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Measurement of Ion Activity Coefficients in Aqueous Solutions of Mixed Electrolyte with a Common Ion: $NaNO_3 + KNO_3$, $NaCl + KCl$, and $NaBr + NaCl$[†]

Eva Rodil,[‡,§] Alberto Arce,[‡,§] Grazyna Wilczek-Vera,[‖] and Juan H. Vera*,[‡]

Department of Chemical Engineering, McGill University, Montreal, Quebec, Canada H3A 2B2, Department of Chemical Engineering, Universidad de Santiago de Compostela, Santiago de Compostela, Spain, and Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A 2K6

This work reports individual ion activity coefficients in aqueous solutions of mixed 1:1 electrolytes with a common ion for the systems $NaNO_3 + KNO_3$, $NaCl + KCl$, and $NaCl + NaBr$ at 298.15 K. These values were obtained from electrode potential measurements of ion-selective-electrodes (ISEs) of the common ion against an Ag−AgCl single-junction reference electrode filled with 4 $mol \cdot kg^{-1}$ KCl solution saturated with AgCl. For the $NaNO_3 + KNO_3$ and $NaCl + KCl$ systems, experiments were carried out at cation molal fractions of sodium of 0.75, 0.5, and 0.25, and for the $NaCl + NaBr$ system, experiments were carried out at an anion molal fraction of chloride of 0.5. For $NaNO_3 + KNO_3$, single ion activity coefficients were obtained up to 2.4 $mol \cdot kg^{-1}$ total nitrate concentration, and for the $NaCl + KCl$ and $NaCl + NaBr$ systems, up to 4 $mol \cdot kg^{-1}$ of total chloride and sodium concentrations, respectively. The Henderson equation was used to estimate the value of the liquid−junction potential.

Introduction

At very low molalities m_{ik} of an ion i in aqueous solution k, the Debye−Hückel equation[1] can be used to calculate single ion activity coefficients of ion i, $\gamma_{i,k}$. However, in many physiological processes and in seawater or salt lakes, the molality of electrolyte in solution is much higher than the range of applicability of the Debye−Hückel equation. The details of a controversy about the measurability of single ion activity coefficients using ion-selective-electrodes, ISEs, against a single junction reference electrode have been discussed elsewhere.[2,3] The basic question is whether an estimate of the effect of the junction potential existing between the sample solution and the standard solution used in the reference electrode would have a significant effect on the values obtained for the ionic activity coefficients. The authors of this work maintain that both experimental evidence[4−6] and theoretical work[2−4,7] demonstrate that ion-selective-electrodes[8] allow the measurement of ionic activity coefficients. In the references quoted above, it has been demonstrated that using the proper method to reduce the data obtained for the electrode potential largely cancels the effect of the error that could be introduced by a poor estimate of the junction potential. Thus, we maintain that ionic activity coefficient of a ion i, $\gamma_{i,k}$, at a molality $m_{i,k}$ can be obtained from the response of an ISE due to the presence of the individual ion i, up to a molality of about 1.5 $mol \cdot kg^{-1}$. In this nomenclature, the subscript k is used to identify the value of the molality of ion i. The results presented in this work are based in the confidence obtained by the authors from their previous experience in verifying the negligible effect of the junction potential in the final values of ionic activity coefficients.

In the potentiometric convention used in this work,[5] we consider a cell of the type:

Reference Electrode | Reference Solution (*r*) || Sample Solution (*k*) | ISE (*i*)

The electrode potential $E_{i,k}$ of an ISE sensitive to ion i, measured against an Ag−AgCl reference electrode, immersed in the same solution of molality $m_{i,k}$, of ion i, is related to the individual ionic activity coefficient $\gamma_{i,k}$ by[9]

$$E_{i,k} = E_i^0 + S_i \ln(m_{i,k}\gamma_{i,k}) + E_{J,k} \tag{1}$$

where E_i^0 is the standard potential of the ISE; S_i is the slope of the response of the ISE; and $E_{J,k}$ is the potential created by the liquid junction J formed due to the necessary contact between the sample solution and a standard solution flowing out of the reference electrode. This latter term has been usually approximated by the Henderson equation, which in the potentiometric convention for 1:1 electrolytes, using a 4 $mol \cdot L^{-1}$ KCl solution in the reference electrode, takes the form

$$E_{j,k}^{\mathrm{H}} = -59.155\frac{[\sum c_+\lambda_+^\infty - \sum c_-\lambda_-^\infty]_k + 11.6}{[\sum c_+\lambda_+^\infty + \sum c_-\lambda_-^\infty]_k - 623} \log \frac{[\sum c_+\lambda_+^\infty + \sum c_-\lambda_-^\infty]_k}{623} \tag{2}$$

where c_i is the concentration of ion i in moles per liter and λ_i^∞ is the limiting molar ionic conductivity of ion i at infinite dilution. The cations and the anions in the sample solution k are indicated by the subscripts plus and minus, respectively. Values of the limiting conductivities taken from the literature[10] are reported in Table 1. The slope of the response S_i in eq 1 is

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* Corresponding author. Tel.: +1 514 398 4274. Fax: +1 514 398 6678. E-mail address: juan.vera@mcgill.ca.

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[‡] Department of Chemical Engineering, McGill University.

[§] Universidad de Santiago de Compostela.

[‖] Department of Chemistry, McGill University.

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Table 1. Limiting Molar Ionic Conductivity, λ_i^∞, of Ions Used in This Work Taken from Robinson and Stokes[10]

ion	$\lambda_i^\infty/\mathrm{S \cdot cm^2 \cdot mol^{-1}}$
NO_3^-	71.46
Cl^-	76.35
Br^-	78.14
Na^+	50.10
K^+	73.50

positive for cations and negative for anions. In this work, the values of the parameters E_i^0 and S_i, for each ISE in a particular experimental run, were evaluated by a calibration method that helps in canceling error introduced by the estimate of the junction potential.[2,4-6] We report ion activity coefficients in mixed 1:1 electrolytes: $NaNO_3 + KNO_3$, NaCl + KCl, and NaCl + NaBr. Using eqs 1 and 2, ion activity coefficients of the common ion in each system were obtained from electrode potentials of ISEs measured against an Ag−AgCl reference electrode filled with 4 mol·L^{-1} KCl solution saturated with AgCl. The activity coefficients of the other ions were calculated using the values of mean ionic activities available in the literature.[11-13] For the system $NaNO_3 + KNO_3$, we have used the raw electrode potential data previously measured by Mar Marcos-Arroyo. Previous results reported using these data[14] were reduced using the wrong sign for the junction potential. For the systems NaCl + KCl and NaCl + NaBr, new raw data were measured in this work. Thus, the results presented here supersede all previously published values.[14,15]

Experimental Section

Materials. Sodium chloride of 99.5 % purity, potassium chloride of 99.5 % purity, sodium bromide of 99.5 % purity, sodium nitrate of 99.5 % purity, and potassium nitrate of 99.5 % purity were obtained from Sigma-Aldrich, Oakville, ON. All the salts were oven-dried prior to use.

Apparatus and Procedure. A Ross sodium-ion-selective electrode glass body model 84-11, an Accumet chloride-ion-selective electrode polymer body model 13-620-519, an Orion potassium-ion-selective electrode polymer body model 93-19, and an Orion nitrate-ion-selective electrode polymer body model 93-07 were obtained from Fisher Scientific (Montreal). All the measurements were conducted against the single junction Accumet silver chloride reference electrode model 13-620-46 obtained from Fisher Scientific (Montreal), which was filled with 4 mol·L^{-1} KCl solution saturated with AgCl (reference electrode filling solution SP135-500). An Orion pH/ISE meter (MA) model EA 920 with a resolution of ± 0.1 mV was used to monitor the electrode potential measurements with two BNC (Bayonet Neil-Concelman) connectors for ion-selective electrodes and two pin-tip connectors for the reference electrode. The mixtures were prepared by mass using a Mettler AE 240 balance that measured to within ± 0.0001 g.

To condition the electrodes, according to the manufacturer's procedure, the sodium-ion-selective electrode was immersed in 5 mol·L^{-1} NaCl (sodium electrode storage solution, thermo Orion Cat. No 841101) 4 h prior to the measurement; the potassium-ion-selective electrode was immersed in a 0.01 mol·L^{-1} solution of potassium standard 4 h prior to the experiments; and the nitrate-ion-selective electrode was immersed in 0.01 mol·L^{-1} nitrate standard (nitrate standard solution, Thermo Orion Cat. No 930707) 4 h prior to starting the experiments. The single junction reference electrode was filled with fresh internal solution to the level of the fill hole 15 min prior to the measurements.

The measurements were done by measuring the electrode potential of both the anion and the cation ion selective electrodes against a single-junction reference electrode in a glass-jacketed beaker containing approximately 250 mL of solution. All solutions were prepared based on molality, and the water was also weighed. Deionized water with conductivity of less than 1.3 μS·cm^{-1} was used in all the experiments. During the experiments, the solutions were stirred continuously, and temperature was kept constant at (298.2 ± 0.1) K using a thermostatic bath. The readings of the potentiometer were made only when the drift was less than 0.1 mV after 10 min.

The experiments were performed starting with the dilute solution, and solid salt was added to increase the concentration. The large volume of solution (250 mL) and the fact that the experiments at the lower concentration were carried out first decreased the error in molality due to outgoing flow of the internal solution from the reference electrode. Considering that the rate of flow of solution is estimated to be less than 0.07 mL·h^{-1}, the maximum error in molality is estimated to be less than 1 %. For more concentrated solutions, the maximum error in molality is estimated to be less than 0.1 %. Two independent runs of measurements were carried out for each system, and the data collected in each run were reduced independently to obtain ionic activity coefficients. The values reported are the average of the replicates.

Method

To obtain the individual activity coefficients of the common ion in aqueous solutions of the mixed electrolytes under study in this work, we have followed the method described in previous works.[4,5] Activity coefficients of the noncommon ions were calculated from mean ionic activity coefficients of the electrolytes in the mixture by means of the following exact equation

$$\gamma_\pm^2 = \gamma_+ \cdot \gamma_- \tag{3}$$

Mean ionic activity coefficients of the electrolytes in the mixtures were taken from the literature.[11-13] This procedure was applied for data collected at different molal fractions of one of the noncommon ions. The molal fraction of an ion at molality m_i in a mixture of 1:1 electrolyte solution is defined as

$$X_i = \frac{m_i}{\sum m_l} \tag{4}$$

The sum in the denominator runs over all the ions of the same sign in the mixture.

For $NaNO_3 + KNO_3$ and NaCl + KCl systems, sodium cation molal fractions of 0.75, 0.5, and 0.25 have been studied, and for the NaCl + NaBr system, a chloride anion molal fraction of 0.5 was studied. For all systems, activity coefficients of the common ion were measured, i.e., nitrate for the system $NaNO_3 + KNO_3$, chloride for NaCl + KCl, and sodium for NaCl + NaBr. Additional measurements of activity coefficients of nitrate in aqueous solutions of a single electrolyte, $NaNO_3$ or KNO_3, were carried out in this work to have values at cation molal fractions of sodium of 1 and 0 for comparison with the values at other cation molal fractions of sodium. For all mixtures, an attempt was made to measure the activity of the counterions to the common ion using the corresponding ISE. However, only the measurements of the K^+ ISE in the system NaCl + KCl were stable. In all other cases, the ISE potentials were unstable, and no reliable data could be collected. Data for the mean ionic activity coefficients in an aqueous mixture of NaCl + NaBr

Table 2. Activity Coefficients, γ, of Nitrate, Sodium, and Potassium Ions in Aqueous Mixtures of $NaNO_3$ + KNO_3 as a Function of the Total Molality, m, of the Nitrate Ion at Different Cation Molal Fractions of Sodium $X_{Na^+} = m_{Na^+}/(m_{K^+} + m_{Na^+})$

m	$X_{Na^+} = 1$		m	$X_{Na^+} = 3/4$		
$mol \cdot kg^{-1}$	$\gamma_{NO_3^-}$	γ_{Na^+}	$mol \cdot kg^{-1}$	$\gamma_{NO_3^-}$	γ_{Na+}	γ_{K+}
0.0021	0.938	0.942	0.0021	0.948	-	-
0.0032	0.947	0.939	0.0041	0.934	-	-
0.0044	0.936	0.931	0.0061	0.922	-	-
0.0053	0.928	0.936	0.0082	0.906	-	-
0.0064	0.920	0.921	0.0103	0.895	-	-
0.0075	0.906	0.912	0.0343	0.829	-	-
0.0085	0.902	0.903	0.0740	0.774	-	-
0.0105	0.892	0.886	0.1037	0.743	-	-
0.0305	0.836	0.824	0.2023	0.673	-	-
0.0500	0.800	0.804	0.3997	0.584	0.644	0.580
0.0700	0.771	0.791	0.5972	0.528	0.598	0.532
0.0998	0.740	0.778	0.7945	0.486	0.580	0.488
0.1997	0.664	0.758	0.9920	0.447	0.568	0.459
0.2996	0.617	0.740	1.189	0.416	0.557	0.436
0.3993	0.578	0.729	1.387	0.390	0.547	0.416
0.5983	0.528	0.717	1.584	0.367	0.539	0.399
0.7976	0.484	0.710	1.781	0.347	0.530	0.381
0.9968	0.449	0.713	1.979	0.329	0.525	0.364
1.196	0.420	0.712	2.373	0.302	0.511	0.326
1.396	0.397	0.706				
1.595	0.376	0.702				
1.795	0.357	0.704				
1.994	0.342	0.706				
2.493	0.311	0.698				
σ^a	*0.016*	0.018	σ^a	*0.014*	-	-

m	$X_{Na^+} = 1/2$			m	$X_{Na^+} = 1/4$		
$mol \cdot kg^{-1}$	$\gamma_{NO_3^-}$	γ_{Na+}	γ_{K+}	$mol \cdot kg^{-1}$	$\gamma_{NO_3^-}$	γ_{Na+}	γ_{K+}
0.0021	0.945	-	-	0.0022	0.941	-	-
0.0043	0.938	-	-	0.0044	0.938	-	-
0.0064	0.919	-	-	0.0066	0.929	-	-
0.0087	0.905	-	-	0.0087	0.896	-	-
0.0108	0.890	-	-	0.0109	0.889	-	-
0.0308	0.840	-	-	0.0350	0.831	-	-
0.0707	0.781	-	-	0.0750	0.777	-	-
0.1006	0.749	-	-	0.1047	0.746	-	-
0.2013	0.670	-	-	0.2043	0.673	-	-
0.4005	0.582	0.663	0.582	0.4021	0.579	0.684	0.610
0.5980	0.523	0.631	0.538	0.6013	0.515	0.667	0.585
0.7980	0.478	0.617	0.496	0.8003	0.466	0.663	0.548
0.9926	0.443	0.606	0.463	0.9976	0.428	0.663	0.523
1.189	0.412	0.599	0.440	1.196	0.395	0.666	0.507
1.388	0.385	0.596	0.422	1.396	0.365	0.674	0.496
1.590	0.359	0.595	0.407	1.595	0.339	0.683	0.486
1.787	0.338	0.594	0.391	1.794	0.318	0.689	0.473
1.987	0.319	0.593	0.375	1.994	0.297	0.699	0.459
2.384	0.287	0.595	0.342	2.393	0.266	0.716	0.427
σ^a	0.018	-	-	σ^a	0.015	-	-

m	$X_{Na^+} = 0$	
$mol \cdot kg^{-1}$	$\gamma_{NO_3^-}$	γ_{K+}
0.0021	0.938	-
0.0032	0.943	-
0.0042	0.938	-
0.0052	0.944	-
0.0063	0.913	-
0.0074	0.905	-
0.0084	0.900	-
0.0105	0.894	-
0.0306	0.840	-
0.0508	0.804	-
0.0710	0.775	-
0.1012	0.744	-
0.2014	0.658	0.668
0.3016	0.606	0.622
0.4021	0.564	0.589
0.6024	0.500	0.539
0.8030	0.448	0.505
0.9033	0.427	0.493
1.0036	0.404	0.486
1.2041	0.368	0.466
1.4047	0.341	0.446
1.6051	0.316	0.431
1.8057	0.295	0.416
2.0062	0.276	0.401
2.5578	0.236	0.356
σ^a	0.016	-

[a] σ is pooled standard deviation.

are not available in the literature. Thus, for this system, only ion activity coefficients of sodium in the mixture are reported.

For the system $NaNO_3$ + KNO_3, individual activity coefficients of sodium and potassium were calculated with eq 3 using the mean ionic activity coefficients, γ_i, calculated with the equations reported by Harned and Robinson[16]

$$2 \ln \frac{\gamma_{KNO_3}}{\gamma^{\circ}_{KNO_3}} = [2(\phi^{\circ}_{NaNO_3} - \phi^{\circ}_{KNO_3}) + (am + bm^2)]Y_{NaNO_3} + \left[-\frac{1}{2}bm^2\right]Y^2_{NaNO_3} \qquad (5)$$

$$2 \ln \frac{\gamma_{NaNO_3}}{\gamma^{\circ}_{NaNO_3}} = [2(\phi^{\circ}_{KNO_3} - \phi^{\circ}_{NaNO_3}) + (am + bm^2)]Y_{KNO_3} + \left[-\frac{1}{2}bm^2\right]Y^2_{KNO_3} \qquad (6)$$

where Y_l is the molal fraction of the electrolyte; m is the total molality of the electrolyte; and γ°_l and ϕ°_l are, respectively, the mean ionic activity coefficients and the osmotic coefficients of a single electrolyte in aqueous solution at the same total molality of the solution. The values of γ°_l and ϕ°_l used in this work were interpolated from those reported by Robinson and Stokes[10] and Bezboruah et al.,[11] respectively. Parameters a and b of eqs 5 and 6 are -0.0214 $mol^{-1} \cdot kg$ and -0.00338 $mol^{-2} \cdot kg^2$, respectively.[11] The activity coefficients of potassium in aqueous solutions of pure KNO_3 were calculated with eq 3 using mean activity coefficient values of KNO_3 compiled by Zaytsev and Aseyev.[17]

The mean ionic activity coefficients of KCl and NaCl in aqueous solution of NaCl + KCl were calculated using the equations reported by Robinson[13]

$$\log \gamma_{KCl} = \log \gamma^{\circ}_{KCl} - \alpha_{KCl} m_{NaCl} - \beta_{KCl} m^2_{NaCl} \qquad (7)$$

$$\log \gamma_{NaCl} = \log \gamma^{\circ}_{NaCl} - \alpha_{NaCl} m_{KCl} - \beta_{NaCl} m^2_{KCl} \qquad (8)$$

where γ°_l stands for the mean ionic activity coefficient of the electrolyte l in an aqueous solution. In this work, mean ionic activity coefficient values were interpolated from those reported by Robinson and Stokes.[10] In eqs 7 and 8, m_l is the molality of the electrolyte and α_l ($mol^{-1} \cdot kg$) are parameters dependent on the total molality. Their variations with molality are reported by Robinson.[13] The parameters β_{KCl} and β_{NaCl} were fixed by Robinson at 0 $mol^{-2} \cdot kg^2$ and -0.0005 $mol^{-2} \cdot kg^2$, respectively.[13] In all cases, the liquid-junction potential was estimated using the Henderson equation in the potentiometric convention form.

All raw data measured in this work have been filed with ACS as Supporting Information. Pooled standard deviations, σ, for each system are reported at the foot of each column of the tables presenting the results obtained in this work.

Results and Discussion

Individual activity coefficients of nitrate at different total molalities of nitrate, for cation molal fractions of sodium of 1, 0.75, 0.5, 0.25, and 0, in aqueous mixtures of $NaNO_3$ + KNO_3, were calculated from potentials of a nitrate ISE measured against a reference electrode following the method previously described. These values are reported in Table 2 along with individual activity coefficients of sodium and potassium calculated from mean ionic activity coefficients of $NaNO_3$ and KNO_3 obtained using eqs 3, 5, and 6. For all cation molal fractions of sodium, the activity coefficients of sodium are larger than those of nitrate

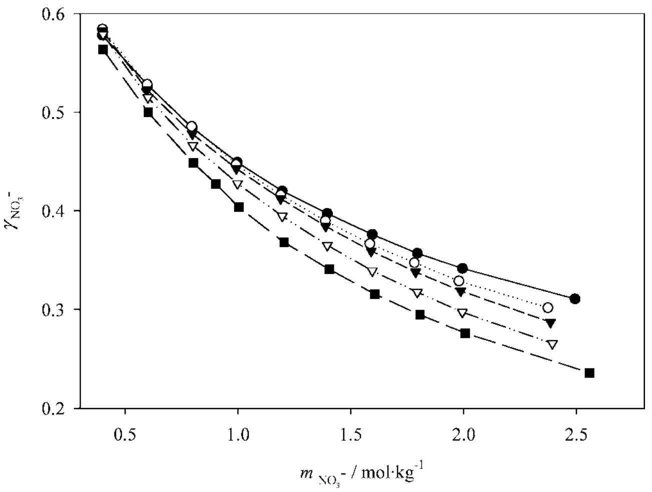

Figure 1. Variation of activity coefficients, γ, of nitrate in solutions of $NaNO_3$ + KNO_3 with total nitrate molality, m, at different cation molal fractions of sodium: —●—, $X_{Na^+} = 1$; ···○···, $X_{Na^+} = 3/4$; - -▼- -, $X_{Na^+} = 1/2$; —··—▽—··—, $X_{Na^+} = 1/4$; - -■- -, $X_{Na^+} = 0$.

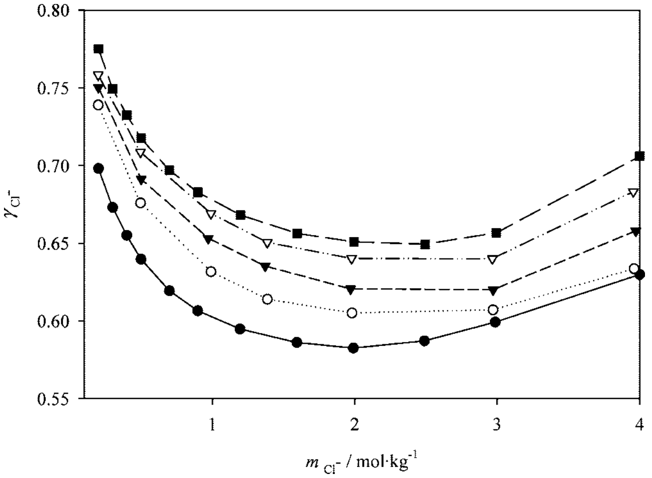

Figure 2. Variation of activity coefficients, γ, of chloride in solutions of NaCl + KCl with total chloride molality, m, at different cation molal fractions of sodium: —●—, $X_{Na^+} = 1$; ···○···, $X_{Na^+} = 3/4$; - -▼- -, $X_{Na^+} = 1/2$; —··—▽—··—, $X_{Na^+} = 1/4$; - -■- -, $X_{Na^+} = 0$.

and potassium. Between nitrate and potassium, the differences are smaller except at a cation molal fraction of 0.25 of sodium. All activity coefficients of nitrate at cation molal fractions of sodium of 0.75, 0.5, and 0.25 lie between those of nitrate in pure $NaNO_3$ and KNO_3, as expected. This comparison is clearly shown in Figure 1. Marcos-Arroyo et al.[14] also reported activity coefficients of individual ions in these mixtures at cation molal fractions of sodium of 0.66 and 0.33; however, these values correspond to cation molal fractions of 0.75 and 0.25, respectively, with an error in the sign of the liquid-junction potential.[5]

In Table 3, experimental individual activity coefficients of chloride and potassium ions in aqueous solutions of NaCl + KCl as a function of the total molality of chloride are reported. The experimental values of the individual activity coefficients of the potassium ion are indicated with an asterisk at the heading of the column. Table 3 also includes the activity coefficients of the sodium and potassium ions calculated with eqs 3, 7, and 8. The differences between the activity coefficients of potassium calculated from experimental ISE potentials and the coefficients calculated from mean ionic activity coefficients of KCl in mixtures of NaCl + KCl are about ± 0.01 for a cation molal fraction of sodium of 0.25. These differences increase with the cation molal fraction of sodium, being about ± 0.05 at the highest cation molal fraction of sodium. Khoshkbarchi et al.[15] reported activity coefficients of individual ions in these mixtures at 0.66, 0.5, and 0.33 cation molal fractions of sodium; however, these values were also calculated with the wrong sign for the liquid-junction potential.[5]

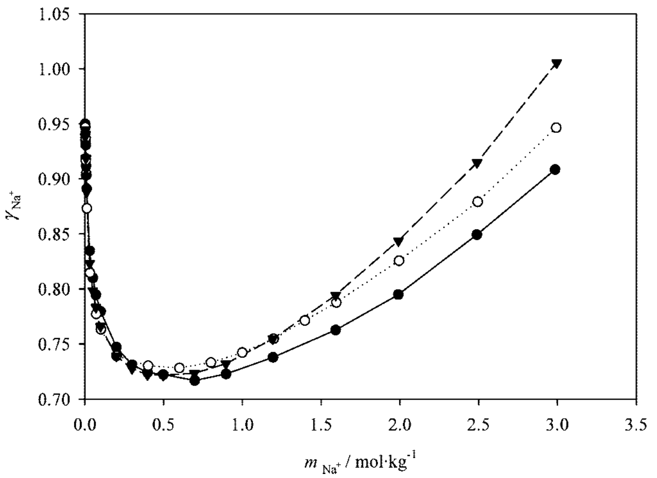

Figure 3. Variation of activity coefficients, γ, of sodium in solutions of NaCl + NaBr with total sodium molality, m, at different anion molal fractions of chloride: —●—, $X_{Cl^-} = 1$; ···○···, $X_{Cl^-} = 1/2$; - -▼- -, $X_{Cl^-} = 0$.

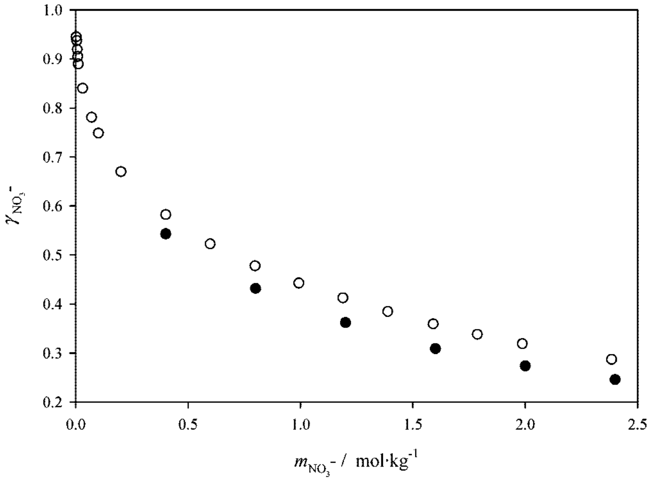

Figure 4. Activity coefficients of the nitrate ion in NaCl + KCl mixtures, at a sodium cation molal fraction of 0.5, as a function of the total nitrate molality: full symbols are the values calculated with the wrong sign for the junction potential and previously reported in the literature;[14] open symbols are the values calculated in this work from the same raw data using the correct sign for the junction potential.

Table 4 presents the individual activity coefficients of the sodium ion in aqueous solutions of NaBr + NaCl at 0.5 anion molal fraction of chloride as a function of the total molality of sodium.

Figure 2 shows the variation of chloride activity coefficients with the total molality of chloride in aqueous solutions of NaCl + KCl for different cation molal fractions of sodium. The activity coefficients of chloride in aqueous solutions of pure NaCl, and of pure KCl, obtained from a previous work[6] are included in Figure 2 for comparison. As can be seen, activity coefficients of chloride at cation molal fractions of sodium of 0.75, 0.5, and 0.25 are between those at 1 and 0 as expected, with all the plots showing a minimum near a chloride molality of 2 mol·kg^{-1}.

Table 3. Activity Coefficients, γ, of Chloride, Sodium, and Potassium Ions in Aqueous Mixtures of NaCl + KCl as a Function of the Total Molality, m, of the Chloride Ion at Different Cation Molal Fractions of Sodium $X_{Na^+}[m_{Na^+}/(m_{K^+} + m_{Na^+})]$

m	$X_{Na^+} = 3/4$				m	$X_{Na^+} = 1/2$			
mol·kg^{-1}	γ_{Cl-}	γ_{Na+}	γ_{K+}	$\gamma_{K+}{}^{b}$	mol·kg^{-1}	γ_{Cl-}	γ_{Na+}	γ_{K+}	$\gamma_{K+}{}^{b}$
0.0040	0.929	-	-	0.933	0.0041	0.933	-	-	0.934
0.0080	0.913	-	-	0.908	0.0089	0.901	-	-	0.902
0.0120	0.893	-	-	0.887	0.0119	0.890	-	-	0.889
0.0159	0.872	-	-	0.879	0.0158	0.879	-	-	0.880
0.1980	0.739	0.700	0.742	0.691	0.1998	0.750	0.685	0.727	0.722
0.4949	0.676	0.673	0.679	0.626	0.5001	0.691	0.647	0.657	0.646
0.9897	0.632	0.676	0.623	0.567	0.9705	0.653	0.637	0.599	0.584
1.386	0.614	0.692	0.597	0.544	1.370	0.635	0.645	0.570	0.547
1.980	0.605	0.728	0.569	0.513	1.970	0.621	0.674	0.544	0.519
2.970	0.607	0.825	0.555	0.487	2.971	0.620	0.748	0.528	0.492
3.961	0.634	0.950	0.567	0.474	3.972	0.658	0.825	0.525	0.476
σ^{a}	*0.008*	-	-	0.013	σ^{a}	0.014	-	-	0.02

m	$X_{Na^+} = 1/4$			
mol·kg^{-1}	γ_{Cl-}	γ_{Na+}	γ_{K+}	$\gamma_{K+}{}^{b}$
0.0040	0.935	-	-	0.934
0.0080	0.904	-	-	0.908
0.0121	0.889	-	-	0.886
0.0164	0.878	-	-	0.878
0.1978	0.758	0.675	0.719	0.736
0.4946	0.709	0.624	0.638	0.657
0.9895	0.669	0.605	0.576	0.585
1.385	0.651	0.608	0.548	0.547
1.977	0.640	0.622	0.518	0.513
2.966	0.640	0.673	0.497	0.480
3.955	0.683	0.716	0.484	0.460
σ^{a}	0.005	-	-	0.013

[a] σ is pooled standard deviation. [b] Experimental data obtained from stable measurements of the potential of a K^+ ISE.

Table 4. Activity Coefficients, γ, of the Sodium Ion in Aqueous Mixtures of NaBr + NaCl as a Function of the Total Molality, m, of Sodium at an Anion Molal Fraction of Chloride $X_{Cl^-} = [m_{Cl^-}/(m_{Br^-} + m_{Cl^-})] = 1/2$

m/mol·kg^{-1}	γ_{Na+}
0.0021	0.947
0.0042	0.937
0.0062	0.917
0.0083	0.905
0.0124	0.873
0.0322	0.815
0.0720	0.777
0.1018	0.763
0.2016	0.739
0.4011	0.73
0.6003	0.728
0.7995	0.733
0.9991	0.742
1.198	0.755
1.397	0.771
1.596	0.788
1.995	0.826
2.493	0.879
2.992	0.946
3.990	1.108
σ^{a}	0.01

[a] σ is pooled standard deviation.

The variation of the activity coefficients of sodium in aqueous mixtures of NaCl + NaBr with the total molality of sodium at anion molal fraction of chloride of 0.5 is shown in Figure 3. These coefficients are compared with those at cation molal fractions of sodium of 1 and 0 previously published.[6] The differences at different anion molal fraction of chloride are small at low and moderate sodium molality and increase at higher molalities. All plots show a minimum for the activity coefficient of the sodium ion near a sodium molality of 0.5 mol·kg^{-1}.

Figure 4 compares the activity coefficient of the nitrate ion in $NaNO_3$ + KNO_3 mixtures, as a function of the total nitrate molality for a cation molal fraction of sodium of 0.5, measured in this work with the values previously reported in the literature.[14] In this case, both results were generated from the same experimental measurements collected by Mar Marcos-Arroyo. The difference between both results is due only to the fact that the data from the literature[14] was reduced using the wrong sign in eq 2 employed to estimate the junction potential. Notably, this result confirms that an error of sign for the junction potential has a very small effect on the resulting values of the activity coefficients of the ions due to the method used for the calibration of the ISEs in each experimental run.[4,5]

Conclusions

Activity coefficients of the common ion in aqueous solutions of mixed 1:1 electrolytes of $NaNO_3$ + KNO_3, NaCl + KCl, and NaCl + NaBr were studied for different molal fractions of the counterion. Experimental electrode potentials of ion selective electrodes for the common ion were measured at 298.15 K against an Ag−AgCl reference electrode filled with a 4 mol·L^{-1} KCl solution, saturated with AgCl. Activity coefficients of the counterions were calculated from published mean ionic activity coefficients of the electrolytes in these mixtures. Although for all systems an attempt was made to measure the activity of the counterions to the common ion, with the exception of the measurements of the K^+ ISE in the system NaCl + KCl, it was not possible to get a stable response of the ISE. This fact is clearly due to interference between ions of the same sign. Due to the very special nature of the potassium ISE used in this work, it was feasible to get independent information for the activity coefficient of the potassium ion in the NaCl + KCl system. Thus, it was possible to compare these values with those calculated using experimental information for the chloride ion and for the mean ionic activity coefficient of KCl in NaCl + KCl mixtures. The comparison shown in Table 3 is rewarding, as it shows good agreement between the values at low sodium cation molal fraction. The differences increase as the cation molal fraction of sodium increases clearly indicating an interference of the sodium ion with the response of the potassium ISE, exactly as expected. We believe that the more reliable values for the activity coefficients of potassium are those obtained from the independent measurements for the nitrate ion and the mean ionic activity coefficient for KCl. These values are obtained using two pieces of information obtained from measurements that are free from interferences.

Previous studies[4,5] had shown that the values of the activity coefficients of individual ions obtained from the measurements of potentials of ISEs against reference electrodes are quite insensitive to the estimated values for the junction potential. As discussed elsewhere,[4−7] this is a result of the method used to calibrate the ISEs before each individual run of measurements. Perhaps one of the most interesting implications of this study is that, as shown in Figure 4, the same conclusion is valid for the measurement of individual ionic activity coefficients in electrolyte mixtures.

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Supporting Information Available:

Raw data measured in this work have been filed with the ACS. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Pitzer, K. S. *Thermodynamics*, 3rd ed.; McGraw-Hill: New York, 1995; p 316.

(2) Wilczek-Vera, G.; Rodil, E.; Vera, J. H. A complete discussion of the rationale supporting the experimental determination of individual ionic activities. *Fluid Phase Equilib.* **2006**, *244*, 33–45.

(3) Wilczek-Vera, G.; Vera, J. H. On the measurement of individual ion activities. *Fluid Phase Equilib.* **2005**, *236*, 96–110.

(4) Arce, A.; Wilczek-Vera, G.; Vera, J. H. Activities of aqueous Na+ and Cl- ions from homoionic measurements with null junction potentials at different concentrations. *Chem. Eng. Sci.* **2007**, *62*, 3849–3857.

(5) Wilczek-Vera, G.; Rodil, E.; Vera, J. H. On the activity of ions and the junction potential: Revised values for all data. *AIChE J.* **2004**, *50*, 445–462.

(6) Wilczek-Vera, G.; Rodil, E.; Vera, J. H. Towards accurate values of individual ion activities - Additional data for NaCl, NaBr and KCl, and new data for NH4Cl. *Fluid Phase Equilib.* **2006**, *241*, 59–69.

(7) Rodil, E.; Vera, J. H. Erratum to "The activity of ions: analysis of the theory and data for aqueous solutions of MgBr2, CaBr2 and BaBr2 at 298.2 K": [Fluid Phase Equilibria **2003**, *205*, 115−132]. *Fluid Phase Equilib.* **2003**, *211*, 289.

(8) Eisenman, G. *Glass electrodes for hydrogen and other cations*; Dekker: New York, 1967.

(9) Khoshkbarchi, M. K.; Vera, J. H. Measurement and correlation of ion activity in aqueous single electrolyte solutions. *AIChE J.* **1996**, *42*, 249–258.

(10) Robinson, R. A.; Stokes, R. H. *Electrolyte solutions*; Butterworths: London, 1959.

(11) Bezboruah, C. P.; Covington, A. K.; Robinson, R. A. Excess Gibbs energies of aqueous mixtures of alkali metal chlorides and nitrates. *J. Chem. Thermodyn.* **1970**, *2*, 431–437.

(12) Dinane, A.; Guendouzi, M. E.; Mounir, A. Hygrometric determination of water activities, osmotic and activity coefficients of (NaCl + KCl)(aq) at $T = 298.15$ K. *J. Chem. Thermodyn.* **2002**, *34*, 423–441.

(13) Robinson, R. A. Activity Coefficients of Sodium Chloride and Potassium Chloride in Mixed Aqueous Solutions at 25 Degree. *J. Phys. Chem.* **1961**, *65*, 662–667.

(14) Marcos-Arroyo, M. D. M.; Khoshkbarchi, M. K.; Vera, J. H. Activity coefficients of sodium, potassium, and nitrate ions in aqueous solutions of NaNO3, KNO3, and NaNO3+KNO3 at 25 degrees C. *J. Solution Chem.* **1996**, *25*, 983–1000.

(15) Khoshkbarchi, M. K.; Vera, J. H. Measurement and correlation of ion activity coefficients in aqueous solutions of mixed electrolyte with a common ion. *Fluid Phase Equilib.* **1996**, *121*, 253–265.

(16) Harned, H. S.; Robinson, R. A. *Multicomponent Electrolyte Solutions*; Pergamon Press: Oxford, 1968.

(17) Zaytsev, I. D.; Aseyev, G. G. *Properties of Aqueous Solutions of Electrolytes*; CRC Press: Boca Raton, FL, 1992.

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