, E and ln($m\gamma_{\pm}$) are the potentials and natural logarithm of the activity of RbF or CsF in water, respectively. The values of $2k$ are 51.37 and 51.21 for RbF and CsF systems, which is close to the theoretical one (51.38) of the Nernst slope. Our data for the

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Table 2. Potential E, Mean Activity Coefficient $\gamma_{\pm}$, and Osmotic Coefficient Φ, at Different RbF Molalities and Mass Fraction of Ethene Glycol in Ethene Glycol + Water Systems at 298.15 K

m	E			m	E		
mol·kg^{-1}	mV	$\gamma_{\pm}$	Φ	mol·kg^{-1}	mV	$\gamma_{\pm}$	Φ
			$w = 0.00$				
0.0046	116.9	0.9305	0.9772	0.0915	263.9	0.7891	0.9375
0.0096	153.4	0.9047	0.9690	0.1058	270.7	0.7806	0.9359
0.0140	172.3	0.8889	0.9641	0.1293	280.2	0.7690	0.9340
0.0187	186.7	0.8759	0.9601	0.1517	287.8	0.7599	0.9328
0.0232	197.4	0.8654	0.9570	0.1747	294.5	0.7521	0.9320
0.0275	205.8	0.8567	0.9545	0.2107	303.2	0.7421	0.9314
0.0321	213.3	0.8486	0.9522	0.2467	310.7	0.7342	0.9315
0.0367	219.8	0.8414	0.9502	0.2819	317.0	0.7278	0.9319
0.0411	225.4	0.8351	0.9485	0.3349	325.2	0.7202	0.9330
0.0506	235.4	0.8235	0.9455	0.3859	331.9	0.7146	0.9346
0.0596	243.3	0.8141	0.9431	0.4584	340.0	0.7086	0.9373
0.0685	250.0	0.8060	0.9412	0.5332	347.3	0.7043	0.9404
0.0772	255.8	0.7990	0.9396	0.6214	354.6	0.7010	0.9445
			$w = 0.10$				
0.0027	105.5	0.9417	0.9807	0.0686	262.5	0.7938	0.9362
0.0055	140.6	0.9203	0.9738	0.0792	269.1	0.7845	0.9338
0.0093	165.3	0.9007	0.9675	0.0950	277.7	0.7727	0.9309
0.0132	182.4	0.8852	0.9627	0.1111	285.1	0.7624	0.9285
0.0160	191.9	0.8765	0.9600	0.1274	291.5	0.7533	0.9265
0.0188	200.4	0.8684	0.9575	0.1600	302.1	0.7382	0.9233
0.0218	207.6	0.8609	0.9552	0.1942	311.2	0.7252	0.9207
0.0248	213.8	0.8540	0.9531	0.2260	318.2	0.7152	0.9190
0.0311	224.7	0.8416	0.9495	0.2574	324.3	0.7066	0.9175
0.0373	233.4	0.8311	0.9465	0.3154	333.8	0.6934	0.9156
0.0434	240.6	0.8222	0.9439	0.3712	341.5	0.6830	0.9143
0.0494	246.9	0.8143	0.9417	0.4403	349.5	0.6722	0.9131
0.0592	255.6	0.8031	0.9387	0.5024	355.5	0.6640	0.9124
			$w = 0.20$				
0.0031	136.6	0.9301	0.9769	0.0986	303.7	0.7441	0.9213
0.0060	170.0	0.9065	0.9692	0.1154	311.0	0.7327	0.9185
0.0103	195.4	0.8830	0.9616	0.1328	317.6	0.7224	0.9160
0.0130	207.9	0.8714	0.9579	0.1616	326.5	0.7080	0.9126
0.0169	220.2	0.8580	0.9538	0.1889	333.7	0.6965	0.9100
0.0200	228.2	0.8486	0.9508	0.2172	340.0	0.6861	0.9078
0.0230	235.0	0.8406	0.9484	0.2577	347.8	0.6734	0.9050
0.0293	246.6	0.8259	0.9440	0.2983	354.4	0.6624	0.9027
0.0360	256.6	0.8132	0.9402	0.3565	362.5	0.6490	0.8999
0.0423	264.6	0.8027	0.9371	0.4233	370.6	0.6361	0.8971
0.0487	271.0	0.7933	0.9345	0.5054	379.0	0.6226	0.8942
0.0588	279.7	0.7805	0.9309	0.5821	385.8	0.6117	0.8918
0.0694	287.4	0.7690	0.9278	0.6563	389.6	0.6024	0.8895
0.0800	294.2	0.7590	0.9251				
			$w = 0.30$				
0.0029	120.8	0.9357	0.9787	0.0860	283.9	0.7597	0.9228
0.0059	155.2	0.9128	0.9712	0.1056	293.4	0.7435	0.9176
0.0089	175.7	0.8958	0.9657	0.1243	300.8	0.7301	0.9132
0.0121	190.7	0.8820	0.9613	0.1425	307	0.7186	0.9093
0.0154	202.3	0.8702	0.9575	0.1715	315.3	0.7022	0.9037
0.0188	212.1	0.8596	0.9541	0.2000	322.2	0.6880	0.8985
0.0223	220.2	0.8502	0.9511	0.2277	327.9	0.6756	0.8938
0.0257	227.1	0.8419	0.9485	0.2715	335.6	0.6581	0.8867
0.0326	238.3	0.8276	0.9440	0.3144	341.9	0.6426	0.8800
0.0397	247.8	0.8148	0.9400	0.3689	348.7	0.6248	0.8718
0.0471	255.7	0.8035	0.9365	0.4392	355.9	0.6042	0.8615
0.0541	262.2	0.7939	0.9335	0.5190	362.7	0.5832	0.8501
0.0642	270.2	0.7817	0.9297	0.5963	368.2	0.5645	0.8391
0.0754	277.7	0.7697	0.9260				
			$w = 0.40$				
0.0032	157.2	0.9241	0.9750	0.0979	320.0	0.7349	0.9174
0.0066	191.2	0.8972	0.9664	0.1144	327.2	0.7223	0.9134
0.0097	210.6	0.8800	0.9610	0.1308	333.2	0.7111	0.9096
0.0129	224.6	0.8662	0.9567	0.1568	341.5	0.6953	0.9040
0.0160	235.2	0.8548	0.9532	0.1837	348.8	0.6807	0.8984
0.0192	243.8	0.8444	0.9500	0.2110	355.1	0.6672	0.8928
0.0221	250.7	0.8363	0.9476	0.2511	362.9	0.6491	0.8847
0.0284	262.5	0.8212	0.9431	0.2908	369.5	0.6327	0.8766
0.0348	271.9	0.8086	0.9393	0.3467	375.3	0.6114	0.8650
0.0412	279.9	0.7975	0.9361	0.4018	381.3	0.5920	0.8534
0.0482	287.3	0.7868	0.9330	0.4821	388.5	0.5656	0.8361
0.0586	296.4	0.7732	0.9290	0.5601	394.2	0.5418	0.8190
0.0690	303.9	0.7615	0.9255	0.6398	399.2	0.5190	0.8011
0.0795	310.5	0.7509	0.9223				

activity coefficients of RbF and CsF in water were compared with the published values,[18] and the results are both depicted in Figure 2. From Figure 2, we can see that the results are consistent. So it is concluded that the electrode pairs we used have good Nernst response, and they are satisfactory for our study.

For a 1−1 type electrolyte, the Pitzer equations for the mean activity coefficient ($\gamma_{\pm}$) and osmotic coefficient (Φ) can be written as follows:[19]

$$\ln \gamma_{\pm} = f^{\gamma} + mB^{\gamma} + m^2C^{\gamma} \quad (2)$$

$$\Phi - 1 = f^{\varphi} + mB^{\varphi} + m^2C^{\varphi} \quad (3)$$

where

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

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

$$C^{\gamma} = 1.5C^{\varphi} \quad (2c)$$

$$f^{\varphi} = -A_{\varphi}(I^{1/2}/(1 + bI^{1/2})) \quad (3a)$$

$$B^{\varphi} = \beta^{(0)} + \beta^{(1)} \exp(-\alpha I^{1/2}) \quad (3b)$$

$\beta^{(0)}$, $\beta^{(1)}$, and C^{φ} are the parameters of the Pitzer equation. I is the summation of ionic strength over all ions, $I = (1/2)\Sigma(mZ^2)$,

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Table 3. Potential E, Mean Activity Coefficient $\gamma_{\pm}$, and Osmotic Coefficient Φ, at Different CsF Molalities and Mass Fraction of Ethene Glycol in Ethene Glycol + Water Systems at 298.15 K

m / mol·kg^{-1}	E / mV	$\gamma_{\pm}$	Φ	m / mol·kg^{-1}	E / mV	$\gamma_{\pm}$	Φ
			$w = 0.00$				
0.0043	137.9	0.9338	0.9782	0.1003	291.2	0.7892	0.9388
0.0085	171.9	0.9112	0.9711	0.1138	297.2	0.7822	0.9377
0.0128	191.9	0.8953	0.9662	0.1268	302.3	0.7762	0.9369
0.0172	206.4	0.8824	0.9622	0.1455	308.9	0.7689	0.9361
0.0215	217.4	0.8720	0.9596	0.1632	314.3	0.7629	0.9356
0.0258	226.3	0.8630	0.9565	0.1817	319.4	0.7575	0.9354
0.0302	233.8	0.8551	0.9543	0.2045	325.1	0.7517	0.9355
0.0346	240.3	0.8480	0.9523	0.2260	329.7	0.7471	0.9357
0.0391	246.1	0.8416	0.9506	0.2524	335.1	0.7423	0.9363
0.0437	251.3	0.8355	0.9490	0.2823	340.2	0.7377	0.9373
0.0523	260.1	0.8257	0.9466	0.3166	345.9	0.7335	0.9386
0.0608	267.4	0.8173	0.9445	0.3589	352.0	0.7294	0.9406
0.0698	273.9	0.8096	0.9428	0.4086	358.5	0.7259	0.9433
0.0787	279.7	0.8028	0.9414	0.4762	366.2	0.7227	0.9473
0.0875	284.6	0.7968	0.9402				
			$w = 0.10$				
0.0033	141.3	0.9368	0.9792	0.0809	296.7	0.7868	0.9355
0.0063	173.4	0.9162	0.9726	0.0918	302.6	0.7788	0.9336
0.0094	193.6	0.9007	0.9677	0.1028	308.0	0.7717	0.9320
0.0129	208.8	0.8873	0.9636	0.1138	312.7	0.7652	0.9305
0.0165	220.7	0.8761	0.9601	0.1288	318.6	0.7573	0.9288
0.0197	229.4	0.8674	0.9575	0.1434	323.6	0.7504	0.9274
0.0233	237.4	0.8589	0.9550	0.1622	329.4	0.7425	0.9259
0.0268	244.2	0.8515	0.9528	0.1840	335.2	0.7344	0.9243
0.0301	249.7	0.8453	0.9510	0.2096	341.3	0.7260	0.9228
0.0338	255.3	0.8388	0.9492	0.2377	347.2	0.7180	0.9215
0.0413	264.8	0.8275	0.9460	0.2696	353.1	0.7099	0.9202
0.0483	272.3	0.8183	0.9435	0.3034	358.6	0.7024	0.9190
0.0555	278.9	0.8099	0.9413	0.3447	364.5	0.6943	0.9178
0.0629	284.8	0.8024	0.9394	0.3940	370.7	0.6859	0.9167
0.0700	289.9	0.7958	0.9377	0.4516	377.1	0.6773	0.9156
			$w = 0.20$				
0.0031	150.5	0.9338	0.9781	0.0775	305.4	0.7738	0.9303
0.0057	180.2	0.9139	0.9716	0.0868	310.7	0.7662	0.9285
0.0087	201.0	0.8970	0.9662	0.0961	315.4	0.7595	0.9269
0.0114	213.9	0.8852	0.9624	0.1087	321.2	0.7512	0.9251
0.0142	224.7	0.8747	0.9591	0.1242	327.4	0.7422	0.9232
0.0169	233.2	0.8657	0.9563	0.1438	334.2	0.7325	0.9214
0.0197	240.6	0.8576	0.9538	0.1665	341.0	0.7228	0.9198
0.0230	248.0	0.8492	0.9512	0.1917	347.6	0.7137	0.9184
0.0258	253.4	0.8428	0.9493	0.2205	354.2	0.7047	0.9173
0.0329	265.0	0.8284	0.9451	0.2508	360.1	0.6968	0.9166
0.0391	273.2	0.8180	0.9421	0.2845	366.1	0.6891	0.9161
0.0454	280.3	0.8086	0.9394	0.3215	371.8	0.6819	0.9160
0.0515	286.3	0.8005	0.9372	0.3597	377.1	0.6756	0.9160
0.0570	291.8	0.7929	0.9352	0.3997	382.0	0.6699	0.9164
0.0676	299.0	0.7828	0.9325	0.4484	387.4	0.6639	0.9170

Table 3. Continued

m / mol·kg^{-1}	E / mV	$\gamma_{\pm}$	Φ	m / mol·kg^{-1}	E / mV	$\gamma_{\pm}$	Φ
			$w = 0.30$				
0.0031	154.8	0.9290	0.9764	0.0878	318.0	0.7499	0.9225
0.0063	190.1	0.9037	0.9681	0.0985	323.4	0.7417	0.9205
0.0097	211.5	0.8848	0.9620	0.1124	329.7	0.7323	0.9183
0.0134	227.3	0.8691	0.9570	0.1267	335.3	0.7237	0.9165
0.0165	237.5	0.8580	0.9535	0.1444	341.5	0.7144	0.9146
0.0202	247.6	0.8464	0.9499	0.1628	347.1	0.7059	0.9130
0.0231	254.0	0.8387	0.9475	0.1850	353.2	0.6970	0.9115
0.0262	260.2	0.8311	0.9451	0.2103	359.2	0.6882	0.9102
0.0293	265.5	0.8242	0.9431	0.2389	365.2	0.6796	0.9091
0.0326	270.7	0.8175	0.9411	0.2708	371.1	0.6713	0.9083
0.0394	279.8	0.8053	0.9374	0.3066	377.0	0.6633	0.9077
0.0461	287.3	0.7948	0.9344	0.3449	382.6	0.6559	0.9074
0.0531	294.1	0.7852	0.9317	0.3904	388.4	0.6484	0.9074
0.0597	299.7	0.7770	0.9295	0.4353	393.6	0.6420	0.9076
0.0666	304.9	0.7694	0.9275	0.4872	399.0	0.6357	0.9081
0.0768	311.6	0.7594	0.9249				
			$w = 0.40$				
0.0028	174.5	0.9276	0.9759	0.0771	333.4	0.7415	0.9180
0.0053	206.2	0.9040	0.9681	0.0863	338.5	0.7329	0.9157
0.0080	226.3	0.8857	0.9621	0.0988	344.8	0.7225	0.9130
0.0106	239.9	0.8718	0.9575	0.1110	350.0	0.7136	0.9108
0.0134	251.3	0.8591	0.9534	0.1270	356.2	0.7032	0.9084
0.0164	261.0	0.8476	0.9497	0.1419	361.3	0.6947	0.9065
0.0193	268.7	0.8379	0.9466	0.1603	366.8	0.6854	0.9045
0.0222	275.4	0.8291	0.9438	0.1818	372.5	0.6759	0.9026
0.0252	281.3	0.8211	0.9413	0.2062	378.3	0.6664	0.9009
0.0283	286.7	0.8136	0.9390	0.2411	385.4	0.6548	0.8990
0.0341	295.6	0.8008	0.9351	0.2839	392.8	0.6430	0.8974
0.0400	303.0	0.7898	0.9317	0.3215	398.5	0.6342	0.8964
0.0460	309.6	0.7797	0.9288	0.3605	403.7	0.6263	0.8958
0.0522	315.4	0.7707	0.9261	0.4022	408.7	0.6189	0.8954
0.0582	320.4	0.7626	0.9238	0.4514	414.0	0.6113	0.8952
0.0677	327.4	0.7513	0.9206	0.5059	419.2	0.6041	0.8953

where m and Z are the molality and charge number, respectively. For the 1−1 type electrolyte, $I = m$. The parameters b and α are equal to (1.2 and 2.0) kg·mol$^{-1/2}$, respectively.[20] A_{φ} is the Debye−Huckel constant for the osmotic coefficient defined by

$$A_{\varphi} = (1/3)[(2\pi N_0 \rho)/1000]^{1/2}[e^2/(\varepsilon KT)]^{3/2} \quad (4)$$

where N_0, ρ, e, ε, K, and T are Avogadro's number, the density of solvent mixtures, electronic charge, the dielectric constant, Boltzmann's constant, and the temperature. Equation 4 can be simplified as:

$$A_{\varphi} = 1.4006 \cdot 10^6 \cdot \rho^{1/2}(\varepsilon T)^{-3/2} \quad (5)$$

The value of A_{φ} in pure water is 0.3915[19] at 298.15 K. The A_{φ} values for the investigated ethene glycol + water mixtures are given in Table 1, which increase with the addition of ethene glycol in the mixtures. The values of ρ were determined by DMA4500-RXA170 (Anton Paar) and ε are from the literature.[21]

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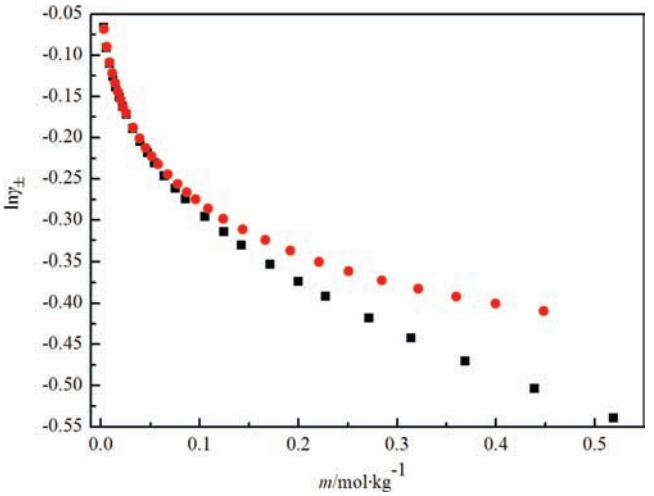

Figure 3. Variation of ln $\gamma_{\pm}$ with m of RbF or CsF for 0.20 mass fraction of ethene glycol in the mixed solvent. ■, RbF; ●, CsF.

Table 4. Pitzer Parameters and Standard Transfer Gibbs Energy for RbF or CsF + Ethene Glycol + Water Systems at 298.15 K

				E^0	SD	$\Delta_t G^0$
w	$\beta^{(0)}$	$\beta^{(1)}$	C^{φ}	mV	mV	kJ·mol^{-1}
			RbF + Ethene Glycol + Water			
0.00	0.1141	0.2842	−0.0105	398.5 ± 0.1	0.09	0
0.10	0.0472	0.3901	0.0020	412.0 ± 0.1	0.06	1.2459
0.20	0.1234	0.2356	−0.0278	424.0 ± 0.1	0.01	2.3543
0.30	0.0291	0.5080	−0.0013	438.1 ± 0.1	0.04	3.6308
0.40	−0.1913	1.0064	0.0068	455.6 ± 0.1	0.08	5.2623
			CsF + Ethene Glycol + Water			
0.00	0.1306	0.2570	−0.0043	420.9 ± 0.1	0.03	0
0.10	0.0362	0.4529	0.0029	437.7 ± 0.1	0.006	1.5628
0.20	0.0941	0.3486	−0.0085	449.5 ± 0.1	0.006	2.6318
0.30	0.0942	0.3725	−0.0098	460.3 ± 0.1	0.005	3.6411
0.40	0.0848	0.4126	−0.0047	479.9 ± 0.1	0.005	5.4414

The mean activity coefficients and osmotic coefficients of RbF or CsF in the ternary mixed systems were calculated by the Pitzer model. The values are listed in Tables 2 and 3. The variation of ln $\gamma_{\pm}$ with the molalities of RbF or CsF is shown in Figure 2. It can be seen that a decrease of the mean activity coefficient for RbF or CsF with the ethene glycol content increased and with the molality of RbF or CsF increased. The values of osmotic coefficients Φ have the same trend as the mean activity. As depicted in Figure 3, at the same ethene glycol content, the mean activity coefficient of CsF is higher than that of RbF. This may be caused by the smaller electronegativity difference between Rb^+ and F^- than that of Cs^+ and F^-.

The standard Gibbs energy of transfer is one of the most useful available thermodynamic properties of solution. It can be calculated from E^0 values according to the following equation:[22]

$$\Delta_t G^0 = F(E^0{}_s - E^0{}_w) + 2RT(\ln \rho_w/\rho_s) \qquad (6)$$

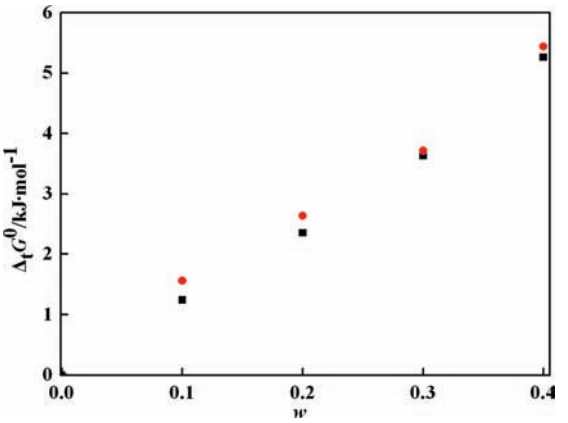

Figure 4. Standard Gibbs energy of transference from water to ethene glycol + water for RbF and CsF. ■, RbF; ●, CsF.

where $\Delta_t G^0$ is the standard Gibbs energy of solvent of RbF or CsF. $E^0{}_w$ and $E^0{}_s$ are the standards of electromotive force of RbF or CsF in pure water and in mixed solvents, respectively. ρ_w and ρ_s are density of water and mixed solvents, respectively. The $\Delta_t G^0$ values are listed in Table 4.

If the electrostatic component of $\Delta_t G^0$ is assumed to be well-described by the Born model of ion solvation, then for RbF or CsF it should be expressed[23] by the following equation:

$$\Delta_t G^0 = 69.25(1/\varepsilon_s - 1/\varepsilon_w)(1/r_+ + 1/r_-) \qquad (7)$$

where ε_s and ε_w are the dielectric constants of the mixed solvent and water; r_+ and r_- are the crystal radii of the cation and anion.

Figure 4 is the relationship between standard transfer Gibbs energy $\Delta_t G^0$ and the ratio of w in the mixed solvent. $\Delta_t G^0$ are all positive obviously, which indicates that the transference of RbF or CsF from water to the ethene glycol + water mixed solvents is not spontaneous. This shows that the solvation power of Rb^+ or Cs^+ decreases when the mass fraction of ethene glycol in the mixed solvents increased. When w was a certain value, $\Delta_t G^0$ of RbF + ethene glycol + water was larger than that of CsF + ethene glycol + water system because the radius of Rb^+ is smaller than that of Cs^+.

■ CONCLUSION

Using the galvanic cell consisting of Rb-ISE or Cs-ISE and F-ISE electrodes, we determined the potential of RbF or CsF in the ethene glycol + water mixtures. The experimental data were calculated by the Pitzer model. The mean activity coefficients, osmotic coefficients, and the Gibbs energies of transfer were obtained along with the corresponding parameters for the model.

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REFERENCES

(1) Lietzke, M. H.; O'Brien, H. A., Jr. Electromotive Force Studies in Aqueous Solutions at Elevated Temperatures. X. Thermodynamic Properties of HCl-KCl, HCl-RbCl, HCl-CsCl, HCl-$MgCl_2$, HCl-$CaCl_2$, HCl-$SrCl_2$, and HCl-$AlCl_3$ Mixtures. *J. Phys. Chem.* **1968**, *72*, 4408–4414.

(2) Wang, J.; Liu, W.; Fan, J.; Lu, J. Mean Activity Coefficients of NaCl in Glucose−Water and Sucrose−Water Mixtures at 298.15 K. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 3281–3285.

(3) Hernández-Luis, F.; Galleguillos, H. R.; Fernández-Mérida, L.; González-Díaz, O. Activity Coefficients of NaCl in Aqueous Mixtures with ε-Increasing Co-solvent: Formamide−Water Mixtures at 298.15 K. *Fluid Phase Equilib.* **2009**, *275*, 116–126.

(4) Esteso, M. A.; Gonzalez-Diaz, O. M.; Hernandez-Luis, F.; Fernandez-Merida, L. Activity Coefficients for NaCl in Ethanol + Water Mixtures at 25 °C. *J. Solution Chem.* **1989**, *18*, 277–288.

(5) Yao, J.; Yan, W.; Xu, Y.; Han, S. Activity Coefficients for NaCl in MeOH + H_2O by Electromotive Force Measurements at 308.15 and 318.15 K. *J. Chem. Eng. Data* **1999**, *44*, 497–500.

(6) Ma, Y. Y.; Li, S. N.; Zhai, Q. G.; Jiang, Y. C.; Hu, M. C. Activity Coefficients of Potassium Chloride in Ethene Glycol Water Mixtures Using Electromotive Force Measurements at (278.15, 288.15, 298.15, and 308.15) K. *J. Chem. Eng. Data* **2010**, *55*, 1573–1579.

(7) Lopes, A.; Farelo, F.; Ferra, M. I. Activity Coefficients of Potassium Chloride in Water + Ethanol Mixtures. *J. Solution Chem.* **1999**, *28*, 117–131.

(8) Lopes, A.; Farelo, F.; Ferra, M. I. Activity Coefficients of Sodium Chloride in Water + Ethanol Mixtures: A Comparative Study of Pitzer and Pitzer−Simonson models. *J. Solution Chem.* **2001**, *30*, 757–770.

(9) Deyhimi, F.; Ebrahimi, A.; Roohi, H.; Koochaki, K. Determination of Activity Coefficients, Osmotic Coefficients, and Excess Gibbs Free Energies of HCl in *N*,*N*-Dimethylformamide + Water Mixed Solvent Systems by Potentiometric Measurements. *J. Chem. Eng. Data* **2004**, *49*, 1185–1188.

(10) Deyhimi, F.; Karimzadeh, Z. Pitzer and Pitzer−Simonson−Clegg Modeling Approaches: Ternary HCl + 2-Propanol +Water Electrolyte System. *J. Solution Chem.* **2010**, *39*, 245–257.

(11) Hernández-Luis, F.; Vázquez, M.; Esteso, M. Activity Coefficients for NaF in Methanol + Water and Ethanol + Water Mixtures at 25 °C. *J. Mol. Liq.* **2003**, *108*, 283–301.

(12) Hernández-Luis, F.; Galleguillos, H.; Vázquez, M. Activity Coefficients of NaF in (Glucose + Water) and (Sucrose + Water) Mixtures at 298.15 K. *J. Chem. Thermodyn.* **2004**, *36*, 957–964.

(13) Hernández-Luis, F.; Galleguillos-Castro, H.; Esteso, M. Activity Coefficients of NaF in Aqueous Mixtures with ε-increasing Co-solvent: Formamide + Water Mixtures at 298.15 K. *Fluid Phase Equilib.* **2005**, *227*, 245–253.

(14) Hu, M. C.; Cui, R. F.; Li, S. N.; Jiang, Y. C.; Xia, S. P. Determination of Activity Coefficients for Cesium Chloride in Methanol + Water and Ethanol + Water Mixed Solvents by Electromotive Force Measurements at 298.15 K. *J. Chem. Eng. Data* **2007**, *52*, 357–362.

(15) Cui, R. F.; Hu, M. C.; Jin, L. H.; Li, S. N.; Jiang, Y. C.; Xia, S. P. Activity Coefficients of Rubidium Chloride and Cesium Chloride in Methanol + Water Mixtures and a Comparative Study of Pitzer and Pitzer−Simonson−Clegg Models (298.15 K). *Fluid Phase Equilib.* **2007**, *251*, 137–144.

(16) Hu, M. C.; Tang, J.; Li, S. N.; Xia, S. P.; Cui, R. F. Activity Coefficients of Cesium Chloride and Cesium Sulfate in Aqueous Mixtures Using an Electromotive Force Method at 298.15 K. *J. Chem. Eng. Data* **2007**, *52*, 2224–2227.

(17) Hu, M. C.; Zhang, W. J.; Li, S. N.; Zhai, Q. G.; Jiang, Y. C. Thermodynamic Investigation of a Ternary Mixed Electrolyte (CsCl/$MgCl_2$/H_2O) System Using Electromotive Force Measurement at 298.15 K. *J. Chem. Eng. Data* **2009**, *54*, 2023–2027.

(18) Hamer, W. J.; Wu, Y. C. Osmotic Coefficients and Mean Activity Coefficients of Uni-univalent Electrolytes in Water at 25 °C. *J. Phys. Chem. Ref. Data* **1972**, *1*, 1047–1100.

(19) Pitzer, K. S. Thermodynamics of electrolytes. I. Theoretical Basis and General Equation. *J. Phys. Chem.* **1973**, *77*, 268–277.

(20) Koh, D. S. P.; Khoo, K. H.; Chan, C. Y. The Application of the Pitzer Equations to 1−1 Electrolytes in Mixed Solvents. *J. Solution Chem.* **1985**, *14*, 635–651.

(21) Kumbharkhane, A. C.; Puranik, S. M.; Mehrotra, S. C. Temperature Dependent Dielectric Relaxation Study of Ethene Glycol-Water Mixtures. *J. Solution Chem.* **1992**, *21*, 201–212.

(22) Feakins, D.; Voice, P. J. Studies in Ion Solvation in Non-aqueous Solvents and Their Aqueous Mixtures: Part 14. Free Energies of Transfer of the Alkali-metal Chlorides from Water to 10∼99% (*w*/*w*) Methanol + Water Mixtures at 25 °C. *J. Chem. Soc., Faraday Trans.* **1972**, *168*, 1390–1405.

(23) Senanayake, G.; Hefter, G. Gibbs Energies of Transfer of Fluoride Salts from Water to Aqueous Alcohol Mixtures. *Monatsh. Chem.* **2003**, *134*, 669–677.