J. Chem. Eng. Data **2007,** *52,* 357−362

Determination of Activity Coefficients for Cesium Chloride in Methanol−Water and Ethanol−Water Mixed Solvents by Electromotive Force Measurements at 298.15 K

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Activity coefficients for CsCl in different methanol−water and ethanol−water mixed solvents were determined at 298.15 K by electromotive force (EMF) measurements of the cell: Cs-ISE|CsCl (*m*), alcohol (*Y*), H_2O (100 − *Y*)|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 good Nernstian response. The experimental data were calculated using the Pitzer model. Standard cell potentials and Pitzer parameters were obtained. From these, mean activity coefficients of CsCl, osmotic coefficients of the mixtures, standard Gibbs free energies of transference of CsCl from water to methanol−water or ethanol−water mixtures, and the corresponding medium effects were calculated.

Introduction

The determination of the mean activity coefficients for electrolytes in organic−water systems is very important not only for developing electrolyte solution theories but also for research in various areas such as electroanalysis, environmental chemistry, industrial chemistry as well as biochemistry, etc. For our work, it is useful to help people find new ways to separate and purify the rare cesium and rubidium salts, which are plentiful in western China.

Measurement of electromotive force (EMF) is one of the commonly used methods to determine the mean activity coefficients because of its simplicity, high speed, and accuracy. Actually, in many previous works, people have used such a method to determine the activity coefficients of NH_4Cl in different mixed ethanol−water[1] and 1-propanol−water[2] systems at 25 °C; NaCl in methanol−water systems;[3] KCl in ethanol−water systems;[4] and NaCl in ethanol−water systems.[5] Furthermore, Hernández-Luis et al.,[6,7] Zhang et al.,[8,9] and Deyhimi et al.[10] also undertook similar studies.

For our work, EMF measurement was employed. Calculations of standard cell potentials of each condition and Pitzer parameters were made by using the Pitzer equation.[13] Moreover, mean activity coefficients of CsCl, osmotic coefficients of the mixed solvent systems, the standard Gibbs free energies of transference of CsCl from water to alcohol−water mixtures, and medium effects are discussed.

Experimental Section

Materials. Cesium chloride (Shanghai, China), analytical grade (mass % > 99.5), was dried overnight in an oven (T = 573 to 673 K) and then stored over silica gel in a desiccator before use. Methanol (or ethanol) of analytical grade, from Xi'an, was fractionally distilled, and the intermediate fraction was used. The refractive index was used as a measure of purity. Experimental values for the refractive index were 1.32644 (methanol) and 1.35928 (ethanol), which were obtained using an Anton Paar Co. model RXA 170 refractometer. Water was deionized and then redistilled in the presence of a small amount of $KMnO_4$. Its specific conductance was approximately (1.0 to 1.2) × 10^{-4} $S\cdot m^{-1}$.

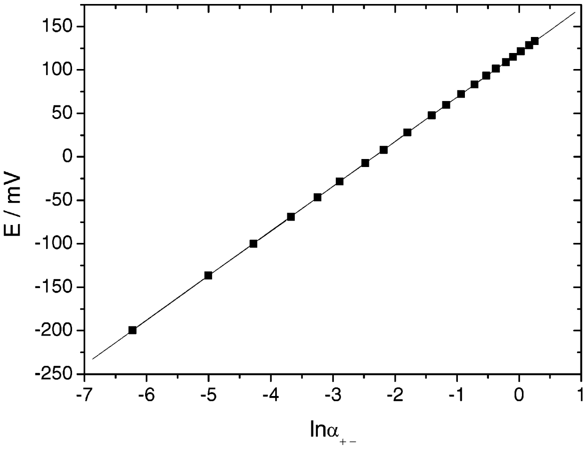

Figure 1. Response of Cs-ISE and Ag|Ag electrode pair for several aqueous solutions of CsCl.

Apparatus and Procedure. The Cs-ISE was a PVC membrane type based on valinomycin and was filled with 0.1 $mol\cdot L^{-1}$ CsCl as the internal liquid. The technique has been described by Wu et al.[11] The Ag|AgCl electrode was a thermal-electrolytic type. Both electrodes were prepared in our laboratory and were standardardized before use. They showed good Nernstian response.[12] In this work, EMF measurements of the cell, Cs-ISE|CsCl (*m*), alcohol (*Y*), H_2O(100 − *Y*)|Ag|AgCl, were carried out at different molalities of CsCl in mixtures containing (0, 10, 20, 30, and 40) wt % of alcohol (alcohol = methanol and ethanol) at 298.15 K. In the cell, *Y* is the mass fraction percent of methanol or ethanol, *m* is the molality of CsCl, and a cesium ion-selective electrode (Cs-ISE) was employed. It belongs to the type of galvanic cells without a liquid junction.

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

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10.1021/je060278s CCC: $37.00

Table 1. Electromotive Force (E), Mean Activity Coefficients ($\gamma_\pm$), and Osmotic Coefficients (φ) at Different CsCl Molality and Weight Percent of Methanol in the Methanol−Water Systems at 298.15 K

m^a	E^a	$\gamma_\pm$	φ	m^a	E^a	$\gamma_\pm$	φ	m^a	E^a	$\gamma_\pm$	φ	m^a	E^a	$\gamma_\pm$	φ
0 % Methanol															
0.0021	−199.3	0.9504	0.9835	0.0704	−28.2	0.7902	0.9320	0.4890	59.7	0.6335	0.8864	1.4636	109.0	0.5530	0.8829
0.0074	−136.5	0.9129	0.9711	0.1111	−7.0	0.7565	0.9218	0.6418	72.1	0.6103	0.8808	1.6556	115.2	0.5490	0.8897
0.0158	−99.9	0.8801	0.9604	0.1550	8.3	0.7304	0.9140	0.8254	83.3	0.5897	0.8770	1.8747	121.6	0.5475	0.9001
0.0301	−68.8	0.8455	0.9493	0.2385	28.2	0.6950	0.9036	1.0307	93.3	0.5731	0.8759				
0.0477	−46.5	0.8168	0.9403	0.3731	47.8	0.6569	0.8927	1.2254	101.4	0.5619	0.8775				
10 % Methanol															
0.0038	−158.3	0.9307	0.9770	0.0831	−9.6	0.7673	0.9251	0.3832	59.5	0.6408	0.8873	1.1550	107.1	0.5372	0.8535
0.0089	−116.6	0.8993	0.9667	0.1182	6.5	0.7403	0.9170	0.5149	72.2	0.6138	0.8788	1.3894	114.9	0.5198	0.8482
0.0196	−78.8	0.8613	0.9544	0.1592	20.1	0.7163	0.9099	0.6582	83.0	0.5908	0.8713	1.6631	122.5	0.5036	0.8441
0.0334	−52.4	0.8301	0.9444	0.2102	32.9	0.6932	0.9030	0.7939	91.1	0.5730	0.8654				
0.0543	−29.6	0.7981	0.9345	0.2810	45.7	0.6683	0.8956	0.9507	98.8	0.5558	0.8596				
20 % Methanol															
0.0024	−169.5	0.9386	0.9794	0.0546	−18.8	0.7732	0.9234	0.1749	33.7	0.6708	0.8898	0.3521	64.3	0.6036	0.8687
0.0054	−129.6	0.9110	0.9701	0.0786	−1.9	0.7430	0.9133	0.2054	40.7	0.6556	0.8849	0.4013	69.9	0.5908	0.8646
0.0124	−88.8	0.8724	0.9570	0.1049	11.2	0.7178	0.9050	0.2370	47.0	0.6419	0.8806	0.4531	75.1	0.5788	0.8608
0.0217	−62.6	0.8396	0.9458	0.1268	19.7	0.7006	0.8994	0.2668	52.2	0.6305	0.8771				
0.0345	−40.2	0.8080	0.9351	0.1502	27.0	0.6850	0.8943	0.3085	58.5	0.6165	0.8727				
30 % Methanol															
0.0018	−171.6	0.9419	0.9807	0.0670	2.9	0.7550	0.9198	0.2739	65.0	0.6189	0.8669	0.7333	103.8	0.4903	0.7970
0.0055	−116.6	0.9049	0.9685	0.0750	8.3	0.7457	0.9167	0.3453	74.6	0.5911	0.8533	0.8374	108.5	0.4721	0.7869
0.0102	−85.9	0.8775	0.9596	0.1102	25.4	0.7123	0.9051	0.4301	83.4	0.5631	0.8385	0.9437	112.9	0.4563	0.7789
0.0206	−51.9	0.8385	0.9469	0.1564	40.9	0.6791	0.8927	0.5286	91.4	0.5355	0.8231				
0.0415	−18.8	0.7917	0.9318	0.2086	53.2	0.6493	0.8805	0.6402	98.8	0.5091	0.8079				
40 % Methanol															
0.0027	−138.0	0.9186	0.9718	0.0818	19.5	0.6412	0.8580	0.2373	60.6	0.4939	0.7854	0.5386	89.2	0.3788	0.7217
0.0085	−82.0	0.8598	0.9501	0.1066	30.0	0.6062	0.8415	0.2772	66.3	0.4718	0.7738	0.6557	95.5	0.3520	0.7046
0.0206	−40.6	0.7928	0.9238	0.1351	39.2	0.5737	0.8258	0.3234	71.8	0.4499	0.7621	0.8029	101.5	0.3244	0.6847
0.0371	−13.9	0.7352	0.8998	0.1704	48.2	0.5410	0.8096	0.3906	78.5	0.4233	0.7475				
0.0563	4.0	0.6880	0.8792	0.2039	54.9	0.5156	0.7966	0.4545	83.6	0.4022	0.7355				

[a] Units: m in mol·kg^{-1}; E in mV.

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. Voltage readings were taken when they were stable to 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

In order to check the response of the electrodes, aqueous solutions of CsCl were measured at several molalities. The mean activity coefficients of different systems were calculated at 298.15 K, using the Pitzer equation. As shown in Figure 1, a plot of E against ln α_{+-} produced a straight line, and the value of E^0 for each cell was 120.2 mV. The value of k was 25.68 mV, where α_{+-}, E, E^0, and k are the mean activity of CsCl, the measured potential, the standard potential, and the Nernstian slope of the cell, respectively. They were evaluated using a linear regression method, and the linear correlation coefficient was 0.9999. It was clear that the value of k was close to theoretical one (25.69 mV) for the Nernstian slope. It was therefore concluded that the electrode pairs we used had a good Nernstian response and were satisfactory enough for our research.

The cell was employed to determine the EMF values of CsCl in the mixed solvents at 298.15 K. The experimental mean activity coefficients of CsCl in the mixtures were calculated from the following Nernst equation:

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

where $\gamma_\pm$ is the mean activity coefficient of CsCl, $k = RT/F$; R, T, and F are the universal gas constant, absolute temperature, and Faraday constant, respectively. The EMF values for each system and the molalities are listed in Tables 1 and 2.

The application of the Pitzer model both in aqueous and in organic−water mixed systems was found to be successful in many previous studies in this area.[1−10] Therefore, it was used to describe the mean activity coefficients in the present work. For 1−1 type electrolytes, the Pitzer equations[13] for the mean activity coefficient ($\gamma_\pm$) and osmotic coefficient (φ) can be written as:

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

$$\varphi - 1 = f^{\varphi} + mB^{\varphi} + m^2C^{\varphi} \tag{3}$$

where

$$f^{\gamma} = -A^{\varphi}x \tag{2a}$$

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

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

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

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

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

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

In these equations, $\beta^{(0)}$, $\beta^{(1)}$, and C^{φ} are the parameters of the Pitzer equation, which were obtained by fitting the equations to the experimental data; α and b are assumed to be fixed parameters whose values are 2.0 and 1.2 kg$^{1/2}$·mol$^{-1/2}$, respectively, and which were proved to be suitable for alcohol

Table 2. Electromotive Force (E), Mean Activity Coefficients ($\gamma_{\pm}$), and Osmotic Coefficients (φ) at Different CsCl Molality and Weight Percent of Ethanol in the Ethanol−Water Systems at 298.15 K

m^a	E^a	$\gamma_{\pm}$	φ	m^a	E^a	$\gamma_{\pm}$	φ	m^a	E^a	$\gamma_{\pm}$	φ	m^a	E^a	$\gamma_{\pm}$	φ
0 % Ethanol															
0.0055	−155.9	0.9212	0.9734	0.0927	−21.4	0.7499	0.9142	0.3179	33.3	0.6334	0.8750	0.8135	73.5	0.5432	0.8511
0.0126	−115.6	0.8862	0.9614	0.1211	−9.3	0.7261	0.906	0.4036	43.5	0.6098	0.8678	0.9521	80.3	0.5294	0.8491
0.0271	−79.0	0.8430	0.9465	0.1536	1.3	0.7041	0.8984	0.5061	53.3	0.5876	0.8614	1.1004	86.7	0.5174	0.8481
0.0454	−54.6	0.8074	0.9342	0.1932	11.5	0.6822	0.8910	0.6085	61.0	0.5700	0.8569				
0.0657	−37.3	0.7789	0.9243	0.2482	22.4	0.6578	0.8829	0.7082	67.6	0.5558	0.8536				
10 % Ethanol															
0.0392	−46.7	0.7965	0.9291	0.1738	20.1	0.6614	0.8827	0.3788	54.0	0.5841	0.8591	0.6807	77.5	0.5207	0.8334
0.0601	−27.1	0.7610	0.9166	0.2156	29.7	0.6401	0.8761	0.4197	58.3	0.5737	0.8557	0.7774	83.5	0.5037	0.8229
0.0892	−9.3	0.7255	0.9041	0.2600	37.7	0.6216	0.8704	0.4781	63.7	0.5602	0.8511				
0.1194	3.5	0.6979	0.8947	0.2977	43.6	0.6082	0.8664	0.5345	68.2	0.5484	0.8466				
0.1478	12.9	0.6773	0.8879	0.3314	48.2	0.5975	0.8632	0.6031	73.3	0.5350	0.8407				
20 % Ethanol															
0.0065	−122.1	0.8950	0.9642	0.1178	12.6	0.6721	0.8818	0.3070	53.2	0.5674	0.8382	0.6276	82.2	0.4863	0.7958
0.0174	−73.9	0.8390	0.9443	0.1523	23.6	0.6448	0.8709	0.3628	60.2	0.5487	0.8296	0.7141	87.2	0.4711	0.7857
0.0330	−44.0	0.7917	0.9272	0.1848	32.1	0.6237	0.8623	0.4135	65.6	0.5340	0.8224	0.8217	92.3	0.4541	0.773
0.0522	−23.1	0.7523	0.9125	0.2182	39.0	0.6055	0.8547	0.4752	71.0	0.5182	0.8143				
0.0804	−3.7	0.7112	0.8970	0.2528	45.2	0.5891	0.8478	0.5450	76.5	0.5026	0.8057				
30 % Ethanol															
0.0178	−58.9	0.8146	0.9352	0.1772	41.6	0.5766	0.8394	0.4043	73.5	0.4698	0.7825	0.6307	88.9	0.4069	0.7341
0.0332	−30.0	0.7617	0.9155	0.2510	55.4	0.5325	0.8181	0.4464	77.2	0.4563	0.7735	0.6894	91.7	0.3934	0.7211
0.0541	−8.4	0.7139	0.8970	0.2861	60.1	0.5156	0.8093	0.4892	80.0	0.4436	0.7644				
0.1133	23.2	0.6311	0.8633	0.3242	65.0	0.4992	0.8003	0.5297	83.0	0.4324	0.7558				
0.1446	33.3	0.6017	0.8506	0.3580	69.3	0.4861	0.7926	0.5688	85.5	0.4222	0.7475				
40 % Ethanol															
0.0050	−106.9	0.8497	0.9498	0.0555	−6.3	0.5397	0.8507	0.2180	35.5	0.3152	0.6492	0.3134	44.7	0.2601	0.5326
0.0293	−30.5	0.6448	0.9033	0.1284	20.0	0.3975	0.8273	0.2439	39.2	0.2984	0.6203				
0.0412	−17.2	0.5902	0.8739	0.1846	32.2	0.3403	0.6842	0.2749	42.0	0.2804	0.5833				

[a] Units: m in mol·kg^{-1}; E in mV.

Table 3. Values of the Density (d), Dielectric Constant (D), and Parameter (A^{φ}) of the Pitzer Equation for the Methanol−Water and Ethanol−Water Mixtures at 298.15 K

wt %	d/g·cm^{-3}	D	A^{φ}	wt %	d/g·cm^{-3}	D	A^{φ}
	Methanol−Water[a]				Ethanol−Water[b]		
0	0.9971	78.3	0.3921	0[a]	0.9971	78.3	0.3921
10	0.9799	74.2	0.4214	10	0.9804	72.8	0.4337
20	0.9645	70.0	0.4562	20	0.9664	67.0	0.4877
30	0.9481	65.4	0.5008	30	0.9505	61.0	0.5564
40	0.9319	60.9	0.5521	40	0.9315	55.0	0.6437

[a] Values are taken from ref 14. [b] Values are taken from ref 15.

Table 4. Pitzer Parameters for CsCl in the Methanol−Water and Ethanol−Water Solvents at 298.15 K

wt %	$\beta^{(0)}$	$\beta^{(1)}$	C^{φ}	E^0/mV	SD[a]/mV
		Methanol			
0	−0.0056	0.2712	0.0230	120.2	0.22
10	−0.0025	0.3315	0.0071	131.6	0.22
20	0.0543	0.1097	−0.0332	143.8	0.24
30	−0.2124	0.8124	0.1057	156.2	0.26
40	0.0751	−0.6506	−0.0779	170.8	0.16
		Ethanol			
0	0.0250	−0.0138	0.0038	115.5	0.14
10	0.1867	−0.3256	−0.1540	131.3	0.18
20	0.0376	−0.0554	−0.0574	143.1	0.16
30	0.0418	−0.1093	−0.1304	158.8	0.16
40	1.2204	−3.2356	−3.0580	173.6	0.39

[a] SD, standard deviation of the fit.

Table 5. Values of Standard Free Energy of Transference (ΔG_t^0) of CsCl from Water to Methanol−Water and Ethanol−Water Mixtures at 298.15 K

wt %	E^0 / mV	ΔE^0 / mV	ΔG_t^0 / kJ·mol^{-1}	wt %	E^0 / mV	ΔE^0 / mV	ΔG_t^0 / kJ·mol^{-1}
	Methanol				Ethanol		
0	120.2			0	115.5		
10	131.6	11.4	1.19	10	131.3	15.8	1.61
20	143.8	23.6	2.44	20	143.1	27.5	2.81
30	156.2	36.0	3.72	30	158.8	43.2	4.41
40	170.8	50.6	5.22	40	173.8	58.3	5.96

(methanol or ethanol)−water mixed systems by Koh et al.[14] A^{φ} is the Debye−Hückel constant for the osmotic coefficient defined by

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

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

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

The A^{φ} values in the different solvents are listed in Table 3. Combining eq 2 and eq 3, the values for E^0 and the Pitzer parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^{φ} of each alcohol−water mixture could be optimized using a simplex method from EMF data. These values are shown in Table 4, with the fitting standard deviation. The Pitzer parameters obtained were then substituted into eq 4 for calculation of the osmotic coefficients at each molality, and the values are listed in Tables 1 and 2.

Plots of ln $\gamma_{\pm}$ versus m for both mixed solvents are shown in Figures 2 and 3. It is obvious that ln $\gamma_{\pm}$ decreases with an increase in m and also decreases at a given m value with increasing mass fraction percent of alcohols used in the systems. To explain this situation, we take ion−ion and ion−solvent interactions into consideration. From the results, it can be assumed that for methanol−water mixtures, the relative permittivity of the mixed solvent decreases when the mass

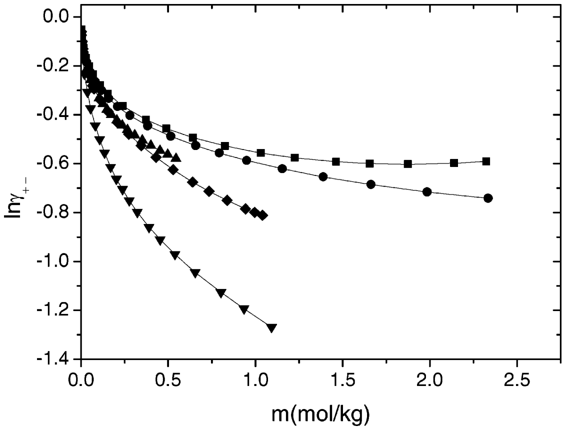

Figure 2. Natural logarithm of mean activity coefficient for CsCl vs its molality in various mass fraction percents of methanol−water solvents at 298.15 K: ■, 0 % MeOH; ●, 10 % MeOH; ▲, 20 % MeOH; ◆, 30 % MeOH; ▼, 40 % MeOH.

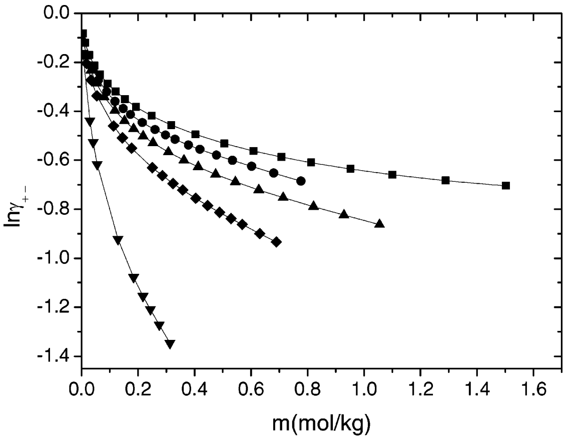

Figure 3. Natural logarithm of mean activity coefficient for CsCl vs its molality in various mass fraction percents of ethanol−water solvents at 298.15 K: ■, 0 % EtOH; ●, 10 % EtOH; ▲, 20 % EtOH; ◆, 30 % EtOH; ▼, 40 % EtOH.

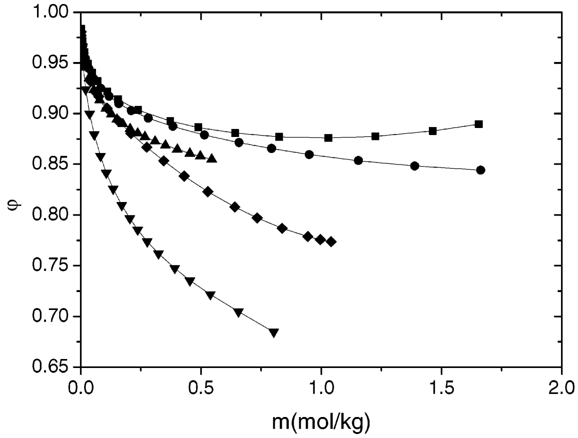

Figure 4. Osmotic coefficient vs molality of CsCl in various mass fraction percents of methanol−water solvents at 298.15 K: ■, 0 % MeOH; ●, 10 % MeOH; ▲, 20 % MeOH; ◆, 30 % MeOH; ▼, 40 % MeOH.

fraction of methanol increases, while the ion−ion interaction is more significant than the ion−solvent interaction. The same effects are observed in the ethanol−water mixtures. Moreover, Figures 4 and 5 show the relationship between osmotic coefficients (φ) of the mixtures (methanol−water and ethanol−water) and the molalities of CsCl. They look similar to the plots of ln $\gamma_{\pm}$ versus m.

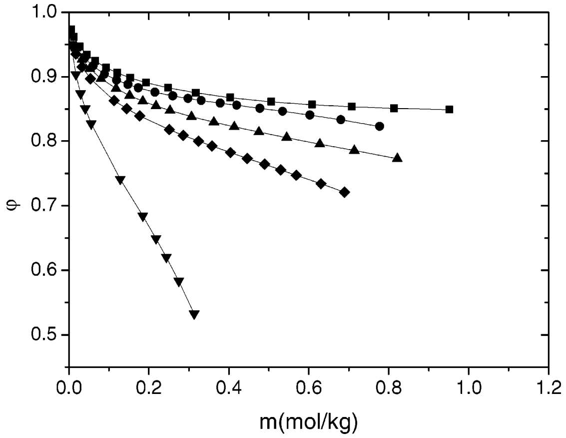

Figure 5. Osmotic coefficient vs molality of CsCl in various mass fraction percents of ethanol−water solvents at 298.15 K: ■, 0 % EtOH; ●, 10 % EtOH; ▲, 20 % EtOH; ◆, 0 % EtOH; ▼, 40 % EtOH.

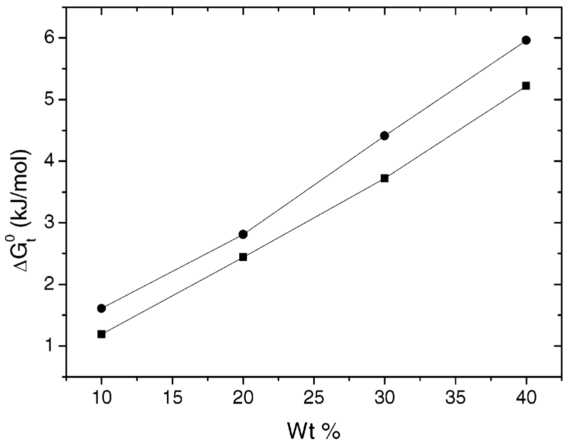

Figure 6. Standard free energy of transference, ΔG_t^0, from water to methanol−water and ethanol−water mixtures for CsCl at 298.15 K: ■, MeOH−water; ●, EtOH−water.

The standard free 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:[16]

$$\Delta G_t^0 = F(E_m^0 - E_w^0) + 2RT\ln(d_w/d_m) \qquad (6)$$

where subscripts w and m refer to the water and mixed solvent, respectively. Other symbols have their usual meaning. On the basis of the results obtained before, the values of ΔG_t^0 for each system were calculated and are listed in Table 5. These values were then plotted for the methanol−water system against the methanol percentages together with the corresponding data for the ethanol−water system and are presented in Figure 6. It can be seen that both systems have a similar variation, although the line for ethanol−water is a little higher than that of the methanol−water system. The energies for methanol−water are less than for ethanol−water for a given percentage. This phenomenon may be explained by the fact that CsCl is more solvated in the former system. These values are always positive, which indicates that the transference of CsCl from water to the alcohol−water mixed solvents is not spontaneous.

It is well-known that different electrolytes have different activity coefficients in different solvents. Medium effects can be used to describe such differences. According to the definition

Table 6. Primary, Secondary, and Total Medium Effect at Different CsCl Molality and Weight Percent of Methanol in the Methanol−Water Systems at 298.15 K

m/mol·kg^{-1}	PEM	SEM	TME	m/mol·kg^{-1}	PEM	SEM	TME	m/mol·kg^{-1}	PEM	SEM	TME	m/mol·kg^{-1}	PEM	SEM	TME
10 % Methanol															
0.0038	0.0963	−0.0026	0.0937	0.0831	0.0963	−0.0082	0.0881	0.3832	0.0963	−0.0114	0.0849	1.1550	0.0963	−0.0195	0.0768
0.0089	0.0963	−0.0060	0.0903	0.1182	0.0963	−0.0064	0.0899	0.5149	0.0963	−0.0149	0.0815	1.3894	0.0963	−0.0248	0.0715
0.0196	0.0963	−0.0041	0.0922	0.1592	0.0963	−0.0045	0.0918	0.6582	0.0963	−0.0164	0.0800	1.6631	0.0963	−0.0361	0.0602
0.0334	0.0963	−0.0018	0.0945	0.2102	0.0963	−0.0056	0.0907	0.7939	0.0963	−0.0169	0.0794				
0.0543	0.0963	−0.0112	0.0851	0.2810	0.0963	−0.0058	0.0906	0.9507	0.0963	−0.0175	0.0788				
20 % Methanol															
0.0024	0.1994	−0.0023	0.1971	0.0546	0.1994	−0.0250	0.1744	0.1749	0.1994	−0.0179	0.1815	0.3521	0.1994	−0.0412	0.1583
0.0054	0.1994	−0.0082	0.1912	0.0786	0.1994	−0.0246	0.1748	0.2054	0.1994	−0.0238	0.1756	0.4013	0.1994	−0.0445	0.1549
0.0124	0.1994	−0.0119	0.1876	0.1049	0.1994	−0.0260	0.1734	0.2370	0.1994	−0.0289	0.1705	0.4531	0.1994	−0.0474	0.1521
0.0217	0.1994	−0.0118	0.1876	0.1268	0.1994	−0.0054	0.1940	0.2668	0.1994	−0.0329	0.1666				
0.0345	0.1994	−0.0125	0.1869	0.1502	0.1994	−0.0121	0.1874	0.3085	0.1994	−0.0374	0.1621				
30 % Methanol															
0.0018	0.3042	−0.0022	0.3020	0.0670	0.3042	−0.0242	0.2800	0.2739	0.3042	−0.0400	0.2642	0.7333	0.3042	−0.0901	0.2141
0.0055	0.3042	−0.0109	0.2933	0.0750	0.3042	−0.0250	0.2792	0.3453	0.3042	−0.0511	0.2531	0.6307	0.3042	−0.0973	0.2070
0.0102	0.3042	−0.0139	0.2903	0.1102	0.3042	−0.0005	0.3037	0.4301	0.3042	−0.0620	0.2422	0.6894	0.3042	−0.1037	0.2006
0.0206	0.3042	−0.0141	0.2901	0.1564	0.3042	−0.0150	0.2892	0.5286	0.3042	−0.0726	0.2316				
0.0415	0.3042	−0.0164	0.2878	0.2086	0.3042	−0.0276	0.2766	0.6402	0.3042	−0.0828	0.2214				
40 % Methanol															
0.0027	0.4276	−0.0109	0.4167	0.0818	0.4276	−0.0500	0.3776	0.2373	0.4276	−0.1427	0.2849	0.5386	0.4276	−0.2219	0.2057
0.0085	0.4276	−0.0264	0.4012	0.1066	0.4276	−0.0710	0.3566	0.2772	0.4276	−0.1575	0.2701	0.6557	0.4276	−0.2415	0.1861
0.0206	0.4276	−0.0385	0.3891	0.1351	0.4276	−0.0911	0.3365	0.3234	0.4276	−0.1723	0.2553	0.8029	0.4276	−0.2632	0.1644
0.0371	0.4276	−0.0514	0.3762	0.1704	0.4276	−0.1119	0.3157	0.3906	0.4276	−0.1906	0.2370				
0.0563	0.4276	−0.0229	0.4047	0.2039	0.4276	−0.1284	0.2992	0.4545	0.4276	−0.2053	0.2223				

Table 7. Primary, Secondary, and Total Medium Effect at Different CsCl Molality and Weight Percent of Ethanol in the Ethanol−Water Systems at 298.15 K

m/mol·kg^{-1}	PEM	SEM	TME	m/mol·kg^{-1}	PEM	SEM	TME	m/mol·kg^{-1}	PEM	SEM	TME	m/mol·kg^{-1}	PEM	SEM	TME
10 % Ethanol															
0.0392	0.1335	−0.0126	0.1209	0.1738	0.1335	−0.0227	0.1108	0.3788	0.1335	−0.0207	0.1129	0.6807	0.1335	−0.0420	0.0915
0.0601	0.1335	−0.0017	0.1318	0.2156	0.1335	−0.0237	0.1099	0.4197	0.1335	−0.0204	0.1131	0.7774	0.1335	−0.0632	0.0704
0.0892	0.1335	−0.0118	0.1217	0.2600	0.1335	−0.0232	0.1103	0.4781	0.1335	−0.0214	0.1121				
0.1194	0.1335	−0.0179	0.1156	0.2977	0.1335	−0.0224	0.1112	0.5345	0.1335	−0.0241	0.1094				
0.1478	0.1335	−0.0211	0.1124	0.3314	0.1335	−0.0216	0.1120	0.6031	0.1335	−0.0305	0.1031				
20 % Ethanol															
0.0065	0.2324	−0.0031	0.2293	0.1178	0.2324	−0.0348	0.1976	0.3070	0.2324	−0.0501	0.1823	0.6276	0.2324	−0.0713	0.1611
0.0174	0.2324	−0.0162	0.2162	0.1523	0.2324	−0.0409	0.1915	0.3628	0.2324	−0.0513	0.1811	0.7141	0.2324	−0.0869	0.1455
0.0330	0.2324	−0.0222	0.2102	0.1848	0.2324	−0.0447	0.1877	0.4135	0.2324	−0.0527	0.1797	0.8217	0.2324	−0.1138	0.1186
0.0522	0.2324	−0.0096	0.2228	0.2182	0.2324	−0.0470	0.1854	0.4752	0.2324	−0.0557	0.1767				
0.0804	0.2324	−0.0236	0.2088	0.2528	0.2324	−0.0486	0.1838	0.5450	0.2324	−0.0611	0.1713				
30 % Ethanol															
0.0178	0.3651	−0.0285	0.3366	0.1772	0.3651	−0.0812	0.2838	0.4043	0.3651	−0.1101	0.2550	0.6307	0.3651	−0.1487	0.2164
0.0332	0.3651	−0.0114	0.3537	0.2510	0.3651	−0.0930	0.2721	0.4464	0.3651	−0.1153	0.2498	0.6894	0.3651	−0.1640	0.2010
0.0541	0.3651	−0.0317	0.3334	0.2861	0.3651	−0.0972	0.2679	0.4892	0.3651	−0.1213	0.2438				
0.1133	0.3651	−0.0637	0.3013	0.3242	0.3651	−0.1014	0.2637	0.5297	0.3651	−0.1278	0.2373				
0.1446	0.3651	−0.0736	0.2915	0.3580	0.3651	−0.1050	0.2601	0.5688	0.3651	−0.1350	0.2300				
40 % Ethanol															
0.0050	0.4927	−0.0278	0.4649	0.0555	0.4927	−0.1526	0.3400	0.2180	0.4927	−0.3306	0.1621	0.3134	0.4927	−0.3872	0.1055
0.0293	0.4927	−0.0852	0.4074	0.1284	0.4927	−0.2592	0.2335	0.2439	0.4927	−0.3466	0.1461				
0.0412	0.4927	−0.1192	0.3735	0.1846	0.4927	−0.3078	0.1848	0.2749	0.4927	−0.3648	0.1279				

made by Owen,[17] the fundamental relationship between total, primary, and secondary medium effects can be written as follows:

$$\log(\gamma/\gamma^0) = \log \gamma_0 + \log(\gamma^*/\gamma^0) \tag{7}$$

where γ^0, γ_0, and γ^* stand for the mean activity coefficients in infinite dilute solvent, pure water, and infinite dilute mixed solvent, respectively. Furthermore, $\log(\gamma/\gamma^0)$, $\log \gamma_0$, and $\log(\gamma^*/\ \gamma^0)$ were defined as the total medium effect (TME), the primary medium effect (PME), and the secondary medium effect (SME). PME can be calculated by

$$\log \gamma_0 = F(E^0_{(s)} - E^0_{(w)})/(2RT \ln 10) \tag{8}$$

These values are shown in Tables 6 and 7. From these results, it is obvious that the PME and TME for different molalities of CsCl in both mixed solvents are always positive. A decrease in SME, which is always negative, with increasing molality is observed clearly. The reason why such situations occur may relate to the variation of the interaction between the cesium and chloride ions.

Conclusion

The galvanic cell consisting of Cs-ISE and Ag|AgCl electrodes can be used to study the thermodynamic properties of the CsCl−MeOH−H_2O and CsCl−EtOH−H_2O systems with great precision, provided the contents of alcohol is (0 to 40) %. We have presented in this work results concerning the determination of the mean activity coefficients for CsCl in methanol−water and ethanol−water mixtures, osmotic coefficients, along with a comparative study of the standard Gibbs free energies of transference of CsCl from water to methanol−water and ethanol−water mixed solvents by using the Pitzer model. Medium effects are calculated in this work.

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Received for review June 17, 2006. Accepted January 19, 2007.

JE060278S