Thermodynamic Study of RbCl or CsCl in the Mixed Solvent DMF + H₂O by Potentiometric Measurements at 298.15 K

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The mean activity coefficient of RbCl or CsCl in *N*,*N*-dimethylformamide (DMF) + water mixtures was determined by potentiometric measurements at 298.15 K in the range $w = 0.10$ to 0.40 DMF. The Pitzer model was adopted to describe the behavior of the electrolytes. We also obtained the osmotic coefficients and the Gibbs energies of transfer of rubidium or cesium chloride from water to DMF + water mixtures.

Introduction

The behavior of aqueous solutions of electrolytes is of interest because of their importance in areas such as chemistry, biology, process engineering, desalination, and atmospheric processes. To date, there has been a growing interest in the measurement of the thermodynamic properties of electrolytes in mixed solvents. For example, Koh et al.[1] obtained the activity coefficients of the alkali metal chlorides in methanol + water mixtures at 25 °C. Hernandez-Luis et al. determined the activity coefficients of NaCl in ethanol + water, fructose + water, formamide + water, and PEG 4000 + water mixtures.[2−5] Lopes et al. investigated the activity coefficients of KCl or NaCl in ethanol + water mixtures.[6,7] Moreover, Deyhimi et al. measured the activity coefficient of NH₄Cl in some mixed solvents.[8,9]

N,*N*-Dimethylformamide (DMF) is widely used as a solvent and reaction medium in different fields such as chemical synthesis and chemical engineering processes. Some investigations have been performed on the activity coefficients of electrolytes in DMF + water mixtures. For example, Maestre reported the activity coefficients of NaCl in DMF + water mixtures.[10] Deyhimi and co-workers determined the activity coefficients, osmotic coefficients, and excess Gibbs energies of HCl in DMF + water mixed solvent systems.[11] For the ternary system RbCl + DMF + H₂O, reports are found in the literature[12] at 25 °C but with molalities only up to 0.08 mol·kg⁻¹.

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,[13,14] CsCl + Cs₂SO₄ + H₂O,[15] CsCl + MgCl₂ + H₂O[16]), we present herein the activity coefficients, osmotic coefficients, and standard transfer Gibbs energy for RbCl or CsCl at different concentrations of DMF + water mixtures from (0.10 to 0.40) mass fraction DMF.

Experimental Section

RbCl and CsCl (purity > 0.9950, Shanghai) were recrystallized[17] and dried overnight in a muffle furnace (*T* = 500 K). Afterward, the salts were stored over silica gel in a desiccator

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before use. DMF was analytical grade high purity (purity > 0.9950, Shanghai). Double-distilled deionized water was used in our experiments.

The Ag−AgCl electrode was the thermal-electrolytic type prepared by us according to the guidance described by Ives and Janz.[18] The Rb or Cs ion-selective electrodes (Rb- or Cs-ISE) were a PVC membrane type based on valinomycin and were filled with 0.1 mol·L⁻¹ RbCl or CsCl as the internal liquid. Both electrodes were calibrated before use and showed good Nernstian response. The galvanic cells without liquid junction arrangements in this work were as follows

(a) Rb-ISE|RbCl(*m*), DMF(*w*), H₂O|Ag|AgCl

(b) Cs-ISE|CsCl(*m*), DMF(*w*), H₂O|Ag|AgCl

In the cells, *m* is the molality of RbCl or CsCl in the mixtures and *w* the mass fraction of DMF (*w* = 0.00, 0.10, 0.20, 0.30, and 0.40). As usual, all the measurements were performed under stirring conditions, and the temperature in the cell was maintained 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.).

Results and Discussion

The experimental mean activity coefficients of RbCl or CsCl in the mixtures were calculated from the following Nernstian equation

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

where $\gamma_{\pm}$ is the mean activity coefficient of RbCl or CsCl, and $k(RT/F)$ is the ideal Nernstian slope in which the symbols (R, T, and F) have their usual meanings. E^0 is the standard potential of cells (a) and (b).

The cell calibration of the electrode should be done before the determination. Combining the Nernst eq 1 with the single 1−1 electrolyte Pitzer equation,[19] we obtained the mean activity coefficient of RbCl or CsCl in pure water. As shown in Figure
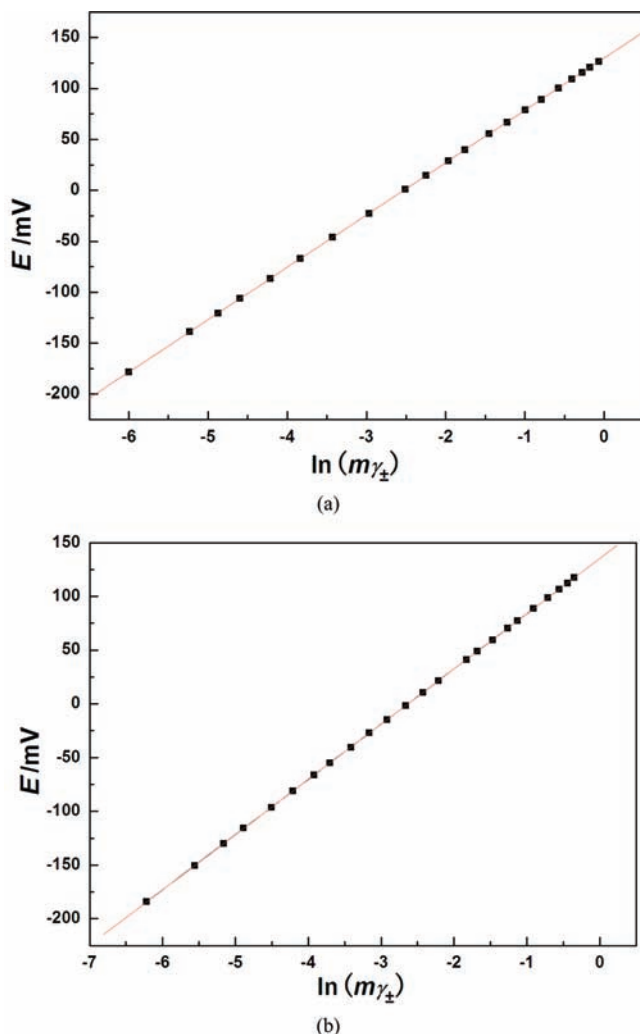
(a)

(b)

Figure 1. Response of Rb-ISE (a) or Cs-ISE (b) and the Ag/AgCl electrode pair in the mixture at 298.15 K.

1, a plot of E against $\ln(m\gamma_\pm)$ produced a straight line, with a linear correlation of 0.9999. The values of k are (25.70 ± 0.01) mV and (25.68 ± 0.01) mV for the RbCl and CsCl systems, respectively, which are close to the theoretical one (25.69 mV) of the Nernst slope. For comparison, the published values[22] and our data for the activity coefficients of RbCl are both depicted in Figure 2. Figure 2 shows that the two results are consistent. So it is concluded that the electrode pairs we used have good Nernstian response, and they are satisfactory for our study. The EMF values for the studied systems are listed in Tables 1 and 2.

For 1−1 type electrolytes, 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

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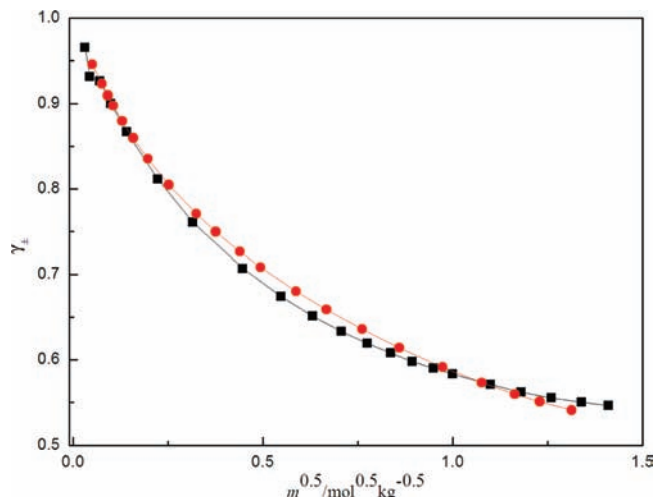

Figure 2. Comparisons between this work and the reference data for mean activity coefficients of RbCl in water at 298.15 K: ■, ref 1; ●, this work.

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

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

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

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

$\beta^{(0)}$, $\beta^{(1)}$, and C^φ are the parameters of the Pitzer equation. I is the summation of ionic strength over all ions, $I = (1/2)\sum(mZ^2)$, where m and Z are the molality and charge number, respectively. For 1−1 type electrolytes, $I = m$. The parameters b and α are equal to $(1.2$ and $2.0)$ kg·mol$^{-1/2}$,[1] respectively. A_φ is the Debye−Huckel constant for the osmotic coefficient defined by

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

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

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

The values of ρ, ε, and A_φ are shown in Table 3.

The mean activity coefficients and the osmotic coefficient of RbCl or CsCl in the ternary mixed system were calculated by the Pitzer model by means of a curve-fitting computer program (Solver in Excel). The variation of $\gamma_\pm$ with the square root of the molalities of RbCl or CsCl is shown in Figure 3. It can be seen that the mean activity coefficient for RbCl or CsCl decreases with a DMF content increase and with an increase in the molality of RbCl or CsCl. The values of Φ have the same trend as the mean activity. As depicted in Figure 4, at the same DMF content, the mean activity coefficient of RbCl is higher than that of CsCl. This is due to the smaller resistance force of Rb$^+$ than that of Cs$^+$ influenced by the radius of the ions.

Table 1. Potential E, Mean Activity Coefficient $\gamma_\pm$, and Osmotic Coefficient Φ at Different RbCl Molalities and Mass Fraction of DMF in DMF + H_2O Systems at 298.15 K

m / mol·kg⁻¹	E / mV	$\gamma_\pm$	ϕ	m / mol·kg⁻¹	E / mV	$\gamma_\pm$	ϕ
			$w = 0.00$				
0.0026	−178.4	0.9456	0.9820	0.2437	39.8	0.7084	0.9112
0.0058	−138.8	0.9226	0.9746	0.3448	55.5	0.6804	0.9031
0.0084	−120.3	0.9093	0.9703	0.4450	67.0	0.6589	0.8965
0.0112	−106.3	0.8978	0.9666	0.5796	78.7	0.6359	0.8892
0.0168	−86.5	0.8798	0.9609	0.7380	89.3	0.6140	0.8821
0.0251	−67.2	0.8598	0.9547	0.9482	100.3	0.5913	0.8747
0.0388	−46.2	0.8354	0.9474	1.1590	109.0	0.5732	0.8693
0.0637	−22.6	0.8048	0.9384	1.3543	115.8	0.5597	0.8661
0.1054	1.0	0.7708	0.9287	1.5108	120.6	0.5508	0.8647
0.1411	14.6	0.7499	0.9229	1.7245	126.4	0.5408	0.8645
0.1930	29.1	0.7265	0.9163				
			$w = 0.10$				
0.0025	−168.0	0.9452	0.9818	0.2597	54.0	0.6801	0.8968
0.0046	−137.2	0.9275	0.9759	0.3030	60.9	0.6659	0.8919
0.0068	−118.3	0.9140	0.9716	0.3887	71.9	0.6422	0.8836
0.0114	−92.5	0.8930	0.9647	0.4505	78.4	0.6278	0.8784
0.0159	−76.4	0.8773	0.9596	0.5606	87.9	0.6057	0.8702
0.0204	−64.2	0.8645	0.9555	0.6447	93.8	0.5914	0.8648
0.0274	−49.9	0.8480	0.9502	0.7396	99.6	0.5772	0.8593
0.0365	−36.2	0.8308	0.9447	0.8241	104.0	0.5658	0.8551
0.0492	−21.5	0.8116	0.9386	0.9472	109.6	0.5515	0.8498
0.0679	−6.6	0.7892	0.9316	1.0841	115.5	0.5377	0.8451
0.0903	6.2	0.7682	0.9250	1.2561	121.8	0.5231	0.8408
0.1178	18.4	0.7475	0.9185	1.4157	126.8	0.5120	0.8384
0.1513	29.7	0.7272	0.9121	1.5722	131.4	0.5029	0.8376
0.2094	44.2	0.6994	0.9031	1.7224	134.9	0.4957	0.8381
			$w = 0.20$				
0.0019	−168.0	0.9497	0.9832	0.2365	63.6	0.6666	0.8881
0.0036	−134.1	0.9317	0.9772	0.3124	75.7	0.6386	0.8777
0.0054	−114.3	0.9188	0.9729	0.3785	84.1	0.6185	0.8699
0.0091	−88.3	0.8979	0.9660	0.4561	91.9	0.5967	0.8618
0.0128	−71.4	0.8819	0.9607	0.5267	97.8	0.5825	0.8553
0.0185	−54.0	0.8629	0.9544	0.6085	103.6	0.5662	0.8484
0.0259	−37.8	0.8434	0.9479	0.6826	108.2	0.5531	0.8427
0.0333	−25.9	0.8275	0.9426	0.8674	117.9	0.5254	0.8305
0.0424	−14.6	0.8112	0.9373	0.9663	122.4	0.5129	0.8250
0.0536	−3.6	0.7944	0.9317	1.0657	126.6	0.5016	0.8201
0.0682	7.4	0.7762	0.9257	1.1987	131.2	0.4882	0.8145
0.0900	20.2	0.7539	0.9183	1.3523	136.0	0.4748	0.8094
0.1171	32.4	0.7317	0.9108	1.4920	139.8	0.4643	0.8059
0.1569	45.6	0.7056	0.9019	1.6265	143.1	0.4554	0.8035
0.2045	57.2	0.6807	0.8932	1.7438	145.7	0.4486	0.8022
			$w = 0.30$				
0.0016	−157.9	0.9507	0.9834	0.2817	86.1	0.6091	0.8577
0.0032	−123.0	0.9321	0.9772	0.3349	93.4	0.5885	0.8487
0.0046	−103.7	0.9194	0.9728	0.3821	98.8	0.5724	0.8415
0.0077	−78.6	0.8988	0.9658	0.4470	105.1	0.5530	0.8325
0.0108	−62.1	0.8826	0.9602	0.5143	110.5	0.5354	0.8241
0.0154	−45.0	0.8637	0.9537	0.5790	115.1	0.5203	0.8168
0.0217	−28.5	0.8428	0.9464	0.6640	120.4	0.5027	0.8082
0.0297	−14.0	0.8217	0.9390	0.7439	124.6	0.4881	0.8009
0.0407	0.7	0.7984	0.9307	0.8696	130.5	0.4681	0.7910
0.0547	14.3	0.7745	0.9222	0.9990	135.8	0.4506	0.7824
0.0730	27.3	0.7496	0.9131	1.1154	139.9	0.4369	0.7759
0.0963	39.8	0.7238	0.9036	1.2260	143.3	0.4255	0.7709
0.1268	52.0	0.6966	0.8932	1.3255	146.2	0.4164	0.7672
0.1718	65.3	0.6648	0.8808	1.4161	148.7	0.4088	0.7645
0.2216	76.0	0.6367	0.8694				
			$w = 0.40$				
0.0023	−116.3	0.9368	0.9786	0.0913	57.8	0.6953	0.8873
0.0032	−98.9	0.9257	0.9747	0.1248	71.2	0.6594	0.8719
0.0054	−74.6	0.9064	0.9679	0.1703	84.1	0.6213	0.8548
0.0074	−58.4	0.8916	0.9627	0.2387	97.8	0.5774	0.8341
0.0101	−43.3	0.8752	0.9569	0.3263	109.6	0.5349	0.8127
0.0132	−31.0	0.8602	0.9514	0.4253	119.2	0.4978	0.7929
0.0160	−21.6	0.8479	0.9469	0.5276	127.6	0.4671	0.7758
0.0209	−8.8	0.8294	0.9401	0.6184	133.3	0.4445	0.7628
0.0311	9.5	0.7989	0.9287	0.7017	137.5	0.4265	0.7522
0.0393	20.3	0.7790	0.9210	0.7745	140.8	0.4125	0.7438
0.0519	32.9	0.7535	0.9110	0.8415	143.5	0.4010	0.7369
0.0674	44.5	0.7277	0.9007				

Table 2. Potential E, Mean Activity Coefficient $\gamma_\pm$, and Osmotic Coefficient Φ at Different CsCl Molalities and Mass Fraction of DMF in DMF + H_2O Systems at 298.15 K

m / mol·kg⁻¹	E / mV	$\gamma_\pm$	ϕ	m / mol·kg⁻¹	E / mV	$\gamma_\pm$	ϕ
			$w = 0.00$				
0.0021	−184.3	0.9495	0.9831	0.1212	10.5	0.7282	0.9072
0.0041	−150.5	0.9309	0.9767	0.1552	21.6	0.7055	0.8995
0.0062	−130.0	0.9167	0.9719	0.2419	41.2	0.6633	0.8854
0.0083	−115.8	0.9053	0.9680	0.2877	48.8	0.6462	0.8798
0.0125	−96.2	0.8870	0.9618	0.3692	59.6	0.6216	0.8720
0.0170	−81.3	0.8711	0.9564	0.4742	70.4	0.5968	0.8643
0.0232	−66.4	0.8533	0.9502	0.5587	77.5	0.5807	0.8594
0.0295	−54.7	0.8384	0.9451	0.7257	88.6	0.5549	0.8518
0.0402	−40.3	0.8173	0.9379	0.9267	98.8	0.5311	0.8451
0.0531	−27.1	0.7969	0.9308	1.1179	106.7	0.5130	0.8399
0.0695	−14.7	0.7758	0.9235	1.2879	112.5	0.4993	0.8358
0.0926	−1.7	0.7519	0.9153	1.4455	117.4	0.4881	0.8323
			$w = 0.10$				
0.0027	−155.8	0.9417	0.9804	0.1649	39.6	0.6911	0.8936
0.0060	−116.1	0.9158	0.9715	0.2323	54.7	0.6574	0.8821
0.0091	−95.8	0.8986	0.9657	0.2952	65.0	0.6333	0.8739
0.0166	−66.5	0.8685	0.9553	0.3795	75.8	0.6077	0.8654
0.0195	−59.1	0.8597	0.9523	0.4498	83.1	0.5903	0.8597
0.0253	−46.5	0.8437	0.9467	0.5643	92.6	0.5671	0.8521
0.0345	−31.9	0.8229	0.9395	0.6541	98.8	0.5518	0.8472
0.0501	−14.4	0.7956	0.9300	0.8352	109.0	0.5267	0.8388
0.0626	−4.1	0.7778	0.9238	0.9900	115.9	0.5090	0.8326
0.0778	5.9	0.7597	0.9174	1.1344	121.5	0.4947	0.8272
0.0997	17.1	0.7380	0.9099	1.2730	126.2	0.4823	0.8222
0.1258	27.5	0.7168	0.9025	1.3879	129.5	0.4729	0.8181
			$w = 0.20$				
0.0135	−58.0	0.8742	0.9570	0.1632	57.2	0.6777	0.8876
0.0207	−37.5	0.8493	0.9483	0.1972	65.4	0.6588	0.8811
0.0257	−27.1	0.8351	0.9433	0.2403	74.0	0.6386	0.8742
0.0302	−19.5	0.8240	0.9394	0.3032	83.9	0.6145	0.8660
0.0356	−11.8	0.8120	0.9351	0.4233	98.1	0.5797	0.8543
0.0442	−1.7	0.7956	0.9293	0.5587	109.7	0.5502	0.8440
0.0559	9.1	0.7766	0.9225	0.7116	119.6	0.5239	0.8338
0.0756	22.9	0.7507	0.9133	0.8761	127.9	0.5001	0.8230
0.0917	31.5	0.7332	0.9071	1.0253	133.9	0.4810	0.8126
0.1161	42.1	0.7111	0.8993	1.1560	138.6	0.4649	0.8024
0.1373	49.6	0.6948	0.8936	1.2812	142.1	0.4510	0.7923
			$w = 0.30$				
0.0021	−128.1	0.9427	0.9806	0.1248	64.9	0.6874	0.8888
0.0047	−89.2	0.9175	0.9719	0.1533	74.0	0.6660	0.8809
0.0067	−71.2	0.9025	0.9667	0.2043	86.2	0.6355	0.8698
0.0091	−56.1	0.8882	0.9617	0.2766	99.1	0.6026	0.8579
0.0137	−36.6	0.8665	0.9540	0.3743	111.8	0.5693	0.8459
0.0185	−22.3	0.8483	0.9475	0.4296	117.4	0.5540	0.8403
0.0253	−7.5	0.8273	0.9400	0.5718	128.9	0.5219	0.8279
0.0327	4.4	0.8084	0.9332	0.7471	139.6	0.4908	0.8143
0.0419	15.8	0.7888	0.9260	0.8933	146.4	0.4689	0.8028
0.0560	29.2	0.7640	0.9169	1.0358	151.8	0.4496	0.7908
0.0764	43.2	0.7357	0.9066	1.1653	156.1	0.4335	0.7788
0.0986	54.5	0.7110	0.8975	1.2802	159.1	0.4190	0.7671
			$w = 0.40$				
0.0022	−100.3	0.9383	0.9791	0.1781	105.7	0.6277	0.8645
0.0043	−65.8	0.9147	0.9708	0.2511	120.0	0.5892	0.8502
0.0066	−45.8	0.8970	0.9646	0.3269	130.7	0.5594	0.8393
0.0163	−1.9	0.8463	0.9464	0.4541	144.3	0.5222	0.8255
0.0240	16.2	0.8194	0.9366	0.5313	150.6	0.5043	0.8186
0.0286	24.4	0.8060	0.9316	0.6451	158.2	0.4818	0.8090
0.0355	34.3	0.7884	0.9251	0.7684	164.7	0.4608	0.7988
0.0452	45.4	0.7675	0.9173	0.9251	171.6	0.4373	0.7849
0.0577	56.4	0.7451	0.9089	1.0650	176.6	0.4178	0.7710
0.0727	66.8	0.7227	0.9004	1.1811	180.1	0.4026	0.7580
0.0999	80.8	0.6903	0.8881	1.2972	182.8	0.3877	0.7435
0.1290	91.9	0.6631	0.8778				

The standard Gibbs energy of transference is one of the most useful available thermodynamic properties of solution. It can be calculated from E^0 values according to the following equation[20]

$$\Delta G_t^0 = F(E_s^0 - E_w^0) + 2RT(\ln d_w/d_s) \quad (6)$$

Table 3. Values of the Density ρ, Permittivity ε, and Debye−Hückel Osmotic Coefficient Parameter A_φ for the DMF + H₂O Mixtures at 298.15 K[19]

w(DMF)	ρ/g·cm⁻³	ε	A_φ
0	0.99704	78.54	0.3915
0.10	0.98613	76.82	0.4025
0.20	0.98115	74.64	0.4192
0.30	0.97613	72.20	0.4395
0.40	0.97151	69.06	0.4687

where ΔG_t^0 is the standard Gibbs energy of solvation of RbCl or CsCl. E_w^0 and E_s^0 are the standard of electromotive force of RbCl or CsCl in pure water and in mixed solvents, respectively. d_w and d_s are the density of water and mixed solvent, respectively, and the ΔG_t^0 values are listed in Table 4.

If the electrostatic component of ΔG_t^0 is assumed to be well described by the Born-model of ion-solvation, then for RbCl or CsCl it should be expressed[21] by the following equation

$$\Delta G_t^0 = Ne^2(1/\varepsilon_s - 1/\varepsilon_w)(1/\gamma_+ + 11/\gamma_-)/2 \quad (7)$$

where N is the Avogadro constant; e is the electron charge; ε_s and ε_w are the dielectric constant of the mixed solvent and water; and γ_+ and γ_- are the crystal radius of the cation and anion.
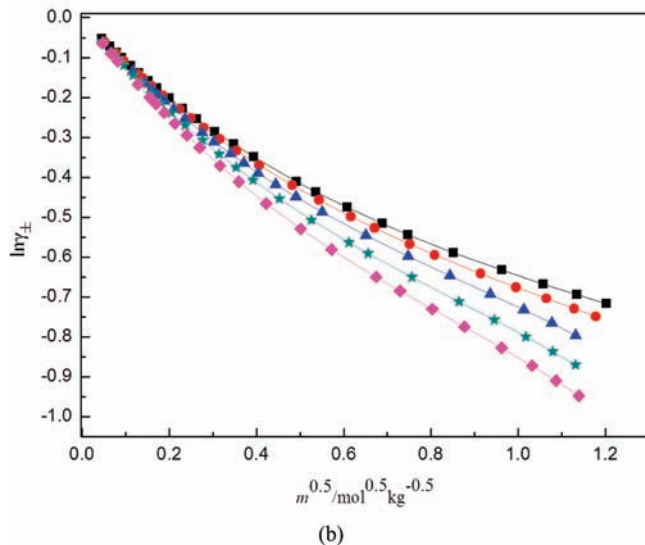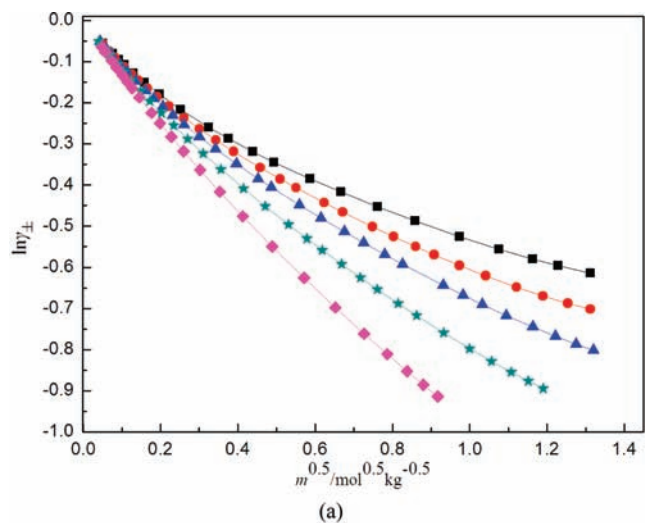
Figure 3. Plot of ln $\gamma_\pm$(RbCl) (a) and ln $\gamma_\pm$(CsCl) (b) vs $m^{0.5}$ of RbCl or CsCl in DMF + H₂O at 298.15 K for different mass fractions of DMF. ■, 0.00 DMF; ●, 0.10 DMF; ▲, 0.20 DMF; ★, 0.30 DMF; ◆, 0.40 DMF.
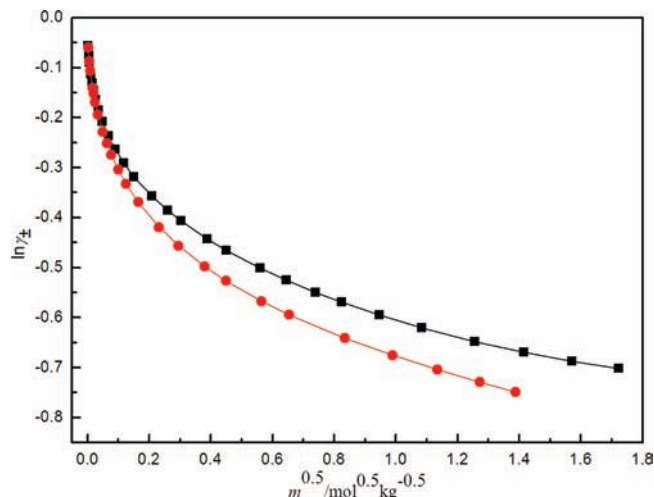
Figure 4. Variation of ln $\gamma_\pm$ with $m^{0.5}$ of RbCl or CsCl for 0.10 mass fraction of DMF in the mixed solvent. ■, RbCl; ●, CsCl.

Table 4. Pitzer Parameters and Standard Transfer Gibb's Energy for RbCl or CsCl + DMF + H₂O Systems at 298.15 K

w	$\beta^{(0)}$	$\beta^{(1)}$	C^φ	E^0 mV	SD mV	ΔG_t^0 kJ·mol⁻¹
			RbCl + DMF + H₂O			
0.00	0.0466	0.12983	−0.0016	129.9 ±0.1	0.16	0
0.10	−0.03870	0.34758	0.02242	130.0 ± 0.1	0.23	1.3380
0.20	−0.04642	0.29856	0.01980	143.3 ± 0.1	0.23	2.8299
0.30	−0.07043	0.18289	0.02775	158.5 ± 0.1	0.24	4.6213
0.40	−0.09531	−0.00742	0.03209	176.8 ± 0.1	0.15	6.8257
			CsCl + DMF + H₂O			
0.00	0.02945	−0.00178	−0.00826	135.3 ± 0.1	0.02	0
0.10	0.03186	−0.01855	−0.01416	151.2 ± 0.1	0.07	1.5889
0.20	0.06911	−0.11384	−0.04868	170.3 ± 0.1	0.09	3.4572
0.30	0.07537	−0.17394	−0.05814	191.1± 0.1	0.06	5.4898
0.40	0.10542	−0.26722	−0.07855	218.2 ± 0.1	0.08	8.1285

Figure 5 is the relationship between the standard transfer Gibbs energy ΔG_t^0 and the ratio of w in the mixed solvent. ΔG_t^0 values are all positive, which indicates that the transference of RbCl or CsCl from water to the DMF + water mixed solvents is not spontaneous. This shows that with an increase of the mass fraction of DMF in the mixed solvents the solvation capacity decreases. When w was a certain value, ΔG_t^0 of RbCl + DMF + H₂O was larger than that of the CsCl + DMF + H₂O system because the radius of Rb⁺ is smaller than that of Cs⁺.
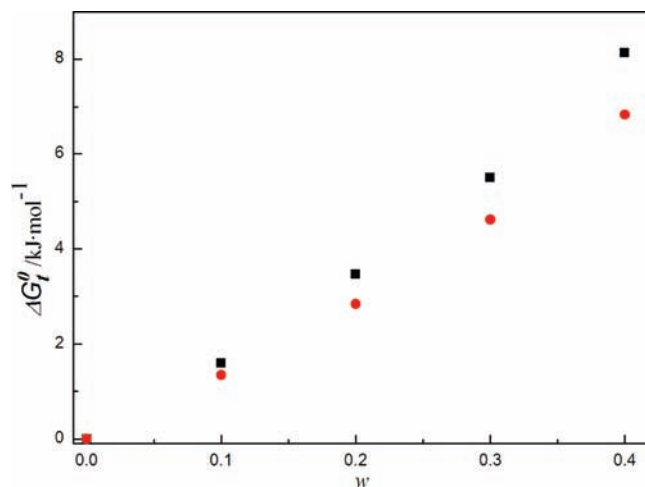
Figure 5. Standard Gibbs energy of transference from water to DMF + H₂O for RbCl and CsCl. ■, RbCl; ●, CsCl.

Conclusion

The mean activity coefficients of RbCl and CsCl in the DMF + H$_2$O mixed solvent were determined by using the galvanic cell consisting of Rb-ISE or Cs-ISE and Ag−AgCl electrodes. Associated with the Pitzer equation, we obtained the activity coefficients and osmotic coefficients of RbCl and CsCl in the mixed solvent at 298.15 K. The values of the standard transfer Gibb's energy of RbCl or the CsCl + DMF + H$_2$O system were also obtained. For RbCl and CsCl systems at the same DMF content, the activity coefficient and the standard transfer Gibb's energy of RbCl are all larger than that of CsCl.

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