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Ionization of Acetic Acid in Aqueous Potassium Chloride Solutions

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ABSTRACT: Stoichiometric ionization constants of acetic acid were determined in the temperature range (10 to 40) °C, from potentiometric titrations in aqueous potassium chloride solutions with molalities up to 3 $\text{mol}\cdot\text{kg}^{-1}$. The electrochemical cell was calibrated in terms of hydrogen ion concentration, and the calculations were performed by means of the SUPERQUAD computer program. The Pitzer theory, widely used in the evaluation of the excess free energy of nonideal electrolyte solutions, was applied to the calculation of the activity coefficient of each chemical species involved in the equilibria, and a good fit was observed at all temperatures. From these results, Pitzer interaction coefficients for potassium acetate were determined. This model was also used to calculate the chloride ion activity coefficient in acetate buffer systems with added potassium chloride, at ionic strengths higher than 0.1 $\text{mol}\cdot\text{kg}^{-1}$, the limit of validity of the Bates−Guggenheim convention.

INTRODUCTION

Thermodynamic ionization constants of ethanoic acid, or acetic acid (HAc), at various temperatures, have been determined very accurately from potentiometric measurements on the Harned cell, without liquid junction, using dilute solutions[1,2] and from conductivity data.[3] However, in many analytical applications, weak acid solutions contain a relatively large amount of a background electrolyte, compared to that of the weak acid, to keep the ionic strength constant to avoid significant variation of the activity coefficients during measurements. Therefore, values for stoichiometric ionization constants of the weak acid in different ionic media are necessary for the evaluation of the system composition. They can be determined experimentally or by calculation of the activity coefficient of each chemical species involved in the equilibrium, provided an adequate equation is known.

The Pitzer theory[4,5] has been widely used in the evaluation of the excess free energy of non ideal electrolyte solutions. It arbitrarily separates electrostatic and specific short-range interactions and enables these to be expressed as virial coefficients. One advantage of this theory is that the second and third virial coefficients for a given salt can be determined from measurements in single salt solutions and be applied in mixed electrolyte solutions. It has been successfully applied to many single and mixed electrolytes, in both aqueous and nonaqueous solutions, with ionic strengths up to saturation. The use of the Pitzer model to calculate single ion activity coefficients for the assignment of pH to the standards for pH determination has been pointed out by Pitzer,[5] and there are reports in the literature that refer to this application.[6−8]

Acetic acid and sodium or potassium acetate can also be used to prepare standards for pH determination.[9−11] In particular, two solutions with different concentrations of acetic acid and sodium acetate have been selected as secondary standards,[11] and the respective pH was calculated from Harned cell measurements,[12] using the Bates-Guggenheim convention[13] for the calculation of the chloride ion activity coefficient, according to the recommended methodology for assigning pH to the standards.[10,11]

There are fewer studies on the acetic acid ionization in potassium chloride than in sodium chloride aqueous media, in the literature. Protonation constants of acetic acid in potassium chloride solutions from potentiometric data at 25 °C have been reported by De Robertis et al.[14] Partanen and co-workers have discussed methods for the calculation of stoichiometric ionization constants of acetic acid in aqueous potassium chloride solutions at 25 °C.[15,16]

This work reports a potentiometric study on the ionization of acetic acid in aqueous potassium chloride solutions with molalities up to 3 $\text{mol}\cdot\text{kg}^{-1}$, in the temperature range (10 to 40) °C. Pitzer's model was applied to the evaluation of the activity coefficient of each chemical species involved in the equilibria. The chloride ion activity coefficients were also evaluated, at the various investigated temperatures, for ionic strengths up to 3 $\text{mol}\cdot\text{kg}^{-1}$, that is, higher than 0.1 $\text{mol}\cdot\text{kg}^{-1}$, the limit of validity of the Bates−Guggenheim convention.[13]

EQUATIONS

The thermodynamic ionization constant of the acetic acid, K, is given by:

$$K = \left(\frac{m_{\text{H}}m_{\text{Ac}}}{m_{\text{HAc}}m^0}\right)\left(\frac{\gamma_{\text{H}}\gamma_{\text{Ac}}}{\gamma_{\text{HAc}}}\right) \tag{1}$$

where m and γ refer to molality and activity coefficient, respectively, of the indicated species and $m^0 = 1\ \text{mol}\cdot\text{kg}^{-1}$ is the standard state molality. The ionic charges have been omitted for simplicity. The stoichiometric ionization constant, $K_{\text{m}} = (m_{\text{H}}m_{\text{Ac}})/(m_{\text{HAc}}m^0)$, was determined from potentiometric titrations, in potassium chloride solutions, by means of the SUPERQUAD computer program.[17]

According to the Pitzer's formalism, the activity coefficients in eq 1 are given by eqs 2 to 4:

$$\begin{aligned}\ln \gamma_{\text{H}} = F &+ m_{\text{Cl}}(2B_{\text{HCl}} + ZC_{\text{HCl}}) \\ &+ m_{\text{K}}(2\theta_{\text{H,K}} + m_{\text{Cl}}\psi_{\text{H,K,Cl}} + m_{\text{Ac}}\psi_{\text{H,K,Ac}}) \\ &+ m_{\text{Cl}}m_{\text{Ac}}\psi_{\text{H,Cl,Ac}} + m_{\text{H}}m_{\text{Cl}}C_{\text{HCl}} \\ &+ m_{\text{K}}(m_{\text{Cl}}C_{\text{KCl}} + m_{\text{Ac}}C_{\text{KAc}}) + 2m_{\text{HAc}}\lambda_{\text{H,HAc}} + ...\end{aligned} \tag{2}$$

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Table 1. Mean Values of the Negative Logarithm of the Stoichiometric Ionization Constant of Acetic Acid in Potassium Chloride Solutions

t	I		t	I	
°C	mol·kg^{-1}	pK_m	°C	mol·kg^{-1}	pK_m
10	0.0151[a]	4.773 (0.027)	30	0.0154[a]	4.647 (0.003)
	0.0362	4.627 (0.048)		0.0597	4.581 (0.002)
	0.0601	4.600 (0.039)		0.1104	4.549 (0.002)
	0.0803	4.586 (0.004)		0.2123	4.516 (0.011)
	0.1108	4.569 (0.047)		0.3142	4.498 (0.004)
	0.2124	4.546 (0.059)		0.4149	4.492 (0.003)
	0.3146	4.539 (0.033)		0.5192	4.494 (0.002)
	0.4167	4.539 (0.027)		1.0485	4.529 (0.002)
	0.5208	4.541 (0.011)		1.5835	4.592 (0.008)
	1.0459	4.591 (0.080)		2.1577	4.680 (0.006)
	1.5840	4.662 (0.043)		2.7474	4.768 (0.029)
	2.1466	4.748 (0.021)		3.3634	4.862 (0.014)
	2.7024	4.838 (0.012)			
	3.3030	4.938 (0.005)			
15	0.0157[a]	4.686 (0.078)	35	0.0155[a]	4.654 (0.004)
	0.0605	4.591 (0.007)		0.0597	4.583 (0.004)
	0.1108	4.562 (0.010)		0.1107	4.544 (0.005)
	0.2114	4.534 (0.003)		0.2128	4.511 (0.006)
	0.3148	4.526 (0.018)		0.3134	4.495 (0.001)
	0.4150	4.523 (0.014)		0.4176	4.490 (0.012)
	0.5199	4.525 (0.003)		0.5185	4.486 (0.001)
	1.0475	4.577 (0.022)		1.0499	4.518 (0.001)
	1.5897	4.648 (0.020)		1.5892	4.586 (0.007)
	2.1506	4.729 (0.028)		2.1480	4.662 (0.003)
	2.7224	4.822 (0.022)		2.7349	4.752 (0.007)
	3.3329	4.925 (0.031)		3.3783	4.844 (0.008)
20	0.0151[a]	4.685 (0.001)	40	0.0153[a]	4.664 (0.004)
	0.0599	4.589 (0.002)		0.0596	4.582 (0.001)
	0.1103	4.552 (0.003)		0.1106	4.552 (0.001)
	0.2119	4.522 (0.001)		0.2124	4.508 (0.003)
	0.3147	4.511 (0.004)		0.3140	4.486 (0.006)
	0.4163	4.511 (0.015)		0.4168	4.483 (0.002)
	0.5201	4.514 (0.002)		0.5204	4.480 (0.004)
	1.0462	4.560 (0.010)		1.0508	4.513 (0.009)
	1.5813	4.621 (0.002)		1.5878	4.575 (0.001)
	2.1538	4.711 (0.003)		2.1480	4.650 (0.006)
	2.7524	4.806 (0.002)		2.7435	4.740 (0.014)
	3.3581	4.903 (0.003)		3.3112	4.824 (0.002)
25	0.0153[a]	4.659 (0.009)			
	0.0594	4.580 (0.019)			
	0.1106	4.552 (0.001)			
	0.2121	4.516 (0.011)			
	0.3145	4.506 (0.004)			
	0.4158	4.500 (0.005)			
	0.5163	4.502 (0.002)			
	1.0458	4.542 (0.001)			
	1.5906	4.610 (0.010)			
	2.1475	4.692 (0.017)			
	2.7697	4.788 (0.003)			
	3.3818	4.884 (0.004)			

[a] Solutions without KCl. Standard deviations are shown in parentheses.

$$\begin{aligned}\ln\gamma_{\mathrm{Ac}} = {} & F + m_{\mathrm{K}}(2B_{\mathrm{KAc}} + ZC_{\mathrm{KAc}}) \\ & + m_{\mathrm{Cl}}(2\theta_{\mathrm{Cl,Ac}} + m_{\mathrm{K}}\psi_{\mathrm{K,Cl,Ac}} + m_{\mathrm{H}}\psi_{\mathrm{H,Cl,Ac}}) \\ & + m_{\mathrm{K}}m_{\mathrm{H}}\psi_{\mathrm{K,H,Ac}} + m_{\mathrm{H}}m_{\mathrm{Cl}}C_{\mathrm{HCl}} \\ & + m_{\mathrm{K}}(m_{\mathrm{Cl}}C_{\mathrm{KCl}} + m_{\mathrm{Ac}}C_{\mathrm{KAc}}) \\ & + 2m_{\mathrm{HAc}}\lambda_{\mathrm{Ac,HAc}} + \ldots \end{aligned} \tag{3}$$

$$\begin{aligned}\ln\gamma_{\mathrm{HAc}} = {} & 2(m_{\mathrm{H}}\lambda_{\mathrm{H,HAc}} + m_{\mathrm{K}}\lambda_{\mathrm{K,HAc}} + m_{\mathrm{Cl}}\lambda_{\mathrm{Cl,HAc}} \\ & + m_{\mathrm{Ac}}\lambda_{\mathrm{Ac,HAc}} + m_{\mathrm{HAc}}\lambda_{\mathrm{HAc,HAc}}) \end{aligned} \tag{4}$$

where

$$F = -A^{\Phi}F_1 + m_{\mathrm{K}}(m_{\mathrm{Cl}}B'_{\mathrm{KCl}} + m_{\mathrm{Ac}}B'_{\mathrm{KAc}}) \tag{5}$$

$$B = \beta^{(0)} + \beta^{(1)}F_2 \tag{6}$$

$$B' = \beta^{(1)}F_3 \tag{7}$$

$$Z = m_{\mathrm{K}} + m_{\mathrm{H}} + m_{\mathrm{Cl}} + m_{\mathrm{Ac}} \tag{8}$$

F_1, F_2, and F_3 are functions of the ionic strength, I/mol·kg^{-1}:

$$\begin{aligned}F_1 = {} & I^{1/2}/[1 + 1.2(I/m^0)^{1/2}] \\ & + \{(2/1.2)\ln[1 + 1.2(I/m^0)^{1/2}]\}(m^0)^{1/2} \end{aligned} \tag{9}$$

$$\begin{aligned}F_2 = {} & [1/(2I/m^0)]\{1 - [1 \\ & + 2(I/m^0)^{1/2}]\exp[-2(I/m^0)^{1/2}]\} \end{aligned} \tag{10}$$

$$\begin{aligned}F_3 = {} & [1/(2I^2)]\{-1 \\ & + [1 + 2(I/m^0)^{1/2} \\ & + 2(I/m^0)]\exp[-2(I/m^0)^{1/2}]\}m^0 \end{aligned} \tag{11}$$

A^{Φ} is the Debye–Hückel limiting law slope coefficient for the osmotic coefficient;[4] B and C are the second and third virial coefficients, respectively, for single electrolytes; $\beta^{(0)}$ and $\beta^{(1)}$ are specific coefficients for each electrolyte; θ and ψ are the second and third order mixing coefficients, respectively, for mixed electrolytes; and λ arises from interactions between ions and neutral chemical species or between molecules. For a weak acid, HA, $B_{\mathrm{HA}} = 0$ and so $B'_{\mathrm{HA}} = 0$.[18] The nondeterminable part of the ionic activity coefficients, which cancels when equations are combined to give mean activity coefficients,[5] has been neglected.

In the acetate buffer solution with added potassium chloride, the chloride ion activity coefficient may be evaluated by eq 12:

$$\begin{aligned}\ln\gamma_{\mathrm{Cl}} = {} & F + m_{\mathrm{K}}(2B_{\mathrm{KCl}} + ZC_{\mathrm{KCl}}) + m_{\mathrm{H}}m_{\mathrm{Cl}}C_{\mathrm{HCl}} \\ & + m_{\mathrm{K}}(m_{\mathrm{Cl}}C_{\mathrm{KCl}} + m_{\mathrm{Ac}}C_{\mathrm{KAc}}) + 2m_{\mathrm{HAc}}\lambda_{\mathrm{Cl,HAc}} \end{aligned} \tag{12}$$

■ EXPERIMENTAL SECTION

Acetic acid solutions, at 0.02 mol·dm^{-3}, were titrated with 1 mol·dm^{-3} potassium hydroxide in aqueous potassium chloride solutions. The volume of the solution used in most titrations

Table 2. Parameters for Calculation of the Ionization Constant of Acetic Acid (eq 13)[a]

t		p_1	p_2	p_3	
°C	p_0	$\mathrm{kg^{1/2}\cdot mol^{-1/2}}$	$\mathrm{kg\cdot mol^{-1}}$	$\mathrm{kg^2\cdot mol^{-2}}$	σ^b
10	4.7490 (0.0078)	−0.732 (0.038)	0.690 (0.050)	−0.128 (0.018)	0.0092
15	4.7567 (0.0083)	−0.774 (0.041)	0.710 (0.055)	−0.130 (0.020)	0.0103
20	4.7559 (0.0084)	−0.799 (0.041)	0.720 (0.055)	−0.132 (0.020)	0.0104
25	4.7469 (0.0061)	−0.792 (0.030)	0.705 (0.040)	−0.128 (0.014)	0.0075
30	4.7455 (0.0062)	−0.796 (0.030)	0.695 (0.040)	−0.124 (0.015)	0.0076
35	4.7519 (0.0056)	−0.824 (0.027)	0.715 (0.036)	−0.131 (0.013)	0.0069
40	4.7610 (0.0052)	−0.855 (0.026)	0.731 (0.034)	−0.134 (0.013)	0.0064

[a] Standard errors are shown in parentheses. [b] Standard error of the fit.

was 5 cm^3. The ionic strength varied from (0.02 to 3) mol·kg^{-1}. This salt (fractopur, from Merck) was dried at 120 °C for 24 h. The KOH and HAc solutions were prepared from Titrisol ampules (Merck) and from Fixanal 38051 (Riedel-de Haen), respectively. The base solution was standardized against potassium hydrogen phthalate and was used to standardize the acetic acid solutions. Purified water, with a resistivity around 18 MΩ cm, obtained from Milli-Q185 Plus (Millipore), was boiled for 30 min to remove dissolved gases, before being used in the solution preparation.

Titrations were carried out in a double-wall glass vessel, under helium atmosphere, and two combined pH glass electrodes (Crison, ref 52-08) were used for the measurements. The temperature was controlled within ± 0.05 °C from (10 to 40) °C. Cell potential differences were obtained by means of an interface with a Molspin pH meter (precision ± 0.01 mV), compatible with the SUPERQUAD program[17] which was used for the calculation of the stoichiometric ionization constants.

The electrodes were calibrated in terms of the hydrogen ion concentration, by means of titrations of 0.01 mol·kg^{-1} HCl, prepared from Titrisol ampules (Merck), with 1 mol·kg^{-1} KOH, at each temperature and ionic strength, according to the method described by Gans and O'Sullivan.[19]

The acetic acid concentrations were low to avoid large variations of the ionic strength along the titrations and to avoid variations in the liquid junction potential. For each solution, the ionic strength was taken as the mean of the calculated values after each addition of titrant, taking into account the concentration of all ionic species involved in the equilibria, as calculated by the SUPERQUAD program. The ionic strength variation during the titrations was more pronounced for those solutions with no added KCl and was negligible for the other solutions.

The required ionization constants of water, in potassium chloride media, were obtained from literature data.[20]

RESULTS AND DISCUSSION

Ionization Constants. The stoichiometric ionization constants of acetic acid (pK_m = −log K_m), calculated in molar units from the SUPERQUAD program, were converted to the molality scale by means of the densities of KCl solutions available in the literature.[21] For each experiment (three replicates for each ionic strength and temperature), readings were taken with two combined pH glass electrodes, so six values each were computed for pK_m. The mean values and the respective standard deviations are listed in Table 1.

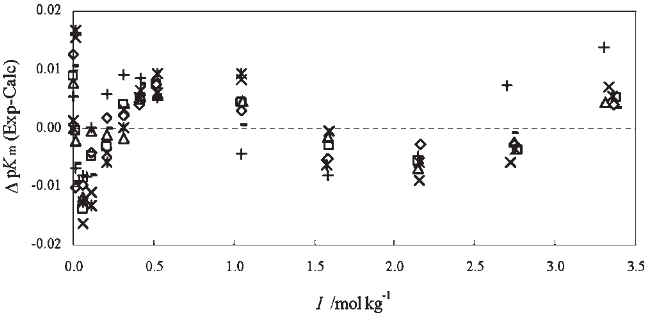

Figure 1. Differences between experimental pK_m values and those predicted by eq 13 at: +, 10 °C; ×, 15 °C; ∗, 20 °C; □, 25 °C; ◇, 30 °C; −, 35 °C; △, 40 °C.

Several empirical equations were tested to express the ionic strength dependence of pK_m, and a reasonably good fit of eq 13 to the experimental data was obtained at all temperatures. The first point of the data set at 10 °C was considered an outlier and was not taken into account in further calculations. Published thermodynamic ionization constants[1,2] were also included in the data sets.

$$\mathrm{p}K_m = p_0 + p_1 I^{1/2} + p_2 I + p_3 I^{3/2} \tag{13}$$

The values of the adjustable parameters, p_0, p_1, p_2, and p_3, are given in Table 2. A smooth variation of these parameters with the temperature was not found. Nevertheless, eq 13 is useful to calculate pK_m of acetic acid in aqueous KCl solutions. A plot of the residuals against ionic strength, at the studied temperatures, is shown in Figure 1. The points scatter more at low concentrations, indicating greater difficulty in reproducing experimental data.

Equations 1 to 4 were used to apply the Pitzer model to this system. In these solutions, the hydrogen ion and total acetate (acetic acid and acetate ion) molalities are very small compared to that of KCl, except for the first solution of each set (Table 1). So this solution was not included in the following calculations, and those terms involving m_{H}, m_{HAc} or m_{Ac} in eqs 2 to 4 were neglected. Thus, from eqs 1 to 4, pK of acetic acid can be expressed by eq 14:

$$\begin{aligned}\mathrm{p}K = \mathrm{p}K_m - (2/\ln 10)(&F + m_{\mathrm{Cl}}B_{\mathrm{HCl}} + 0.5m_{\mathrm{Cl}}ZC_{\mathrm{HCl}} \\ &+ m_{\mathrm{K}}B_{\mathrm{KAc}} + 0.5m_{\mathrm{K}}ZC_{\mathrm{KAc}} + m_{\mathrm{K}}\theta_{\mathrm{H,K}} \\ &+ 0.5m_{\mathrm{K}}m_{\mathrm{Cl}}\psi_{\mathrm{H,K,Cl}} + m_{\mathrm{Cl}}\theta_{\mathrm{Cl,Ac}} \\ &+ 0.5m_{\mathrm{K}}m_{\mathrm{Cl}}\psi_{\mathrm{K,Cl,Ac}} + m_{\mathrm{K}}m_{\mathrm{Cl}}C_{\mathrm{KCl}} \\ &- m_{\mathrm{K}}\lambda_{\mathrm{K,HAc}} - m_{\mathrm{Cl}}\lambda_{\mathrm{Cl,HAc}})\end{aligned} \tag{14}$$

Table 3. Pitzer Coefficients for HCl and KCl and Debye−Hückel Parameter for the Osmotic Coefficient (A^{ϕ})

		HCl			KCl		
t	A^{ϕ}	$\beta^{(0)}$	$\beta^{(1)}$	C	$\beta^{(0)}$	$\beta^{(1)}$	C
°C	$\mathrm{kg}^{1/2}\cdot\mathrm{mol}^{-1/2}$	$\mathrm{kg}\cdot\mathrm{mol}^{-1}$	$\mathrm{kg}\cdot\mathrm{mol}^{-1}$	$\mathrm{kg}^2\cdot\mathrm{mol}^{-2}$	$\mathrm{kg}\cdot\mathrm{mol}^{-1}$	$\mathrm{kg}\cdot\mathrm{mol}^{-1}$	$\mathrm{kg}^2\cdot\mathrm{mol}^{-2}$
10	0.3821	0.1821	0.2924	0.00086	0.03966	0.1961	−0.000038
15	0.3852	0.1806	0.2931	0.00071	0.04256	0.2015	−0.00017
20	0.3882	0.1790	0.2938	0.00055	0.04545	0.2086	−0.00029
25	0.3915	0.1775	0.2945	0.00040	0.04835	0.2122	−0.00042
30	0.3949	0.1760	0.2952	0.00024	0.05125	0.2176	−0.00055
35	0.3985	0.1744	0.2959	0.00009	0.05414	0.2229	−0.00067
40	0.4023	0.1729	0.2966	−0.00006	0.05704	0.2283	−0.00080

Table 4. Parameters To Calculate pK_m by the Pitzer Formalism[a]

t			P_1	P_2	P_3	
°C	pK[b]	P_0	$\mathrm{kg}\cdot\mathrm{mol}^{-1}$	$\mathrm{kg}\cdot\mathrm{mol}^{-1}$	$\mathrm{kg}^2\cdot\mathrm{mol}^{-2}$	σ[c]
10	4.762	4.7632 (0.0010)	0.0828 (0.0056)	0.497 (0.019)	0.0016 (0.0011)	0.0012
15	4.758	4.7570 (0.0017)	0.0915 (0.0077)	0.458 (0.028)	0.0007 (0.0015)	0.0015
20	4.756	4.7554 (0.0033)	0.106 (0.015)	0.379 (0.054)	−0.0013 (0.0030)	0.0029
25	4.756	4.7546 (0.0022)	0.112 (0.010)	0.342 (0.036)	−0.0021 (0.0019)	0.0020
30	4.759	4.7602 (0.0028)	0.126 (0.013)	0.257 (0.046)	−0.0039 (0.0024)	0.0025
35	4.763	4.7627 (0.0026)	0.134 (0.012)	0.222 (0.043)	−0.0056 (0.0022)	0.0023
40	4.769	4.7684 (0.0035)	0.143 (0.016)	0.166 (0.057)	−0.0061 (0.0030)	0.0031

[a] Standard errors are shown in parentheses. [b] From ref 2. [c] Standard error of the fit.

The function Y, given by eq 15, includes the experimental pK_m values (Table 1), the Pitzer model coefficients for aqueous HCl and KCl indicated in Table 3, calculated at each temperature from available data,[5] and the mixing coefficients[5] $\theta_{\mathrm{H,K}} = 0.005$ kg·mol^{-1} and $\psi_{\mathrm{H,K,Cl}} = -0.007$ kg^2·mol^{-2}. The Debye−Hückel limiting law slope coefficient, A^{Φ}, is also given in Table 3. Since m_{KCl} and I have identical values, Y can be given by eq 15:

$$Y = \mathrm{p}K_m - (2/\ln 10)(F + IB_{\mathrm{HCl}} + 0.5IZC_{\mathrm{HCl}} + I^2C_{\mathrm{KCl}} + I\theta_{\mathrm{H,K}} + 0.5I^2\psi_{\mathrm{H,K,Cl}}) \qquad (15)$$

Equation 16 was then obtained from eqs 14 and 15, neglecting the third-order mixing parameter $\psi_{\mathrm{K,Cl,Ac}}$:

$$Y = P_0 + P_1X_1 + P_2X_2 + P_3X_3 \qquad (16)$$

where $X_1 = (2/\ln 10)I$, $X_2 = (2/\ln 10)IF_2$, and $X_3 = (1/\ln 10)IZ$. The adjustable parameters, $P_{0,1,2,3}$, were obtained by regression analysis and are shown in Table 4. P_0 corresponds to the ionization constant at zero ionic strength, and its values, in the temperature range under consideration, are close to those obtained by Harned and Ehlers[1,2] using dilute solutions in the Harned cell, as also indicated in Table 4.

The parameters P_i (i = 1, 2, 3) show a linear variation with temperature:

$$P_i = a_i + b_i(t/°\mathrm{C} - 25) \qquad (17)$$

The coefficients a_i and b_i are presented in Table 5.

The variation of pK_m with $I^{1/2}$ is illustrated in Figure 2, according to the Pitzer's equations, at (10, 25, and 40) °C. Similar plots were obtained at other temperatures. Differences between experimental pK_m and calculated by Pitzer's equations were plotted against I, at all temperatures, and are shown in Figure 3.

Table 5. Parameters To Be Used in Equation 17[a]

P_i	a_i	b_i	σ[b]
P_1	0.1134 (0.0007)	0.00204 ($7\cdot10^{-5}$)	0.0019
P_2	0.3315 (0.0046)	−0.0114 ($5\cdot10^{-4}$)	0.012
P_3	−0.0024 (0.0002)	−0.00027 ($2\cdot10^{-5}$)	0.0004

[a] Standard errors are shown in parentheses. [b] Standard error of the fit.

Pitzer Interaction Coefficients. From eqs 14 to 16, the Pitzer interaction coefficients for KAc were evaluated by means of the following expressions: $P_1 = \beta^{(0)}_{\mathrm{KAc}} + \theta_{\mathrm{Cl,Ac}} - (\lambda_{\mathrm{K,HAc}} + \lambda_{\mathrm{Cl,HAc}})$, $P_2 = \beta^{(1)}_{\mathrm{KAc}}$ and $P_3 = C_{\mathrm{KAc}}$. The $\theta_{\mathrm{Cl,Ac}}$ value (−0.00545 kg·mol^{-1}), suggested by Manohar and Ananthaswamy,[22] was determined in their study of acetic acid in sodium chloride media. Partanen[15] considered $\lambda_{\mathrm{Cl,HAc}} = 0$ and calculated $\lambda_{\mathrm{K,HAc}}$ (0.044 kg·mol^{-1}) from measurements on the Harned cell.[23] The temperature dependence of these two parameters is expected to be very small and was here neglected. Then they were used to determine $\beta^{(0)}_{\mathrm{KAc}}$ at the various temperatures. Table 6 presents the Pitzer coefficients $\beta^{(0)}$, $\beta^{(1)}$ and C for KAc which are close to those published by Pitzer and Mayorga[24] based on experimental data from single salt solutions at 25 °C. The values indicated by De Robertis et al.[14] were obtained from potentiometric titrations, with $\theta_{\mathrm{Cl,Ac}} = 0$, $\psi_{\mathrm{Cl,K,Ac}} = 0$, and $\lambda_{\mathrm{K,HAc}} = 0.094$ kg·mol^{-1} in their calculations.

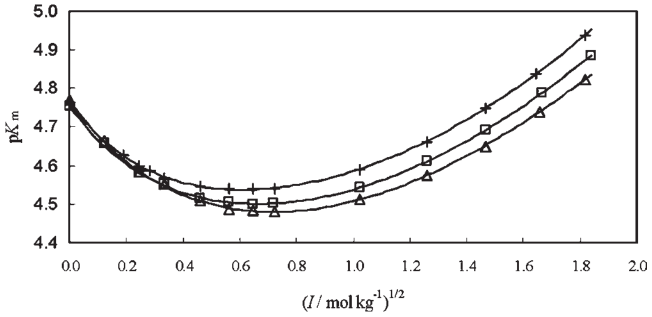

Figure 2. Ionic strength dependence of pK_m, according to Pitzer's formalism, at: +, 10 °C; □, 25 °C; △, 40 °C.

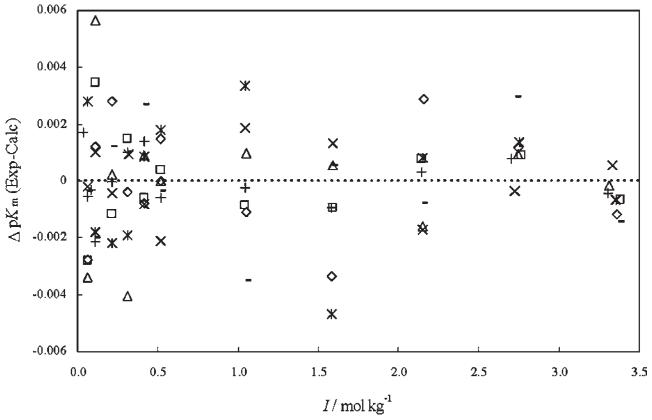

Figure 3. Differences between experimental pK_m and calculated by Pitzer equations at: +, 10 °C; ×, 15 °C; ∗, 20 °C; □, 25 °C; ◇, 30 °C; −, 35 °C; △, 40 °C.

Table 6. Pitzer Interaction Coefficients for KAc

t	$\beta^{(0)}$	$\beta^{(1)}$	C
°C	kg·mol^{-1}	kg·mol^{-1}	kg^2·mol^{-2}
10	0.132	0.497	0.0016
15	0.141	0.458	0.0007
20	0.155	0.379	−0.0013
25	0.161	0.342	−0.0021
	0.1587[a]	0.3251[a]	−0.0033[a]
	0.228[b]	0.143[b]	−0.0042[b]
30	0.175	0.257	−0.0039
35	0.184	0.222	−0.0056
40	0.192	0.166	−0.0061

[a] From ref 24. [b] From ref 14.

Table 7. Temperature Dependence of the Pitzer Parameters: $P = A + B\,(t/°\mathrm{C} - 25)$

P	A	B	σ^a
$\beta^{(0)}$	0.1625 (0.0007)	0.00204 ($7 \cdot 10^{-5}$)	0.0019
$\beta^{(1)}$	0.3315 (0.0046)	−0.0114 ($5 \cdot 10^{-4}$)	0.0122
C	−0.0024 (0.0001)	−0.00027 ($1 \cdot 10^{-5}$)	0.0004

[a] Standard error of the fit; standard coefficient errors are shown in parentheses.

Table 8. Values of $(-\log \gamma_{\mathrm{Cl}})$ for Acetate Buffer Systems with Ionic Strengths of (0.01 and 0.1) mol·kg^{-1}

t	0.01 mol·kg^{-1}		0.1 mol·kg^{-1}	
°C	B-G	Pitzer	B-G	Pitzer
10	0.0434	0.0444	0.1070	0.1151
15	0.0437	0.0447	0.1078	0.1154
20	0.0440	0.0450	0.1087	0.1154
25	0.0444	0.0454	0.1096	0.1157
30	0.0448	0.0457	0.1105	0.1158
35	0.0452	0.0460	0.1114	0.1162
40	0.0456	0.0464	0.1124	0.1166

Table 9. Chloride Ion Activity Coefficient $(-\log \gamma_{\mathrm{Cl}})$ in Two Acetate Buffers ($m_{\mathrm{HAc}} = m_{\mathrm{KAc}} = 0.1$ mol·kg^{-1} and $m_{\mathrm{HAc}} = m_{\mathrm{KAc}} = 0.01$ mol·kg^{-1}) with Added Potassium Chloride at 25 °C

m_{KCl}		
mol·kg^{-1}	$m_{\mathrm{Ac}} = 0.01$ mol·kg^{-1}	$m_{\mathrm{Ac}} = 0.1$ mol·kg^{-1}
0	0.0454	0.1157
0.1	0.1189	0.1458
0.5	0.1891	0.1976
1.0	0.2199	0.2243
1.5	0.2348	0.2374
2.0	0.2422	0.2438
2.5	0.2451	0.2460
3.0	0.2400	0.2455

The values obtained in the present study show a linear variation with temperature; hence, they can be easily evaluated with the information given in Table 7.

Chloride Ion Activity Coefficient. According to the recommended procedure for assigning pH values to standards for pH determination,[11] the Bates–Guggenheim convention[13] is applied for the calculation of the chloride ion activity coefficient. However, if standards with an ionic strength higher than 0.1 mol·kg^{-1} were developed, a model of electrolyte solutions that takes into account both electrostatic and specific interactions should be used.

Using the Pitzer model, for the acetate buffer system with added KCl, the chloride ion activity coefficient can be evaluated by eq 12. Table 8 gives the results of this calculation for two buffer solutions of HAc and KAc with ionic strengths of (0.1 and 0.01) mol·kg^{-1} in which $m_{\mathrm{Cl}} = 0$. For comparison, the Bates–Guggenheim convention was also applied, and as can be observed in the same table, the biggest difference, in terms of pH, between the two approaches is 0.008 for the more concentrated solution at 10 °C and is close to 0.001 for the other buffer. In this calculation, it was considered that $\lambda_{\mathrm{Cl,HAc}} = 0$. If it were assumed that $\lambda_{\mathrm{K,HAc}} = 0$ and $\lambda_{\mathrm{Cl,HAc}} = 0.044$ kg·mol^{-1}, the differences would be lower than 0.005 for both buffers in this temperature range.

The chloride ion activity coefficient was also calculated by eq 12 when potassium chloride is added to those buffers, and the results, at 25 °C, are indicated in Table 9.

CONCLUSIONS

Stoichiometric ionization constants of acetic acid were determined in potassium chloride aqueous solutions with molalities up to 3 $\text{mol}\cdot\text{kg}^{-1}$, from potentiometric titrations, in the temperature range (10 to 40) °C. The Pitzer model was applied for the calculation of the activity coefficients of the chemical species involved in the equilibria, and a good fit of those equations to the experimental data was observed.

The specific interaction coefficients for KAc, here obtained, enable the computation of the chloride ion activity coefficient in acetate buffer systems with a potassium ion. This formulation could replace the Bates–Guggenheim convention, if acetate standard buffers were developed, with added potassium chloride to increase the ionic strength to match test solutions, hence reducing the residual liquid junction potential in pH measurements.

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