Application of Pitzer Equations for Quaternary Systems: NaCl–NaNO₃–NaOAc–H₂O and KCl–KNO₃–KOAc–H₂O at 25 °C

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Electromotive force measurements were carried out on the NaCl–NaNO₃–NaOAc–H₂O and KCl–KNO₃–KOAc–H₂O systems at constant total ionic strengths of 0.5, 1.0, 2.0, and 3.0 mol/kg and at 25 °C using a cell consisting of a sodium ion-selective electrode or potassium ion-selective electrode and an Ag/AgCl electrode. The results were analyzed in terms of the Harned equation and by the Pitzer formalism.

Introduction

A current problem in the field of electrolyte solutions is the prediction of the thermodynamic properties of mixed electrolyte solutions from the properties of single electrolyte solutions. Activity coefficients are of primary importance in describing accurately the thermodynamic behavior of aqueous mixed electrolyte solutions. The lack of accurate activity coefficient data leads to large errors in calculating solubilities in multicomponent electrolyte systems (1). We have reported the activity coefficients of NaCl in the ternary systems NaCl–NaNO₃–H₂O (2) and NaCl–NaOAc–H₂O (3) and the activity coefficients of KCl in the ternary systems KCl–KNO₃–H₂O (4) and KCl–KOAc–H₂O (5). As part of our continuing program on activity coefficients in aqueous electrolyte solutions, we have extended our measurements to the quaternary systems NaCl–NaNO₃–NaOAc–H₂O and KCl–KNO₃–KOAc–H₂O. The activity coefficients of NaCl in NaCl–NaNO₃–NaOAc–H₂O and KCl in KCl–KNO₃–KOAc–H₂O systems were studied by an electromotive force (emf) method at constant total ionic strengths of 0.5, 1.0, 2.0, and 3.0 mol/kg at 25 °C. The experimentally determined activity coefficient data are treated in terms of the Harned equation (6) in order to get Harned coefficients. In addition, the data are used to test the applicability of the Pitzer equations (7–12) for such multicomponent electrolyte solutions and, thereby, explain the trends in the activity coefficient values of NaCl and KCl in ternary and quaternary electrolyte systems on the basis of the activity coefficient values of the pure electrolytes.

Experimental Section

The cell consisted of an M ion-selective electrode and an Ag/AgCl electrode (13) immersed in a mixture of aqueous MCl–MNO₃–MOAc solution placed in a double-walled glass vessel whose temperature was maintained constant within ±0.01 °C by circulation of thermostated water. The cell arrangement was

M	MCl (*m*A)	Ag/AgCl
ion-selective	+	electrode
electrode	MNO₃ (*m*B)	
	+	
	MOAc (*m*C)	

where M = K⁺ or Na⁺.

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Analytical grade sodium chloride, potassium chloride, sodium nitrate, potassium nitrate, sodium acetate, and potassium acetate were used as such. The stock solutions were standardized volumetrically using AgNO₃ and by cation exchange methods. The results obtained by these two methods agreed within 0.08%. Deionized, doubly distilled water was used for preparation of solutions. All solutions and dilutions were made using weight burets. The electrodes were connected to a high-impedance (∼10¹² Ω) unit gain amplifier. The output of this amplifier was measured by a Keithley 5½ digit electrometer/multimeter (model DMM 191). The accuracy of the emf measurements was ±0.01 mV. Three sets of experiments were carried out at a given ionic strength. In the first set of experiments, NaCl solution was put in the double-walled glass vessel and water was added in aliquots using a weight buret. The potential was noted after every dilution. This set was performed to calibrate the electrodes. In the second set, NaCl solution was put in the glass vessel and a mixture of the second electrolyte (NaNO₃ and NaOAc solutions having half of the total ionic strength of NaCl solution in order to maintain constant total ionic strength) was added in aliquots. The third set consisted of a mixture of the second electrolyte taken into the glass vessel and aliquots of NaCl solution was added. This set of data is used to test the reproducibility and accuracy of results.

Treatment of Data

The emfs of the M ion-selective electrode vs an Ag/AgCl electrode in aqueous MCl–MNO₃–MOAc system are given by the relation

$$E_{\text{MCl–MNO}_3\text{–MOAc}} =$$
$$E_0 + k \log (a_M a_{Cl} + K' a_M a_{NO_3} + K'' a_M a_{OAc}) \quad (1)$$

where $K' a_M a_{NO_3}$ and $K'' a_M a_{OAc}$ terms will take into account the effect of the same solution (MNO₃–MOAc) on the cell emf and $k = RT \ln 10/F$ which is the Nernst slope. In pure MCl solution, $a_{MNO_3} = 0$, $a_{MOAc} = 0$, and eq 1 becomes

$$E_{MCl} = E_0 + k \log (a_M a_{Cl}) \quad (2)$$

At each ionic strength the emf data obtained in the calibration run were fitted to the above eq 2 using a least-squares procedure to find E_0 and k values (the activity coefficient values of pure NaCl and KCl solutions at a given concentration were taken from the literature (1)).

In pure MNO₃ solution, $a_{MCl} = 0$ and $a_{OAc} = 0$.

$$E_{MNO_3} = E_o + k \log (K'a_M a_{NO_3}) \qquad (3)$$

$$K' = \frac{1}{a_{MNO_3}^2} \times 10^{(E_{MNO_3} - E_o)/k} \qquad (4)$$

Similarly for pure MOAc solution

$$K'' = \frac{1}{a_{MOAc}^2} \times 10^{(E_{MOAc} - E_o)/k} \qquad (5)$$

The selectivity coefficient values (K' and K'') at all ionic strengths studied are of the magnitude $<1 \times 10^{-5}$ reported in earlier papers (2-5). Thus, the second and third terms on the right-hand side of eq 1 can be neglected, and as $a_M = (m_A + m_B + m_C)\gamma_M$ and $a_{Cl} = m_{Cl}\gamma_{Cl}$, eq 1 becomes

$$\gamma_\pm^2 = \frac{1}{m_M m_{Cl}} \times 10^{(E_{MCl-MNO_3-MOAc} - E_o)/k} \qquad (6)$$

The activity coefficients of MCl in aqueous an MCl-MNO$_3$-MOAc system were calculated by substituting the cell emfs ($E_{MCl-MNO_3-MOAc}$) in eq 6 determined at different ionic strength fractions of y_B, where $y_B = (m_B + m_C)/(m_A + m_B + m_C)$. The experimental activity coefficient data of NaCl in aqueous NaCl-NaNO$_3$-NaOAc and KCl in KCl-KNO$_3$-KOAc systems determined at I = 0.5, 1.0, 2.0, and 3.0 mol/kg are given in Tables I and II. The plots of log γ_{MX} vs y_B at all the experimental ionic strengths are shown in Figure 1.

Results and Discussion

The activity coefficient data of NaCl or KCl in the quaternary systems at each ionic strength were treated in terms of the Harned equation (7):

$$\log \gamma_A = \log \gamma_A^o - \alpha_{AB} y_B - \beta_{AB} y_B^2 \qquad (7)$$

where γ_A^o is the activity coefficient value of pure NaCl or KCl at the same ionic strength as the respective mixtures. The Harned coefficients measure the effect of an added electrolyte (aqueous NaNO$_3$-NaOAc) on the activity coefficient values of aqueous NaCl solution. These coefficients (α_{AB}) were calculated at every ionic strength using a least-squares procedure, and these values along with corresponding RMSD values are summarized in Table III. The data seem to need a β_{AB} term at higher ionic strengths (I = 2.0 and 3.0 mol/kg), but from Figure 1 it looks to be insignificant.

The activity coefficient data were further analyzed using the Pitzer formalism. According to the Pitzer equations, the mean activity coefficients of NaCl, KCl, NaNO$_3$, KNO$_3$, NaOAc, and KOAc in pure solutions can be calculated using the equation given below:

$$\ln \gamma_{MX} = f' + 2IB_{MX} + I^2 B'_{MX} + 1.5I^2 C_{MX}^\phi \qquad (8)$$

where

$$f' = -A_\phi\left\{\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b}\ln (1 + bI^{1/2})\right\}$$

A_ϕ = 0.391 45, and the term b is an empirical parameter equal to 1.2 at 25 °C (14).

The parameters B_{MX} and B'_{MX} are interactions of oppositely charged ions representing measurable combinations of the second virial coefficients of pure electrolytes. They are described as functions of ionic strength by the following expressions:

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g(\alpha I^{1/2})$$

$$B'_{MX} = \beta_{MX}^{(1)} g'(\alpha I^{1/2})/I$$

$$g(x) = 2\{1 - (1 + x) \exp(-x)\}/x^2$$

$$g'(x) = -2\{1 - (1 + x + 0.5x^2) \exp(-x)\}/x^2$$

The values of parameters $\beta_{MX}^{(0)}, \beta_{MX}^{(1)}$, and C_{MX}^ϕ for pure aqueous electrolytes are given in Table IV.

The experimental activity coefficient data of NaCl or KCl in the mixtures were further analyzed using the Pitzer equations.

$$\ln \gamma_{NaCl} = -A_\phi\left\{\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b}\ln (1 + bI^{1/2})\right\} +$$
$$I^2(1 - y_B)B'_{NaCl} + 0.5I^2 y_B B'_{NaNO_3} + 0.5I^2 B'_{NaOAc} +$$
$$0.5I(2 - y_B)(2B_{NaCl} + 2IC_{NaCl}) + 0.25Iy_B(2B_{NaNO_3} +$$
$$2IC_{NaNO_3}) + 0.25Iy_B(2B_{NaOAc} + 2IC_{NaOAc}) +$$
$$0.25Iy_B(2\theta_{Cl-NO_3} + I\psi_{Cl-NO_3-Na}) + 0.25Iy_B(2\theta_{Cl-OAc} +$$
$$I\psi_{Cl-OAc-Na}) + 0.25I^2 y_B(1 - y_B)(\psi_{Cl-NO_3-Na} + \psi_{Cl-OAc-Na}) +$$
$$(1/8)I^2 y_B{}^2\psi_{NO_3-OAc-Na} + I^2(1 - y_B)C_{NaCl} + 0.5I^2 y_B C_{NaNO_3} +$$
$$0.5I^2 y_B C_{NaOAc} \qquad (9)$$

The terms B_{MX} and B'_{MX} can be calculated using the pure electrolyte parameters given in Table IV. The mixing parameters θ_{Cl-NO_3} and ψ_{Cl-NO_3-Na} were obtained from the corresponding ternary systems with common ions such as NaCl-NaNO$_3$-H$_2$O from our earlier work (2-5), and these values are listed in Table V.

The activity coefficient values of NaCl calculated by substituting these values in eq 9 are in good agreement with the experimental activity coefficient data with RMSD = 4.56 $\times 10^{-4}$. The same equation holds for the system containing K ions by replacing Na ions by K ions in eq 9. The activity coefficient values calculated using eq 9 are in good agreement with experimental activity coefficient data of KCl with RMSD = 5.67 $\times 10^{-4}$. These RMSD values clearly show the usefulness of the Pitzer treatment for calculating the activity coefficients of multicomponent electrolyte mixtures in the present study.

The activity of water at every ionic strength in the quaternary systems NaCl-NaNO$_3$-NaOAc-H$_2$O and KCl-KNO$_3$-KOAc-H$_2$O at 25 °C has been calculated using the relation given below:

$$\sum m_i \phi = -55.51 \ln a_{H_2O} \qquad (10)$$

where ϕ is the osmotic coefficient of the mixture which could be calculated using the Pitzer equation.

$$\phi = \frac{2}{\sum m_i}\left\{\frac{-A_\phi I^{1/2}}{(1 + bI^{1/2})} + \sum_{c<a}\sum m_c m_a (B_{ca}^\phi + ZC_{ca}) + \right.$$
$$\sum_{c<c'}\sum m_c m_{c'}(\phi_{cc'}^\phi + \sum_a m_a \psi_{cc'a}) +$$
$$\left.\sum_{a<a'}\sum m_a m_{a'}(\phi_{aa'}^\phi + \sum_c m_c \psi_{aa'c})\right\} \qquad (11)$$

where

$$B_{ca}^\phi = \beta_{ca}^{(0)} + \beta_{ca}^{(1)} \exp(-2I^{1/2})$$

Table I. Mean Activity Coefficients of NaCl in the NaCl–NaNO₃–NaOAc–H₂O System at 25 °C

m_{NaCl}/(mol/kg)	m_{NaNO_3}[a]/(mol/kg)	emf/V	log $\gamma_{\pm}$	m_{NaCl}/(mol/kg)	m_{NaNO_3}[a]/(mol/kg)	emf/V	log $\gamma_{\pm}$
	$I = 0.5$				$I = 1.0$		
0.5000	0.0000	0.1176	−0.1667	1.0000	0.0000	0.1513	−0.1823
0.4500	0.0250	0.1149	−0.1668	0.9009	0.0496	0.1486	−0.1827
0.4090	0.0455	0.1124	−0.1669	0.8197	0.0902	0.1460	−0.1840
0.3749	0.0626	0.1102	−0.1670	0.7519	0.1241	0.1439	−0.1833
0.3460	0.0770	0.1081	−0.1671	0.6452	0.1774	0.1399	−0.1837
0.3213	0.0894	0.1062	−0.1672	0.5651	0.2175	0.1365	−0.1840
0.2811	0.1095	0.1028	−0.1673	0.4763	0.2619	0.1319	−0.1853
0.2367	0.1317	0.0984	−0.1674	0.3427	0.3287	0.1236	−0.1847
0.1632	0.1684	0.0888	−0.1676	0.2811	0.3595	0.1184	−0.1855
0.1333	0.1834	0.0836	−0.1677	0.2068	0.3966	0.1106	−0.1851
0.0976	0.2012	0.0756	−0.1677	0.1153	0.4424	0.0956	−0.1854
0.0541	0.2230	0.0605	−0.1678				
	$I = 2.0$				$I = 3.0$		
2.0000	0.0000	0.1877	−0.1749	3.0000	0.0000	0.2118	−0.1466
1.8116	0.0942	0.1850	−0.1764	2.7393	0.1304	0.2091	−0.1496
1.6556	0.1722	0.1825	−0.1775	2.5203	0.2398	0.2067	−0.1520
1.5244	0.2378	0.1803	−0.1784	2.1726	0.4137	0.2025	−0.1557
1.4126	0.2937	0.1783	−0.1792	1.9095	0.5453	0.1988	−0.1584
1.2316	0.3842	0.1746	−0.1804	1.7031	0.6485	0.1957	−0.1604
1.0332	0.4834	0.1700	−0.1817	1.4433	0.7784	0.1911	−0.1628
0.9308	0.5346	0.1672	−0.1823	1.1460	0.9270	0.1849	−0.1655
0.7346	0.6327	0.1610	−0.1835	0.7083	1.1459	0.1722	−0.1690
0.4498	0.7751	0.1483	−0.1850	0.4014	1.2993	0.1573	−0.1714
0.2534	0.8733	0.1334	−0.1860				

[a] $m_{NaOAc} = m_{NaNO_3}$.

Table II. Mean Activity Coefficients of KCl in the KCl–KNO₃–KOAc–H₂O System at 25 °C

m_{KCl}/(mol/kg)	m_{KNO_3}[a]/(mol/kg)	emf/V	log $\gamma_{\pm}$	m_{KCl}/(mol/kg)	m_{KNO_3}[a]/(mol/kg)	emf/V	log $\gamma_{\pm}$
	$I = 0.5$				$I = 1.0$		
0.5000	0.0000	0.1593	−0.1872	1.0000	0.0000	0.1911	−0.2184
0.4504	0.0248	0.1566	−0.1873	0.9018	0.0491	0.1884	−0.2187
0.4098	0.0451	0.1542	−0.1874	0.8212	0.0894	0.1861	−0.2180
0.3472	0.0764	0.1499	−0.1876	0.7539	0.1231	0.1838	−0.2192
0.3226	0.0887	0.1480	−0.1877	0.6476	0.1762	0.1797	−0.2205
0.3012	0.0994	0.1462	−0.1877	0.5676	0.2162	0.1765	−0.2198
0.2660	0.1170	0.1430	−0.1878	0.4809	0.2596	0.1722	−0.2200
0.2318	0.1341	0.1395	−0.1879	0.3461	0.3270	0.1637	−0.2203
0.1653	0.1674	0.1308	−0.1881	0.2093	0.3954	0.1507	−0.2210
0.1351	0.1824	0.1257	−0.1881	0.1169	0.4416	0.1358	−0.2208
0.0990	0.2005	0.1177	−0.1882				
0.0550	0.2225	0.1026	−0.1883				
	$I = 2.0$				$I = 3.0$		
2.0000	0.0000	0.2240	−0.2408	3.0000	0.0000	0.2444	−0.2438
1.8148	0.0926	0.2214	−0.2416	2.7303	0.1349	0.2419	−0.2451
1.6612	0.1694	0.2191	−0.2422	2.5053	0.2474	0.2395	−0.2461
1.5314	0.2343	0.2169	−0.2427	2.1507	0.4247	0.2355	−0.2475
1.3244	0.3378	0.2131	−0.2434	1.8837	0.5582	0.2320	−0.2484
1.1012	0.4494	0.2083	−0.2441	1.5885	0.7058	0.2275	−0.2492
0.8516	0.5742	0.2017	−0.2448	1.4982	0.7509	0.2260	−0.2494
0.7446	0.6277	0.1982	−0.2450	0.9984	1.0008	0.2155	−0.2503
0.6158	0.6921	0.1933	−0.2453	0.7485	1.1258	0.2081	−0.2506
0.4574	0.7713	0.1856	−0.2455	0.4278	1.2861	0.1937	−0.2507
0.2582	0.8709	0.1710	−0.2458				

[a] $m_{KOAc} = m_{KNO_3}$.

$$C_{ca} = \frac{C^{\phi}_{ca}}{2|Z_M Z_X|^{1/2}}$$

$$\phi^{\phi}_{ij} = {}^{s}\theta_{ij} + {}^{E}\theta_{ij} + I{}^{E}\theta'_{ij}$$

$$Z = \sum_i m_i |Z_i|$$

and the other terms have their usual significance.

The terms B^{ϕ}_{ca} and C_{ca} were computed from the Pitzer pure electrolyte parameters using Table IV. The higher order electrostatic terms (${}^{E}\theta_{ij}$ and ${}^{E}\theta'_{ij}$) for these mixtures are zero. The ${}^{s}\theta_{ij}$ and ψ_{ijk} values could be obtained from our earlier work and are listed in Table V. Hence, calculated water activities in both these quaternary systems were found to be almost the same at all the ionic strengths studied in the present investigation. The plots of water activity vs y_B for the aqueous NaCl–NaNO₃–NaOAc system are shown in Figure 2 at constant total ionic strengths of 0.5, 1.0, 2.0, and 3.0 mol/kg and 25 °C. It is clear from Figure 2 that the water activities are constant for ionic strengths up to 2 mol/kg for the entire composition range of y_B. But the activity of water increases slightly with an increase in y_B at ionic strength 3.0 mol/kg.

The activity coefficients of MCl as a function of y_B at $I = 1.0$ mol/kg and at 25 °C for the MCl–MNO₃–MOAc–H₂O system and corresponding ternary systems are plotted in Figure 3. This figure clearly shows that the activity coefficient values of NaCl are (i) increased by the addition of NaOAc and (ii) decreased by the addition of NaNO₃.
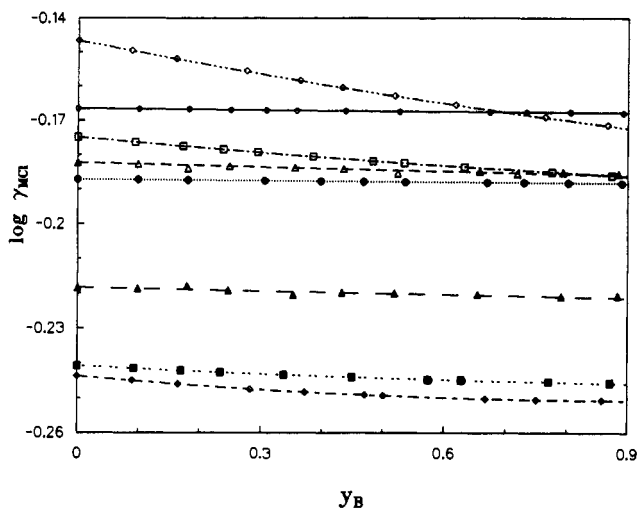
Figure 1. Mean activity coefficients of MCl in the quaternary systems at 25 °C: o, $I = 0.5$; △, $I = 1.0$; □, $I = 2.0$; and ◇, $I = 3.0$ mol/kg for NaCl; ●, $I = 0.5$; ▲, $I = 1.0$; ■, $I = 2.0$; and ◆, $I = 3.0$ mol/kg for KCl.

Table III. Harned Coefficients for the Activity Coefficient Data of MCl in the Quaternary Systems at 25 °C

system	I	α_{AB}	β_{AB}	RMSD × 10⁴
NaCl-NaNO₃-NaOAc-H₂O	0.5	0.0012		4.59
	1.0	0.0041		2.76
	2.0	0.0158	-0.0036	3.49
	3.0	0.0351	-0.0074	3.76
KCl-KNO₃-KOAc-H₂O	0.5	0.0011		4.25
	1.0	0.0034		3.61
	2.0	0.0090	-0.0037	2.99
	3.0	0.0154	-0.0085	3.12

Table IV. Ion Interaction Parameters

salt	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ
NaCl	0.077 22	0.251 83	0.001 06
NaNO₃	0.003 88	0.211 51	-0.000 06
NaOAc	0.137 23	0.341 95	-0.004 74
KCl	0.046 61	0.224 31	-0.000 44
KNO₃	-0.085 11	0.105 18	0.007 73
KOAc	0.152 83	0.355 13	-0.004 32

Table V. $^s\theta_{ij}$ and ψ_{ijk} Values

component			parameter		
i	j	k	$^s\theta_{ij}$	ψ_{ijk}	ref
Cl	NO₃	Na	0.0164	-0.007 6	2
		K		-0.004 7	4
Cl	OAc	Na	-0.005	-0.002 05	3
		K		-0.002 99	5

These trends in the activity coefficients of the electrolytes studied can be explained on the basis of the activity coefficient values of the pure electrolytes involved in these mixtures.

The activity coefficient values of pure aqueous electrolytes are dependent on the nature and size of ions which constitute these electrolytes. The larger the size of the anion, the larger will be its activity coefficient value in the presence of a given cation. Therefore, it is evident from Figure 4 that the activity coefficient values decrease in the order given below at a given concentration:

$$\text{NaOAc} > \text{NaCl} > \text{NaNO}_3$$

$$\text{KOAc} > \text{KCl} > \text{KNO}_3$$

The nitrate ion has a smaller effective radius due to close approach of the cations in a direction perpendicular to its molecular plane. For the ternary mixtures reported in the
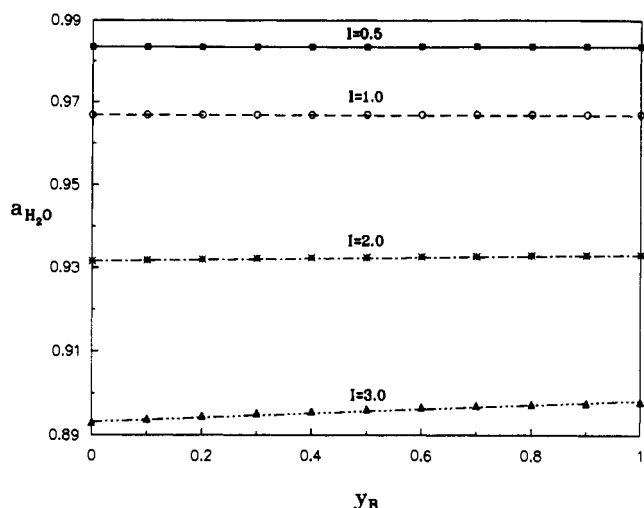

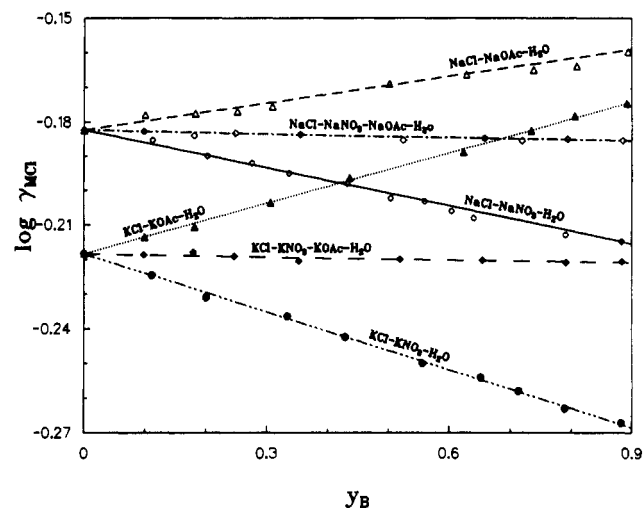**Figure 2.** Activity of water in the NaCl-NaNO₃-NaOAc-H₂O system at 25 °C.

Figure 3. Mean activity coefficients of MCl in their aqueous ternary and quaternary mixtures at 25 °C and $I = 1.0$ mol/kg.
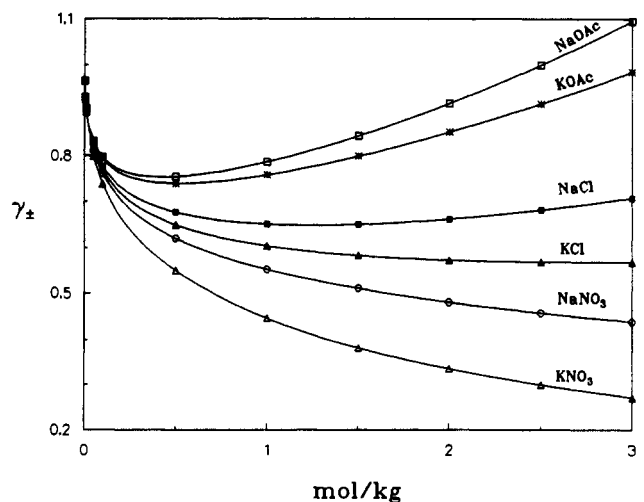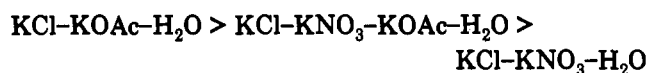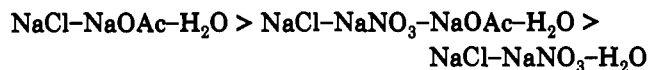

Figure 4. Mean activity coefficients of pure electrolytes at 25 °C.

earlier paper, it was observed that the activity coefficient values of NaCl were increased by the addition of NaOAc but decreased by the addition of NaNO₃. This is because aqueous NaOAc which has high values of activity coefficients is expected to increase the activity coefficient value of NaCl. In the same way NaNO₃ which has lower activity coefficient

values than NaCl is expected to decrease the activity coefficient values of NaCl. Similarly the activity coefficient values of KCl by addition of KOAc and KNO$_3$ could be explained on the same basis. The activity coefficients of NaCl and KCl in the quaternary system as compared to the corresponding ternary systems follow the sequence given below:

$$NaCl-NaOAc-H_2O > NaCl-NaNO_3-NaOAc-H_2O >$$
$$NaCl-NaNO_3-H_2O$$

$$KCl-KOAc-H_2O > KCl-KNO_3-KOAc-H_2O >$$
$$KCl-KNO_3-H_2O$$

These trends can be explained using the activity coefficient values of pure electrolytes as discussed above. The addition of NaOAc increases the activity coefficient value of NaCl, but the addition of NaNO$_3$ decreases the activity coefficient values of NaCl. Thus, the addition of both these salts (NaOAc–NaNO$_3$) increases the activity coefficient values of NaCl to a greater extent than addition of NaNO$_3$ alone. The same trend is applicable for the quaternary system containing KCl.

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