

# Electrical Conductivity of Concentrated $\text{H}_2\text{TiF}_6 + \text{HF} + \text{H}_2\text{O}$ Mixtures

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The electrical conductivity of  $\text{H}_2\text{TiF}_6$  (1) + HF (2) +  $\text{H}_2\text{O}$  (3) mixtures was measured in a wide range of mass fractions ( $0\% < w_1 < 55\%$  and  $0\% < w_2 < 11\%$ ) and temperature ( $15\text{ }^\circ\text{C} < t < 35\text{ }^\circ\text{C}$ ) by means of an automatic system based on the “electrodeless conductivity” technique. The results were fitted to a polynomial equation in  $w_1$ ,  $w_2$ , and  $t$  using a Mathematica package (Tkondru). The resulting model is able to reproduce experimental data with an uncertainty below 5%.

## Introduction

Different fluorotitanates of commercial interest are commonly obtained in the fluoride derivative manufacturing industry by reaction of fluorotitanic acid ( $\text{H}_2\text{TiF}_6$ ) with an appropriate chloride salt. The most important of them, potassium fluorotitanate, is mainly used in abrasive grinding wheels and to incorporate titanium into aluminum alloys.<sup>1</sup>

The production of  $\text{H}_2\text{TiF}_6$  usually involves the dissolution of solid titanium oxide ( $\text{TiO}_2$ ) into hydrofluoric acid (HF) in a discontinuous or a continuous process. Usually, less  $\text{TiO}_2$  than the stoichiometric quantity is added so the reaction is not complete. The process results in a  $\text{H}_2\text{TiF}_6$  solution with a slight excess of HF (1–4%) which confers better physicochemical properties to the final product. A good control of the process is therefore mandatory if a final product of quality is to be obtained.

In-line control of chemical processes in the fluoride derivative manufacturing industry is not an easy task. The list of potential control variables is short, because of the special characteristics of the fluoride-containing acids (highly corrosive toward glass and its derivatives). Properties commonly used in other industrial applications, such as pH, density, viscosity, concentration determined by selective electrodes, etc., are not readily applicable. It is possible nowadays, however, to measure the conductivity of solutions using plastic probes.<sup>2,3</sup> This turns conductivity into an excellent candidate for in-line control of chemical processes in which HF and its derivatives are involved.

A conductivity-based in-line control of the industrial production of  $\text{H}_2\text{TiF}_6$  requires a knowledge of the dependence of the conductivity of the  $\text{H}_2\text{TiF}_6$  (1) + HF (2) +  $\text{H}_2\text{O}$  (3) ternary system with (i) the  $\text{H}_2\text{TiF}_6$  mass fraction,  $w_1$ , (ii) the HF mass fraction,  $w_2$ , and (iii) temperature,  $t$ . As the  $\text{H}_2\text{TiF}_6$  manufacturing processes are carried out at atmospheric pressure, the dependence of conductivity with pressure is not required. Most relevant conductivity data on single electrolyte solutions have been reviewed by Lobo.<sup>4</sup> No information concerning the conductivity of  $\text{H}_2\text{TiF}_6$  aqueous solutions and only one reference on the conductiv-

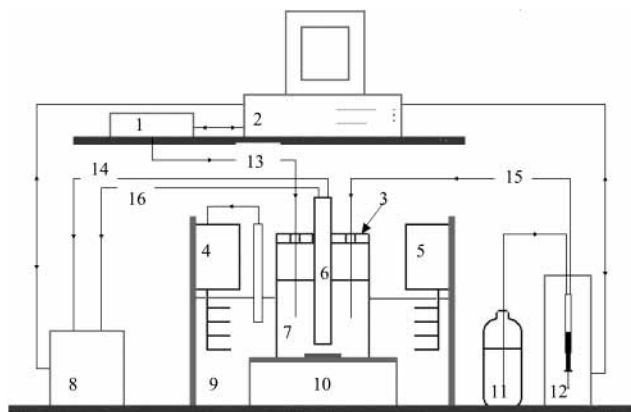
ity of HF +  $\text{H}_2\text{O}$  mixtures is cited in that work. To our knowledge, no work has been published reporting electrical conductivities of aqueous mixtures of  $\text{H}_2\text{TiF}_6$  and HF.

The accurate measurement of the conductivity of concentrated mixtures of  $\text{H}_2\text{TiF}_6 + \text{HF} + \text{H}_2\text{O}$  is not straightforward using conventional techniques, e.g., the classical two electrodes of known cell constant. Using the classical technique, polarization of the electrodes may occur during the measurement of high conductivities, resulting in false conductivity measurements.<sup>3</sup> The so-called “electrodeless conductivity” or “induced conductivity”<sup>5,6</sup> technique uses radiofrequencies to measure the conductivity of a solution. Two toroids inside a plastic probe are immersed in the solution to be tested, so that direct contact between the toroids and the solution is avoided. “Electrodeless conductivity” is, consequently, an appropriate technique to measure high conductivities, and it has been widely used in some industrial applications.<sup>2,7</sup>

In engineering applications, raw data are not of practical use. Alternatively, a mathematical model enabling a fast interpolation of the required property at different conditions is normally used. The model is usually obtained by any correlation method, e.g., regression analysis of data, rather than by complicate theoretical considerations.<sup>8</sup> Several empirical models have been used to fit conductivity data of multicomponent concentrated electrolytes over a temperature range.<sup>9–11</sup> When enough data are available, polynomials in concentration and temperature are usually preferred.<sup>12</sup> Nonlinear regression analysis is generally required to fit conductometric data of concentrated electrolytes to polynomial models. When multicomponent systems are considered, or if the effect of temperature on the conductivity of a single electrolyte is to be taken into account, multivariate nonlinear regression of data must be done. Several computer programs and software packages are nowadays commercially available to make multivariate nonlinear regression of data.<sup>13–17</sup>

In this work, the conductivity of a series of aqueous mixtures of  $\text{H}_2\text{TiF}_6$  and HF has been measured by an automated system based on the “electrodeless conductivity” technique. Multivariate nonlinear regression of the obtained data have been performed, via a computer program that looks for the simplest polynomial which best fits the

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**Figure 1.** Automated system to measure the electrical conductivity of solutions. DC generator (1); personal computer (2); reactor (3); thermostat (4); cooler (5); probe (6); solution (7); conductimeter (8); oil bath (9); submersible magnetic stirrer (10); reagent (11); automatic buret (12); Coulometric additions (13); temperature measurement (14); addition of liquid reagents (15); conductivity measurement (16).

**Table 1.** Mass Fractions,  $w$ , and Densities,  $\rho$ , of the  $\text{H}_2\text{TiF}_6$  (1) +  $\text{HF}$  (2) +  $\text{H}_2\text{O}$  (3) Mixtures Used as Stock Solutions

$100w_1$	$100w_2$	$\rho/(\text{g}\cdot\text{cm}^{-3})$
$47.9 \pm 0.5$	$10.8 \pm 0.3$	$1.519 \pm 0.008$
$54.1 \pm 0.5$	$4.6 \pm 0.1$	$1.558 \pm 0.006$
$56.5 \pm 0.5$	$2.71 \pm 0.07$	$1.583 \pm 0.009$
$58.2 \pm 0.6$	$0.70 \pm 0.02$	$1.603 \pm 0.010$

experimental data. As a result, an empirical model that explains the variability of data and allows adequate estimation of the conductivity of the  $\text{H}_2\text{TiF}_6 + \text{HF} + \text{H}_2\text{O}$  electrolytic system in the ranges of composition and temperature investigated is presented.

## Experimental Section

**Materials and Reagents.** Electrical conductivities were measured by means of an automated conductometric titration station (Figure 1) fully controlled by a program written in QuickBasic, CONDUCTO. Both the experimental setup and the controlling software have been developed in our research group.<sup>18–20</sup> It has already been used to measure conductivities of electrolyte solutions.<sup>11,21,22</sup> A full description of the system can be found elsewhere.<sup>19</sup>

The procedure to calibrate the apparatus has also been previously described.<sup>22–24</sup> This procedure uses a polynomial in HCl concentration and temperature which correctly fits (RSD = 0.41%) selected bibliographic data<sup>25</sup> to produce reference conductivity data from nearly (0 up to 1100)  $\text{mS}\cdot\text{cm}^{-1}$ .

$\text{H}_2\text{TiF}_6 + \text{HF}$  aqueous mixtures of different composition were provided by Derivados del Fluor, S. A. (DDF, Ontón, Cantabria, Spain). Four different mixtures were used as stock solutions in this work. The composition of those solutions (Table 1) was determined by acid–base titration following the same procedure than in DDF.<sup>26</sup> MilliQ quality water (Millipore water purification system, with  $\kappa < 0.05$   $\mu\text{S}\cdot\text{cm}^{-1}$ ) was used in all of the experiments.

All plastics and glassware were thoroughly washed with tap water, immersed in an aqueous  $\text{HNO}_3$  bath ( $w = 10\%$ ) overnight, again washed with tap water, and finally rinsed with MilliQ quality water before use.

**Experimental Procedure.** The experimentation was designed as a series of dilution processes which were conductometrically monitored.

Each mixture in Table 1 acted as a starting point of a series of three dilution processes. In the first one,  $(300.0 \pm 0.2)$   $\text{cm}^3$  of the original mixture were diluted with six  $(30.00 \pm 0.01)$   $\text{cm}^3$  portions of water.  $(300.0 \pm 0.2)$   $\text{cm}^3$  of the resulting solution were again diluted in the same way in a second dilution process. This was repeated in a third dilution process, using  $(300.0 \pm 0.2)$   $\text{cm}^3$  of the solution resulting from the second step. In this way, the conductivity of different compositions was measured at the three temperatures of about (20, 25, and 35)  $^\circ\text{C}$ .

The same procedure was repeated in each dilution process: the Teflon-made titration vessel was located on the surface of the magnetic stirrer immersed into the paraffin oil bath and thermostated at the working temperature, and the measuring probe was inserted into the vessel through the corresponding hole. After thermal stabilization of the system, the Pt100 included in the conductivity probe was calibrated against an external precalibrated thermometer, and the conductivity reading was corrected to  $0.000$   $\text{mS}\cdot\text{cm}^{-1}$ .  $(300.0 \pm 0.2)$   $\text{cm}^3$  of the solution to be diluted was added to the vessel. Both the conductivity and the temperature of the solution inside the vessel were monitored until thermal stabilization of the system. The conductivity of the solution at the working temperature was measured and stored. Afterward, the dilution process was automatically performed according to defined parameters.

According to the input file, after each addition of water, 2 h elapsed before the first measurement of temperature was taken. The temperature was then measured after every 5 min until thermal stabilization (working temperature  $\pm 0.3$   $^\circ\text{C}$ ). The program then checked the conductivity of the solution every 5 min. When the standard deviation of the last three conductivities was less than the 0.2% of the mean, both the conductivity and the temperature were recorded, the next programmed addition of water occurred, and the measuring algorithm was repeated. The solution inside the vessel was continuously stirred by a magnetic bar throughout the dilution process.

Considering the eventual errors of the volumetric material used and the uncertainties in the mass fractions and densities of the stock solutions, an uncertainty in  $w_1$  and  $w_2$  about  $\pm 1.3\%$  and  $\pm 2.2\%$ , respectively, has been estimated. The conductimeter manufacturer gives indications so that the imprecision is smaller than  $\pm 2\%$  in the conductivity measurement.

**Data Treatment.** Multivariate nonlinear regression analysis of ( $\kappa$ ,  $w_1$ ,  $w_2$ , and  $t$ ) data was accomplished by a computer program based on the Nonlinear Regress package in Mathematica<sup>16</sup> (Tkondur<sup>27</sup>). Briefly, Tkondur looks for the polynomial which best fits ( $\kappa$ ,  $w_1$ ,  $w_2$ , and  $t$ ) conductivity data of liquid mixtures of two electrolytes. Starting from a general polynomial in  $w_1$ ,  $w_2$ , and  $t$  and using statistical parameters defined by the user, Tkondur (i) determines the lowest grade in each independent variable ( $w_1$ ,  $w_2$ , and  $t$ ) necessary to fit data with a predetermined accuracy and (ii) simplifies the resulting model by removing the adjustable parameters which are not statistically significant. More details about working with Tkondur can be found elsewhere.<sup>27</sup>

## Results and Discussion

The measured conductivities are shown in Table 2, together with the corresponding values of mass fraction and

**Table 2. Measured Conductivities,  $\kappa$ , of the Ternary System  $\text{H}_2\text{TiF}_6$  (1) +  $\text{HF}$  (2) +  $\text{H}_2\text{O}$  (3) at Different Mass Fractions,  $w$ , and Temperatures,  $t^a$** 

$100w_1$	$100w_2$	$t/^\circ\text{C}$	$\kappa/(\text{mS}\cdot\text{cm}^{-1})$	$100w_1$	$100w_2$	$t/^\circ\text{C}$	$\kappa/(\text{mS}\cdot\text{cm}^{-1})$	$100w_1$	$100w_2$	$t/^\circ\text{C}$	$\kappa/(\text{mS}\cdot\text{cm}^{-1})$
47.9	10.8	19.4	546	26.5	6.0	25.3	728	41.5	6.8	35.4	777
44.9	10.1	19.8	589	25.0	5.6	25.3	714	39.5	6.5	35.2	806
42.3	9.5	19.8	622	23.6	5.4	25.2	700	37.6	6.2	36.2	832
40.0	9.0	19.8	648	23.8	5.4	25.5	703	35.0	5.7	36.3	853
37.9	8.5	19.7	668	21.9	5.0	25.5	677	32.7	5.4	36.1	860
36.0	8.1	19.7	681	20.4	4.6	25.5	652	30.7	5.0	35.9	860
34.3	7.8	19.6	689	19.1	4.3	25.4	626	29.0	4.8	36.0	854
34.3	7.7	19.6	690	17.9	4.0	25.4	602	27.4	4.5	35.8	842
32.0	7.2	19.7	697	16.8	3.8	25.3	578	25.9	4.3	35.7	827
29.9	6.7	19.6	696	15.9	3.6	25.3	555	25.9	4.3	36.5	836
28.1	6.3	19.7	692	54.1	4.6	25.5	521	24.0	4.0	36.6	811
26.5	6.0	19.8	682	50.8	4.3	25.6	577	22.3	3.7	36.5	782
25.0	5.6	19.7	671	47.9	4.1	25.5	624	20.8	3.4	35.4	753
23.8	5.4	19.7	657	45.4	3.9	25.3	663	19.5	3.2	35.3	724
56.5	2.7	19.7	440	43.0	3.7	25.3	694	18.3	3.0	35.2	696
53.1	2.5	19.9	500	40.9	3.5	25.3	718	36.9	2.4	36.1	842
50.2	2.4	19.8	548	39.0	3.3	25.3	734	34.5	2.3	36.1	845
47.5	2.3	19.6	591	39.0	3.3	25.7	745	32.4	2.1	36.0	841
45.1	2.2	19.6	625	36.3	3.1	25.7	762	30.6	2.0	35.8	831
42.9	2.1	19.5	652	34.0	2.9	25.7	769	28.9	1.9	35.7	816
41.0	2.0	19.4	674	31.9	2.7	25.6	767	27.4	1.8	36.1	817
41.0	2.0	19.6	672	30.1	2.6	25.6	763	25.3	1.7	36.1	790
38.1	1.8	19.7	695	28.5	2.4	25.6	753	23.6	1.5	36.0	761
35.7	1.7	19.8	708	27.0	2.3	25.6	741	22.0	1.4	36.0	731
33.6	1.6	19.8	713	27.0	2.3	25.7	746	20.7	1.4	35.9	703
31.7	1.5	19.7	712	24.9	2.1	25.6	722	19.5	1.3	35.8	675
30.0	1.4	19.7	707	23.2	2.0	25.5	698	18.4	1.2	35.6	648
28.4	1.4	19.7	698	21.7	1.8	25.4	672	54.1	2.3	36.5	599
28.4	1.4	19.2	695	20.3	1.7	25.5	647	50.8	2.2	36.6	664
26.3	1.3	19.4	680	19.1	1.6	25.5	623	47.9	2.0	36.5	718
24.4	1.2	19.4	660	18.1	1.5	25.4	600	45.3	1.9	36.4	762
22.8	1.1	19.4	638	56.5	2.7	25.7	473	43.0	1.8	36.4	795
21.4	1.0	19.4	616	53.1	2.5	25.7	534	40.9	1.7	36.3	820
20.2	1.0	19.4	594	50.2	2.4	25.6	586	39.0	1.7	36.5	837
19.1	1.0	19.3	573	47.5	2.3	25.5	630	36.3	1.5	36.6	855
58.2	0.7	19.6	413	45.1	2.2	25.4	667	33.9	1.4	36.6	858
54.8	0.7	19.8	473	42.9	2.1	25.3	695	31.9	1.4	36.4	853
51.7	0.6	19.8	524	41.0	2.0	26.0	730	30.0	1.3	36.3	844
49.0	0.6	19.7	568	38.1	1.8	26.0	754	28.4	1.2	36.1	829
46.6	0.6	19.6	605	35.7	1.7	25.9	766	26.9	1.1	36.0	813
44.3	0.5	19.5	634	33.6	1.6	25.9	769	26.9	1.2	36.4	813
42.3	0.5	19.4	658	31.7	1.5	25.7	768	24.9	1.1	36.4	804
42.3	0.5	19.6	662	30.0	1.4	25.8	761	23.1	1.0	36.4	775
39.5	0.5	19.8	690	28.5	1.4	25.7	750	21.6	0.9	36.2	745
37.0	0.4	19.7	703	28.4	1.4	25.9	750	20.2	0.9	36.1	715
34.7	0.4	19.6	711	26.3	1.3	25.9	731	19.1	0.8	36.0	687
32.8	0.4	19.6	712	24.4	1.2	25.8	708	18.0	0.8	35.8	659
31.0	0.4	19.5	707	22.8	1.1	25.7	684	57.1	1.1	36.5	534
29.5	0.4	19.5	699	21.4	1.0	25.6	659	53.7	1.0	36.4	602
29.5	0.4	20.2	695	20.2	1.0	25.6	636	50.7	1.0	36.4	661
27.3	0.3	20.5	684	19.1	1.0	25.5	612	48.0	0.9	36.3	710
25.4	0.3	20.5	665	58.2	0.7	25.9	448	45.6	0.9	36.2	752
23.7	0.3	20.5	641	54.8	0.7	26.0	510	43.4	0.8	36.0	784
22.3	0.3	20.5	621	49.0	0.6	25.9	609	41.4	0.8	35.9	807
21.0	0.3	20.5	601	46.6	0.6	25.8	649	41.4	0.8	36.4	809
19.8	0.2	20.4	580	44.3	0.5	25.7	676	38.6	0.7	36.4	835
47.9	10.8	25.5	588	42.3	0.5	25.7	704	36.2	0.7	36.2	848
45.0	10.1	25.6	632	42.3	0.5	25.8	716	34.0	0.7	36.2	851
42.3	9.5	25.5	668	39.5	0.5	25.7	744	32.1	0.6	36.1	846
40.0	9.0	25.5	695	37.0	0.4	25.7	759	30.3	0.6	35.9	839
37.9	8.5	25.5	716	34.7	0.4	25.6	765	28.8	0.6	36.6	843
36.0	8.1	25.3	731	32.8	0.4	25.6	767	26.6	0.5	36.5	820
34.3	7.7	25.5	740	31.0	0.4	25.6	767	24.8	0.5	36.4	793
34.3	7.7	25.5	743	52.3	8.6	35.5	570	23.1	0.5	36.2	765
31.9	7.2	25.5	749	49.1	8.1	35.6	637	21.7	0.4	36.3	737
29.9	6.7	25.0	746	46.3	7.6	35.6	693	20.5	0.4	36.1	710
28.1	6.3	25.4	736	43.8	7.2	35.4	740	19.3	0.4	35.8	684

<sup>a</sup> Estimated imprecision in the conductivity measurement: lower than  $\pm 2\%$  of the measurement.

temperature. A data set composed by the experimental data obtained in this work ( $\kappa$ ,  $w_1$ ,  $w_2$ , and  $t$ ) and bibliographic conductometric data of  $\text{H}_2\text{TiF}_6$ <sup>21</sup> and  $\text{HF}$ <sup>28,29</sup> single aqueous

solutions, ( $\kappa$ ,  $w_1$ , and  $t$ ) and ( $\kappa$ ,  $w_2$ , and  $t$ ), was used to determine the simplest polynomial able to reproduce experimental data with the required accuracy. The proce-

**Table 3. Fit of Experimental (This Work) and Bibliographic Data<sup>21,28,29</sup> to the Polynomials Proposed in This Work<sup>a</sup>**

data considered	model	$N$	$N_p$	$\sigma$	$R^2$	$\text{Prob}(t)$	$N_i$	$N_j$
$(\kappa, w_1, \text{ and } t)$	eq 1	156	6	3.44	0.9990	$1 \times 10^{-14}$	4	
$(\kappa, w_2, \text{ and } t)$	eq 2	54	1	1.65	0.9980	0.02		1
$(\kappa, w_1, w_2, \text{ and } t)$	eq 5	201	4	1.30	0.9993	$1 \times 10^{-14}$		

<sup>a</sup>  $N$ , number of data considered in each fit;  $N_p$ , number of adjustable parameters in the model;  $\sigma$ , standard deviation of the fit (eq 6);  $R^2$ , coefficient of determination (eq 3);  $\text{Prob}(t)$ , probability of an adjustable parameter to be zero;  $N_i$ , maximum degree considered in  $\text{H}_2\text{TiF}_6$  mass fraction;  $N_j$ , maximum degree considered in HF mass fraction.

ture to find the polynomial, divided into two different steps, is briefly described as follows:

1. Successive fit of  $(\kappa, w_1, \text{ and } t)$  and  $(\kappa, w_2, \text{ and } t)$  data to eqs 1 and 2, respectively.

$$\kappa = \sum_{j=1}^{N_j} \sum_{k=0}^{N_i} a_{0jk} w_1^j t^k \quad (1)$$

$$\kappa = \sum_{j=1}^{N_j} \sum_{k=0}^{N_i} a_{0jk} w_2^j t^k \quad (2)$$

where  $\kappa$  is the specific conductivity,  $w_1$  and  $w_2$  are the mass fractions of  $\text{H}_2\text{TiF}_6$  and HF, respectively,  $t$  is temperature in °C,  $N_i$  and  $N_j$  are the maximum degrees considered in  $w_1$  and  $w_2$ , and  $a_{0jk}$  and  $a_{ijk}$  are adjustable parameters to be calculated by data fitting. Data were first fitted to eq 1 (or 2) with  $N_i = 1$  (or  $N_j = 1$ ). Fitting of data was repeated with  $N_i + 1$  (or  $N_j + 1$ ) until a predetermined difference between calculated and experimental data required to the fit was obtained. That difference was defined in terms of the so-called coefficient of determination ( $R^2$ , eq 3):<sup>30,31</sup>

$$R^2 = 1 - \frac{\sum_{i=1}^N (\kappa_{\text{calc}} - \kappa)^2}{\sum_{i=1}^N (\bar{\kappa} - \kappa)^2} \quad (3)$$

where  $N$ ,  $\kappa_{\text{calc}}$ ,  $\kappa$ , and  $\bar{\kappa}$  are, respectively, the number of points used in the fit, the conductivity calculated by the model, the experimental conductivity, and the average of all of the experimental conductivities considered in the fit.

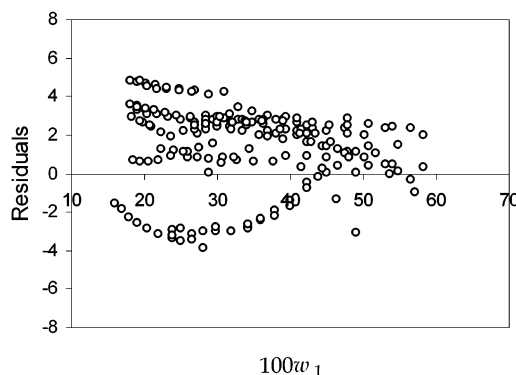
The models were later simplified by removing from the equation those adjustable parameters with a probability to be zero higher than 2%. The probability to be zero,  $\text{Prob}(t)$ , was computed using the statistical parameter  $t_i$  (eq 4) and taking into account the degrees of freedom of the fit:<sup>31</sup>

$$t_i = \frac{a_i}{\sigma_{ai}} \quad (4)$$

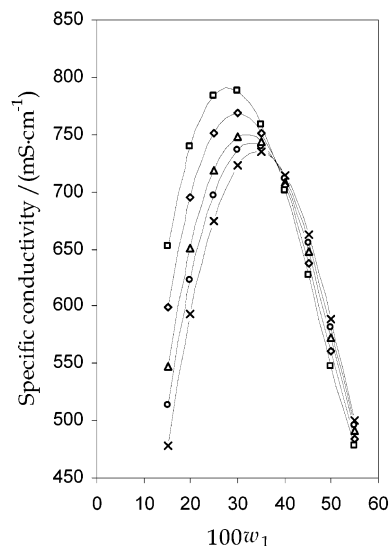
where  $a_i$  is one of the adjustable parameters of the polynomial considered and  $\sigma_{ai}$  is the standard deviation associated to the parameter.

2. Simultaneous fit of  $(\kappa, w_1, \text{ and } t)$ ,  $(\kappa, w_2, \text{ and } t)$ , and  $(\kappa, w_1, w_2, \text{ and } t)$  data to eq 5.

$$\kappa = \sum_{i=1}^{N_i} \sum_{k=0}^{N_j} a_{0ik} w_1^i t^k + \sum_{j=1}^{N_j} \sum_{k=0}^{N_i} a_{0jk} w_2^j t^k + \sum_{i=1}^{N_i} \sum_{j=1}^{N_j} \sum_{k=0}^{N_i} a_{ijk} w_1^i w_2^j t^k \quad (5)$$



**Figure 2.** Residuals (as  $100(\kappa_{\text{calc}} - \kappa)/\kappa$ ) computed using the model proposed to explain the variability of  $(\kappa, w_1, \text{ and } t)$ ,  $(\kappa, w_2, \text{ and } t)$ , and  $(\kappa, w_1, w_2, \text{ and } t)$  data of the  $\text{H}_2\text{TiF}_6$  (1) + HF (2) +  $\text{H}_2\text{O}$  (3) chemical system.



**Figure 3.** Conductometric behavior of the  $\text{H}_2\text{TiF}_6$  (1) + HF (2) +  $\text{H}_2\text{O}$  (3) electrolytic system as described by the proposed model at 25 °C.  $w_2$ : ×, 0%; ○, 2%; △, 4%; ◇, 7%; □, 10%.

**Table 4. Adjustable Parameters Which Best Fit  $(\kappa, w_1, \text{ and } t)$ ,  $(\kappa, w_2, \text{ and } t)$ , and  $(\kappa, w_1, w_2, \text{ and } t)$  Data of the  $\text{H}_2\text{TiF}_6$  (1) + HF (2) +  $\text{H}_2\text{O}$  (3) Chemical System to the Proposed Model (Eq 5)**

$i, j$	$a_{ij0}/(\text{mS}^{-1}\cdot\text{cm})$	$i, j$	$a_{ij1}/(\text{mS}^{-1}\cdot\text{cm}\cdot\text{°C}^{-1})$
0, 1	$12.89 \pm 0.06$	0, 1	0
1, 0	$26.4 \pm 0.1$	1, 0	$0.350 \pm 0.003$
1, 1	$-0.39 \pm 0.04$	1, 1	$(6.2 \pm 0.6) \times 10^{-2}$
2, 0	0	2, 0	0
2, 1	0	2, 1	$(-2.8 \pm 0.3) \times 10^{-3}$
3, 0	$(-1.33 \pm 0.02) \times 10^{-2}$	3, 0	$(-1.35 \pm 0.06) \times 10^{-4}$
3, 1	0	3, 1	$(3.1 \pm 0.4) \times 10^{-5}$
4, 0	$(1.19 \pm 0.03) \times 10^{-4}$	4, 0	$(1.10 \pm 0.09) \times 10^{-6}$
4, 1	0	4, 1	0

where  $a_{ijk}$  are adjustable parameters to be calculated by data fitting and the rest of symbols have the same meaning than before. Data were first fitted to eq 5 using the values of  $N_i$  and  $N_j$ ,  $a_{0ik}$ , and  $a_{0jk}$  found in the previous step. The model was later simplified by removing from the equation those  $a_{ijk}$  adjustable parameters with a probability to be zero,  $\text{Prob}(t)$ , higher than 2%.

This procedure to fit conductometric data of aqueous mixtures of two electrolytes at varying temperature to eq 5 has already been successfully used before.<sup>11,22,23,32</sup>

Table 3 shows the values of  $R^2$  and  $\text{Prob}(t)$  finally selected in each step of the procedure to fit the conductivity data, the number of data ( $N$ ) considered in each case, the



number of adjustable parameters in the model ( $N_p$ ), the best degrees in mass fraction ( $N_i$  and  $N_j$ ), and the standard deviation of each fit ( $\sigma$ , eq 6):

$$\sigma = \sqrt{\frac{\sum_{i=1}^N (\kappa_{\text{calc}} - \kappa)^2}{N - N_p}} \quad (6)$$

The values of the adjustable parameters which best fit data to the model are shown in Table 4. A plot of the residuals (computed as  $100((\kappa_{\text{calc}} - \kappa)/\kappa)$ ) obtained for the selected model is shown in Figure 2. To illustrate the dependence of the conductivity of the system with the composition and temperature, the conductivity predicted by the model at 25 °C has been plotted in Figure 3.

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