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(Received 26 August 1985

In revised form 1 July 1986)

ACTIVITY COEFFICIENTS OF TETRAETHYLAMMONIUM PERCHLORATE IN AQUEOUS SOLUTIONS.

by

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Abstract.- Mean ionic activity coefficients of tetraethylammonium (TEA) perchlorate in aqueous solutions have been calculated from the effect of the TEA salt on the perchloric acid activity coefficients. Acid activity coefficients have been determined by measuring the emf of a concentration cell.

Parameters β^0 , β^1 and C^0 in Pitzer's equations have also been calculated for a series of substituted ammonium salts using both previously reported data and our TEA perchlorate values.

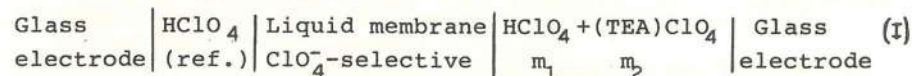
Key words.- Activity coefficients, tetraethylammonium perchlorate, electrochemical cell measurements.

INTRODUCTION

An exact thermodynamic study of electrosorption requires the knowledge of the activity values of the system components in the homogeneous solution phase. In order to apply with exactness the electrocapillary equation to the mercury-(C_2H_5)₄NClO₄, HClO₄ aqueous solution interphase, we must know TEA perchlorate activity values in perchloric acid solutions and its effect on the acid activity values.

Both osmotic and activity coefficients for tetraalkylammonium halides [1-4] were determined using the isopiestic method. Values obtained by this method for some substituted ammonium halides, nitrates and perchlorates were also repor-

ted[5-8]. But the relative low solubility of TEA perchlorate (<0.2m) was an important hindrance to be studied by this method. Then, we calculate TEA perchlorate activity coefficients from the TEA salt effect on the perchloric acid activity coefficients, which are determined by measuring the emf of the following concentration cell with a liquid membrane[9]:



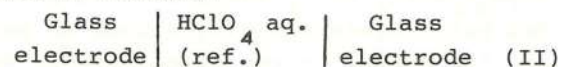
The liquid membrane has a Nernstian response in respect to the perchlorate anion[9]:

$$E = (RT/F) \ln [m_1(m_1+m_2) \gamma_{\pm}^2 / (m \gamma_{\pm, \text{ref.}})^2] \quad (1)$$

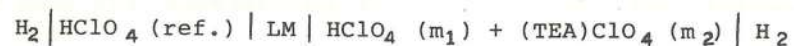
and activity coefficients are analyzed by means of Pitzer's equations[10], obtaining the parameters β^0 and β^1 for TEA perchlorate.

EXPERIMENTAL

The cell design and measuring procedure have been described previously[9]. The liquid membrane consists of a tetraheptylammonium perchlorate solution(0.001m) in ethylbromide, that moreover to have Nernstian response to perchlorate, prevents TEA perchlorate solubility. However, the influence of this compound on the liquid membrane has also been analyzed. In order to eliminate asymmetry potential contributions of both glass electrodes (in the range of tenths of millivolts) a second cell is used[9]:



and since the liquid membrane does not present asymmetry potential[9], $E = E_I - E_{II}$ represents the emf of the equivalent cell:



Apparatus and Reagents

The emf measurements were made with a Precision Decade Potentiometer (Scientific PYE Instruments 7600), using an Electrometer(Keithley 610C) of high input impedance($>10^{14} \Omega$) as a null point detector. Both cells were thermostated at $25 \pm 0.05^\circ\text{C}$ with a circulator thermostat(Haake D8-G), and isolated from static currents by a Faraday cage. HClO₄ Suprapur Merck and (TEA)ClO₄ Carlo Erba Polarographic Quality were used, together with twice distilled water(once over permanganate), to prepare the solutions. TEA perchlorate was previously recrystallized and dried under vacuum.

RESULTS

Table 1 summarizes mean ionic activity coefficients for perchloric acid in mixtures HClO₄+(TEA)ClO₄ calculated by means of equation (1). The reference solution activity coefficient has been calculated using Pitzer's equation with $\beta^0=0.1853$ and $\beta^1=0.2695$ [9].

If mixture parameters would be considered zero and the contribution of C^γ terms negligible[9] because the low ionic strength, Pitzer's equation for a mixture of two 1:1 electrolytes with a common ion[10] becomes:

$$\ln \gamma_{MX} = f^{\gamma} + m B_{MX}^{\gamma} + m_{NX} (B_{NX}^{\phi} - B_{MX}^{\phi}) \quad (2)$$

where

$$f^{\gamma} = -A_{\phi} [m^{1/2} / (1+bm^{1/2}) + (2/b) \ln(1+bm^{1/2})] \quad (3)$$

$$B_{MX}^{\gamma} = 2\beta^0 + 2\beta^1 / (\alpha^2 m) [1 - (1 + \alpha m^{1/2} - (\alpha^2 m / 2) \exp(-\alpha m^{1/2}))] \quad (4)$$

$$B_{MX}^{\phi} = \beta^0 + \beta^1 \exp(-\alpha m^{1/2}) \quad (5)$$

with the values $A_{\phi} = 0.392$, $\alpha = 2.0$ and $b = 1.2$ [10]. MX denotes perchloric acid and NX TEA perchlorate, $m = m_{MX} + m_{NX}$. Since β^0 and β^1 for perchloric acid are known, terms in equation (2) can be reordered:

Table 1.- Mean ionic activity coefficients of HClO₄ in mixtures with (TEA)ClO₄ by emf measurements.

	$m(\text{HClO}_4)$ $10^{-2} \text{ mol Kg}^{-1}$	$m(\text{TEAClO}_4)$ $10^{-2} \text{ mol Kg}^{-1}$	E mV	$\gamma_{\pm}(\text{HClO}_4)$
+	1.003	1.096	16.83	0.865
	1.026	1.917	24.46	0.838
	1.004	2.766	29.09	0.820
	1.004	3.522	32.90	0.805
	1.002	3.482	32.53	0.804
	0.998	3.974	34.39	0.794
	1.002	4.404	36.29	0.788
	0.994	5.150	38.20	0.770
++	9.990	3.065	3.91	0.751
	9.942	3.896	4.63	0.742
	10.039	5.765	6.99	0.723
	9.965	6.646	7.37	0.713
	9.997	8.185	8.69	0.699

+ $m_{\text{ref.}} = 1.001 \cdot 10^{-2}$, $\gamma_{\text{ref.}} = 0.904$
 ++ $m_{\text{ref.}} = 1.0016 \cdot 10^{-1}$, $\gamma_{\text{ref.}} = 0.794$

$$F = \ln \gamma_{\text{MX}} - f^{\gamma} - m B_{\text{MX}}^{\gamma} + m_{\text{NX}} B_{\text{MX}}^{\phi} = m_{\text{NX}} [\beta_{\text{NX}}^{\circ} + \beta_{\text{MX}}^{\phi} \exp(-\alpha m^{\frac{1}{2}})] \quad (6)$$

and a non-linear regression procedure allow us to find the parameters for TEA perchlorate within the concentration range studied: $\beta^{\circ} = -1.1828$ and $\beta^{\phi} = 0.6995$.

TEA perchlorate activity coefficients in aqueous solution have been calculated at rounded molalities from Pitzer's equation for 1:1 electrolytes with the calculated parameters (table 2).

Moreover, as commented in reference[9], Bromley's equation for 1:1 electrolyte mixtures, at moderate ionic strength, takes the form:

$$\log \gamma_{\text{MX}} = 1/(2(m_{\text{MX}} + m_{\text{NX}})) ((2m_{\text{MX}} + m_{\text{NX}}) \log \gamma_{\text{MX}}^{\circ} + m_{\text{NX}} \log \gamma_{\text{NX}}^{\circ}) \quad (7)$$

Table 2.- Mean ionic activity coefficients of (TEA)ClO₄.

m	γ^a	γ^b
0.001	0.963	0.963
0.005	0.919	0.919
0.01	0.886	0.885
0.02	0.839	0.838
0.03	0.803	0.801
0.04	0.773	0.770
0.05	0.745	0.742
0.06	0.720	0.716
0.07	0.697	0.693
0.08	0.675	0.671
0.09	0.655	0.650
0.1	0.636	0.630
0.12	0.600	0.593
0.14	0.567	0.560
0.16	0.536	0.529
0.18	0.508	0.500

a) $\beta^{\circ} = -1.1828$, $\beta^{\phi} = 0.6995$
 b) $\beta^{\circ} = -1.2103$, $\beta^{\phi} = 0.6713$

where γ° represents the individual activity coefficients at the same ionic strength of the mixture. As $\gamma_{\text{HClO}_4}^{\circ}$ is known, then $\gamma_{(\text{TEA})\text{ClO}_4}^{\circ}$ can be calculated easily. We can use again Pitzer's equation for 1:1 electrolytes conveniently rearranged to find parameters β° and β^{ϕ} :

$$\ln \gamma^{\circ} - f^{\gamma} = 2m \beta^{\circ} + (\beta^{\phi}/2) [1 - (1 + 2m^{\frac{1}{2}} - 2m) \exp(-2m^{\frac{1}{2}})] \quad (8)$$

and a regression procedure leads to $\beta^{\circ} = -1.2103$ and $\beta^{\phi} = 0.6713$.

As table 2 shows, activity coefficients calculated by both procedures only deviate slightly as concentration increases. This demonstrates the reability of simple equation (7) in

estimating activity coefficients in electrolyte mixtures.

Finally, we notice the liquid membrane response deviates from the expected behaviour for TEA perchlorate concentration below 10^{-2} m (table 3). The concentration range with a negligible influence of the liquid membrane can be obtained from a linear plot of function $G = F - \beta^1 m_{NX} \exp(-2m^{1/2})$ (see equation (6)) in front of m_{NX} (figure 1).

DISCUSSION

Lindenbaum and Boyd[1] and Wen et al.[3,4] showed that both osmotic and activity coefficients for a series of symmetric tetraalkylammonium halides, follow the sequence $F^- > Cl^- > Br^- > I^-$ for any cation. On the other hand, the cation sequence is TMA(methyl) > TEA > TPA(propyl) > TBA(butyl) for I^- and Br^- , changing to the reverse for F^- and for Cl^- at moderate concentrations.

More recently, Bonner[6] studied both TMA and TEA nitrates and nitrate anion can be inserted in the sequence in between Br^- and I^- for both cations. The estimated osmotic coefficients for the perchlorates of these cations[6] in the limit of the isopiestic method, lead to conclude that TMA perchlorate would be situated in between nitrate and iodide, whereas TEA perchlorate would lie in between bromide and nitrate. On the contrary, our measurements indicate that TEA perchlorate activity coefficients are lower than those of iodide, the sequence being completed on the right with perchlorate anion ($F^- > Cl^- > Br^- > NO_3^- > I^- > ClO_4^-$).

To test our experimental conclusion, we have reexamined previously reported data for other ammonium salts. Thus, from the osmotic coefficients determined by Esvál and Tyree [11] for ammonium perchlorate, those calculated by Wishaw and Stokes[12] for ammonium nitrate and chloride and those calculated by Bonner for methylsubstituted ammonium perchlorates [8], nitrates[7] and chlorides[5] we conclude that the general sequence is for any cation $Cl^- > NO_3^- > ClO_4^-$. It is also noted that activity coefficients for perchlorate anion[8] strongly decreases as ammonium salt is more substi-

Table 3 .- Effect of TEA cations on the membrane response

m (HClO ₄)	m (TEAClO ₄)	E	γ _t	γ° (HClO ₄)	γ° (TEAClO ₄)
10 ⁻²	mol Kg ⁻¹	mV			
0.994	0.308	6.40	0.901	0.894	0.954
1.009	0.393	8.29	0.894	0.890	0.918
0.996	0.591	10.66	0.886	0.885	0.891
1.004	0.702	12.39	0.880	0.882	0.874

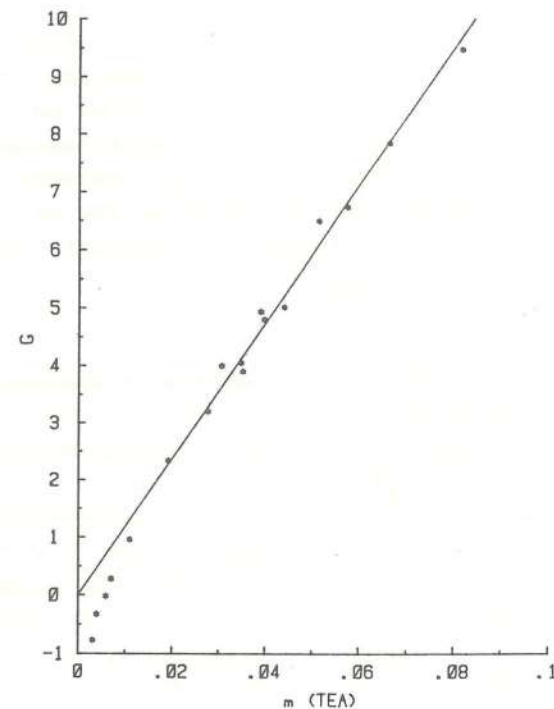


Fig.1.- Plot of the function $G = F - \beta^1 m_{NX} \exp(-2m^{1/2})$ versus the tetraethylammonium perchlorate molality for several solutions outlined in Table 1.

tuted. Our TEA perchlorate values also agree with this variations.

Nevertheless, the preceding considerations are however general and they may be altered within a concentration range, especially for the centered elements in the sequence (Cl^- , Br^-). Also, important discrepancies among reported data by several authors can be found in the literature: activity coefficients reported by Bonner[8] for ammonium perchlorate are greater than those of nitrate in contrast with the values reported by Esvál and Tyree[11].

The order of activity coefficients for any ammonium salt ($\text{Cl}^- > \text{NO}_3^- > \text{ClO}_4^-$) can be explained by the lowering of anion solvation. Thus, the greater hydration of chloride anion and the structure-promoter character of tetraalkylammonium cations[13] would explain both the greater activity coefficients and the cation sequence TBA>TPA>TEA>TMA at moderate concentration. Perchlorate anion is a solvent structure-breaker like Iodide ion and this explains the very low

Table 4.- Pitzer's parameters for several substituted ammonium salts.

salt	β^0	β^1	C^ϕ	m	σ	ref.
$\text{NH}_2\text{MeClO}_4$	-0.0338	0.0075	0.0035	0.1-4	0.0015	8
$\text{NH}_2\text{Me}_2\text{ClO}_4$	-0.0435	-0.1196	0.0024	0.1-7.5	0.0015	8
$\text{NHMe}_3\text{ClO}_4$	-0.1204	-0.1265	0.0161	0.1-1.8	0.002	8
NH_3MeCl	0.0651	0.0398	-0.0036	0.1-7.5	0.0012	5
$\text{NH}_2\text{Me}_2\text{Cl}$	0.0582	0.0495	-0.0024	0.1-6.5	0.0012	5
NH_3MeNO_3	-0.0054	0.1180	0.0001	0.1-9.5	0.003	7
$\text{NH}_2\text{Me}_2\text{NO}_3$	0.0054	0.1085	-0.0004	0.1-6	0.0023	7
NHMe_3NO_3	-0.0003	-0.0831	0.0008	0.1-8.5	0.0048	7
NMe_4NO_3	0.0128	-0.2225	0.0011	0.1-7	0.0028	6
NEt_4NO_3	-0.0388	-0.7246	0.0057	0.1-8	0.0076	6
NH_4I	0.0568	0.2906	-0.0031	0.1-7.5	0.0017	6
NEt_4ClO_4	-1.1828	0.6995	-	< 0.2	0.0023	t.w.

values of activity coefficients. TEA perchlorate activity coefficients are even lower than values predicted by the Debye-Hückel law. Ion pair formation can be postulated to minimize the ion-solvent interaction [1], being important even in dilute solutions.

ACKNOWLEDGEMENTS

We are indebted to the CIRIT(Generalitat de Catalunya) for the partial financial support given for this study.

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(Received 21 February 1986

In revised form 12 May 1986)