Activity Coefficients of Potassium Chloride in Ethylene Glycol−Water Mixtures Using Electromotive Force Measurements at (278.15, 288.15, 298.15, and 308.15) K

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The mean activity coefficients of KCl were determined in ethylene glycol−water mixed solvents, in the range of (10, 20, 30, and 40) % ethylene glycol, from the electromotive force (EMF) data at (278.15, 288.15, 298.15, and 308.15) K. The Pitzer and extended Debye−Hückel equations were used to describe the nonideal behavior of the electrolyte, and the corresponding activity and osmotic coefficients were determined. Moreover, the standard Gibbs energy of transference of KCl−ethylene glycol−water was evaluated.

1. Introduction

In recent years, there has been a growing interest in the measurement or prediction of the thermodynamic properties of electrolytes in mixed solvents. This is, in part, because of their applications in various areas like biochemistry, environmental chemistry, oceanography, geochemistry, and so forth.[1,2] Activity coefficients like other related thermodynamic parameters (osmotic coefficients, Gibbs excess energies of mixture or of transference) can be directly used to analyze the ion−ion and ion−solvent interactions occurring in the mixtures and estimate the nonideality of the mixture in equilibrium.

In the past decades, several methods have been used to determine the activity coefficients of electrolytes in solutions, such as electrodynamic balance,[3] static vapor pressure[4,5] measurement, and electromotive force (EMF)[6−8] measurement. The EMF method[9,10] is widely used to determine the activity coefficient of electrolytes in solution because of its characteristics of simplicity and convenience in comparison with the other foregoing techniques.

There have been a number of studies using the EMF method to determine the mean activity coefficients of alkali metal halides in electrolyte aqueous solutions or aqueous−organic mixtures. For example, Vera et al.[11] determined individual anionic activity coefficients in aqueous electrolyte solutions of LiCl and LiBr. Lopes et al.[12−14] obtained mean activity coefficients of NaCl/KCl and NaCl + KCl in water−ethanol mixtures. Hernández-Luis et al. investigated the activity coefficients for NaF in methanol−water and ethanol−water mixtures at 25 °C.[15] Moreover, they measured the behavior of NaF in organic water mixtures with ε, increasing cosolvent (i.e., formamide−water, ethylene carbonate−water),[16,17] and NaCl in formamide−water mixtures.[18] Activity coefficients of NaCl in PEG 4000−H_2O[19] have also been determined.

In previous work, we have determined the mean activity coefficients of electrolyte−mixture−solvent (MeOH/EtOH−water)[20−22] ternary systems. Owing to the scarcity of thermodynamic information of electrolytes in ethylene glycol−H_2O,[23−25] the aim of this work is to extend our previous research and enrich the available data on the mean activity coefficients and other information of KCl in ethylene glycol−H_2O. In this paper, the EMF measurements were performed for the KCl−ethylene glycol−H_2O system at (278.15 to 308.15) K, with molalities of KCl up to about 1.4 mol·kg^{-1} and ethylene glycol content ranging from (10 to 40) %. The experimental data were fitted to the Pitzer and extended Debye−Hückel equations. The mean activity coefficients, osmotic coefficients, and the standard Gibbs energy of transference of KCl−ethylene glycol−water were also calculated.

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2. Experimental Section

Potassium chloride (purity ≥ 99.5 %, Shanghai) was dried in an electrical oven at about 383 K for 48 h before use. It was stored in a desiccator without further purification. Ethylene glycol (99.8 %, Shanghai) and double-distilled water with specific conductivity of (1.0 to 1.2)·10^{-4} S·m^{-1} were used in our experiments.

The potassium ion−selective electrode, which was a poly(vinyl chloride) membrane type based on valinomycin, was filled with aqueous KCl as an internal liquid. The technique has been described by Wu et al.[26] The Ag/AgCl electrode of the thermal electrolytic type was used as internal reference electrodes, prepared following the procedure described by Bates.[27] They both were calibrated before use and showed good Nernstian response and selectivity.

The cell vessel was a glass double-walled container, enabling the circulation of water from a thermostat. The solution in the vessel was stirred by a magnetic stirrer, and the temperature was kept constant at (278.15, 288.15, 298.15, and 308.15) K (± 0.02 K). The ion analyzer used was an Orion-868 (U.S.) with a precision of ± 0.1 mV. Each concentration of the solution was prepared by directly weighing the materials, using a Sartorius electronic balance (Germany), with a precision of 0.1 mg.

3. Results

The cell used in this work was a galvanic cell without liquid junction:

K-ISE|KCl (m), ethylene glycol (Y), water(1 − Y)|Ag|AgCl (1)

In the cell, m is the molality of KCl in the mixed solvents and Y the percentage (by weight) of ethylene glycol in the mixture.

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Table 1. Experimental Electromotive Force, *E*, Mean Activity Coefficients, $\gamma_{\pm}$, and Osmotic Coefficient, Φ, at Different KCl Molalities and Weight Percent of Ethylene Glycol in the Ethylene Glycol−Water System at (278.15, 288.15, 298.15, and 308.15) K

m	E			m	E			m	E			m	E		
mol·kg^{-1}	mV	$\gamma_{\pm}$	Φ	mol·kg^{-1}	mV	$\gamma_{\pm}$	Φ	mol·kg^{-1}	mV	$\gamma_{\pm}$	Φ	mol·kg^{-1}	mV	$\gamma_{\pm}$	Φ
						$T = 278.15$ K									
						0 % Ethylene Glycol									
0.0025	−61.0	0.9474	0.9824	0.2770	148.8	0.6787	0.8956	0.0340	58.4	0.8398	0.9471	1.0633	202.8	0.5488	0.8522
0.0054	−24.7	0.9254	0.9752	0.3883	163.1	0.6474	0.8854	0.0510	76.3	0.8137	0.9387	1.2463	209.3	0.5333	0.8475
0.0083	−5.3	0.9100	0.9701	0.5559	177.6	0.6129	0.8738	0.0752	93.2	0.7863	0.9299	1.4048	213.9	0.5220	0.8444
0.0140	18.5	0.8876	0.9627	0.7102	187.3	0.5888	0.8656	0.1147	111.3	0.7540	0.9197	1.5466	218.2	0.5131	0.8424
0.0224	39.7	0.8637	0.9549	0.8997	196.6	0.5653	0.8576	0.1839	131.7	0.7149	0.9072				
						10 % Ethylene Glycol									
0.0026	−51.0	0.9429	0.9811	0.2503	151.0	0.6688	0.8901	0.0264	54.0	0.8462	0.9486	1.0878	208.8	0.5212	0.8388
0.0053	−18.5	0.9215	0.9739	0.3861	167.9	0.6269	0.8760	0.0396	72.0	0.8200	0.9400	1.2607	215.3	0.5060	0.8334
0.0079	−0.3	0.9066	0.9688	0.5386	181.4	0.5935	0.8646	0.0608	90.4	0.7896	0.9299	1.3962	218.5	0.4956	0.8298
0.0131	22.5	0.8841	0.9613	0.7073	192.3	0.5657	0.8548	0.0947	109.6	0.7548	0.9184	1.5302	221.9	0.4863	0.8266
0.0180	37.0	0.8679	0.9559	0.8892	201.3	0.5421	0.8463	0.1482	129.1	0.7167	0.9059				
						20 % Ethylene Glycol									
0.0015	−70.2	0.9536	0.9844	0.2801	162.8	0.6426	0.8796	0.0254	59.4	0.8403	0.9467	1.0027	211.4	0.5028	0.8224
0.0031	−36.0	0.9349	0.9782	0.4034	176.7	0.6047	0.8652	0.0411	80.6	0.8083	0.9361	1.1046	215.1	0.4919	0.8178
0.0046	−17.0	0.9218	0.9739	0.5208	186.7	0.5769	0.8541	0.0637	99.8	0.7757	0.9253	1.1953	218.1	0.4830	0.8141
0.0082	9.1	0.8996	0.9664	0.6424	194.8	0.5535	0.8443	0.0987	118.7	0.7400	0.9134	1.2770	220.5	0.4757	0.8112
0.0116	25.1	0.8834	0.9611	0.7592	201.1	0.5346	0.8362	0.1403	133.6	0.7090	0.9029	1.3652	222.7	0.4684	0.8085
0.0172	42.0	0.8631	0.9543	0.8877	206.9	0.5167	0.8284	0.2032	149.3	0.6743	0.8910	1.4965	226.5	0.4586	0.8051
						30 % Ethylene Glycol									
0.0013	−65.8	0.9528	0.9845	0.2717	168.8	0.6228	0.8686	0.0258	69.1	0.8297	0.9427	0.9071	213.6	0.4806	0.8044
0.0028	−32.0	0.9341	0.9778	0.3770	181.3	0.5861	0.8533	0.0398	88.1	0.7992	0.9324	1.0113	217.5	0.4674	0.7983
0.0044	−10.0	0.9187	0.9728	0.4804	190.6	0.5578	0.8409	0.0613	107.0	0.7655	0.9208	1.1422	221.9	0.4529	0.7918
0.0076	14.5	0.8970	0.9654	0.5852	197.9	0.5341	0.8300	0.0951	125.2	0.7275	0.9076	1.2876	226.4	0.4391	0.7862
0.0107	30.0	0.8809	0.9600	0.6974	204.4	0.5127	0.8199	0.1319	138.7	0.6970	0.8967	1.4287	230.0	0.4277	0.7823
0.0166	49.7	0.8570	0.9520	0.8092	209.5	0.4945	0.8111	0.1960	155.3	0.6575	0.8821				
						40 % Ethylene Glycol									
0.0013	−59.1	0.9506	0.9833	0.2900	178.7	0.5902	0.8506	0.0330	88.7	0.8011	0.9329	0.8362	216.2	0.4523	0.7794
0.0025	−28.2	0.9330	0.9774	0.3777	188.3	0.5571	0.8344	0.0500	106.8	0.7686	0.9216	0.9506	221.5	0.4363	0.7721
0.0050	4.4	0.9081	0.9691	0.4681	195.8	0.5292	0.8200	0.0838	128.9	0.7233	0.9054	1.0589	224.9	0.4236	0.7674
0.0080	25.5	0.8873	0.9622	0.5565	202.1	0.5062	0.8077	0.1344	148.4	0.6769	0.8878	1.1826	228.5	0.4117	0.7648
0.0131	47.7	0.8616	0.9535	0.6453	207.5	0.4864	0.7971	0.1986	163.9	0.6347	0.8705	1.3187	232.3	0.4014	0.7651
0.0213	69.3	0.8319	0.9434	0.7408	212.0	0.4680	0.7873								
						$T = 288.15$ K									
						0 % Ethylene Glycol									
0.0026	−65.4	0.9460	0.9819	0.2433	145.4	0.6945	0.9043	0.0362	59.6	0.8346	0.9456	0.9633	205.3	0.5828	0.8792
0.0050	−33.2	0.9269	0.9757	0.3142	156.6	0.6736	0.8989	0.0512	75.5	0.8123	0.9386	1.1423	212.3	0.5695	0.8768
0.0077	−12.6	0.9118	0.9707	0.4008	167.2	0.6536	0.8940	0.0744	92.6	0.7864	0.9306	1.3008	217.8	0.5594	0.8750
0.0129	12.0	0.8901	0.9636	0.5060	177.4	0.6346	0.8896	0.1053	108.1	0.7607	0.9229	1.4400	222.3	0.5515	0.8736
0.0183	27.9	0.8733	0.9580	0.6305	186.7	0.6167	0.8858	0.1534	124.9	0.7316	0.9144	1.5672	225.6	0.5450	0.8724
0.0260	44.5	0.8543	0.9519	0.7893	195.5	0.5987	0.8821								
						10 % Ethylene Glycol									
0.0024	−59.9	0.9447	0.9816	0.1943	143.3	0.7028	0.9056	0.0269	54.5	0.8459	0.9493	0.8676	207.2	0.5714	0.8680
0.0048	−27.3	0.9244	0.9750	0.2763	158.7	0.6729	0.8969	0.0418	74.6	0.8185	0.9406	1.0392	214.7	0.5555	0.8639
0.0071	−8.4	0.9104	0.9703	0.3805	172.3	0.6450	0.8889	0.0652	94.7	0.7880	0.9311	1.2063	221.3	0.5426	0.8609
0.0118	16.5	0.8889	0.9633	0.5448	187.7	0.6131	0.8797	0.0988	113.3	0.7571	0.9217	1.3529	226.1	0.5330	0.8591
0.0167	32.7	0.8721	0.9578	0.7021	198.4	0.5904	0.8732	0.1452	130.3	0.7267	0.9126	1.4886	229.7	0.5252	0.8580
						20 % Ethylene Glycol									
0.0016	−70.5	0.9512	0.9838	0.3028	170.9	0.6523	0.8892	0.0385	79.5	0.8157	0.9400	1.1515	225.7	0.5203	0.8421
0.0034	−34.2	0.9313	0.9772	0.4356	186.2	0.6179	0.8774	0.0575	97.6	0.7882	0.9314	1.2427	228.9	0.5130	0.8400
0.0052	−13.6	0.9171	0.9726	0.5513	196.2	0.5947	0.8690	0.0826	113.8	0.7615	0.9232	1.3245	231.7	0.5070	0.8385
0.0088	10.6	0.8965	0.9657	0.6751	204.5	0.5743	0.8614	0.1136	128.1	0.7367	0.9157	1.3978	234.0	0.5021	0.8375
0.0121	25.8	0.8819	0.9610	0.8040	211.6	0.5565	0.8547	0.1472	139.7	0.7155	0.9092	1.4641	235.8	0.4980	0.8369
0.0175	43.0	0.8630	0.9549	0.9358	217.7	0.5410	0.8490	0.2186	156.9	0.6817	0.8987				
0.0251	59.9	0.8425	0.9484	1.0506	221.9	0.5294	0.8450								
						30 % Ethylene Glycol									
0.0015	−62.9	0.9500	0.9834	0.2015	162.9	0.6740	0.8941	0.0225	64.6	0.8420	0.9480	0.8365	221.2	0.5268	0.8368
0.0030	−30.6	0.9322	0.9773	0.2701	175.3	0.6461	0.8843	0.0315	80.2	0.8208	0.9412	0.9341	225.5	0.5151	0.8325
0.0044	−11.1	0.9188	0.9731	0.3793	189.5	0.6120	0.8714	0.0440	95.4	0.7981	0.9340	0.9943	228.0	0.5086	0.8303
0.0072	12.1	0.8998	0.9669	0.4861	199.7	0.5859	0.8610	0.0661	113.7	0.7682	0.9246	1.1107	232.6	0.4975	0.8273
0.0102	28.2	0.8843	0.9617	0.6009	208.2	0.5629	0.8515	0.0976	131.2	0.7373	0.9149	1.2573	237.4	0.4860	0.8254
0.0144	44.1	0.8671	0.9561	0.7280	215.7	0.5419	0.8428	0.1361	146.0	0.7092	0.9058	1.3999	242.0	0.4771	0.8257
						40 % Ethylene Glycol									
0.0012	−62.7	0.9511	0.9838	0.2284	177.1	0.6445	0.8835	0.0243	78.3	0.8260	0.9428	0.8668	230.5	0.4991	0.8218
0.0024	−30.4	0.9333	0.9778	0.3099	189.7	0.6138	0.8718	0.0373	97.8	0.7970	0.9335	0.9504	234.6	0.4889	0.8177
0.0036	−11.0	0.9201	0.9735	0.3988	200.7	0.5870	0.8609	0.0561	116.5	0.7669	0.9240	1.0391	237.9	0.4793	0.8143
0.0060	12.8	0.9007	0.9669	0.4843	208.5	0.5655	0.8516	0.0822	133.4	0.7364	0.9143	1.1590	242.5	0.4682	0.8113
0.0085	29.7	0.8848	0.9618	0.5870	216.0	0.5437	0.8418	0.1267	152.8	0.6995	0.9024	1.2957	246.5	0.4578	0.8099
0.0121	46.1	0.8670	0.9560	0.6726	221.3	0.5281	0.8347	0.1673	164.0	0.6743	0.8940				
0.0168	61.2	0.8487	0.9501	0.7818	226.8	0.5108	0.8269								
						$T = 298.15$ K									
						0 % Ethylene Glycol									
0.0025	−72.7	0.9465	0.9821	0.1458	124.1	0.7404	0.9189	0.0272	44.6	0.8519	0.9517	0.7187	196.8	0.6245	0.8942
0.0049	−38.7	0.9271	0.9759	0.2002	138.2	0.7169	0.9127	0.0384	61.2	0.8318	0.9454	0.8905	206.2	0.6109	0.8934

Table 1. Continued

m	E			m	E			m	E			m	E		
mol·kg^{-1}	mV	$\gamma_\pm$	Φ	mol·kg^{-1}	mV	$\gamma_\pm$	Φ	mol·kg^{-1}	mV	$\gamma_\pm$	Φ	mol·kg^{-1}	mV	$\gamma_\pm$	Φ
						$T = 298.15$ K									
						0 % Ethylene Glycol									
0.0077	−17.0	0.9114	0.9707	0.2643	150.5	0.6961	0.9076	0.0529	76.5	0.8116	0.9392	1.0897	215.7	0.5990	0.8939
0.0132	9.3	0.8888	0.9634	0.3687	166.2	0.6714	0.9020	0.0731	91.9	0.7899	0.9328	1.2399	221.7	0.5921	0.8952
0.0190	27.1	0.8713	0.9578	0.5383	183.8	0.6442	0.8968	0.1027	107.5	0.7660	0.9259	1.3977	227.4	0.5862	0.8972
						10 % Ethylene Glycol									
0.0021	−72.2	0.9477	0.9825	0.1668	139.1	0.7207	0.9136	0.0228	46.2	0.8550	0.9528	0.7839	209.2	0.5981	0.8847
0.0043	−35.3	0.9270	0.9759	0.2324	154.3	0.6948	0.9068	0.0347	66.2	0.8306	0.9452	0.9516	217.8	0.5839	0.8832
0.0067	−14.3	0.9121	0.9709	0.3297	170.2	0.6670	0.8997	0.0514	84.6	0.8057	0.9376	1.1185	225.2	0.5731	0.8833
0.0115	12.1	0.8896	0.9637	0.4605	185.3	0.6401	0.8932	0.0758	102.7	0.7791	0.9299	1.2654	230.9	0.5658	0.8848
0.0160	28.1	0.8738	0.9586	0.6240	199.0	0.6158	0.8878	0.1158	122.4	0.7484	0.9212	1.4026	235.7	0.5605	0.8872
						20 % Ethylene Glycol									
0.0014	−81.4	0.9534	0.9845	0.2205	161.7	0.6835	0.9031	0.0272	64.3	0.8352	0.9461	0.8991	224.6	0.5702	0.8769
0.0030	−42.2	0.9334	0.9780	0.2903	174.1	0.6614	0.8977	0.0385	80.9	0.8132	0.9393	1.0136	229.9	0.5607	0.8749
0.0047	−20.6	0.9191	0.9732	0.4115	189.8	0.6333	0.8911	0.0532	96.1	0.7913	0.9327	1.1138	234.2	0.5532	0.8734
0.0086	9.0	0.8954	0.9654	0.5235	200.5	0.6138	0.8866	0.0758	112.6	0.7660	0.9253	1.2049	237.4	0.5470	0.8721
0.0125	26.8	0.8783	0.9598	0.6441	209.7	0.5971	0.8829	0.1061	128.3	0.7407	0.9181	1.2871	240.2	0.5419	0.8711
0.0176	43.6	0.8604	0.9541	0.7832	218.4	0.5813	0.8794	0.1445	142.4	0.7169	0.9117	1.3614	242.9	0.5375	0.8703
						30 % Ethylene Glycol									
0.0014	−68.7	0.9505	0.9837	0.1918	165.9	0.6838	0.9013	0.0291	78.5	0.8246	0.9429	0.8366	230.5	0.5513	0.8603
0.0029	−33.9	0.9320	0.9773	0.2455	177.0	0.6627	0.8952	0.0399	93.4	0.8039	0.9365	0.9331	235.3	0.5413	0.8575
0.0043	−14.1	0.9190	0.9731	0.3310	190.3	0.6366	0.8874	0.0557	108.8	0.7807	0.9294	1.0216	238.9	0.5332	0.8553
0.0072	11.1	0.8987	0.9665	0.4253	201.4	0.6140	0.8804	0.0763	123.9	0.7574	0.9225	1.0963	242.0	0.5270	0.8540
0.0100	27.5	0.8838	0.9617	0.5227	210.3	0.5951	0.8743	0.0976	135.2	0.7385	0.9170	1.2133	246.3	0.5184	0.8525
0.0142	44.4	0.8662	0.9560	0.6221	218.0	0.5789	0.8691	0.1338	149.6	0.7135	0.9098	1.2945	249.5	0.5132	0.8520
0.0198	60.3	0.8479	0.9502	0.7314	224.5	0.5638	0.8642								
						40 % Ethylene Glycol									
0.0012	−64.4	0.9498	0.9835	0.2163	181.9	0.6565	0.8931	0.0218	76.0	0.8308	0.9446	0.8397	240.7	0.5308	0.8518
0.0024	−31.3	0.9319	0.9774	0.3082	197.2	0.6252	0.8839	0.0323	94.5	0.8052	0.9366	0.9154	244.4	0.5225	0.8490
0.0036	−11.6	0.9187	0.9730	0.4005	209.0	0.6013	0.8763	0.0482	113.2	0.7770	0.9280	1.0273	248.9	0.5116	0.8455
0.0064	17.3	0.8957	0.9655	0.4933	217.8	0.5819	0.8698	0.0717	131.5	0.7472	0.9191	1.0777	250.4	0.5072	0.8442
0.0090	33.2	0.8802	0.9604	0.5803	224.2	0.5664	0.8645	0.1098	151.3	0.7133	0.9094	1.2133	255.5	0.4965	0.8414
0.0123	48.4	0.8642	0.9552	0.6687	230.9	0.5527	0.8596	0.1567	167.2	0.6840	0.9010	1.2796	258.7	0.4919	0.8405
0.0161	61.3	0.8492	0.9504	0.7464	235.9	0.5421	0.8559								
						$T = 308.15$ K									
						0 % Ethylene Glycol									
0.0025	−76.2	0.9451	0.9819	0.1962	140.1	0.7209	0.9159	0.0332	53.8	0.8402	0.9484	0.9162	213.6	0.6138	0.9004
0.0050	−41.4	0.9256	0.9755	0.2752	156.1	0.6962	0.9104	0.0491	73.0	0.8165	0.9413	1.0872	221.4	0.6044	0.9020
0.0073	−21.7	0.9123	0.9712	0.3636	169.4	0.6759	0.9064	0.0750	93.7	0.7889	0.9334	1.2509	228.5	0.5978	0.9046
0.0099	−6.5	0.9007	0.9673	0.4739	182.0	0.6570	0.9033	0.1006	108.1	0.7687	0.9279	1.3969	233.5	0.5934	0.9076
0.0151	14.7	0.8818	0.9613	0.6044	193.8	0.6402	0.9011	0.1313	120.9	0.7499	0.9230	1.5264	238.9	0.5906	0.9109
0.0226	34.7	0.8616	0.9550	0.7598	204.5	0.6252	0.9001								
						10 % Ethylene Glycol									
0.0019	−79.0	0.9484	0.9830	0.1807	147.1	0.7146	0.9133	0.0297	59.4	0.8382	0.9478	1.0428	229.4	0.5836	0.8892
0.0038	−44.3	0.9298	0.9768	0.2705	165.7	0.6837	0.9056	0.0426	77.1	0.8163	0.9412	1.1848	234.9	0.5766	0.8912
0.0074	−10.1	0.9064	0.9692	0.4077	185.0	0.6518	0.8981	0.0598	93.7	0.7941	0.9347	1.3146	240.6	0.5718	0.8941
0.0114	11.2	0.8884	0.9634	0.5463	198.9	0.6291	0.8933	0.0862	111.5	0.7689	0.9276	1.4262	244.6	0.5689	0.8975
0.0154	26.7	0.8738	0.9588	0.7040	209.9	0.6101	0.8900	0.1240	129.0	0.7427	0.9205	1.5265	247.5	0.5671	0.9012
0.0214	42.8	0.8569	0.9535	0.8765	221.2	0.5946	0.8886								
						20 % Ethylene Glycol									
0.0015	−79.5	0.9508	0.9838	0.2907	180.2	0.6670	0.9004	0.0312	73.3	0.8278	0.9447	1.0966	241.5	0.5610	0.8781
0.0034	−38.4	0.9296	0.9767	0.4112	196.3	0.6385	0.8926	0.0458	92.1	0.8035	0.9375	1.1891	245.3	0.5563	0.8794
0.0051	−18.5	0.9160	0.9722	0.5164	206.3	0.6195	0.8874	0.0657	109.4	0.7792	0.9306	1.2718	248.4	0.5528	0.8812
0.0087	9.2	0.8946	0.9654	0.6392	216.7	0.6017	0.8828	0.0965	128.0	0.7519	0.9230	1.3455	251.3	0.5503	0.8833
0.0122	26.5	0.8789	0.9605	0.7636	225.1	0.5873	0.8797	0.1349	144.1	0.7271	0.9163	1.4362	254.6	0.5480	0.8866
0.0174	43.7	0.8612	0.9549	0.8807	230.6	0.5762	0.8780	0.2057	163.9	0.6946	0.9077				
0.0228	57.7	0.8463	0.9503	0.9938	237.3	0.5675	0.8775								
						30 % Ethylene Glycol									
0.0016	−63.6	0.9466	0.9824	0.2171	178.2	0.6750	0.9003	0.0251	74.7	0.8329	0.9457	0.8836	242.6	0.5550	0.8683
0.0031	−30.9	0.9290	0.9764	0.3327	198.3	0.6389	0.8900	0.0349	90.9	0.8121	0.9394	0.9891	247.7	0.5465	0.8678
0.0042	−14.6	0.9182	0.9731	0.4430	210.8	0.6140	0.8827	0.0497	107.9	0.7882	0.9322	1.0854	252.1	0.5402	0.8684
0.0074	13.7	0.8964	0.9658	0.5532	220.8	0.5945	0.8771	0.0704	124.7	0.7633	0.9250	1.2294	257.4	0.5328	0.8710
0.0122	39.2	0.8732	0.9583	0.6621	228.8	0.5788	0.8730	0.0997	141.3	0.7372	0.9176	1.3730	263.0	0.5279	0.8756
0.0168	54.9	0.8560	0.9530	0.7803	236.6	0.5650	0.8698	0.1460	160.1	0.7073	0.9093				
						40 % Ethylene Glycol									
0.0012	−67.5	0.9501	0.9832	0.2491	196.5	0.6442	0.8910	0.0218	80.4	0.8292	0.9441	0.8051	250.0	0.5431	0.8646
0.0036	−10.1	0.9177	0.9726	0.3468	211.2	0.6156	0.8831	0.0313	98.0	0.8055	0.9369	0.8958	254.7	0.5349	0.8639
0.0058	14.4	0.8987	0.9665	0.4451	222.3	0.5938	0.8769	0.0434	113.8	0.7827	0.9300	1.0012	259.4	0.5269	0.8641
0.0085	33.1	0.8815	0.9608	0.5547	232.7	0.5745	0.8716	0.0638	132.2	0.7544	0.9216	1.0913	263.1	0.5214	0.8652
0.0109	46.1	0.8686	0.9568	0.6457	239.4	0.5614	0.8682	0.0950	151.1	0.7236	0.9129	1.2037	268.1	0.5160	0.8679
0.0151	62.1	0.8510	0.9511	0.7252	244.9	0.5516	0.8661	0.1513	173.8	0.6860	0.9025	1.3290	273.1	0.5118	0.8725

Table 2. Values of Average Molecular Mass (M), Dielectric Constant D, Density ρ, Debye−Hückel Constants (A, B), and Pitzer Constants (A_Φ) in the Weight Percentage of Ethylene Glycol−Water Mixtures at (278.15, 288.15, 298.15, and 308.15) K

% (by weight)	M / g·mol^{-1}	D	ρ / g·cm^{-3}	A / kg$^{1/2}$·mol$^{-1/2}$	B / kg$^{1/2}$·mol$^{-1/2}$·Å^{-1}	A_Φ / kg$^{1/2}$·mol$^{-1/2}$
			278.15 K			
0	18.02	85.48	1.00000	0.4971	0.3261	0.3820
10	19.40	82.98	1.01528	0.5243	0.3335	0.4025
20	21.00	79.60	1.03127	0.5625	0.3432	0.4317
30	22.89	76.92	1.04698	0.5966	0.3518	0.4579
40	25.16	73.24	1.06250	0.6469	0.3632	0.4965
			288.15 K			
0	18.02	81.82	0.99909	0.5038	0.3274	0.3867
10	19.40	79.07	1.01363	0.5342	0.3354	0.4100
20	21.00	75.83	1.02870	0.5730	0.3451	0.4398
30	22.89	73.47	1.04354	0.6051	0.3531	0.4645
40	25.16	69.87	1.05827	0.6571	0.3646	0.5044
			298.15 K			
0	18.02	78.24	0.99707	0.5114	0.3288	0.3921
10	19.40	75.23	1.01096	0.5462	0.3376	0.4192
20	21.00	72.30	1.02525	0.5838	0.3468	0.4481
30	22.89	70.09	1.03928	0.6158	0.3547	0.4727
40	25.16	66.47	1.05325	0.6712	0.3666	0.5152
			308.15 K			
0	18.02	74.80	0.99407	0.5199	0.3303	0.3990
10	19.40	71.62	1.00744	0.5586	0.3398	0.4288
20	21.00	68.90	1.02109	0.5960	0.3488	0.4575
30	22.89	66.87	1.03445	0.6274	0.3563	0.4816
40	25.16	63.39	1.04779	0.6842	0.3683	0.5251

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

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

where E stands for the EMF of the cell and E^0 is the standard potential of cell (1). $\gamma_\pm$ is the mean activity coefficient of KCl, $k = RT/F$ for the Nernst slope, with R and F as the universal gas constant and the Faraday constant, respectively.

To check the response of the electrodes, the EMF of aqueous solutions of KCl at several molalities was determined. The activity coefficients of KCl in water were calculated using the Pitzer equation at 298.15 K. The values of E^0 and k are (238.1 and 25.64) mV (theoretical value of k: 25.69 mV), with a standard deviation and correlation coefficient of 0.25 and 0.9999, respectively. It is obvious that the electrode pair used here has a satisfactory Nernstian response and is appropriate for our research. Hence, the mean activity coefficients of KCl in mixed solvents can be calculated, and the results obtained by use of the Pitzer equation are listed in Table 1.

For 1−1 type electrolytes, such as KCl, the extended Debye−Hückel equations for the mean activity coefficient ($\gamma_\pm$) are written as:[28,29]

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

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. A and B are the Debye−Hückel constants given by:

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

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

where ρ, D, and T stand for the density and relative permittivity (static dielectric constant) of the solvent and the temperature, respectively.

The Pitzer equations for the mean activity coefficient ($\gamma_\pm$) and osmotic coefficient (Φ) are written as:[30,31]

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

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

where

Table 3. Values of E^0 and the Debye−Hückel and Pitzer Parameters for KCl in Ethylene Glycol−Water Solvents at (278.15, 288.15, 298.15, and 308.15) K

	Debye−Hückel parameters					Pitzer parameters				
% (by weight)	a / Å	C / kg·mol^{-1}	D / kg^2·mol^{-2}	E^0 / mV	SD[a]	$\beta^{(0)}$ / kg·mol^{-1}	$\beta^{(1)}$ / kg·mol^{-1}	C^φ / kg^2·mol^{-2}	E^0 / mV	SD
				278.15 K						
0	3.8612	−0.0272	0.0069	229.0	0.22	−0.0111	0.2198	0.0091	229.0	0.22
10	4.1573	−0.0651	0.0261	236.2	0.20	−0.0030	0.1787	0.0037	236.2	0.24
20	3.7619	−0.0408	0.0058	244.2	0.28	−0.0375	0.2931	0.0166	244.4	0.29
30	3.8490	−0.0725	0.0162	253.4	0.21	−0.0649	0.3233	0.0282	253.6	0.20
40	5.1982	−0.1920	0.0744	262.8	0.24	−0.1606	0.5316	0.0840	263.0	0.26
				288.15 K						
0	3.5078	0.0142	−0.0018	233.7	0.24	0.0373	0.1693	−0.0058	233.6	0.24
10	4.0281	−0.0155	0.0059	242.2	0.26	0.0078	0.2736	0.0062	242.1	0.27
20	4.5481	−0.0428	0.0110	251.5	0.19	−0.0325	0.4252	0.0215	251.4	0.17
30	4.6587	−0.0639	0.0173	262.1	0.18	−0.0745	0.5212	0.0452	261.9	0.15
40	4.7895	−0.0712	0.0142	272.7	0.26	−0.0966	0.6365	0.0554	272.6	0.27
				298.15 K						
0	3.8879	0.0119	0.0037	238.3	0.25	0.0342	0.2419	0.0047	238.1	0.25
10	4.4431	−0.0132	0.0109	248.2	0.18	0.0048	0.3693	0.0188	248.1	0.18
20	4.0981	0.0092	−0.0019	259.1	0.10	0.0315	0.3569	−0.0010	258.9	0.10
30	4.5665	−0.0264	0.0083	270.5	0.18	−0.0210	0.5020	0.0237	270.3	0.15
40	4.4013	−0.0057	−0.0075	282.2	0.22	−0.0253	0.6007	0.0245	282.0	0.26
				308.15 K						
0	4.1512	0.0125	0.0049	244.2	0.20	0.0322	0.3045	0.0091	244.0	0.19
10	4.8724	−0.0206	0.0139	253.0	0.28	0.0018	0.4253	0.0245	255.5	0.27
20	5.0970	−0.0339	0.0187	267.5	0.28	−0.0292	0.5594	0.0389	267.3	0.27
30	4.9628	−0.0394	0.0212	280.4	0.25	−0.0371	0.5867	0.0444	280.1	0.25
40	4.9212	−0.0369	0.0222	293.7	0.26	−0.0357	0.6627	0.0488	293.4	0.26

[a] SD: standard deviation.

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

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

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

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

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

In these equations, $\beta^{(0)}$, $\beta^{(1)}$, and C^{φ} are the parameters of the Pitzer equations, and α and b are assumed to be fixed parameters whose values are (2.0 and 1.2) $kg^{1/2}\cdot mol^{-1/2}$. I is the ionic strength in the molarity scale, and m is the concentration of the electrolyte in molarity. A_{φ} is the Debye−Hückel constant for the osmotic coefficient defined by:

$$A_{\varphi} = (1/3)[(2\pi N_0\rho)/1000]^{1/2}[e^2/(DKT)]^{3/2} \quad (6a)$$

where N_0, ρ, D, and K are Avogadro's number, the density of solvent mixtures, the dielectric constant, and Boltzmann's constant, respectively. After the values of the fundamental physical constants are introduced to eq 6a, it becomes

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

The values of ρ, D, and M of the mixture, as well as the constants A, B, and A_{φ} are shown in Table 2. The values of the dielectric constant in the different solvent compositions were taken from the literature,[32,33] and the density data were measured by us using a densimeter (DMA4500). Introducing eqs 3 and 4 into eq 2, the Debye−Hückel parameters a, c, and d, and the Pitzer parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^{φ} with E^0 are obtained and are listed in Table 3.

4. Discussion

It can be seen that the standard deviations and E^0 values of the same system obtained from the extended Debye−Hückel and the Pitzer models are very close. The values of parameter a (related to the size of the ion) in the extended Debye−Hückel equation was obtained. In all cases, a is greater than the sum of the crystallographic radii (3.2 Å),[34] which can be explained by the solvation of the ions.[35] The Pitzer parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^{φ} values could be optimized by the algorithm of the Nelder and Mead simplex method[36] from the EMF data.

The mean activity coefficients of KCl in mixed solvents can be calculated using the extended Debye−Hückel and the Pitzer models, and the results obtained by the Pitzer equation are listed in Table 1. The plots of $\gamma_{\pm}$ with the molality of KCl in mixed solvents for these systems at the investigated temperatures are similar. As an example, Figure 1 is shown for the system at 278.15 K. It can be seen that $\gamma_{\pm}$ decreases with an increase of the ethylene glycol content in the mixed solvent at a given temperature. For a given percentage (by weight) of ethylene glycol, $\gamma_{\pm}$ increases with an increase of temperature. This phenomenon can be explained by the short-range interactions of ion−ion and ion−solvent in the mixture.[29] It is necessary to note that Manzoni et al.[23] have also reported the activity coefficients for the KCl system at 298.15 K in the range of (0 to 80) % (by weight of ethylene glycol). The comparison of our and Manzoni's activity coefficient data are both depicted in Figure 2. It can be seen that two series of data are basically coincident within our investigated concentration range. Furthermore, the osmotic coefficients (Φ) of KCl−ethylene glycol−water show a similar variation as $\gamma_{\pm}$.

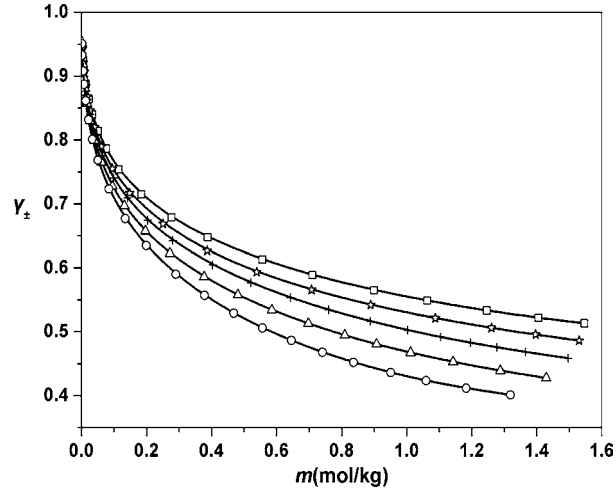

Figure 1. Variation of mean activity coefficient $\gamma_{\pm}$ with the molality of KCl in ethylene glycol−water solvents at 278.15 K: □, 0 %; ☆, 10 %; +, 20 %; △, 30 %; ○, 40 % ethylene glycol.

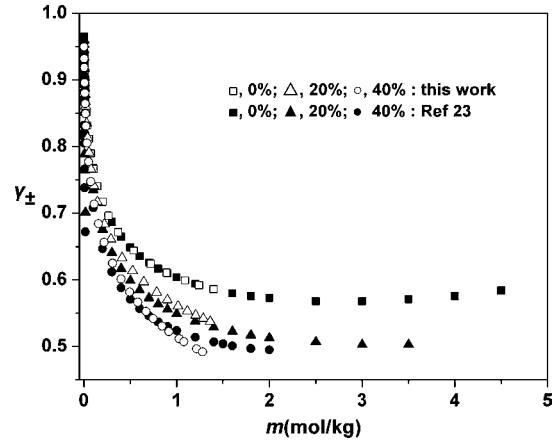

Figure 2. Comparison of our and Manzoni's activity coefficient data for the KCl + ethylene glycol + water system at 298.15 K.

Table 4. Standard Gibbs Energy of Transference for the KCl + Ethylene Glycol + Water System at (278.15, 288.15, 298.15, and 308.15) K

% (by weight)	ΔG_t^0 / kJ·mol^{-1}	% (by weight)	ΔG_t^0 / kJ·mol^{-1}
278.15 K		288.15 K	
0	0.00	0	0.00
10	0.63	10	0.76
20	1.34	20	1.58
30	2.16	30	2.53
40	3.01	40	3.49
298.15 K		308.15 K	
0	0.00	0	0.00
10	0.89	10	1.04
20	1.86	20	2.11
30	2.90	30	3.29
40	3.96	40	4.51

The standard energy of transference, ΔG^0_t, is one of the most useful thermodynamic properties of solution. It can be calculated from E^0 values according to the following equation:

$$\Delta G_t^0 = F(E_m^0 - E_w^0) + 2RT\ln(d_w/d_m) \quad (7)$$

where subscripts w and m refer to the water and mixed solvent, respectively. Other symbols have their usual mean-

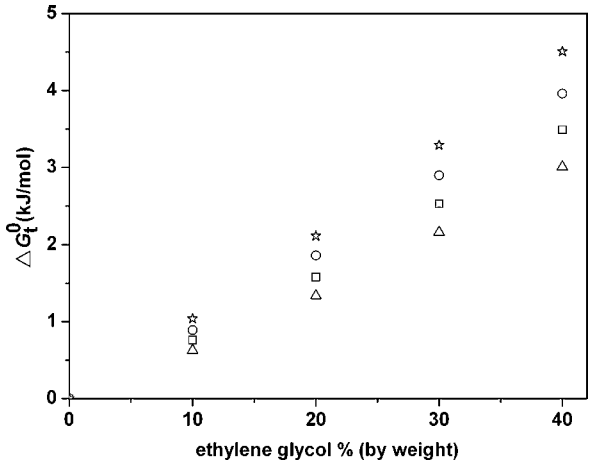

Figure 3. Plot of the standard free energy of transference, ΔG^0_t, vs the weight percentage of ethylene glycol for KCl at different temperatures: △, 278.15 K; □, 288.15 K; ○, 298.15 K; ☆, 308.15 K.

ing. It can be observed that ΔG^0_t increases with an increase of ethylene glycol in the mixture at a given temperature. At the same percentage (by weight) of ethylene glycol, ΔG^0_t increases with an increase of temperature, along with ΔG^0_t becoming more positive (see Table 4 and Figure 3). This phenomenon shows that the transference of KCl from water to the water−ethylene glycol mixed solvents is not a spontaneous process.

5. Conclusion

In this work, using the galvanic cell consisting of K−ISE and Ag−AgCl electrodes, we have obtained the mean activity coefficients of KCl in the KCl + ethylene glycol + H_2O ternary system at (278.15, 288.15, 298.15, and 308.15 K). We used the Pitzer equation for getting the parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^{φ} and osmotic coefficients; meanwhile, the parameters *a*, *c*, and *d* were obtained by the extended Debye−Hückel equation. In addition, the standard energy of transference at different temperatures was estimated. In this paper, the two thermodynamic models could correlate the experimental data well, and the basic thermodynamic data may be useful for further research applications.

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