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How much do we know about the activity of individual ions?

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ABSTRACT

Data of activity of individual ions reported in the literature by nine authors are compared in graphical form. Visual observation of the plots clearly shows that for some systems the data are in fair agreement and it can be used to test theories of electrolyte solutions. For systems that the data show discrepancy between different researchers, it is possible to judge which data are out of the trend showed by the majority of the other studies. Only a few systems appear to need further measurements. This compilation of results is the first of its class in modern times and not only helps in showing the consistency between data from different laboratories but it also indicates for what systems data are still needed.

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1. Introduction

Thanks to a publication from D.P. Zarubin [1] we became aware of the work of T. Hurlen [2–5] on the measurement of the activity of individual ions in aqueous solutions. The information about these manuscripts of Hurlen was almost impossible to get in the Western Hemisphere before the advent of the academic databases and search engines. The net result is that it is now clear that values of the activity coefficients of individual ions have long been available in the literature. Other than Hurlen, at least Shatkay and Lerman [6,7] had also reported similar measurements. There is also an early work of Szabo [8]. However, to have their work published, these researchers had to pay lip service to the prevailing opinion and admit, as the paradigm required, that theory did not support the concept of individual activity of ions. Hurlen carefully presented his results as “a convenient” scale of single-ion activities useful for interpreting his electrode kinetic studies. Shatkay and Lerman had to state that the fact the “activity measured is that of the individual ion can be disputed on theoretical grounds.” As shown in Table 1 we have been, perhaps, among the first researchers of modern times that have stated without apologies that we believe to be dealing with the real values of the activity of individual ions. As the time passed, other researchers also published measurements of the activity of individual ions [9–11].

Notably, Malatesta first [12] and the Zarubin next [1] developed relations of the activity coefficient of single ions with the mean ionic activity coefficient of the electrolyte and the transference number of the ion. This very important new development was emphasized in a response to Zarubin [13].

In addition, two new theories of electrolyte aqueous solutions have been recently presented in the literature [14–16] confirming the trends shown by the experimental measurements of the individual activities of the ions.

In this work we demonstrate the consistency of the experimental results obtained in different laboratories by different researchers as a way of preparing the material for testing new theories.

2. Results

Table 1 gives the details of different experimental techniques that have been used to determine the activities of individual ions and shows the chronology of the publications reporting experimental results.

First we consider the results for aqueous solutions of sodium salts. As the measurements reported were performed at different concentrations, and any smoothing equation would introduce its own bias, a graphical comparison is probably the most direct way of proceeding. Fig. 1 presents the comparison of experimentally measured individual activity coefficients of Na^+ and Cl^- in the aqueous NaCl system determined in five different laboratories with significantly different experimental techniques (see Table 1). In addition to our original results from 2004 [19], we also included later measurements done with the improved experimental set-up [20] and the results of obtained with Ag/AgCl reference electrode filled with 2 M NH_4Cl instead of a saturated KCl solution as it was done before.

Fig. 2a depicts comparison of our data with results reported by Hurlen et al. [5] for aqueous solutions of NaBr. We used Na ISE

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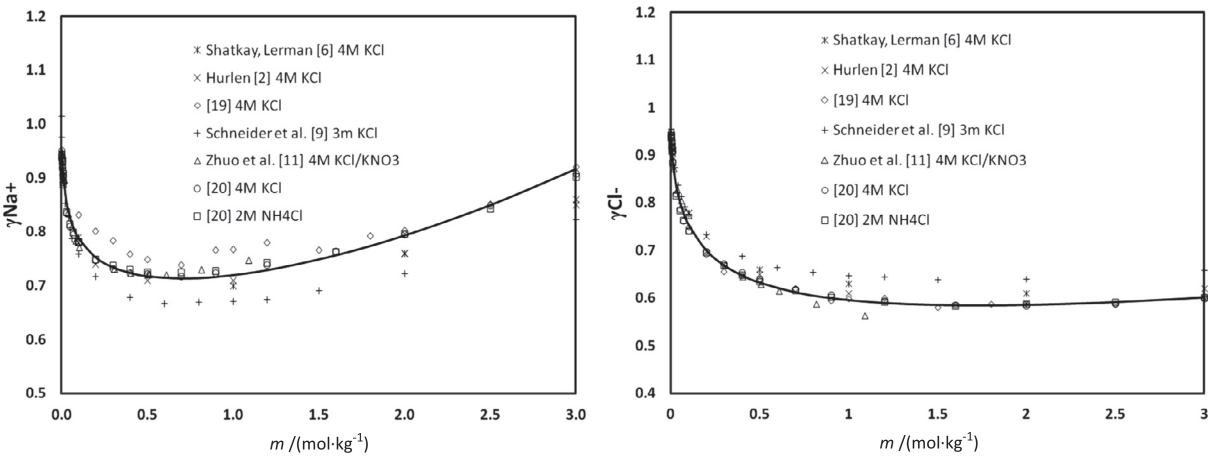
Table 1
Summary of different techniques used for the measurements of ionic activity coefficients. All measurements were performed at 25 °C.

ISE cation	ISE anion	Reference electrode	Runs	Calibration
Szabo, 1935 [8]				
Pt|H_2, HCl	Hg|HgCl, HCl	Liquid chains of cells of identical electrodes were measured	Discontinuous	At low concentration range, junction potential evaluated through diffusion potentials measured in the same study
Shatkay and Lerman, 1969 [6,7]				
Glass sodium electrode	Ag, AgCl	SCE, KCl bridge	Discontinuous	By taking $\gamma_\pm = 0.903$ for 0.01 m NaCl. Henderson eq. for junction potential [17]
Hurlen, 1979–1983, [2–5]				
Calculated	[2,3] Ag/AgCl electrode [4] Ag/AgBr electrode [5] Hg/Hg_2SO_4 electrode	SCE, SJ, inner solution sat. KCl	Discontinuous	$\gamma_- = \gamma_\pm$ for sat. KCl aq. Henderson eq. for junction potential [17]
Khoshkbarchi and Vera, 1996 [18]				
Na ISE K ISE	Cl ISE Br ISE	Ag/AgCl, SJ, inner solution sat. KCl	Continuous	Based on 2 points at intermediate concentrations, Henderson eq. for junction potential [17], wrong sign for E_j
Schneider et. al., 2003–2004 [9,10]				
Na ISE, K ISE	Cl ISE	Ag/AgCl, inner solution:	Continuous	Extended Debye–Hückel eq. used up to $I_m = 0.01$ m 1. E^o and S fitted
		3 m KCl [9]		2. S Nernstian, E^o fitted
Ca ISE		3 M KCl [10]		Henderson eq. for junction potential [17]
Vera at al., 1999–2009 [19–23]				
K ISE, Na ISE	Br ISE, Cl ISE, F ISE, NO_3 ISE	Ag/AgCl, SJ, inner solutions: KCl, NaCl, CsCl or NH_4Cl	Continuous	Based directly on least square fit of several points in the dilute region
Zhuo et al., 2008 [11]				
Na glass ISE	Br ISE, Cl ISE, F ISE	Ag/AgCl, DJ, inner solution: KCl, outer solution: 10% KNO_3	Continuous	Based on one intermediate point and a model equation with 2 parameters. Uses all points of the run for the fit. Assumes E_j = const.
Sakaida and Kakiuchi, 2011 [24]				
Pt|H_2,H^+	Ag|AgCl	Ionic liquid salt bridge	Discontinuous	Use of DHL at 0.01 M HCl aq.

Note: SJ – single junction, DJ – double junction, DHL – Debye–Hückel limiting law.



a. Individual activity coefficients of Na+

b. Individual activity coefficients of Cl-

Fig. 1. Comparison of different experimental results obtained for the individual ionic activity coefficients in the aqueous solutions of NaCl. Inner solutions of reference electrodes are listed by the corresponding reference.

and Br ISE. Our measurements were performed at different times and with different inner electrolytes in the single junction Ag/AgCl reference electrode. Hurlen's measurements of anion data were done with Ag/AgBr electrode, while the activity coefficients for the Na^+ ions were calculated from the mean ionic activity coefficient data. Fig. 2b presents data for the system of aqueous Na_2SO_4. In our study [19] we used the Na^+ sensitive glass electrode to measure the activity of the sodium ion. The activities of the sulfate ion were calculated from the mean ionic activity coefficient. Hurlen [5] on the other hand measured only the anion using Hg/Hg_2SO_4 electrode and the activity of cation was calculated.

Figs. 3 and 4a depict a comparison of results for 1:1 chlorides LiCl, CsCl and NH_4Cl, while Fig. 4b presents the results for LiBr system. In all these cases the measurements were done for anions only, while the missing information for cations was calculated from the mean ionic activity coefficient data. Due to the use of Ag/AgCl and Ag/AgBr electrodes Hurlen [2,4] could extend his measurements up to 4 m, while the use of an Cl ISE and Br ISE limited the range of measurements to 3 m.

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