Mean Activity Coefficients in the Ternary $NaCl-NaNO_3-H_2O$ and $NaBr-NaNO_3-H_2O$ Systems at 298.15 K

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The mean activity coefficients of NaCl in the $NaCl-NaNO_3-H_2O$ system and NaBr in the $NaBr-NaNO_3-H_2O$ system have been measured at 298.15 K over the range of ionic strengths from 0.3 to 6 *m*. The measurements were made by an electrochemical cell using ion-selective electrodes (ISE). The data were collected with an Orion millivolt (mV) meter, Model EA 920, using Na-ISE against Cl-ISE and Br-ISE as reference electrodes. The experimental mean activity coefficients of NaCl and NaBr obey Harned's Rule. The mean activity coefficients of $NaNO_3$ were calculated by using the Gibbs-Duhem equation.

Introduction

Aqueous electrolyte solutions play an important role in chemical, biological, and environmental systems. Experimental thermodynamic studies of single-salt aqueous solutions involve measurements of mean activity coefficients of the electrolytes and the osmotic coefficient of the solvent. However, most of the experimental data collected on ternary systems refer only to activity or osmotic pressure of the solvent. Individual measurements of the mean activity coefficients of salts are rarely reported. Generally two methods are widely used to measure the activity coefficients of nonvolatile electrolytes in solution. These are solvent activity methods and electrochemical cell techniques. In solvent activity methods, one first calculates the activity coefficient of the solvent by measuring the equilibrium pressure of the pure solvent vapor phase over the binary mixture and then uses the Gibbs-Duhem equation to calculate the mean ionic activity coefficient of the electrolyte. One of the traditional solvent activity methods is the isopiestic method. The mean ionic activity coefficients of several hundred single-salt aqueous solutions and their free energies of mixing have been determined by means of the isopiestic method (*1-4*). This technique suffers from two main drawbacks. The attainment of equilibrium needs a great deal of skill, and it can take several days to obtain reliable data. Another disadvantage is that this technique is cumbersome to use for multicomponent electrolyte solutions. McKay and Perring (*5*) have proposed an isopiestic method for multicomponent mixtures. Even when reliable data are obtained for the osmotic coefficient of the solvent, the mean ionic activity coefficients of the individual salts cannot be obtained easily.

The electrochemical methods allow a direct calculation of the activity of an electrolyte by measurement of the electrochemical potential of ions in an electrochemical cell. In contrast to vapor pressure measurements, this technique is very useful for the measurement of the chemical potential or activity of electrolytes in very dilute binary electrolyte mixtures. Many experimental data for binary aqueous electrolyte solutions have been measured with this method (*4*, *6*, *7*). This technique can be adapted for multicomponent solutions provided that each electrode is selective only to one specific ion. Mean ionic activity coefficients for some ternary systems have been reported in the literature (*2*, *8-15*). However, due to limitations of the application of ion-selective electrodes (ISE) to multicomponent mixtures, experimental measurements reported for ternary aqueous electrolyte solutions are not as many as those for binary systems.

The study reported in this paper was undertaken to provide thermodynamic mean activity coefficient data for the $NaCl-NaNO_3-H_2O$ and $NaBr-NaNO_3-H_2O$ systems at various ionic strengths and 298.15 K. The first system, previously measured by Lanier (*12*), was selected so as to be able to standardize the experimental procedure and to verify the reproducibility of the data. The second system was measured because it provides a useful complement to the previous one, and, to the best of our knowledge, no experimental data for the mean activity coefficient have been reported for it.

Apparatus, Chemicals, and Procedure

The main features of the apparatus that was designed and constructed to carry out electromotive force (emf) measurements are a thermostatic cell, ion-selective electrodes, reference electrodes, a thermostatic bath, a mV meter, a temperature probe, and magnetic stirrer. Figure 1 shows a schematic diagram of the experimental system. The thermostatic cell consists of a vertical aluminum cylindrical vessel. The top lid has a circular hole to allow the insertion of an approximately 500-mL sample beaker. The beaker is sealed in position by a metal flange, cushioned by a rubber ring, and held in place by three screws. The electrodes and the temperature probe are inserted through a rubber stopper into the beaker. The solution is agitated by a magnetic stirrer. The temperature of the thermostatic cell is controlled by water from a thermostatic bath, which circulates in the concentric chamber between the beaker and the aluminum cylinder. The temperature of water in the thermostatic bath is stabilized by using an additional cooling bath with an immersed cooling coil. The temperature of the sample solution is held at 298.15 ± 0.1 K.

To monitor the potential of the ions, an Orion PH/ISE meter Model EA 920 was used. This model has a large, easy-to-read, custom LCD (liquid crystal display). It has two inputs with BNC (Bayonet Neil-Concelman) connectors for the indicator ISE's and two inputs with pin-tip connectors for reference electrodes. Since we wanted to use an ISE as a reference electrode, a BNC-pin-tip adapter was connected to the reference ISE and inserted into the pin-tip reference input. For measurements of potential of the ions, the following four Orion ISE's were used: (1) Ross sodium glass ISE (Model 84-11), (2) bromide solid-state ISE (Model 94-35), (3) chloride solid-state ISE (Model 94-17B), and (4) nitrate ion-exchange ISE (Model 93-07).

The temperature of the sample was monitored by an Orion automatic temperature compensation (ATC) probe (Model 917001). This probe transmits a signal to the mV meter, which automatically corrects pH and mV measurements for variation in the electrode slope due to temperature changes.

The following reagent grade salts were used without further purification: (1) sodium bromide, NaBr (Anachemia, AC-8272), (2) sodium chloride, NaCl (Anachemia, AC-8304), and (3) sodium nitrate, $NaNO_3$ (A & C, 5337). A purification water unit was used to prepare very high quality deionized water. First, tap water was passed through an absorber column to provide

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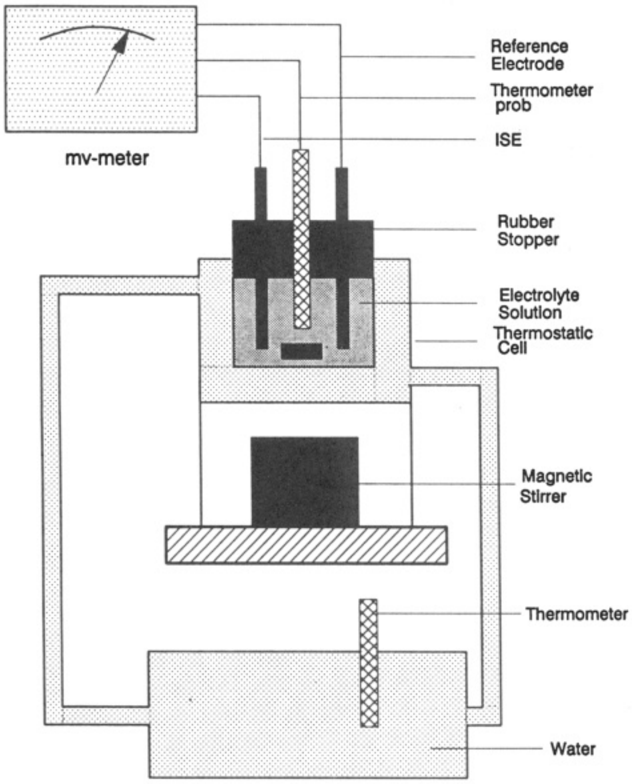

Figure 1. Schematic view of the experimental apparatus.

water free of most organic materials and then through two ion-exchange columns to remove all ionized minerals down to a level of 4 ppb or less. Finally water was passed through a distillation unit to get very high quality pure water. The stock solution of binary aqueous solutions of the salts were prepared initially for the total ionic strengths of the experimental run. The solutions were prepared by weighing the salts and then dissolving them in the required amount of pure deionized distilled water.

Harned's Rule

Harned's rule is a linear model that has been widely used for the interpretation of changes of mean ionic activity coefficients of electrolytes in ternary aqueous solutions. For a ternary mixture of water, electrolyte 1 and electrolyte 2 with a constant total ionic strength I ($I = I_1 + I_2$) and a varying ionic strength of salt 2, i.e., I_2, it was empirically found that, in many cases, the logarithm of the mean activity coefficient of salt 1, $\ln \gamma_{\pm 1}$, varied linearly with I_2 or with I_2/I (*2, 4, 7*) and then

$$\ln \gamma_{\pm 1} = \ln \gamma^{\circ}_{\pm 1} - \alpha'_{12} I_2 \tag{1}$$

where $\gamma^{\circ}_{\pm 1}$ is the mean ionic activity coefficient of a pure electrolyte 1 in an aqueous solution at the same total ionic strength of the mixture, i.e., I. The coefficient α'_{12} is an empirical coefficient that is called Harned's coefficient of salt 1, and it may be a function of the total ionic strength I. The ionic strength of a salt is defined as (*7*)

$$I = \frac{1}{2}\sum_j m_j Z_j^2$$

where m_j and Z_j are the molality and the charge number of ion j, respectively. The original Harned's rule used base 10 logarithm, i.e., $\alpha'_{12} = (\ln 10)\alpha_{12}$, where α_{12} is the value reported for Harned's coefficient in the literature. When the ionic strength of electrolyte 1 approaches zero, i.e., $I_1 = 0$, the trace activity coefficient of electrolyte 1 in the ternary mixture is obtained. Thus, with substitution of $I_2 = I$ in eq 1, the trace activity coefficient of salt 1 can be written as

$$\ln \gamma^{\mathrm{tr}}_{\pm 1} = \ln \gamma^{\circ}_{\pm 1} - \alpha'_{12} I \tag{2}$$

Trace activity coefficients are very important in electrolyte solutions because they facilitate a more detailed comparison of the effect of one electrolyte on the other in the mixture. Equations similar to eqs 1 and 2 can also be written for electrolyte 2. By substituting eq 2 in eq 1, we can obtain another useful equation as

$$\ln \gamma_{\pm 1} = \ln \gamma^{\mathrm{tr}}_{\pm 1} + \alpha'_{12} I_1 \tag{3}$$

Equation 3 is useful for the calculation of mean ionic activity coefficients of salts in terms of their own ionic strength. This makes it possible to compare these values with those of the mean activity coefficient of the electrolyte in a binary aqueous mixture at the same ionic strength of the ternary system. Clearly when I_1 tends to zero, in a ternary mixture, the trace activity coefficient of electrolyte 1 is obtained.

Calibration of ISE's in Binary Solutions

Before the ISE's are used in ternary systems, they should be calibrated in the binary solutions and the slope of the electrode's response should be experimentally determined. Some researchers (*9, 12*) have assumed that the ISE's have Nernstian behavior, and they have used the Nernstian slope in their calculations. Although this method saves time, it introduces unnecessary errors, so in our calculations we have used the slopes that we determined by regression analysis of the experimental values of emf measurements in binary solutions. Moreover, the selectivity coefficient of ISE's should be determined if any of the other ions in the solution interfere with the electrode of interest. According to Nikolsky (*16–18*), the potential of an ISE can be expressed by the following equation:

$$E = E' \pm \frac{S}{Z_i} \ln (a_i + K_{ij} a_j^{Z_i/Z_j}) \tag{4}$$

where a_i and a_j are the activities of ion i and j, respectively, and K_{ij} is the potentiometric selectivity coefficient of ISE selective to ion i toward ion j as an interfering ion. The constant E' is the electromotive force (emf) of the measuring circuit of ISE; it depends on the activity of the ions in the inner solution and on the type of internal reference electrode of the ISE. The slope of the electrode is shown by S.

The ISE's were calibrated in three aqueous solutions of NaBr, $NaNO_3$, and NaCl. We will only describe in detail the calibration of the sodium and bromide ISE's in NaBr aqueous solution and the results for the other ISE's will then be presented. The following cell was set up to calibrate the sodium and bromide electrodes.

detector electrode	binary solution	ref electrode
Na–ISE	$NaBr–H_2O$	Br–ISE
Br–ISE		single-junction electrode (SJE)

In calibrations of the ISE's we always used an ISE as a reference electrode. As indicated by Kakabadse (*19*), "An elegant way of overcoming liquid-junction potential is to use one ion-selective electrode as a reference electrode for another." However in all measurements we also used a single and sometimes a double junction reference electrode in order to check the accuracy of the data. The calibration was started with a concentrated binary solution, and after the system reached equilibrium and the potential was measured, the solution was diluted by adding pure deionized water. When a single-junction reference electrode is used, using the Nikolsky equation, the cell equations for ISE's can be written as

$$E^{\circ}_{S}(\mathrm{Na}^+) = E'_{S}(\mathrm{Na}^+) + S_1 \ln a(\mathrm{Na}^+) \tag{5}$$

$$E^{\circ}_{S}(\mathrm{Br}^-) = E'_{S}(\mathrm{Br}^-) - S_2 \ln a(\mathrm{Br}^-) \tag{6}$$

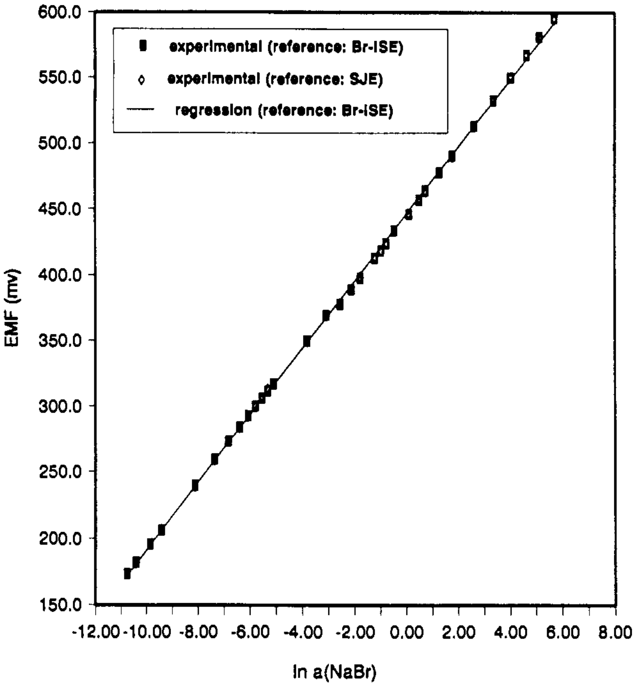

Figure 2. Calibration of Na-ISE toward Br-ISE and a single-junction reference electrode in aqueous solution of NaBr at 298.2 K. Note that points ■ and ◇ coincide in each and every case.

Then, assuming $S_1 \simeq S_2 \simeq (S_1 + S_2)/2$, subtracting the above equations, and expressing the activity of ions in terms of the mean activity coefficient of NaBr lead to (*6*)

$$E°_S(\mathrm{NaBr}) = E'_S(\mathrm{NaBr}) + \left(\frac{S_1 + S_2}{2}\right) \ln\, [m°(\mathrm{NaBr})\ \gamma°_\pm(\mathrm{NaBr})]^2 \quad (7)$$

where

$$E'_S(\mathrm{NaBr}) = E'_S(\mathrm{Na^+}) - E'_S(\mathrm{Br^-})$$

In the above equations S_1 and S_2 are the slopes of the Na-ISE and the Br-ISE against the single-junction electrode, respectively, and $m°(\mathrm{NaBr})$ and $\gamma°_\pm(\mathrm{NaBr})$ are the molality and mean ionic activity coefficient of NaBr in the binary solution.

Alternatively if we write the cell equation when the bromide ISE is used as a reference electrode, the result is

$$E°(\mathrm{NaBr}) = E'(\mathrm{NaBr}) + S \ln\, [m°(\mathrm{NaBr})\ \gamma°_\pm(\mathrm{NaBr})]^2 \quad (8)$$

As can be seen from the comparison of eqs 7 and 8, the same form of calibration equation for the sodium ISE is obtained when we use a single-junction reference electrode or when we use a bromide ISE as a reference electrode. The terms $E'(\mathrm{NaBr})$ and $E'_S(\mathrm{NaBr})$ correspond to the same cell constant. The terms S and $(S_1 + S_2)/2$ are the slope of the sodium ISE when we use the bromide electrode or the single-junction electrode as a reference electrode, respectively, and they should be the same (*6*). As an example Figure 2 shows the calibration of the Na-ISE when the Br-ISE and the single-junction electrode were used as reference electrodes. Within the experimental error, the results are equivalent and the points of the two calibrations are superimposed one over the other. We can also write the same form of the calibration equation for the case when a double-junction reference electrode is used. The calibrations using an ISE as a reference electrode are preferred because they eliminate the effect of liquid-junction potentials. Similar results were obtained for the other ISE's and are not reported in detail here. The activity of the NaBr and of the other salts in the binary salt-water solutions were calculated by the use of the mean activity coefficients of the respective salts from the tabulations of Hamer and Wu (*20*).

A similar setup of cells was prepared for the other binary solutions of interest, and calibration curves were obtained in the same manner. All of the calibration parameters were evaluated by linear regression analysis of the experimental points. Figures 3 and 4 show the calibration lines of the sodium ISE against chloride and nitrate ISE's. As is evident from the figures, the responses of sodium ISE in binary aqueous solutions of NaBr, NaCl, and $NaNO_3$ are straight lines. The cell constants and slope of sodium ISE in the various binaries are shown in Table

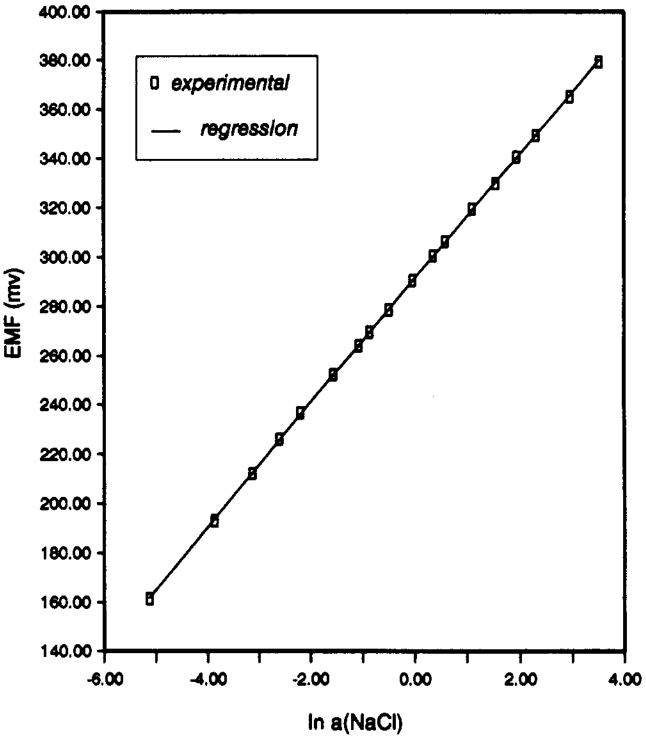

Figure 3. Calibration of Na-ISE toward Cl-ISE in an aqueous solution of NaCl at 298.2 K.

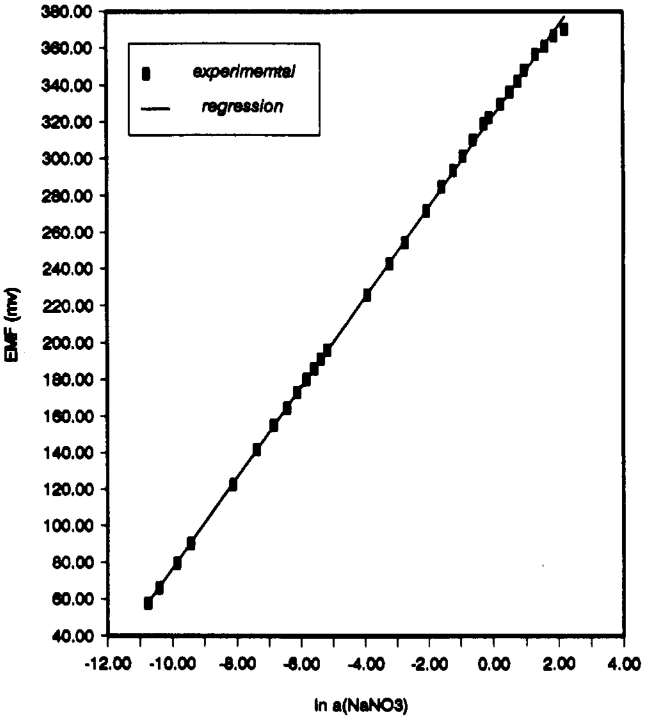

Figure 4. Calibration of Na-ISE toward NO_3-ISE in an aqueous solution of $NaNO_3$ at 298.2 K.

Table I. Slopes and Electrochemical Constants of the Various ISE's in Different Binary Aqueous Solutions at 298.15 K[a]

ISE	ref electrode (ISE)	binary solution	max molality	E', mV	S	correlation coeff × 100%
Na^+	Br^-	NaBr	9.0	445.91	25.48	99.97
Na^+	NO_3^-	$NaNO_3$	8.0	307.88	24.52	99.82
Na^+	Cl^-	NaCl	6.0	291.12	25.21	99.99

[a] $E = E' + S \ln a$, a = activity.

I. The theoretical value of S at 298.15 K is 25.69 mV. This is the slope of an ISE in the case of Nernstian behavior when the natural logarithm is used for the activity of the ions. As is evident from Table I, the slope of Na-ISE toward NO_3-ISE as a reference electrode is sub-Nernstian; however the other slopes of Na-ISE toward Br-ISE and Cl-ISE within the accuracy of our experiments are almost Nernstian.

Measurements for Ternary Systems

For each of the $NaCl$-$NaNO_3$-H_2O and $NaBr$-$NaNO_3$-H_2O systems, an emf cell was arranged. For instance, for the aqueous solution of NaBr and $NaNO_3$, the following cell was set up:

detector electrode	ternary solution	ref electrode
Na-ISE	NaBr (I_1) $NaNO_3$ (I_2)	Br-ISE

The potential of a Na-ISE toward a Br-ISE was measured at different values of the molalities of the salts with constant total ionic strength ($I = I_1 + I_2$) of the solution. In calculations of the mean ionic activity coefficients, the measurements were obtained by using the Br-ISE as a reference electrode. The experimental procedure was as follows. A 200-mL binary solution of NaBr of total ionic strength I was placed in the beaker. The sodium and the bromide ISE's were immersed in the solution. The temperature probe and the pH electrode were also placed in the mixture to check the temperature and the variation of the pH of the solution. All the electrodes were allowed to stay in binary NaBr mixture for 1 h so that the stability of the potentials to within ±0.1 mV could be ascertained. The potential of Na-ISE toward Br-ISE was monitored for binary solutions of NaBr at a given ionic strength I. With use of the Nikolsky equation, with $K_{ij} = 0$, the emf of the Na-ISE toward the Br-ISE as a reference electrode for the binary NaBr solution can be written as

$$E^\circ(\mathrm{NaBr}) = E'(\mathrm{NaBr}) + S \ln\,[I\gamma^\circ_\pm(\mathrm{NaBr})]^2 \qquad (9)$$

where $\gamma^\circ_\pm$(NaBr) is the mean activity coefficient of NaBr in the binary aqueous solution at the same ionic strength of the ternary system and S is 25.47 mV, as obtained by the calibration described in the previous section.

After measurements in the binary NaBr solution, $NaNO_3$ solution of a similar ionic strength I was added. In principle, when two binary aqeuous solutions of the same ionic strength are mixed, the total ionic strength of the ternary mixture will be the same as the ionic strength of the binaries. A titration technique was used to alter the composition of the mixture. This method allows one to minimize errors arising from sudden shifts in potential that are unrelated to changes in solution composition. Thus the cell was not disturbed during a series of measurements, and the electrodes were always in place during the measurements. Due to the limitations in the volume of the beaker, two sets of potential measurements were made. In the first set, the experimental measurements were carried out by starting with NaBr solution and using $NaNO_3$ as titrant, and, in the second set, the order was reversed. In the central region of composition, the two runs overlap. This is used as a test for reproducibility of the data. The two half-curves must overlap smoothly, otherwise either there is an error in emf measurements or the electrodes are not reversible. After a certain volume of titrant was added and the solution was allowed to reach equilibrium (15-30 min), the potential of the Na-ISE toward the Br-ISE in the ternary mixture can be written as

$$E(\mathrm{NaBr}) = E'(\mathrm{NaBr}) + S \ln\,[I_1(I_1 + I_2)[\gamma_\pm(\mathrm{NaBr})]^2] \qquad (10)$$

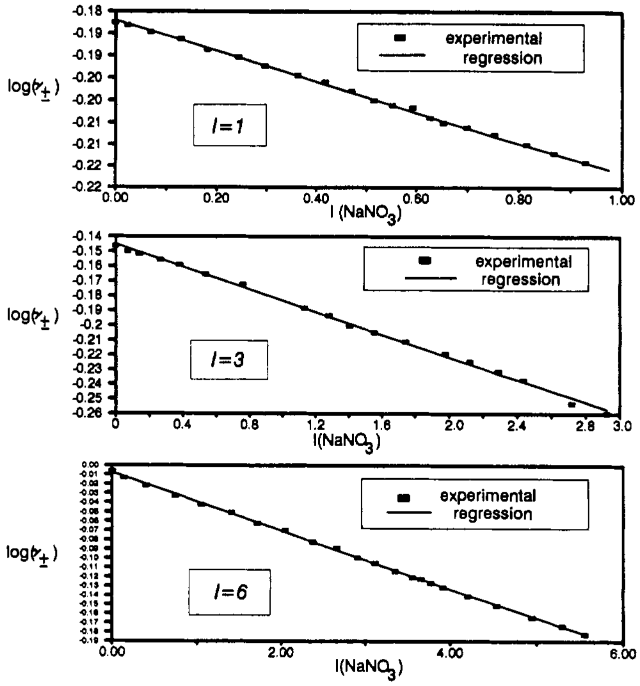

Figure 5. Mean activity coefficient of NaCl in aqueous solutions of NaCl and $NaNO_3$ at ionic strengths of 1, 3, and 6 and 298.2 K.

Repeated experimental measurements under different conditions showed that the bromide ISE is completely selective to bromide ions and does not have any interference with nitrate ions. Thus one can assume a zero value for $K_{\mathrm{Br-NO_3}}$. With subtraction of eq 9 from eq 10 and after rearrangement, with $I_1 = I$(NaBr), one obtains

$$\ln \gamma_\pm(\mathrm{NaBr}) = \ln \gamma^\circ_\pm(\mathrm{NaBr}) + \ln\left(\frac{I}{I(\mathrm{NaBr})}\right)^{1/2} + \frac{E(\mathrm{NaBr}) - E^\circ(\mathrm{NaBr})}{2S} \qquad (11)$$

Equation 11 was used to calculate the logarithm of the mean activity coefficient of NaBr from emf measurements. The measurements in the ternary aqueous system of NaBr and $NaNO_3$ have been carried out at 298.15 K over the total ionic strength range of 0.3-6. Figure 5 shows the change of the logarithm of the mean activity coefficient of NaBr versus the ionic strength of $NaNO_3$ at various total ionic strengths. Table II shows the numerical values of the mean activity coefficients of NaBr at 298.15 K over various ionic strengths of the ternary mixture.

Similarly, with the same procedure, the following equation can be obtained for the $NaCl$-$NaNO_3$-H_2O system

$$\log \gamma_\pm(\mathrm{NaCl}) = \log \gamma^\circ_\pm(\mathrm{NaCl}) + \log\left(\frac{I}{I(\mathrm{NaCl})}\right)^{1/2} + \frac{E(\mathrm{NaCl}) - E^\circ(\mathrm{NaCl})}{2(2.303)S} \qquad (12)$$

where $\gamma^\circ_\pm$(NaCl) is the mean activity coefficient of NaCl in the binary $NaCl$-H_2O solution of ionic strength I. We used base 10 logarithm in order to compare the result of the $NaCl$-$NaNO_3$-H_2O system with Lanier's results (*12*). Equation 12 was used to calculate the mean activity coefficient of NaCl in the mixture. Experiments were performed for three different total ionic strengths of 1, 3, and 6 at 298.15 K. Figure 6 and Table

Table II. Mean Ionic Activity Coefficient of NaBr in Ternary Aqueous Solutions of NaBr and $NaNO_3$ at Various Total Ionic Strengths (I) and 298.15 K

I(NaBr)	$\ln \gamma_\pm$	I(NaBr)	$\ln \gamma_\pm$	I(NaBr)	$\ln \gamma_\pm$	I(NaBr)	$\ln \gamma_\pm$
I = 0.3		I = 0.5		I = 1		I = 2	
0.300	−0.327	0.500	−0.361	1.000	−0.375	2.000	−0.315
0.286	−0.328	0.476	−0.368	0.953	−0.383	1.906	−0.324
0.273	−0.330	0.455	−0.370	0.909	−0.385	1.820	−0.336
0.261	−0.333	0.426	−0.373	0.852	−0.391	1.741	−0.346
0.245	−0.335	0.400	−0.379	0.801	−0.396	1.636	−0.361
0.231	−0.339	0.371	−0.382	0.742	−0.401	1.513	−0.375
0.214	−0.341	0.345	−0.386	0.691	−0.406	1.408	−0.388
0.200	−0.344	0.313	−0.391	0.646	−0.408	1.316	−0.400
0.182	−0.346	0.286	−0.396	0.589	−0.415	1.303	−0.401
0.167	−0.347	0.263	−0.402	0.542	−0.418	1.235	−0.408
0.159	−0.351	0.244	−0.405	0.501	−0.421	1.199	−0.412
0.154	−0.351	0.228	−0.405	0.466	−0.424	1.171	−0.416
0.140	−0.352	0.209	−0.409	0.427	−0.427	1.101	−0.425
0.131	−0.354	0.193	−0.414	0.393	−0.431	1.096	−0.426
0.126	−0.355	0.179	−0.412	0.356	−0.434	1.017	−0.434
0.120	−0.356	0.172	−0.415	0.329	−0.434	0.993	−0.436
0.111	−0.357	0.149	−0.419	0.311	−0.438	0.938	−0.441
0.110	−0.357	0.123	−0.423	0.260	−0.444	0.884	−0.452
0.102	−0.360	0.100	−0.429	0.201	−0.448	0.845	−0.452
0.097	−0.360	0.075	−0.431	0.150	−0.454	0.797	−0.463
0.082	−0.363	0.046	−0.435	0.091	−0.461	0.735	−0.464
0.069	−0.364	0.024	−0.442	0.048	−0.464	0.648	−0.470
0.055	−0.368					0.549	−0.485
0.039	−0.369					0.465	−0.492
0.027	−0.372					0.370	−0.506
0.014	−0.374					0.263	−0.520
						0.183	−0.532
						0.096	−0.547
I = 3		I = 4		I = 5		I = 6	
3.000	−0.203	4.000	−0.068	5.000	0.080	6.000	0.232
2.859	−0.213	3.813	−0.089	4.767	0.042	5.722	0.203
2.731	−0.231	3.643	−0.116	4.555	0.018	5.469	0.168
2.559	−0.255	3.487	−0.135	4.361	−0.003	5.237	0.139
2.407	−0.276	3.277	−0.163	4.100	−0.034	4.924	0.097
2.231	−0.299	3.091	−0.185	3.796	−0.069	4.646	0.061
2.078	−0.310	2.873	−0.215	3.534	−0.098	4.321	0.019
1.945	−0.330	2.684	−0.238	3.253	−0.131	4.039	−0.020
1.775	−0.353	2.443	−0.275	2.970	−0.165	3.791	−0.053
1.734	−0.363	2.241	−0.297	2.733	−0.192	3.471	−0.093
1.632	−0.370	2.071	−0.316	2.530	−0.215	3.201	−0.124
1.615	−0.379	2.019	−0.329	2.329	−0.239	2.970	−0.151
1.511	−0.383	1.924	−0.337	2.157	−0.260	2.740	−0.179
1.406	−0.398	1.797	−0.353	2.088	−0.269	2.542	−0.197
1.389	−0.400	1.758	−0.358	2.029	−0.275	2.513	−0.205
1.315	−0.411	1.594	−0.378	1.903	−0.290	2.395	−0.220
1.261	−0.416	1.587	−0.374	1.694	−0.315	2.169	−0.245
1.246	−0.422	1.350	−0.409	1.517	−0.338	1.900	−0.277
1.075	−0.442	1.159	−0.429	1.320	−0.362	1.589	−0.311
0.940	−0.464	0.937	−0.460	1.099	−0.389	1.228	−0.367
0.786	−0.482	0.746	−0.483	0.850	−0.422	0.916	−0.399
0.607	−0.500	0.531	−0.509	0.666	−0.447	0.560	−0.440
0.452	−0.520	0.370	−0.527	0.465	−0.478	0.294	−0.471
0.276	−0.543	0.194	−0.550	0.244	−0.508	0.151	−0.488
0.145	−0.561			0.125	−0.518		

III show the logarithm of mean activity coefficient of NaCl at ionic strengths 1, 3, and 6 and 298.15 K.

Results

The $NaCl$-$NaNO_3$-H_2O System. As Figure 6 shows, the behavior of the logarithm of the mean ionic activity coefficient with respect to the ionic strength of $NaNO_3$ is linear for all the mixtures of constant total ionic strength studied here. Therefore one can fit the experimental points by the Harned's rule. Table IV shows the Harned's coefficients, α_{12}, obtained by the present experiments and the coefficients reported by Lanier (*12*). As one can see, the values differ slightly in the third significant figure. Following Harned and Owen (*2*), the results were reported with only three significant figures for the present experiments. This is consistent with the reproducibility of the present results. It should be mentioned that there are some important differences between Lanier's experiment and the present study. Lanier (*12*) in his measurements used an Ag/AgCl reference electrode, and in the present experiments a Cl-ISE was used as a reference electrode. An Orion sodium glass Ross electrode was used in the present study, but Lanier (*12*) used a sodium glass electrode from Beckman. Lanier in his calculation of the mean activity coefficient of NaCl in the mixed-salt solution used the difference of the potential between test solution and saturated binary NaCl solution. In the present experiments, as shown in eq 12, the difference of potential between the test solution and the binary NaCl solution at the same total ionic strength of the mixture was used. As a minor detail even the experimental techniques were different. In this work for each experiment the stock solution for a specified total ionic strength was prepared separately. While Lanier initially prepared the concentrated stock solutions for both salts and then diluted the solutions to obtain solutions of total ionic

Table III. Mean Ionic Activity Coefficient of NaCl in Ternary Aqueous Solutions of $NaNO_3$ and NaCl at Various Total Ionic Strengths (I) and 298.15 K

I(NaCl)	log $\gamma_\pm$	I(NaCl)	log $\gamma_\pm$	I(NaCl)	log $\gamma_\pm$
I = 1		I = 3		I = 6	
1.000	−0.182	3.000	−0.146	6.000	−0.006
0.976	−0.183	2.929	−0.150	5.862	−0.013
0.931	−0.185	2.861	−0.152	5.605	−0.021
0.871	−0.186	2.735	−0.155	5.258	−0.033
0.818	−0.189	2.619	−0.159	4.952	−0.042
0.756	−0.190	2.462	−0.165	4.595	−0.051
0.704	−0.192	2.239	−0.172	4.286	−0.062
0.637	−0.194	1.867	−0.188	3.954	−0.070
0.582	−0.196	1.718	−0.193	3.617	−0.082
0.529	−0.198	1.594	−0.200	3.334	−0.089
0.484	−0.200	1.443	−0.205	3.091	−0.099
0.447	−0.201	1.257	−0.211	2.882	−0.104
0.406	−0.202	1.020	−0.219	2.643	−0.113
0.373	−0.204	0.876	−0.224	2.441	−0.120
0.346	−0.205	0.708	−0.231	2.336	−0.122
0.300	−0.206	0.565	−0.237	2.227	−0.126
0.247	−0.208	0.280	−0.253	2.082	−0.131
0.185	−0.210	0.075	−0.260	1.790	−0.141
0.132	−0.212			1.460	−0.151
0.070	−0.214			1.052	−0.164
0.025	−0.217			0.704	−0.173
				0.443	−0.182

Table IV. Harned's Coefficient, α_{12}, for the Ternary System $NaCl-NaNO_3-H_2O$ at Various Total Ionic Strengths (I) and 298.15 K

	I = 1	I = 3	I = 6
α_{12}(present study)	0.035	0.038	0.032
α_{12}(Lanier)	0.0370	0.0336	0.035

strength 1 and 3. Although we believe that Lanier introduced error by neglecting the interference of nitrate ions toward the Ag/AgCl electrode, for the sake of comparison of results, the same path was followed. Finally, it is worth noticing that the mV meter used in measurements has a precision of ±0.1 mV. As shown by the calculations of the mean activity coefficient, a difference of ±0.01 mV in the emf values causes the Harned's coefficient to change in its third significant figure.

The $NaBr-NaNO_3-H_2O$ System. As Figure 5 shows, the behavior of the logarithm of the mean ionic activity coefficient with respect to the ionic strength of $NaNO_3$ was linear for all the mixtures of constant total ionic strength studied here. Therefore one can fit the experimental points by the Harned's rule. The results for Harned's coefficients, regression coefficient, and number of experimental points for each experiment are shown in Table V. The trace mean activity coefficient of NaBr in the ternary system $NaBr-NaNO_3-H_2O$ can be calculated by using eq 2. As explained in the previous section, the data can also be fitted by using eq 3. Figure 7 shows the comparison of the mean activity coefficient of NaBr in the binary aqueous solution of NaBr and in the ternary system. The straight lines were produced by eq 2 for various total ionic strengths, and the square symbols show the logarithm of the mean activity coefficient of NaBr in the binary mixture $NaBr-H_2O$. The straight lines are drawn through the corresponding

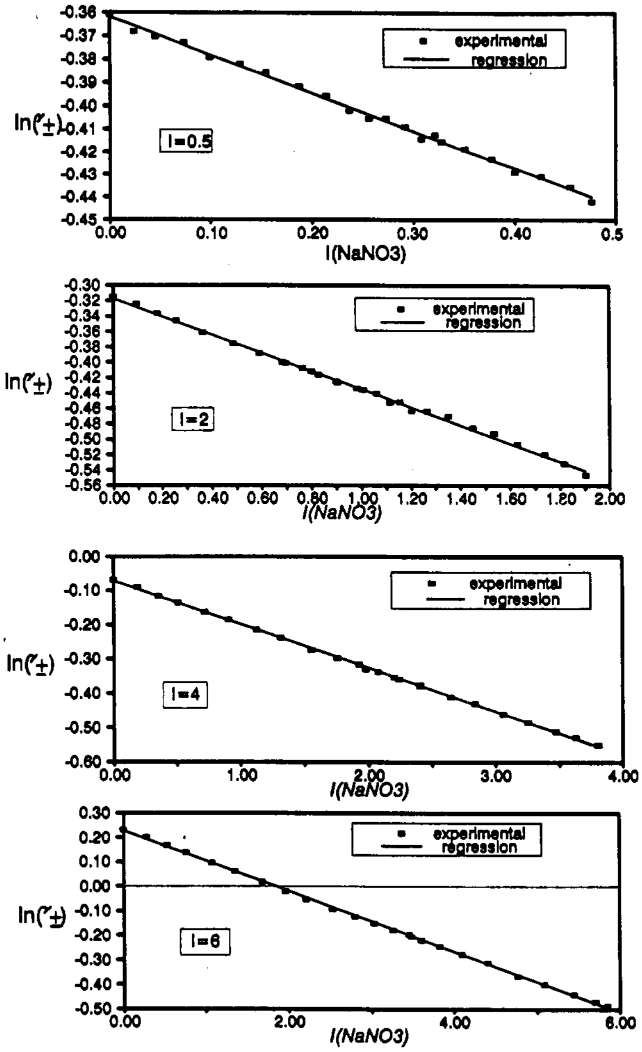

Figure 6. Mean activity coefficient of NaBr in aqueous solutions of NaBr and $NaNO_3$ at ionic strengths of 0.5, 2, 4, and 6 and 298.2 K.

binary points at the same total ionic strengths. This kind of behavior was also observed to be the characteristic of hydrochloric acid in halide solutions (*2*). From Table V, one can see that, within the accuracy of the present measurements, Harned's coefficient α'_{12} is virtually constant at total ionic strengths higher than 2. At lower ionic strengths the value of α'_{12} decreases, and it presents a minimum in the region of total ionic strength 1 with an increase at lower ionic strengths. The fact that at low ionic strengths α'_{12} increases and at high ionic strengths it levels off has also been observed for other ternary systems such as HCl in CsCl, KCl, NaCl, etc. (*2*). It would have been desirable to repeat experiments to confirm the presence of a minimum of α'_{12} as a function of I. However, experiments started from the high concentration regions and three Br-ISE's were damaged before reliable values could be obtained. Measurements with a new (different) electrode can, sometimes,

Table V. Harned's Coefficients α'_{12} and α'_{21} for Aqueous Solutions of NaBr and $NaNO_3$ at Various Total Ionic Strengths (I) and 298.15 K[a]

	I = 0.3	I = 0.5	I = 1	I = 2	I = 3	I = 4	I = 5[b]	I = 6
α'_{12}	0.166	0.164	0.090	0.118	0.127	0.127	0.121	0.124
α'_{21}	−0.081	−0.060	−0.120	−0.083	−0.075	−0.076	−0.082	−0.075
$\alpha'_{12} + \alpha'_{21}$	0.085	0.104	−0.030	0.035	0.051	0.051	0.039	0.049
correlation coeff × 100	99.71	99.67	99.74	99.79	99.92	99.95	99.91	99.95
no. of observations	26	22	22	28	25	24	25	21
std error of α'_{12}	0.002	0.002	0.001	0.001	0.001	0.001	0.001	0.001

[a] $\ln \gamma_\pm(NaBr) = \ln \gamma^\circ_\pm(NaBr) - \alpha'_{12}I_2$; $\ln \gamma_\pm(NaNO_3) = \ln \gamma^\circ_\pm(NaNO_3) - \alpha'_{21}I_1$. [b] For I = 5, measurements were made with a different Br-ISE, as explained in the text.

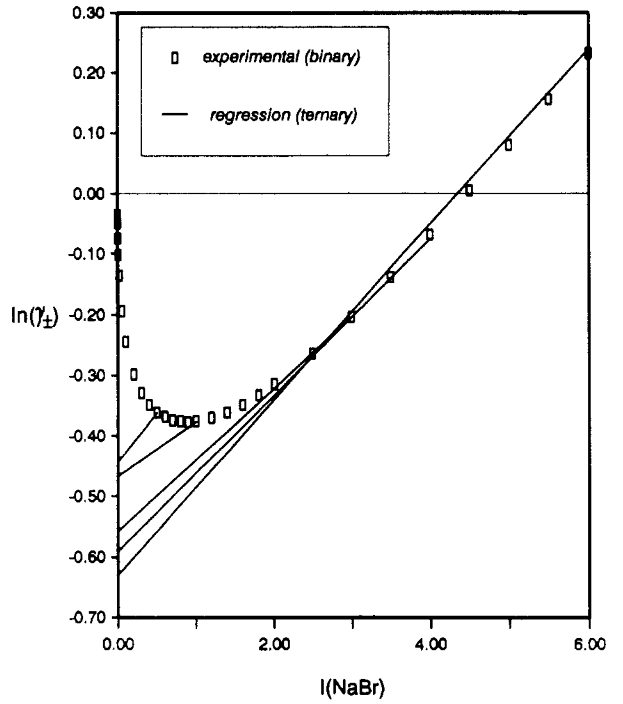

Figure 7. Comparison of the mean ionic activity coefficient of NaBr in a binary aqueous solution of NaBr and in ternary aqueous solutions of NaBr and $NaNO_3$ at various total ionic strengths and 298.2 K.

produce variations, as shown in Table V. Thus, the question of whether or not there is a minimum remains unanswered.

Mean Activity Coefficient of $\boldsymbol{NaNO_3}$. Initially an attempt was made to measure the emf of the Na-ISE with reference to the NO_3-ISE or to monitor the potential of the NO_3-ISE against a double-junction electrode so that the mean activity coefficient of $NaNO_3$ could be obtained directly. However, it was observed that the data collected was not reproducible; i.e., the emf data obtained by starting from the binary system of NaBr and using $NaNO_3$ as titrant was different from the data obtained with NaBr as titrant starting from the $NaNO_3$ binary system. In other words, it was concluded that the NO_3-ISE was not reversible in the ternary NaBr-$NaNO_3$-H_2O system. Therefore, with the assumption that the mean activity coefficient of $NaNO_3$ obeys Harned's rule and with use of the Gibbs-Duhem equation, the Harned's coefficient for $NaNO_3$ can be obtained provided that the total ionic strength of the ternary system is kept constant. The general derivation of the equation is presented at Appendix A. The relation for ternary uni-univalent systems, as shown by Harned and Owen (*2*), can be written as

$$\alpha'_{21} = \alpha'_{12} + \frac{2}{I^2}\int_0^I I \, \mathrm{d} \ln \left[\frac{\gamma^\circ_\pm(\mathrm{NaNO_3})}{\gamma^\circ_\pm(\mathrm{NaBr})}\right]$$
$$= \alpha'_{12} + \frac{2}{I}[\phi^\circ(\mathrm{NaNO_3}) - \phi^\circ(\mathrm{NaBr})] \qquad (13)$$

According to Harned and Owen (*2*), the validity of eq 13 is determined by the accuracy of the linear variation of the logarithm of the mean activity coefficients of the electrolytes at constant total ionic strengths. Thus Harned's rule should be valid for both salts in order to apply eq 13. Following Pitzer (*7*) and Harned and Owen (*2*), with use of the Harned's rule for both salts and the cross differentiation of the mean activity coefficients, the following relation can be obtained

$$\frac{\mathrm{d}}{\mathrm{d}I}(K_1\nu_2\alpha'_{21} + K_2\nu_1\alpha'_{12}) = 0 \qquad (14)$$

where

$$K_k = \tfrac{1}{2}(\nu^+_k Z_{+k}^2 + \nu^-_k Z_{-k}^2)$$

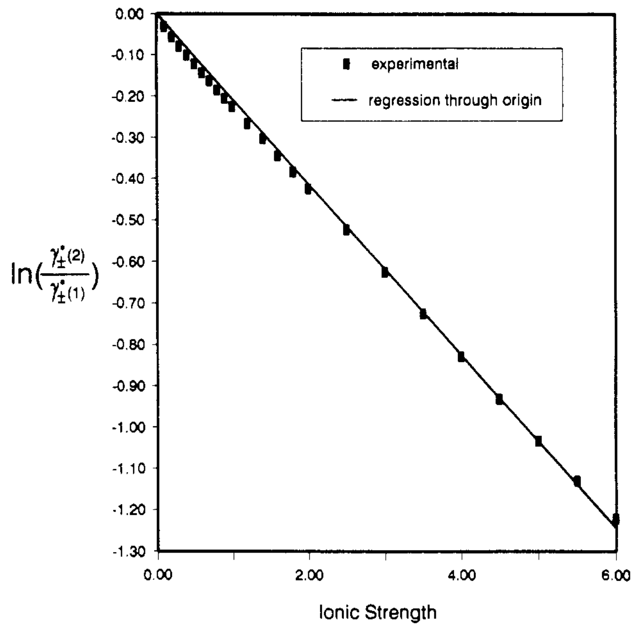

Figure 8. Logarithm of the ratio of the mean ionic activity coefficient of $NaNO_3$ and NaBr in the respective binary mixtures at the same ionic strength as that of the ternary system and 298.2 K.

Thus, with eq 14 for a uni-univalent system, the second salt will obey Harned's rule if the following relation is valid:

$$\alpha'_{12} + \alpha'_{21} = \text{constant} \qquad (15)$$

To test the validity of this equation, α'_{12} was obtained by regression of the experimental data. As proposed by Åkerlöf and Thomas (*2*), according to Harned and Owen (*2*), α'_{21} can be evaluated by assuming that the ratio of the mean ionic activity coefficients of the salts in the respective binaries is linear at high total ionic strengths. As shown by Figure 8, the ratio of the mean activity coefficients for the binaries NaBr-H_2O and $NaNO_3$-H_2O at high ionic strengths can be written as

$$\ln\left(\frac{\gamma^\circ_\pm(\mathrm{NaNO_3})}{\gamma^\circ_\pm(\mathrm{NaBr})}\right) = -CI \qquad (16)$$

Substituting eq 16 in eq 13, one readily obtains

$$\alpha'_{12} - \alpha'_{21} = C \qquad (17)$$

and combining eqs 16 and 17 gives

$$(\alpha'_{21} - \alpha'_{12})I = \ln\left(\frac{\gamma^\circ_\pm(\mathrm{NaNO_3})}{\gamma^\circ_\pm(\mathrm{NaBr})}\right) \qquad (18)$$

Using Harned's Rule, writing the trace activity coefficient equations for both salts, and combining these equations with eq 18 produce the following relation between the trace activity coefficients:

$$\ln \gamma^{\mathrm{tr}}_\pm(\mathrm{NaNO_3}) = \ln \gamma^{\mathrm{tr}}_\pm(\mathrm{NaBr}) \qquad (19)$$

Therefore if the ratio of the mean activity coefficients in the binaries is linear, the mean activity coefficients of trace electrolytes in the solution are equal. The Harned's coefficient, α'_{21}, can be calculated either by eq 17 at high ionic strengths, where the ratio of the mean ionic activity coefficients in the binaries is linear, or with eq 13 using the difference of the osmotic coefficients of salts over whole range of ionic strengths. To have consistent results, the osmotic coefficients of the salts reported by Robinson and Stokes (*4*) were used to calculate the values of α'_{21}, which are shown in Table V. As is evident from Table V, at high concentration of the salts in the mixture, α'_{12} does not change significantly with the total ionic strengths of the solutions and eq 15 is satisfied within experimental error.

Table VI. Activity Coefficients of Trace Electrolytes in the $NaBr-NaNO_3-H_2O$ System at 298.15 K

total ionic strength, I	$\ln \gamma^{tr}_{\pm}(NaBr)$	$\ln \gamma^{tr}_{\pm}(NaNO_3)$
0.3	−0.376	−0.382
0.5	−0.444	−0.451
1	−0.467	−0.486
2	−0.553	−0.572
3	−0.578	−0.603
4	−0.578	−0.592
5	−0.525	−0.550
6	−0.513	−0.539

Table VI shows the trace mean activity coefficient of NaBr and $NaNO_3$ at various total ionic strengths of the mixture. These trace activity coefficients were calculated by using eq 2 for NaBr and a similar equation for $NaNO_3$. The trace activity coefficients, to a reasonable degree, satisfy eq 19.

Discussion

Recapitulating, the emf cell technique was used to obtain experimental data for the mean activity coefficient of NaBr in the ternary $NaBr-NaNO_3-H_2O$ system. Harned's coefficient, α'_{12}, was calculated by regression analysis of the data, and α'_{21} was evaluated by using eq 13. Activity coefficients of the trace salts were computed, and it was found that both activity coefficients of the trace electrolytes are nearly equal. As stated by Harned and Owen (*2*), all these results indicate that the linear variation of ln $\gamma_{\pm}$, as expressed by Harned's rule, is a good first approximation and can be utilized in the treatment of many mixtures.

With the above elements in mind, errors and drift can be discussed. Experimental errors in the measurements come from various sources. One of the most important sources of uncertainty comes from the precision of the millivolt (mV) measurements. As discussed by Harned and Owen (*2*), for 1–1 halide mixtures, errors in the emf of ±0.1, ±0.2, and ±0.2 mV at total ionic strengths 0.5, 1, and 3 m, respectively, cause an error in α'_{12} almost equal to ±0.01, ±0.01, and ±0.005 (based on the natural logarithm) at these ionic strengths. Thus, the errors are more pronounced at ionic strengths less than unity. Although it is difficult to estimate the errors, the consistency of the results shows that for the present measurements an accuracy in α'_{12} of ±0.005 at high ionic strengths and ±0.01 at low ionic strengths may be obtained. The accuracy of α'_{21} is less certain so that one may expect an error of ±0.01 for high ionic strengths and ±0.02 for low ionic strengths.

Another source of error is the electrode drift. Following Freiser's discussion (*17*), the drift in ISE's can usually be categorized as one of three types. (1) A parallel drift is characterized by a shift of the calibration line for an electrolyte system in which the slope of the line does not change. (2) A concentration-dependent drift occurs when the slope of the calibration line changes "For example, one might observe a negative emf drift at high concentration and a positive drift at low concentration. Normally, the drift results in a decrease in the slope of the calibration line indicating a degradation in the electrode response [sub-Nernstian] (*17*)." This effect is most commonly observed with liquid ISE's. Fortunately in the measurements of the $NaBr-NaNO_3-H_2O$ system, this kind of drift is not applicable. (3) A random drift is characterized by the absence of a regular trend, i.e., nonuniform both in the direction and magnitude of the drift. This kind of drift usually happens with the electrodes that are used many times, particularly at high concentrations. It is impossible to correct this type of drift reliably, and the use of a brand new electrode is required. It should be mentioned that in the present measurements three Br-ISE's were used. Using a new electrode requires a new calibration. Moreover, a new electrode has a different lot number, and it may have a different asymmetry potential. Temperature fluctuations, an unstable liquid junction, excessive cell resistance, nonequilibrium state of the system, pressure variations, etc., are examples of other causes of potential drift. In dilute mixtures drifts are more pronounced because the equilibrium potential will be approached more slowly.

In the present experiments pure deionized water was used to prepare the stock solutions. In some cases it was necessary to use different lot numbers of reagent salts, and this may result in errors in the comparison of the experimental results. Also, sample calculations showed that within the precision of the mV meter (±0.1) used in this work, the third decimal place of α'_{12} is only approximate.

Following Harned and Owen (*2*), in a ternary system with a common ion, the following relations for uni-univalent electrolyte mixtures are valid, if the assumption of specific ionic interaction of Brönsted is true, for the ternary system.

$$\alpha'_{12} + \alpha'_{21} = 0 \qquad (20)$$

$$\ln \gamma^{tr}_{\pm 1} = \ln \gamma^{tr}_{\pm 2} \qquad (21)$$

Although for the present system the activity coefficients of the trace electrolytes are almost equal, α'_{12} is not equal to $-\alpha'_{21}$, as it can be seen from Table V. This may be due to experimental errors discussed above, or it may suggest that the theory of Brönsted, which leads to the result that the sum of Harned's coefficients is zero, is not strictly valid due to the effect of the third ion. However, from eq 13, it can be shown that relation 20 is valid for the $NaCl-NaNO_3-H_2O$ system so that the Harned's coefficient α'_{21} for $NaNO_3$ can be obtained by $\alpha'_{21} = -\alpha'_{12}$.

Glossary

a	activity
C	regression constant
E	potential of ion-selective electrode
I	ionic strength
$I(k), I_k$	ionic strength of electrolyte k
K_k	salt number of electrolyte k
K_{ij}	potentiometric selectivity coefficient
m	molality
S	slope of calibration line
$Y(i)$	ionic strength fraction of ion i
Y_k	ionic strength fraction of electrolyte k
Z_i	charge number of ion i

Greek Letters

$\alpha_{12}, \alpha'_{12}$	Harned's coefficient of salt 1, $\alpha'_{12} = (\ln 10)\alpha_{12}$
$\gamma_{\pm}$	mean ionic activity coefficient
ν^+	stoichiometric number of cations
ν^-	stoichiometric number of anions
ν_k	stoichiometric number of electrolyte k
ϕ	osmotic coefficient

Subscripts

±	mean ionic
i, j	ions i and j
k	electrolyte k
S	single-junction electrode
w	water

Superscripts

+	cation
−	anion
°	measurements in binary electrolyte solution
tr	trace

Appendix A

The Gibbs–Duhem equation for a single liquid-phase ternary system at constant temperature, neglecting the small effect due

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to equilibrium pressure changes, can be written as

$$n_1\,d\mu_1 + n_2\,d\mu_2 + n_w\,d\mu_w = 0 \qquad (A1)$$

where n_1 and n_2 are the number of moles of salts and n_w is the number of moles of water. The corresponding chemical potentials are μ_1, μ_2, and μ_w. The chemical potentials of the salts and water can be written in terms of their activity, and the number of moles can be expressed in terms of ionic strength. Therefore, for the ternary aqueous mixture eq A1 can be written as

$$\frac{I_1}{K_1}\,d\ln a_1 + \frac{I_2}{K_2}\,d\ln a_2 = -55.51\,d\ln a_w \qquad (A2)$$

where

$$K_k = \tfrac{1}{2}(\nu^+_k Z_{+k}^2 + \nu^-_k Z_{-k}^2)$$

the activity of the salt k can be written as (*4*, *7*)

$$a_k = \nu_{\pm k} m^{\nu_k}{}_k \gamma^{\nu_k}{}_{\pm k}$$

thus

$$d\ln a_k = \nu_k\,d\ln(m_k\gamma_{\pm k}) = \nu_k\,d\ln\left(\frac{I_k}{K_k}\gamma_{\pm k}\right) \qquad (A3)$$

With use of eq A3 for both electrolytes and with the assumption that Harned's rule is valid for both salts, then eq A2 yields

$$\left(\frac{\nu_1}{K_1}\alpha'_{12} + \frac{\nu_2}{K_2}\alpha'_{21}\right)Y_1\,dY_1 - \frac{\nu_2}{K_2}\alpha'_{21}\,dY_1 + \left(\frac{\nu_1}{K_1} - \frac{\nu_2}{K_2}\right)\frac{dY_1}{I} = -\frac{55.51}{I^2}\,d\ln a_w \qquad (A4)$$

where $Y_1 = I_1/I$ and $I_2 = (1 - Y_1)I$ with $I = I_1 + I_2$ constant. Equation A4 is then integrated at constant I and T from $Y_1 = 0$ (pure salt 2) to $Y_1 = 1$ (pure salt 1) to give

$$\frac{1}{2}\left(\frac{\nu_1}{K_1}\alpha'_{12} + \frac{\nu_2}{K_2}\alpha'_{21}\right) - \frac{\nu_2}{K_2}\alpha'_{21} + \frac{1}{I}\left(\frac{\nu_1}{K_1} - \frac{\nu_2}{K_2}\right) = -\frac{55.51}{I^2}\ln\left(\frac{a^\circ_w(1)}{a^\circ_w(2)}\right) \qquad (A5)$$

The activity of water can be written in terms of its osmotic coefficient (*2*), thus, at a total ionic strength I

$$\ln a^\circ_w = -\frac{\nu_k m_k}{55.51}\phi^\circ_k = -\frac{\nu_k I}{55.51 K_k}\phi^\circ_k \qquad (A6)$$

with

$$\phi^\circ_k = 1 + \frac{1}{I}\int_0^I d\ln\gamma^\circ_{\pm k} \qquad (A7)$$

Thus combining eq A5 with A7 gives

$$\frac{\nu_1}{K_1}\alpha'_{12} - \frac{\nu_2}{K_2}\alpha'_{21} = \frac{2}{I^2}\int_0^I I\,d\ln\left[\frac{(\gamma^\circ\pm_1)^{\nu_1/K_1}}{(\gamma^\circ{}_{\pm 2})^{\nu_2/K_2}}\right] = \frac{2}{I}\left[\frac{\nu_1}{K_1}(\phi^\circ_1 - 1) - \frac{\nu_2}{K_2}(\phi^\circ_2 - 1)\right] \qquad (A8)$$

Registry No. NaCl, 7647-14-5; $NaNO_3$, 7631-99-4; NaBr, 7647-15-6.

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Low-Pressure Isobaric Vapor–Liquid Equilibria of Ethanol/Water Mixtures Containing Electrolytes

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Experimental vapor–liquid equilibrium data at low pressure are presented for ethanol/water mixtures containing sodium chloride and calcium chloride at constant molalities. In addition, the results for an ethanol/water mixture saturated with sodium chloride are given. The saturation concentrations of ethanol/water mixtures at boiling temperature and 123.1 mbar are reported. The data are compared with the predicted results using an extended UNIQUAC model for electrolyte systems published by Macedo et al.

Introduction

In the past few years, local composition models like NRTL and UNIQUAC have been extended for the application to vapor–liquid equilibria of electrolyte systems (*1–3*). The most recent model was presented by Macedo et al. (*1*). For several alcohol/water/salt mixtures, model parameters depending on salt concentration have been published. These parameters were evaluated from previously published experimental data measured at atmospheric pressure. To verify the applicability of the model parameters at other conditions, low-pressure vapor–liquid equilibria were measured.

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