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Activity Coefficients of RbCl in Ethylene Glycol + Water and Glycerol + Water Mixed Solvents at 298.15 K

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ABSTRACT: Activity coefficients for RbCl in different ethylene glycol + water and glycerol + water mixed solvents were determined at 298.15 K using potentiometric measurements. The Pitzer and extended Debye−Hückel equations were applied to describe the nonideal behavior of the electrolyte, and the corresponding coefficients were determined for each mixed solvent system.

INTRODUCTION

Activity coefficients like other related thermodynamic parameters (osmotic coefficients, Gibbs excess energies of mixture or of transference) are very important in desalination, oceanography, biology, environment, geochemistry, and industry. Potentiometric measurements are commonly used to study the activity coefficient of electrolytes in solution because of their simplicity, high speed, and accuracy. Actually, there have been a number of studies using potentiometric measurements to determine the mean activity coefficients of alkali metal halides in electrolyte aqueous solutions or aqueous + organic mixtures. For example, Deyhimi et al.[1,2] using the galvanic cell consisting of selective membrane electrode (NH_4^+−ISE) and Ag/AgCl electrodes studied thermodynamic modeling of NH_4Cl salt in the ternary $NH_4Cl + NH_4NO_3 + H_2O$ and $NH_4Cl + LiCl + H_2O$ mixed electrolyte systems. Hernández-Luis et al.[3,4] reported the determinations of mean activity coefficients of NaCl or NaBr salt in the ternary NaCl + ethylene carbonate + water and NaBr + ethylene carbonate + water mixed electrolyte systems based on potentiometric measurements at 298.15 K, respectively. Lopes et al.[5,6] investigated the activity coefficients of KCl or NaCl in ethanol + water mixtures. Zhuo et al.[7] determined the activity coefficients for the $CaCl_2$ + amino acid + water system at a temperature of 298.15 K using ion-selective electrodes. Furthermore, Mussini et al.[8] and Vera et al.[9,10] also undertook similar studies.

In our previous work, we had obtained the activity coefficients of CsCl in methanol + water, ethanol + water,[11] and *N*,*N*-dimethylformamide (DMF) + water mixtures.[12] As an extension of this work, we now carry out the investigation on the ternary systems RbCl + ethylene glycol + water and RbCl + glycerol + water at 298.15 K by potentiometric measurements. The potentiometric measurements were performed over the RbCl molality range from (0.0011 to 1.3644) $mol \cdot kg^{-1}$ in mixed solvents. The experimental data were fitted by the Pitzer and extended Debye−Hückel equations. Our goal was to enrich the available data on water + alkali chloride + organic systems. It is expected that such a study could be useful in both viewpoints of fundamental and applied aspects.

EXPERIMENTAL SECTION

Rubidium chloride was purchased from Shanghai China Lithium Industrial Co., Ltd. with a purity greater than 0.9950 in mass fraction. Rubidium chloride was dried overnight in a muffle furnace (T = 500 K) and then stored over silica gel in a desiccator before use. Analytical grade ethylene glycol and glycerol were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China, with a minimum mass fraction 0.9980, and were used without further purification, and the specific conductance of double-distilled deionized water was used in our experiments.

The potentiometric measurements were made on the galvanic cell without liquid junction

$$\mathrm{Rb-ISE}|\mathrm{RbCl}(m),\mathrm{alcohol}(w),\mathrm{water}|\mathrm{Ag}|\mathrm{AgCl} \qquad (1)$$

In the cells, m is the molality of RbCl in different ethylene glycol + water and glycerol + water mixed solvents and w the mass fraction of alcohol (w = 0.00, 0.10, 0.20, 0.30, and 0.40). The uncertainties in the electrolyte molality and mass fraction of ethylene glycol or glycerol are ± 0.0001 and ± 0.01, respectively. As usual, all of the measurements were performed under stirring conditions, and the temperature in the cell was controlled with a precision of ± 0.02 K by employing a double-wall container enabling the circulation of water from a thermostat.

Electrodes, cells, and apparatus in the present study have been described in detail in previous works.[12,13] The potential measurements were carried out with pH/mV meter (Orion-868, U.S.), which precision was ± 0.1 mV. In each mixed solvent system, and for each molality, voltage readings were taken when they were stable within 0.1 mV for at least 5 min.

RESULTS AND DISCUSSION

The potentiometric measurements of the cell can be expressed by the Nernstian equation:

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

where $\gamma_\pm$ is the mean activity coefficient of rubidium chloride, $k = RT/F$ for the Nernst slope, R, T, and F are the universal gas constant, absolute temperature, and Faraday constant, respectively. E^0 is the standard potential of the cell (1). To check the

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Table 1. Values of Average Molecular Mass *M*, Relative Permittivity ε_r, Density ρ, Debye−Hückel constants (A, B) and Debye−Hückel Osmotic Coefficient Parameter A_φ for the Ethylene Glycol + Water and Glycerol + Water Mixtures at 298.15 K

ROH (w)	M / $\mathrm{g \cdot mol^{-1}}$	ε_r	ρ / $\mathrm{g \cdot cm^{-3}}$	A / $\mathrm{kg^{1/2} \cdot mol^{-1/2}}$	B / $\mathrm{kg^{1/2} \cdot mol^{-1/2} \cdot Å^{-1}}$	A_φ / $\mathrm{kg^{1/2} \cdot mol^{-1/2}}$
pure water	18.02	78.24	0.99707	0.5114	0.3288	0.3921
ethylene glycol						
0.10	19.40	75.23	1.01096	0.5462	0.3376	0.4192
0.20	21.00	72.30	1.02525	0.5838	0.3468	0.4481
0.30	22.89	70.09	1.03928	0.6158	0.3547	0.4727
0.40	25.16	66.47	1.05325	0.6713	0.3666	0.5152
glycerol						
0.10	19.60	75.50	1.02075	0.5459	0.3387	0.4190
0.20	21.47	72.90	1.04537	0.5822	0.3488	0.4469
0.30	23.75	70.00	1.07068	0.6262	0.3602	0.4807
0.40	26.57	67.10	1.09669	0.6753	0.3723	0.5183

Table 2. Potential *E*, Mean Activity Coefficients $\gamma_\pm$, and Osmotic Coefficient Φ, at Different RbCl Molalities in Pure Water at 298.15 K

m / $\mathrm{mol \cdot kg^{-1}}$	E / mV	$\gamma_\pm$	Φ	m / $\mathrm{mol \cdot kg^{-1}}$	E / mV	$\gamma_\pm$	Φ
			Pure Water				
0.0041	−155.4	0.9320	0.9773	0.2042	30.7	0.7004	0.9043
0.0062	−135.4	0.9182	0.9727	0.2485	39.4	0.6842	0.9001
0.0105	−109.2	0.8971	0.9657	0.2996	47.8	0.6688	0.8963
0.0150	−92.0	0.8805	0.9602	0.3656	56.6	0.6525	0.8928
0.0214	−74.7	0.8619	0.9540	0.4349	64.6	0.6386	0.8901
0.0323	−55.0	0.8377	0.9461	0.5028	71.4	0.6273	0.8883
0.0429	−41.5	0.8194	0.9402	0.5742	77.2	0.6173	0.8870
0.0597	−25.9	0.7966	0.9329	0.7219	87.5	0.6008	0.8860
0.0789	−13.0	0.7762	0.9265	0.8683	96.0	0.5886	0.8865
0.1017	−1.2	0.7567	0.9205	1.0346	104.0	0.5782	0.8884
0.1327	11.1	0.7356	0.9142	1.1823	110.3	0.5712	0.8910
0.1635	20.0	0.7187	0.9093				

response of the electrodes, the potentiometric measurements were taken for RbCl in pure water with several molalities. The activity coefficients of RbCl in water were calculated at 298.15 K, using the Pitzer equation. The values of $2k$ are 51.36 ± 0.10 mV (theoretical value of $2k$: 51.38 mV), with a standard deviation and linear correlation coefficient of 0.16 and 0.9999. So it can be concluded that the electrode pair used here has a good Nernst response and is satisfactory enough for our study.

The extended Debye−Hückel and Pitzer equations were used to describe the variation of the activity coefficients in the present work. For 1−1 type electrolyte RbCl, the extended Debye−Hückel equations for the mean activity coefficient ($\gamma_\pm$) were written as:[14,15]

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

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:

$$A = 1.8247 \cdot 10^6 \cdot \rho^{1/2}/(\varepsilon_r T)^{3/2}\ \mathrm{kg^{1/2} \cdot mol^{-1/2}} \tag{3a}$$

$$B = 50.2901 \cdot \rho^{1/2}/(\varepsilon_r T)^{1/2}\ \mathrm{kg^{1/2} \cdot mol^{-1/2} \cdot Å^{-1}} \tag{3b}$$

where ρ, ε_r, and T stand for the density, relative permittivity of the solvent, and the thermodynamic temperature, respectively.

The Pitzer equations for the mean activity coefficient ($\gamma_\pm$) were written as:[16]

$$\ln \gamma_\pm = f^\gamma + mB^\gamma + m^2C^\gamma \tag{4}$$

where

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

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

$$C^\gamma = 1.5C^\varphi \tag{4c}$$

Table 3. Potential E, Mean Activity Coefficients $\gamma_{\pm}$, and Osmotic Coefficient Φ, at Different RbCl Molalities in Different Ethylene Glycol + Water Systems at 298.15 K

m / $\text{mol}\cdot\text{kg}^{-1}$	E / mV	$\gamma_{\pm}$	Φ	m / $\text{mol}\cdot\text{kg}^{-1}$	E / mV	$\gamma_{\pm}$	Φ
$w = 0.10$							
0.0034	−156.1	0.9333	0.9777	0.1768	31.9	0.6935	0.8992
0.0053	−134.1	0.9186	0.9727	0.2193	41.4	0.6742	0.8932
0.0085	−110.4	0.8999	0.9665	0.2648	49.7	0.6569	0.8879
0.0142	−85.7	0.8756	0.9583	0.3203	58.2	0.6392	0.8824
0.0178	−74.8	0.8635	0.9543	0.3973	67.6	0.6187	0.8759
0.0217	−65.4	0.8521	0.9505	0.4852	75.9	0.5994	0.8696
0.0313	−47.8	0.8294	0.9429	0.5877	84.8	0.5803	0.8628
0.0416	−34.4	0.8101	0.9366	0.7176	93.2	0.5596	0.8547
0.0573	−19.3	0.7869	0.9289	0.8400	99.4	0.5424	0.8470
0.0768	−5.5	0.7642	0.9216	0.9908	105.7	0.5233	0.8373
0.1051	8.5	0.7385	0.9134	1.1569	112.1	0.5040	0.8257
0.1459	23.2	0.7105	0.9045				
$w = 0.20$							
0.0040	−137.8	0.9240	0.9746	0.1805	41.1	0.6721	0.8874
0.0080	−104.2	0.8970	0.9655	0.2448	54.4	0.6400	0.8748
0.0120	−84.2	0.8777	0.9591	0.2891	61.7	0.6217	0.8671
0.0224	−54.2	0.8425	0.9473	0.3424	68.7	0.6024	0.8588
0.0349	−33.4	0.8132	0.9374	0.4062	75.9	0.5823	0.8497
0.0451	−21.4	0.7946	0.9310	0.5126	85.5	0.5539	0.8362
0.0610	−7.2	0.7710	0.9230	0.6005	90.8	0.5339	0.8262
0.0815	5.6	0.7468	0.9146	0.7379	99.0	0.5074	0.8124
0.1080	18.3	0.7218	0.9058	0.8895	105.9	0.4830	0.7994
0.1400	29.9	0.6973	0.8969	1.0756	113.6	0.4583	0.7864
$w = 0.30$							
0.0017	−169.8	0.9458	0.9819	0.1173	32.3	0.6977	0.8948
0.0036	−132.9	0.9237	0.9744	0.1518	43.5	0.6708	0.8839
0.0052	−113.7	0.9102	0.9699	0.1982	54.9	0.6411	0.8712
0.0123	−72.1	0.8701	0.9563	0.2389	62.7	0.6191	0.8613
0.0157	−60.4	0.8564	0.9517	0.2966	71.6	0.5923	0.8484
0.0208	−46.8	0.8392	0.9458	0.3902	82.4	0.5563	0.8297
0.0277	−33.4	0.8201	0.9392	0.4773	90.2	0.5284	0.8141
0.0364	−20.6	0.8004	0.9324	0.6007	98.7	0.4953	0.7944
0.0483	−7.4	0.7783	0.9246	0.7155	105.0	0.4694	0.7781
0.0638	5.1	0.7549	0.9163	0.9001	112.8	0.4352	0.7560
0.0884	19.8	0.7254	0.9054	1.0487	117.9	0.4128	0.7415
$w = 0.40$							
0.0046	−108.6	0.9074	0.9688	0.1695	57.9	0.6306	0.8652
0.0077	−84.0	0.8840	0.9608	0.2131	67.3	0.6026	0.8522
0.0121	−61.7	0.8597	0.9524	0.2591	75.1	0.5776	0.8398
0.0165	−47.0	0.8407	0.9458	0.3186	83.2	0.5497	0.8250
0.0225	−32.4	0.8197	0.9385	0.3889	90.7	0.5216	0.8089
0.0317	−16.4	0.7942	0.9295	0.4872	99.0	0.4883	0.7883
0.0437	−1.7	0.7679	0.9200	0.5916	105.7	0.4585	0.7683
0.0584	11.4	0.7423	0.9105	0.7239	112.5	0.4266	0.7453
0.0763	23.5	0.7169	0.9009	0.8649	117.9	0.3981	0.7234
0.1085	38.9	0.6808	0.8866	1.0067	122.6	0.3738	0.7038
0.1362	48.7	0.6559	0.8763				

The Pitzer equations for osmotic coefficient (Φ) were given by:[17]

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

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

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

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

$$A_{\varphi} = (1/3)[(2\pi N^0\rho)/1000]^{1/2}[e^2/(\varepsilon_r KT)]^{3/2} \tag{6a}$$

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

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

Table 4. Potential E, Mean Activity Coefficients $\gamma_{\pm}$, and Osmotic Coefficient Φ, at Different RbCl Molalities in Different Glycerol + Water Mixed Systems at 298.15 K

m / mol·kg^{-1}	E / mV	$\gamma_{\pm}$	Φ	m / mol·kg^{-1}	E / mV	$\gamma_{\pm}$	Φ
			$w = 0.10$				
0.0016	−194.8	0.9530	0.9843	0.2932	53.9	0.6573	0.8932
0.0031	−161.7	0.9362	0.9787	0.4183	70.2	0.6284	0.8874
0.0063	−126.0	0.9123	0.9707	0.5656	83.7	0.6047	0.8835
0.0141	−86.7	0.8763	0.9587	0.7563	96.7	0.5826	0.8806
0.0321	−47.8	0.8287	0.9430	0.9086	104.7	0.5689	0.8789
0.0696	−11.3	0.7740	0.9255	1.0899	112.8	0.5553	0.8769
0.1219	14.3	0.7298	0.9122	1.2567	119.2	0.5444	0.8748
0.2001	36.9	0.6889	0.9009	1.3644	122.9	0.5380	0.8732
			$w = 0.20$				
0.0013	−195.6	0.9544	0.9847	0.2673	57.0	0.6413	0.8854
0.0027	−159.6	0.9359	0.9785	0.4419	79.2	0.5993	0.8774
0.0058	−122.7	0.9095	0.9695	0.6365	95.5	0.5707	0.8739
0.0118	−87.8	0.8769	0.9585	0.8072	105.8	0.5528	0.8722
0.0258	−50.1	0.8309	0.9429	0.9597	113.6	0.5397	0.8705
0.0547	−15.2	0.7765	0.9248	1.0658	118.0	0.5316	0.8691
0.1007	12.9	0.7263	0.9087	1.1707	122.2	0.5241	0.8672
0.1663	35.6	0.6827	0.8959	1.2936	126.8	0.5158	0.8645
			$w = 0.30$				
0.0011	−196.7	0.9549	0.9849	0.3443	76.4	0.6109	0.8795
0.0022	−160.7	0.9378	0.9791	0.4615	89.4	0.5866	0.8748
0.0049	−121.7	0.9107	0.9700	0.6300	102.9	0.5610	0.8699
0.0110	−82.1	0.8736	0.9575	0.7584	111.0	0.5455	0.8664
0.0237	−45.5	0.8281	0.9422	0.8909	118.0	0.5315	0.8623
0.0486	−11.8	0.7764	0.9252	1.0095	123.2	0.5201	0.8579
0.0881	15.1	0.7281	0.9100	1.0950	126.9	0.5121	0.8542
0.1429	37.0	0.6866	0.8978	1.2070	130.6	0.5020	0.8488
0.2311	58.6	0.6449	0.8870				
			$w = 0.40$				
0.0012	−183.3	0.9496	0.9831	0.2761	74.3	0.6092	0.8749
0.0021	−153.8	0.9346	0.9780	0.4617	97.0	0.5638	0.8645
0.0043	−118.4	0.9097	0.9696	0.5595	105.3	0.5471	0.8609
0.0088	−83.5	0.8769	0.9585	0.6669	112.9	0.5319	0.8573
0.0186	−47.9	0.8332	0.9437	0.7868	119.7	0.5173	0.8535
0.0402	−12.1	0.7777	0.9251	0.8755	124.5	0.5077	0.8505
0.0723	14.8	0.7293	0.9094	0.9493	127.6	0.5002	0.8478
0.1192	37.2	0.6852	0.8957	1.0564	132.2	0.4899	0.8436
0.1881	57.7	0.6439	0.8839	1.1659	136.3	0.4800	0.8387

The values of ρ, ε_r, and M of the mixture, as well as the constants A, B, and A_{φ}, are shown in Table 1. The values of relative permittivity in the different solvent compositions were taken from the literature,[18] and the density data were measured using a densimeter (Anton Parr DMA4500, Austria, with a precision of ± 0.00001 g·cm^{-3}).

The EMF values and the molalities for each system, together with the activity coefficients of RbCl, are listed in Tables 2, 3, and 4. For comparison, the published values[19] and our data for the activity coefficients of RbCl in pure water are both depicted in Figure 1. Figure 1 shows that the two results are consistent. In addition, the related trend of the mean activity coefficients for RbCl versus the electrolyte molality in various ethylene glycol + water and glycerol + water mixtures are shown in Figures 2 and 3, respectively. It can be seen that the values of $\gamma_{\pm}$ decreases with an increase of alcohol content in the solvent mixture. For a given mass fraction percentage, this trend of the mean activity coefficients compares well with the previously studied mixed alcohol/water systems with a more negative shift in the order: ethanol[20] > ethylene glycol > glycerol. This phenomenon can be interpreted as ion−ion and ion−solvent interactions in the mixture. For ethylene glycol−water and glycerol−water mixed solvents, the relative permittivity of the mixed solvent decreases with an increase of organic solvents, while the ion−ion interaction is more significant than the ion−solvent interaction. The osmotic coefficients (Φ) of the above systems shown similar variation rules with the $\gamma_{\pm}$.

The extended Debye–Hückel parameters a, c, and d and the Pitzer parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^{φ} appearing in Table 5 were calculated considering this two models using a curve fitting computer program. Table 5 also shows the standard potential E^0 and standard deviations calculated by the extended Debye–Hückel and the Pitzer models. As can be seen from the Table 5, the standard deviations and E^0 values are very close from the extended Debye–Hückel and the Pitzer models. The values of E^0 increase with an increase of organic solvent content in mixture. In the extended Debye–Hückel equation, the values of parameter a (related to the size of the ion) were obtained. The parameter a of the extended Debye–Hückel equation in ethylene glycol–water mixtures is higher than the sum of crystallographic radii (3.33 Å)[21] which can be explained by ion solvation. The values of a in glycerol–water mixtures are lower than the sum of the crystallographic radii, which also suggests ionic association.[22]

The standard Gibbs energy of transference ($\Delta G^0{}_t$) is one of the most useful thermodynamic properties of solution. It can be calculated from E^0 values according to the following

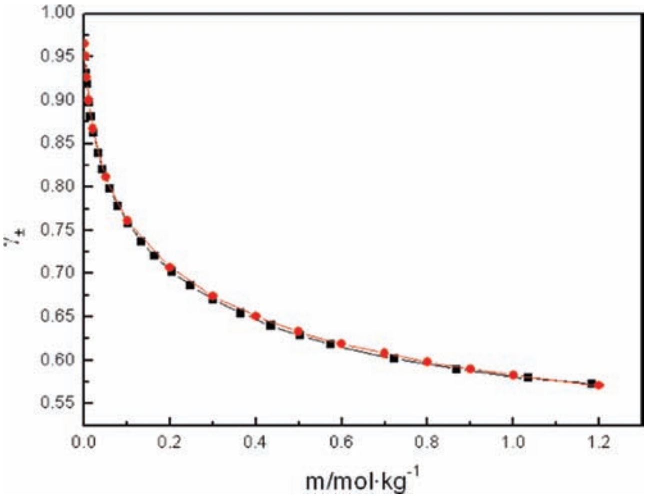

Figure 1. Comparisons between this work and the reference data for mean activity coefficients of RbCl in water at 298.15 K: ●, ref 19; ■, this work.

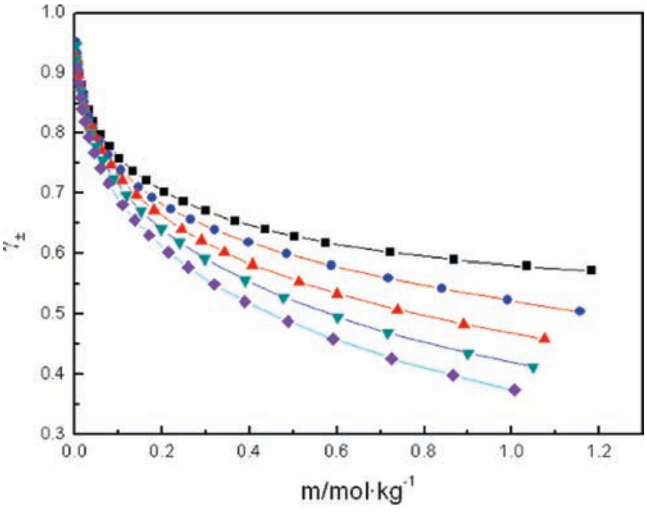

Figure 2. Variation of mean activity coefficient $\gamma_{\pm}$ with the molality of RbCl in the ethylene glycol + water system at 298.15 K: ■, 0.00 ethylene glycol; ●, 0.10 ethylene glycol; ▲, 0.20 ethylene glycol; ▼, 0.30 ethylene glycol; ◆, 0.40 ethylene glycol.

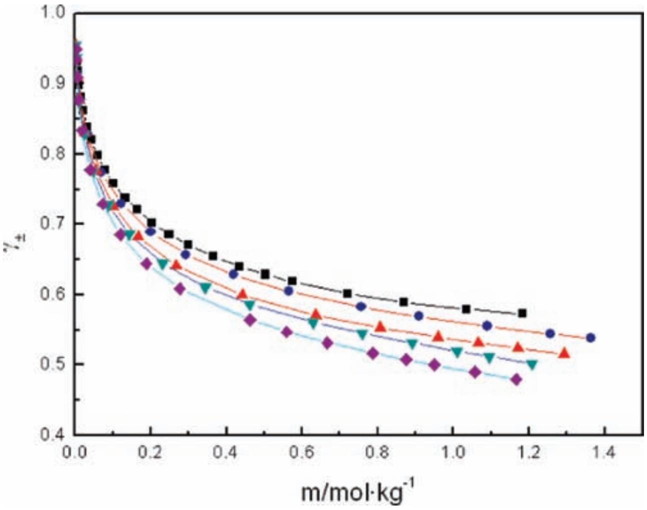

Figure 3. Variation of mean activity coefficient $\gamma_{\pm}$ with molality of RbCl in the glycerol + water system at 298.15 K: ■, 0.00 glycerol; ●, 0.10 glycerol; ▲, 0.20 glycerol; ▼, 0.30 glycerol; ◆, 0.40 glycerol.

Table 5. Values of E^0 and the Debye–Hückel and Pitzer Parameters for RbCl in Ethylene Glycol + Water and Glycerol + Water Mixture Solvents at 298.15 K

	Debye–Hückel parameters					Pitzer parameters				
ROH (w)	a Å	c kg·mol^{-1}	d kg^2·mol^{-2}	E^0 mV	SD	$\beta^{(0)}$ kg·mol^{-1}	$\beta^{(1)}$ kg·mol^{-1}	C^{φ} kg^2·mol^{-2}	E^0 mV	SD
pure water	3.25	0.0198	0.0062	130.5	0.15	0.0478	0.1126	0.0032	130.5	0.15
ethylene glycol										
0.10	3.20	0.0140	−0.0173	139.8	0.20	0.0442	0.1261	−0.0340	139.7	0.21
0.20	4.15	−0.0896	0.0165	149.7	0.26	−0.0856	0.3618	0.0316	149.7	0.25
0.30	4.56	−0.1550	0.0330	160.9	0.19	−0.1580	0.4611	0.0564	161.0	0.19
0.40	4.28	−0.1717	0.0290	172.7	0.11	−0.1726	0.4709	0.0477	172.7	0.11
glycerol										
0.10	3.03	0.0459	−0.0104	138.7	0.18	0.0760	0.1043	−0.0217	138.7	0.18
0.20	2.44	0.0841	−0.0218	147.4	0.31	0.1093	0.0153	−0.0383	147.4	0.31
0.30	2.85	0.0739	−0.0284	156.4	0.25	0.1110	0.1196	−0.0504	156.4	0.27
0.40	3.00	0.0592	−0.0230	166.1	0.33	0.0983	0.1860	−0.0420	166.0	0.33

Table 6. Standard Transfer Gibbs Energy ΔG_t^0 for RbCl + Ethylene Glycol + Water and RbCl + Glycerol + Water Systems at 298.15 K

	ΔE^0	ΔG_t^0		ΔE^0	ΔG_t^0
w	mV	$\mathrm{kJ \cdot mol^{-1}}$	w	mV	$\mathrm{kJ \cdot mol^{-1}}$
	Ethylene Glycol			Glycerol	
0.10	139.7	0.82	0.10	138.7	0.67
0.20	149.7	1.71	0.20	147.4	1.40
0.30	161.0	2.74	0.30	156.4	2.15
0.40	172.7	3.80	0.40	166.0	2.95

equation:

$$\Delta G^0{}_t = F(E^0{}_m - E^0{}_w) + 2RT \ln(\rho_w/\rho_m) \qquad (7)$$

where subscripts w and m refer to the water and mixed solvent, respectively. Other symbols have their usual meaning. The values of $\Delta G^0{}_t$ for each system were calculated and listed in Table 6. From Table 6, it can be observed that $\Delta G^0{}_t$ increase with the increase of ethylene glycol or glycerol in the mixture at 298.15 K; the standard Gibbs energies for glycerol + water are less than for ethylene glycol + water. This phenomenon shows that the transference of RbCl from water to the ethylene glycol + water and glycerol + water mixed solvents is not a spontaneous process.

■ CONCLUSION

In the present work, we have studied the mean activity coefficients of RbCl in different ethylene glycol + water and glycerol + water mixed solvents using potentiometric measurements at 298.15 K. Both the extended Debye−Hückel and Pitzer equations could correlate the experimental data well, and the basic thermodynamic data may be useful for further research applications. On the basis of the obtained Pitzer ion−interaction parameters, the osmotic coefficients (Φ) and the standard energy of transference in RbCl + ethylene glycol + water and RbCl + glycerol + water mixtures were also determined.

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