Conductivity of Concentrated Aqueous Solutions of Several Fluorine-Containing Electrolytes in a Wide Range of Concentrations and Temperatures

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Specific conductivities (κ) of concentrated aqueous solutions of several fluorine containing electrolytes, fluoroboric acid (HBF_4), fluorosilicic acid (H_2SiF_6), and fluorotitanic acid (H_2TiF_6), at mass percents ($100w_{Ac}$) from 10 to 50 at 15, 25, 35, and 45 °C have been measured by making use of an automatic system based on the "electrodeless conductivity" technique. The results have been analyzed in terms of the well-established Casteel−Amis equation and by polynomial equations in the concentration. As a result, empirical models of the type $\kappa = f(100w_{Ac})_t$ have been proposed, which reproduce the results of each chemical system with an overall precision of about ±0.3% and enable the interpolation of conductivity at each temperature in the whole range of concentration studied.

Introduction

Aqueous electrolyte solutions are widely present in such important fields as chemical research, investigations about geothermal systems and biological processes, chemical manufacturing industry (Horvath, 1985), and development of electrochemical devices (Barthel, 1985). Among the thermodynamic and transport properties of such chemical systems more frequently requested by chemists and engineers—density, viscosity, conductivity, transport numbers, diffusion and activity coefficients—experimental data concerning electrical conductivity are the most referenced in the literature (Lobo, 1986, 1989). Nevertheless, the majority of the conductivity information concerns dilute solutions at room temperature (Horvath, 1985). The simple instrumentation needed to measure low conductivities provides very accurate experimental data. As a result, the technique becomes a very useful tool for the interpretation of the structure of the electrolyte solutions and the interactions between the different entities present in the solution (Robinson and Stokes, 1959). Less attention has been paid to concentrated electrolyte solutions, which present much higher values of conductivity. The difficulty of measuring high conductivities in the laboratory with an acceptable accuracy arises from the lack of an appropriate technique, completely avoiding the polarization processes in the interphase between the electrodes and the solution. In fact, quite large differences are often found among the results given by different authors concerning the same concentrated electrolyte solution (Lobo, 1986).

Since Relis (1947, 1951) described the technique to measure conductivities of solutions known as "electrodeless conductivity" or "induced conductivity", which makes use of radio frequencies and needs no direct contact between electrodes and solution, continuous measurement of the conductivity has been extensively used in control and automatization of chemical processes (Stock, 1984) where, frequently, high conductivities are involved. Further improvements of the technique have made it possible to reduce the size of the measuring probe, and consequently, now it is useful for laboratory purposes. Nevertheless, only the automated system for conductimetric titration proposed previously by de Diego et al. (1994) attempts to apply the "electrodeless conductivity" technique to routine laboratory work. It provides a useful tool for the systematic and high-quality measurement of the electrolytic conductivity of concentrated electrolyte solutions.

Control and automation of chemical processes in industry require the implementation of "in line" analysis procedures by the continuous measurement of any changing characteristic parameter in the chemical reaction. The most popular continuous measurement of pH or the use of ion selective electrodes becomes inapplicable under certain conditions, e.g., the presence of fluoride at low values of pH, which usually occurs in the fluorine-derivatives manufacturing industry. In such cases, conductivity can be a good alternative for monitoring a reaction. The dosification and dilution of several fluorine-containing acids would be susceptible to automation by an appropriate conductivity control, if full sets of reliable (κ, $100w$, t) experimental data corresponding to those chemical systems were available.

In this paper we report specific conductivities of the aqueous binary systems $HBF_4 + H_2O$, $H_2SiF_6 + H_2O$, and $H_2TiF_6 + H_2O$. The measurements cover a wide range of composition and temperature. In addition, two equations enabling the interpolation of conductivity data in the whole range of concentration and temperature studied are proposed.

The three acids are in common use in the fluorine-derivatives manufacturing industry as raw materials, intermediates, or final products (Derivados, 1995). An exhaustive review of their physical, thermodynamical, and transport properties (Ryss, 1956), as well as their most important applications (Standen, 1980), can be found elsewhere. In any case, no conductivity data above 0.1 mol·dm^{-3} have been encountered in the literature.

Experimental Details

Materials and Reagents. Concentrations throughout the text are given in g of product per 100 grams of solution

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(100*w*) unless otherwise stated. Concentrated stock solutions of HBF_4, H_2SiF_6, and H_2TiF_6 were prepared by mixing HF solution of $100w \sim 70$ with, respectively, a stoichiometric mass of H_3BO_3, an excess of SiO_2, and an excess of TiO_2. The remaining SiO_2 and TiO_2 were removed by filtration and the concentrations were adjusted by dilution with water. The HF solution of $100w \sim 70$ was purified from a more concentrated one by a procedure similar to that described by Mattison (Mattison, 1972). The analysis of the resulting HF solution yielded very low concentrations of typical contaminants in HF (H_2SiF_6, $100w < 0.0005$; Cl^-, $100w < 0.0005$; sulfates, $100w < 0.0001$; sulfites, $100w < 0.0002$; heavy metals (such as Pb), $100w < 0.000\,05$; Fe, $100w < 0.0001$; phosphates, $100w < 0.0001$; Cu, $100w < 0.000\,01$; As, $100w < 0.000\,005$). H_3BO_3 (Merck, p.a.) was twice recrystallized and SiO_2 and TiO_2 were from Merck, p.a. The results obtained from the analysis of the stock solutions of HBF_4 (Booth and Martin, 1949), H_2SiF_6 (Standen, 1980), and H_2TiF_6 (Ryss, 1956) were as follows:

$$\mathrm{HBF_4}\!: \quad 100w_{\mathrm{HBF_4}} = (49.3 \pm 0.1)$$
$$100w_{\mathrm{H_3BO_3}} < 0.1 \qquad \rho = (1.378 \pm 0.002)\ \mathrm{g{\cdot}cm^{-3}}$$

$$\mathrm{H_2SiF_6}\!: \quad 100w_{\mathrm{H_2SiF_6}} = (45.2 \pm 0.1)$$
$$100w_{\mathrm{HF}} < 0.1 \qquad \rho = (1.445 \pm 0.002)\ \mathrm{g{\cdot}cm^{-3}}$$

$$\mathrm{H_2TiF_6}\!: \quad 100w_{\mathrm{H_2TiF_6}} = (59.0 \pm 0.1)$$
$$100w_{\mathrm{HF}} < 0.1 \qquad \rho = (1.616 \pm 0.002)\ \mathrm{g{\cdot}cm^{-3}}$$

MilliQ quality water (Millipore water purification system) with $\kappa < 0.05\ \mu\mathrm{S{\cdot}cm^{-1}}$ was used throughout.

Conductivity measurements were made with the automated system for conductimetric titration described previously (de Diego et al., 1994). The solution to be titrated is placed in a Teflon-made reactor which is immersed in a thermally isolated parafin-oil bath, thermostated at the work temperature by means of an electrical resistance (Lauda, MT) and a cooler (Selecta). The solution is continuously magnetically stirred (SBS, A-05/B). The upper part of the reactor has several holes for introducing the "electrodeless conductivity" probe (Polymetron, 8332), the autoburet (Crison, MicroBU 2031), and other elements if necessary. The measuring probe is coupled to a conductimeter (Polymetron, Monec 8921). Both the conductimeter and the autoburet are connected to a computer (PC-AT, intel 80 286, 16 mHz, 640 kb memory RAM) by RS-232-C interfaces. A computer program (Conducto) developed in our laboratory, written in Quickbasic 4.5, controls all the steps of the titration assay: monitors the conductivity and temperature of the solution, checks the stability of the signal, and orders new additions of titrant to the autoburet. Calibration was done by following the procedure described by de Diego and Madariaga (1996) with standard solutions of HCl (HCl Fluka, p.a., purified by a method resembling that of Mattison (Mattison, 1972)). The concentration of the HCl stock solution was determined by acid−base titration (Jeffery et al., 1989) with Na_2CO_3, Merck, p.a., and methyl orange, Merck, p.a., as indicator. The pipets and autoburets were calibrated by measuring the mass of the delivered water by a Mettler AJ150 balance (±0.0001 g) at constant temperature.

The data analysis was carried out using NLREG (Sherrod, 1995), a nonlinear regression program which minimizes the sum of the squares of absolute errors between calculated and experimental values and which is based on an algorithm published by Dennis et al. (1981).

Experimental Procedure. The procedure to measure the conductivity of solutions like those of HBF_4, H_2SiF_6, and H_2TiF_6 as a function of the concentration and the temperature has been already described (de Diego et al., 1994), and it will be summarized now. The same measurements were made for each electrolyte at four temperatures close to 15, 25, 35, and 45 °C. In order to cover a wider range of concentrations and taking into account the geometry of the reactor and the measuring probe, three titrations were made at each temperature studied. The first one was the titration of the stock solution of the corresponding acid with water. In the second and third ones, more diluted acid solutions resulting from, respectively, the first and second titrations were titrated again using water as titrant agent. For each case, about $(298.10 \pm 0.25)\ \mathrm{cm^3}$ of solution to be titrated was added to the Teflon reactor and 12 additions of water of $(19.91 \pm 0.02)\ \mathrm{cm^3}$ each were made. The solution in the reactor was magnetically stirred, and its temperature was kept constant within ±0.3 deg. After each addition, the solution was allowed to come to thermal equilibrium, and both the temperature (determined by a resistance thermometer, Pt100, installed inside the conductivity probe, accurate to ±0.1 deg) and the conductivity (accurate to ±0.2% of the measurement) were measured. Before each titration and with the probe in the empty reactor thermostated at the working temperature, the thermocouple was calibrated with the aid of a precalibrated thermometer and zeroing of the conductimeter was carried out. Further information about the parameters of the titrations, stabilization criteria, measuring sign-precision, and correction factors can be found elsewhere (de Diego et al., 1994). The overall precision in the specific conductance was better than ±0.3% of the measurement.

Results

Measured specific conductivities, temperatures, and corresponding acid concentrations are summarized in Table 1.

General polynomial equations in the concentration (eq 1) and the Casteel−Amis equation (eq 2) (Casteel and Amis, 1972) have been frequently used to correlate the specific conductivity with the concentration at constant temperature for several chemical systems consisting of a unique electrolyte in any kind of solvent or mixture of solvents. Both models are described by the following equations:

$$\kappa = \sum_{i=1}^{i} a_i (100w)^i \tag{1}$$

$$\frac{\kappa}{\kappa_{\max}} = \left(\frac{m}{m_{\max}}\right)^x \exp\left[y(m - m_{\max})^2 - \frac{x}{m_{\max}}(m - m_{\max})\right] \tag{2}$$

where a_i are the adjustable coefficients of the polynomial, 100*w* is the solute concentration in mass percent, and for the Casteel−Amis equation, *m* is the molality, $\kappa_{\max}$ is the maximum of conductivity of the system, $m_{\max}$ is the concentration at which $\kappa_{\max}$ is attained, and *x* and *y* are adjustable parameters with no physical meaning. The Casteel−Amis equation has been usually preferred (Barthel and Gores, 1985) because it requires less experimental information to make reliable extrapolations than polynomial equations do and because it contains two parameters, $\kappa_{\max}$ and $m_{\max}$, with a clear graphical meaning. On the other hand, polynomial equations normally offer high-

Table 1. Measured Conductivities (κ) at Temperatures t for Different Mass Percents of HBF_4, H_2SiF_6, and H_2TiF_6, Obtained by Conductimetric Titration Assays

HBF_4

	t = (13.8 ± 0.3) °C		t = (24.7 ± 0.1) °C		t = (36.3 ± 0.2) °C		t = (45.7 ± 0.4) °C			t = (13.8 ± 0.3) °C		t = (24.7 ± 0.1) °C		t = (36.3 ± 0.2) °C		t = (45.7 ± 0.4) °C	
$100w_{HBF_4}$	t/°C	κ/mS·cm^{-1}	t/°C	κ/mS·cm^{-1}	t/°C	κ/mS·cm^{-1}	t/°C	κ/mS·cm^{-1}	$100w_{HBF_4}$	t/°C	κ/mS·cm^{-1}	t/°C	κ/mS·cm^{-1}	t/°C	κ/mS·cm^{-1}	t/°C	κ/mS·cm^{-1}
49.3	13.8	409.4	24.8	487.0	35.9	563.9	44.8	620.1	22.7	14.0	525.1	24.7	606.5	36.7	695.4	45.5	764.1
47.0	13.4	440.6	24.7	519.6	36.1	601.3	45.0	659.8	21.8	13.9	512.7	24.8	597.8	36.6	684.9	45.7	751.3
45.0	13.2	470.2	24.9	548.5	36.3	633.2	45.3	694.0	21.0	13.8	503.5	24.7	587.4	36.5	673.8	45.6	740.0
43.1	13.3	491.8	24.9	572.1	36.5	660.7	45.4	723.0	20.3	13.8	495.5	24.7	577.9	36.5	662.3	45.7	729.5
41.3	13.3	513.5	24.7	592.1	36.5	683.8	45.4	746.7	19.6	13.8	487.0	24.6	568.6	36.4	647.4	45.7	717.9
39.7	13.2	531.4	24.7	606.3	36.5	700.7	45.7	766.5	18.9	13.8	478.8	24.6	559.4	36.2	638.7	46.3	707.4
38.2	13.2	540.7	24.7	620.9	36.5	713.4	45.8	781.6	18.9	14.2	475.8	24.7	561.2	36.2	640.9	45.7	710.3
36.9	13.2	549.0	24.7	633.1	36.5	722.4	45.7	794.7	17.9	14.3	463.9	24.8	542.5	36.2	621.1	45.7	689.7
35.6	13.5	554.3	24.8	642.1	36.5	730.5	45.7	803.8	17.0	14.2	448.9	25.0	526.1	36.2	601.7	45.6	669.0
34.4	13.5	558.9	24.6	648.2	36.3	737.4	45.6	810.4	16.1	14.1	434.5	24.9	510.3	36.2	582.6	46.1	651.5
33.3	13.4	562.2	24.6	652.8	36.3	743.1	45.4	813.9	15.4	14.1	420.6	25.0	493.4	36.2	564.8	46.2	631.7
32.2	13.4	563.2	24.5	655.7	36.2	745.7	45.4	817.2	14.7	14.0	407.1	24.9	477.0	36.3	547.9	46.2	612.3
31.2	13.3	563.9	24.5	657.8	36.1	747.9	45.0	817.9	14.0	14.0	394.9	24.7	462.1	36.2	531.6	46.3	594.5
31.2	14.1	566.6	24.9	655.4	36.2	746.4	45.5	815.7	13.4	14.0	384.7	24.7	450.5	36.3	516.8	46.3	577.7
29.6	14.2	567.0	24.9	654.3	36.3	747.4	45.3	817.4	12.9	13.9	372.3	24.4	436.9	36.2	502.1	46.2	561.6
28.2	14.2	563.4	25.0	649.9	36.4	743.2	45.5	813.7	12.4	13.8	360.7	24.6	426.3	36.2	488.5	46.3	545.8
26.9	14.1	556.5	24.9	643.1	36.5	735.0	45.3	806.1	12.0	13.8	350.7	24.7	415.1	36.2	475.5	46.2	531.1
25.7	14.1	549.9	24.8	635.6	36.5	726.5	45.5	796.4	11.5	13.8	342.4	24.7	404.4	36.1	462.6	46.0	516.5
24.6	14.0	541.0	24.8	626.4	36.6	715.3	45.5	785.6	11.1	13.9	333.0	24.6	393.5	36.0	450.4	45.9	503.0
23.6	14.0	533.1	24.8	616.6	36.6	706.8	45.5	776.2									

H_2SiF_6

	t = (15.2 ± 0.2) °C		t = (25.3 ± 0.2) °C		t = (35.4 ± 0.2) °C		t = (45.2 ± 0.2) °C			t = (15.2 ± 0.2) °C		t = (25.3 ± 0.2) °C		t = (35.4 ± 0.2) °C		t = (45.2 ± 0.2) °C	
$100w_{H_2SiF_6}$	t/°C	κ/mS·cm^{-1}	t/°C	κ/mS·cm^{-1}	t/°C	κ/mS·cm^{-1}	t/°C	κ/mS·cm^{-1}	$100w_{H_2SiF_6}$	t/°C	κ/mS·cm^{-1}	t/°C	κ/mS·cm^{-1}	t/°C	κ/mS·cm^{-1}	t/°C	κ/mS·cm^{-1}
45.2	15.2	474.3	25.7	553.5	35.2	625.1	44.7	690.9	21.2	15.3	609.1	25.3	700.3	35.5	782.7	45.3	872.7
43.2	15.2	516.9	25.6	597.9	35.2	672.7	44.8	747.3	20.4	15.4	597.3	25.2	686.5	35.5	767.1	45.2	855.4
41.4	15.1	553.4	25.8	635.0	35.3	715.7	44.9	795.1	19.6	15.3	587.9	25.3	675.7	35.4	754.4	45.3	839.7
39.7	15.0	578.4	25.7	665.7	35.4	750.7	45.1	831.7	19.0	15.3	577.5	25.2	661.8	35.5	740.4	45.3	823.2
38.2	14.9	601.2	25.7	688.8	35.4	776.3	45.0	861.3	18.3	15.2	566.4	25.2	648.9	35.3	724.0	45.3	810.1
36.7	14.9	616.8	25.6	708.8	35.4	796.2	45.2	887.5	17.7	15.2	554.0	25.1	637.3	35.3	710.9	45.1	791.5
35.4	15.0	632.1	25.5	724.0	35.4	813.1	45.1	903.3	17.7	15.5	555.1	25.3	639.4	35.6	715.4	45.0	789.8
34.2	15.2	643.9	25.5	735.1	35.3	827.6	45.2	917.3	16.7	15.5	538.4	25.3	616.1	35.7	692.8	45.0	761.5
33.0	14.9	649.7	25.5	744.7	35.2	837.0	42.2	928.5	15.9	15.4	519.0	25.3	596.2	35.7	670.3	45.1	738.0
32.0	15.1	655.8	25.4	750.7	35.2	842.0	45.3	933.8	15.1	15.5	501.3	25.3	577.2	35.7	648.1	45.3	716.3
30.9	15.1	659.4	25.3	753.0	35.1	846.9	45.2	938.2	14.4	15.3	484.0	25.2	559.5	35.7	628.3	45.3	691.6
30.0	15.1	661.4	25.2	754.2	35.2	849.9	45.2	943.2	13.7	15.3	469.4	25.2	540.6	35.7	607.2	45.3	668.8
29.1	15.1	661.9	25.2	754.0	35.2	847.7	45.1	940.5	13.1	15.2	453.6	25.1	522.2	35.7	587.1	45.3	647.2
29.1	15.6	664.6	25.4	760.4	35.2	850.3	45.0	944.3	12.6	15.2	438.3	25.1	506.8	35.8	570.5	45.3	628.7
27.6	15.7	664.3	25.4	757.4	35.3	848.2	45.0	941.6	12.1	15.2	426.1	25.1	491.3	35.7	554.1	45.4	610.0
26.3	15.6	657.9	25.5	754.5	35.3	841.7	45.2	935.1	11.6	15.2	412.4	25.0	477.0	35.7	537.5	45.4	593.4
25.1	15.6	649.0	25.5	747.5	35.3	831.8	45.2	926.7	11.2	15.0	401.2	25.0	464.1	35.7	521.9	45.3	574.9
24.0	15.5	640.4	25.4	737.2	35.5	823.4	45.2	912.7	10.8	15.0	389.3	24.9	450.3	35.6	506.5	45.3	560.7
23.0	15.5	632.9	25.4	724.4	35.5	809.5	45.2	900.8	10.4	15.0	379.9	25.0	438.8	35.5	492.9	45.2	544.6
22.0	15.4	621.2	25.4	714.5	35.5	794.8	45.2	887.1									

H_2TiF_6

	$t = (14.8 \pm 0.2)$ °C		$t = (25.2 \pm 0.1)$ °C		$t = (35.6 \pm 0.2)$ °C		$t = (45.2 \pm 0.2)$ °C			$t = (14.8 \pm 0.2)$ °C		$t = (25.2 \pm 0.1)$ °C		$t = (35.6 \pm 0.2)$ °C		$t = (45.2 \pm 0.2)$ °C	
$100w_{H_2TiF_6}$	t/°C	κ/mS·cm^{-1}	t/°C	κ/mS·cm^{-1}	t/°C	κ/mS·cm^{-1}	t/°C	κ/mS·cm^{-1}	$100w_{H_2TiF_6}$	t/°C	κ/mS·cm^{-1}	t/°C	κ/mS·cm^{-1}	t/°C	κ/mS·cm^{-1}	t/°C	κ/mS·cm^{-1}
59.0	14.8	365.9	25.3	428.1	35.5	490.6	44.8	551.6	29.1	14.8	639.5	25.0	721.0	35.5	798.4	45.4	868.5
56.7	14.9	404.9	25.2	468.6	35.7	537.8	44.9	604.1	28.1	14.8	633.5	25.0	712.0	35.5	789.3	45.4	860.0
54.5	14.9	440.2	25.1	507.6	35.6	579.7	45.0	648.9	27.1	14.8	626.1	25.1	702.4	35.5	779.6	45.5	849.6
52.5	14.8	472.2	25.1	542.7	35.6	617.1	45.0	689.0	26.2	14.7	617.9	25.0	692.8	35.5	769.4	45.4	837.6
50.6	14.7	501.5	25.2	574.8	35.7	650.9	45.2	723.9	25.4	14.7	610.1	25.0	682.4	35.5	755.7	45.4	828.2
48.9	14.6	527.7	25.2	604.1	35.8	682.6	45.2	759.3	24.6	14.7	600.0	24.9	671.8	35.5	746.6	45.3	812.8
47.2	14.6	550.4	25.2	629.5	35.8	708.5	45.3	787.6	24.6	15.0	595.6	25.3	668.3	35.3	741.1	44.8	810.7
45.7	14.5	570.9	25.2	652.0	35.8	731.8	45.3	813.0	23.2	14.9	579.5	25.3	650.8	35.5	716.4	44.8	790.4
44.3	14.5	588.2	25.2	670.8	35.8	750.1	45.4	830.8	22.1	14.9	563.3	25.3	631.7	35.4	696.6	44.8	764.8
43.0	14.5	603.4	25.1	686.3	35.8	768.2	45.5	848.0	21.0	14.8	546.8	25.3	609.6	35.5	673.8	45.0	740.3
41.7	14.5	615.9	25.0	699.8	35.7	785.1	45.4	865.3	20.0	14.8	530.6	25.2	590.7	35.5	652.6	44.9	715.6
40.5	14.5	626.2	25.1	709.8	35.7	795.8	45.5	876.1	19.2	14.7	515.2	25.3	573.1	35.6	634.6	45.1	690.8
39.4	14.5	635.1	25.1	718.5	35.7	803.8	45.4	883.8	18.4	14.7	499.8	25.2	556.1	35.6	615.0	45.2	673.4
39.4	15.2	635.0	25.3	724.1	35.2	808.3	45.0	887.3	17.6	14.7	485.5	25.2	539.4	35.6	596.7	45.1	653.2
37.5	15.1	646.4	25.2	736.4	35.3	820.4	45.0	895.0	17.0	14.6	471.6	25.3	524.2	35.6	579.3	45.1	634.1
35.8	15.0	651.2	25.3	740.0	35.4	824.9	45.0	902.6	16.3	14.6	458.4	25.2	508.5	35.6	562.6	45.1	614.8
34.2	15.1	653.2	25.2	740.8	35.5	825.0	45.1	900.6	15.7	14.5	445.6	25.2	493.5	35.6	545.0	45.2	595.9
32.8	15.0	652.3	25.2	739.1	35.5	821.2	45.2	896.5	15.2	14.6	433.7	25.2	480.1	35.5	529.7	45.2	580.1
31.5	14.9	650.1	25.2	734.8	35.4	815.4	45.4	888.2	14.7	14.5	422.2	25.1	467.1	35.5	514.7	45.3	564.5
30.3	14.9	645.1	25.2	728.8	35.4	806.9	45.4	879.6									

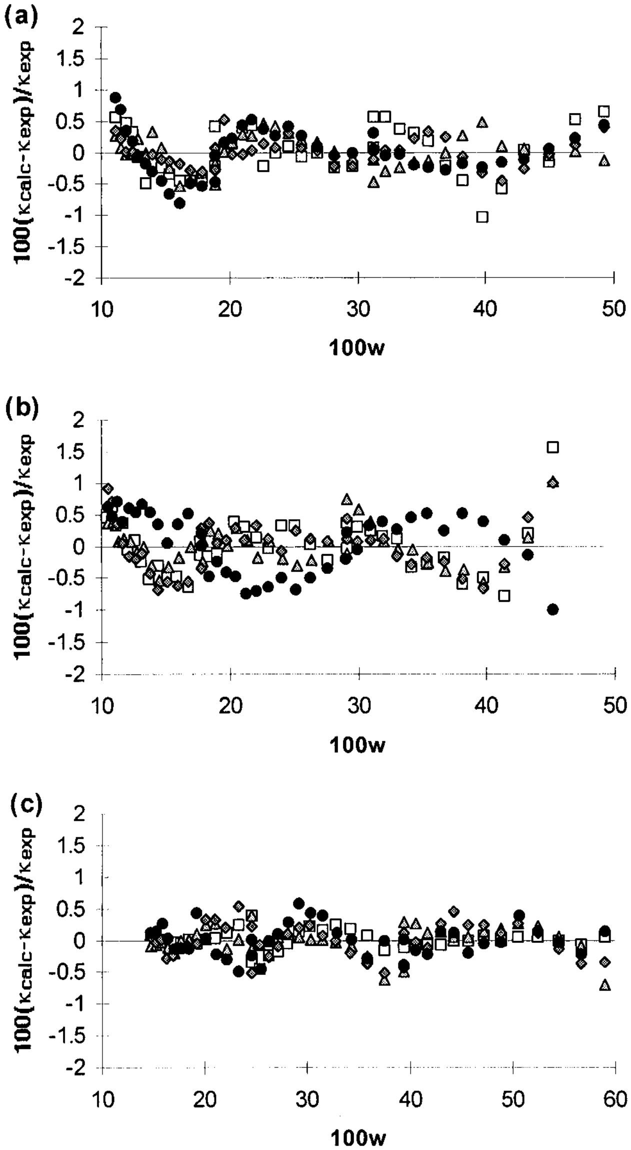

Figure 1. Distribution of the relative errors ($100(\kappa_{calc} - \kappa_{exp})/\kappa_{exp}$) between the experimental conductivities and those calculated by the Casteel–Amis equation with the best sets of adjustable parameters (see Table 2): (a) HBF_4; (b) H_2SiF_6; (c) H_2TiF_6; (□) ~15 °C; (▲) ~25 °C; (◆) ~35 °C; (●) ~45 °C.

quality fits of data with a smaller number of adjustable parameters. If extrapolation is required or in studies in which the determination of the κ_{max} and the m_{max} is of high importance, the Casteel–Amis equation will be preferred but, if high-quality values are to be generated by interpolation, the polynomial equation may be chosen. The validity of the Casteel–Amis equation with the concentration in mass percent (100w) has also been verified for several aqueous electrolytic systems (de Diego, 1996).

Conductimetric results given in Table 1 have been fitted to eq 1 (a fourth degree polynomial has been considered) and eq 2 by means of NLREG. Mass percents have been directly considered in both cases. The best sets of parameters for the Casteel–Amis equation calculated in this way have been collected in Table 2, together with the RSD values (RSD = SQR{Σ(relative errors)^2/(number of observations−number of adjustable parameters)}100) of the fitting processes, and the percentages of variance explained ($\Delta\sigma^2$) in each case. The "t" statistics of each parameter are also given in brackets. This statistic is computed by dividing the estimated value of the parameter by its calculated standard error. It is a measure of the likelihood

Table 2. Best Sets of Parameters Calculated by Fitting Experimental Data of HBF_4, H_2SiF_6, and H_2TiF_6 Aqueous Solutions at Constant Temperature to the Casteel−Amis Equation, Together with the RSD, $\Delta\sigma^2$, and "*t*" Statistic Values (in Parentheses) of Each Fitting Process

HBF_4

	t = (13.8 ± 0.3) °C	t = (24.7 ± 0.1) °C	t = (36.3 ± 0.2) °C	t = (45.7 ± 0.4) °C
κ_{max}/mS·cm^{-1}	567.01 ± 0.55 (1036)	654.68 ± 0.44 (1475)	747.00 ± 0.40 (1852)	818.30 ± 0.69 (1186)
$(100w)_{max}$	31.051 ± 0.055 (566)	30.887 ± 0.042 (742)	30.949 ± 0.035 (896)	30.758 ± 0.056 (549)
x	0.626 ± 0.033 (18.8)	0.709 ± 0.023 (30.5)	0.770 ± 0.018 (41.8)	0.746 ± 0.029 (25.7)
y	$(-7.23 \pm 0.24) \times 10^{-4}$ (29.8)	$(-6.08 \pm 0.17) \times 10^{-4}$ (35.8)	$(-5.32 \pm 0.13) \times 10^{-4}$ (39.7)	$(-5.10 \pm 0.21) \times 10^{-4}$ (24.3)
RSD	0.40	0.27	0.22	0.38
$\Delta\sigma^2$	99.94	99.97	99.98	99.94

H_2SiF_6

	t = (15.2 ± 0.2) °C	t = (25.3 ± 0.2) °C	t = (35.4 ± 0.2) °C	t = (45.2 ± 0.2) °C
κ_{max}/mS·cm^{-1}	664.39 ± 0.65 (1015)	759.56 ± 0.63 (1215)	851.25 ± 0.78 (1093)	945.83 ± 0.78 (1206)
$(100w)_{max}$	28.948 ± 0.048 (601)	29.026 ± 0.042 (696)	29.115 ± 0.046 (627)	29.090 ± 0.042 (696)
x	0.591 ± 0.035 (16.7)	0.647 ± 0.030 (21.4)	0.600 ± 0.033 (18.2)	0.635 ± 0.030 (21.2)
y	$(-9.54 \pm 0.30) \times 10^{-4}$ (31.8)	$(-8.85 \pm 0.25) \times 10^{-4}$ (34.7)	$(-8.90 \pm 0.28) \times 10^{-4}$ (32.0)	$(-8.83 \pm 0.25) \times 10^{-4}$ (34.9)
RSD	0.43	0.33	0.41	0.48
$\Delta\sigma^2$	99.94	99.96	99.94	99.96

H_2TiF_6

	t = (14.8 ± 0.2) °C	t = (25.2 ± 0.1) °C	t = (35.6 ± 0.2) °C	t = (45.2 ± 0.2) °C
κ_{max}/mS·cm^{-1}	654.51 ± 0.26 (2532)	740.13 ± 0.39 (1911)	823.35 ± 0.52 (1576)	900.90 ± 0.55 (1631)
$(100w)_{max}$	33.727 ± 0.026 (1299)	34.135 ± 0.034 (999)	34.456 ± 0.042 (820)	34.826 ± 0.042 (838)
x	0.691 ± 0.018 (38.2)	0.754 ± 0.024 (31.6)	0.789 ± 0.029 (27.5)	0.773 ± 0.028 (27.8)
y	$(-7.04 \pm 0.09) \times 10^{-4}$ (79.0)	$(-6.76 \pm 0.12) \times 10^{-4}$ (57.8)	$(-6.37 \pm 0.14) \times 10^{-4}$ (45.5)	$(-6.16 \pm 0.13) \times 10^{-4}$ (45.7)
RSD	0.16	0.23	0.27	0.26
$\Delta\sigma^2$	99.99	99.98	99.97	99.97

Table 3. Proposed Polynomial Equations To Explain the Variability of the Experimental Data of HBF_4, H_2SiF_6, and H_2TiF_6 Aqueous Solutions at Each Temperature Studied: Best Sets of Calculated Parameters Together with RSD, $\Delta\sigma^2$, and "*t*" Statistic Values (in Parentheses)

HBF_4

	t = (13.8 ± 0.3) °C	t = (24.7 ± 0.1) °C	t = (36.3 ± 0.2) °C	t = (45.7 ± 0.4) °C
a_1/mS·cm^{-1}	36.692 ± 0.080 (459)	43.670 ± 0.093 (470)	50.180 ± 0.060 (836)	56.39 ± 0.10 (567)
a_2/mS·cm^{-1}	−0.6075 ± 0.0038 (160)	−0.7566 ± 0.0044 (172)	−0.8795 ± 0.0029 (303)	−1.0209 ± 0.0047 (217)
a_3/mS·cm^{-1}				
a_4/mS·cm^{-1}	$(1.23 \pm 0.11) \times 10^{-5}$ (11.2)	$(2.85 \pm 0.12) \times 10^{-5}$ (23.8)	$(3.822 \pm 0.081) \times 10^{-5}$ (47.2)	$(5.46 \pm 0.13) \times 10^{-5}$ (40.8)
RSD	0.40	0.39	0.21	0.34
$\Delta\sigma^2$	99.93	99.93	99.98	99.94

H_2SiF_6

	t = (15.2 ± 0.2) °C	t = (25.3 ± 0.2) °C	t = (35.4 ± 0.2) °C	t = (45.2 ± 0.2) °C
a_1/mS·cm^{-1}	44.778 ± 0.065 (694)	51.063 ± 0.081 (634)	57.335 ± 0.060 (952)	63.539 ± 0.083 (765)
a_2/mS·cm^{-1}	−0.7587± 0.0019 (390)	−0.8615 ± 0.0024 (355)	−0.9669 ± 0.0018 (532)	−1.0705 ± 0.0025 (427)
a_3/mS·cm^{-1}				
a_4/mS·cm^{-1}				
RSD	0.58	0.59	0.39	0.48
$\Delta\sigma^2$	99.89	99.87	99.94	99.91

H_2TiF_6

	t = (14.8 ± 0.2) °C	t = (25.2 ± 0.1) °C	t = (35.6 ± 0.2) °C	t = (45.2 ± 0.2) °C
a_1/mS·cm^{-1}	31.601 ± 0.032 (988)	35.086 ± 0.072 (487)	38.696 ± 0.079 (492)	42.036 ± 0.056 (757)
a_2/mS·cm^{-1}				
a_3/mS·cm^{-1}	$(-1.540 \pm 0.006) \times 10^{-2}$ (262)	$(-1.165 \pm 0.013) \times 10^{-2}$ (126)	$(-1.788 \pm 0.014) \times 10^{-2}$ (125)	$(-1.913 \pm 0.010) \times 10^{-2}$ (105)
a_4/mS·cm^{-1}	$(1.372 \pm 0.009) \times 10^{-4}$ (151)	$(1.434 \pm 0.020) \times 10^{-4}$ (70.6)	$(1.547 \pm 0.022) \times 10^{-4}$ (69.9)	$(1.649 \pm 0.016) \times 10^{-4}$ (105)
RSD	0.28	0.58	0.56	0.26
$\Delta\sigma^2$	99.97	99.87	99.88	99.95

that the actual value of the parameter is not zero. The larger the absolute value of "*t*", the less likely that the actual value of the parameter could be zero (Sherrod, 1995). The "*t*" statistic can be considered as a test of the statistical significance of each calculated parameter in the fitting process.

In the case of the Casteel−Amis equation, all the calculated parameters show high values of "*t*" and $\Delta\sigma^2$ ($\Delta\sigma^2 > 99.9$), indicating that the four parameters are needed to give a good fit to the data. Relative errors $(100(\kappa_{calc} - \kappa_{exp})/\kappa_{exp})$ between calculated an experimental data have been plotted in Figure 1.

With regard to the polynomial model, high values of $\Delta\sigma^2$ were obtained but several adjustable parameters showed low values of the "*t*" statistic. New fits of data to eq 1 were attempted after removing one by one the parameters with the lower values of "*t*" statistic. The polynomial equations finally chosen to explain the variability of the experimental data, together with the corresponding values of RSD, $\Delta\sigma^2$, and "*t*" are summarized in Table 3. Further elimination of parameters from the models would have led in each case to poor fits. Relative errors $(100(\kappa_{calc} - \kappa_{exp})/\kappa_{exp})$ between calculated and experimental data have been plotted in Figure 2.

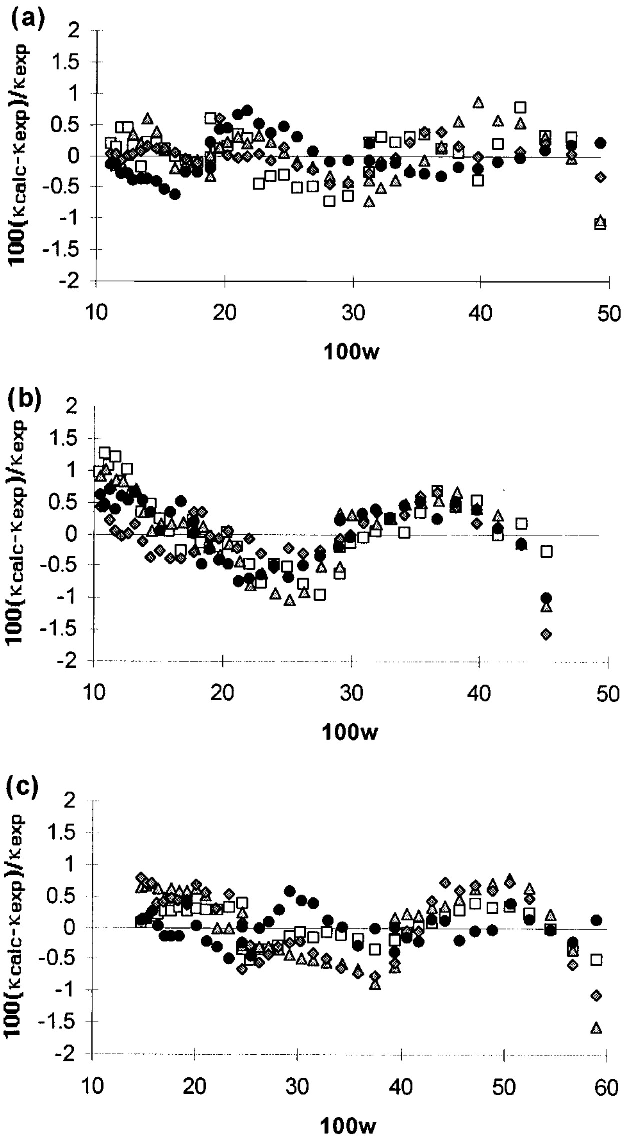

Figure 2. Distribution of the relative errors ($100(\kappa_{\rm calc} - \kappa_{\rm exp})/\kappa_{\rm exp}$) between the experimental conductivities and those calculated by the selected polynomial models with the best sets of adjustable parameters (see Table 3): (a) HBF_4; (b) H_2SiF_6; (c) H_2TiF_6; (□) ~15 °C; (▲) ~25 °C; (◆) ~35 °C; (●) ~45 °C.

Discussion

No other conductivity measurements on the systems studied have been found, so that comparison is not possible. Nevertheless, the obtained κ vs c diagrams at different temperatures show that the conductimetric behavior of each electrolytic system investigated is similar to those of other aqueous electrolyte solutions. A maximum of conductivity is always attained at intermediate concentrations if the solubility of the systems allows it (Valiashko and Ivanov, 1974; Molenat, 1969). Besides, the conductivity values are of the same magnitude as those from other mineral acids such as HCl, HI, HBr (Haase et al., 1965a), HNO_3 (Haase et al., 1965b), $HClO_4$ (Haase et al., 1965c), or H_2SO_4 (Haase et al., 1966).

Increasing temperature tends to increase the conductivity of a chemical system, although the opposite behavior has also been observed in the case of a few electrolyte solutions in very restricted intervals of concentrations (Barthel, 1985). The position of the maximum of conductivity is also influenced by the temperature (Barthel et al., 1979). It usually shifts to higher concentrations with increasing temperature, the amount of this shift being a characteristic of each system. The $(100w)_{\rm max}$ values calculated at different temperatures (see Table 2), taking into account their precisions, confirm the shift to higher concentrations in the case of H_2SiF_6 and H_2TiF_6. On the contrary, the position of the maximum seems not to be significantly influenced by the temperature for HBF_4.

With regard to the models proposed to explain the randomness of the conductivity vs mass percent data, the results confirm the suitability of the Casteel–Amis equation as a general model to fit $(\kappa, 100w)_t$ data from electrolyte solutions. The proposed polynomial equations provide fits of experimental data of similar quality with fewer adjustable parameters. Both models may be applied to the automatic "in line" control of concentrations in industrial processes by continuous measurement of the conductivity.

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