representation by the Grayson–Streed correlation is expected since the Chao–Seader correlation for hydrogen was limited by its data base to temperatures below 260 °C. Grayson and Streed extended the temperature range by using experimental data of their own at temperatures up to 480 °C. Chao–Seader predicted the K values of quinoline in fair agreement with experimental data, but the deviations are up to about 25% at the higher pressures of the lower isotherms. The Grayson–Streed correlation appears to well represent the K values of quinoline up to the highest pressure studied. Both correlations are extrapolated with respect to solubility parameter value to apply to the present system. The result indicates that improvement of the Chao–Seader type correlations to apply to heteroatom-containing hydrocarbons is possible. This conclusion is supported by previous studies in this laboratory (*7–11*).

Glossary

K	vaporization equilibrium ratio, y/x
p	pressure, atm
T	temperature, K
T_r	reduced temperature, T/T_c
$\tilde{V}$	molar volume, mL/g-mol
x_i	mole fraction of component i in the liquid phase
y_i	mole fraction of component i in the gas phase
δ	solubility parameter, $(\mathrm{cal/mL})^{1/2}$
ω	acentric factor

Subscripts

C	critical properties
H	hydrogen
Q	quinoline

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Received for review January 3, 1978. Accepted June 5, 1978. Financial support of this research by the Electric Power Research Institute, RP-367, is acknowledged.

Standard Electromotive Forces of the Cell $\mathrm{Pt;H_{2(1\ atm)},HCl_{(\mathit{m})},AgCl;Ag}$ Containing Mixtures of Dimethyl Sulfoxide and Water between +25 and –12 °C

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Measured emf's for the cell $\mathrm{Pt;H_{2(g,1\ atm)},HCl,AgCl;Ag}$ and derivation of the standard cell potentials are tabulated for water at 25 and 0 °C, for 20% (w/w) $\mathrm{Me_2SO{-}H_2O}$ at +25, 0, and –5.5 °C, and for 30% (w/w) $\mathrm{Me_2SO{-}H_2O}$ at +25, 0, and –12 °C. The determination of standard molal emf's of the hydrogen–silver, silver chloride electrochemical cell containing mixtures of dimethyl sulfoxide ($\mathrm{Me_2SO}$) and water at low temperatures is needed for reliable pH measurements in mixed solvents at normal and subzero temperatures.

Introduction

Reliable pH measurements in mixed solvents are needed at low temperatures, since pH changes may contribute to the injury of biological systems during cooling and freezing (*7*, *31*, *32*). Solutions used for the low-temperature preservation of cells, tissues, and organs usually incorporate a binary mixed solvent due to the addition of a nonelectrolyte compound such as dimethyl sulfoxide ($\mathrm{Me_2SO}$) or glycerol (*25*, *28*). These compounds, often called cryoprotectants, act colligatively to depress the freezing point of the medium and also to reduce the amount of ice at any temperature during freezing. This is thought to be the principal mechanism of cryoprotection (*24*).

Investigations into the factors affecting the low-temperature preservation of smooth muscle tissue (*7*, *31*, *32*) showed that its functional recovery after low-temperature storage in unfrozen media containing $\mathrm{Me_2SO}$ is dependent upon the initial pH of the bathing solution. However, in these and other studies emphasizing pH changes as an important factor for the survival of biological systems after exposure to low temperatures, all measurements of hydrogen ion activity were carried out at ambient temperatures with a glass/calomel cell standardized against aqueous buffers. These measurements were subject to errors of unknown magnitude on account of the indeterminable asymmetry potential of the glass membrane and the liquid junction potentials within the cell, and as a result the true pH of the tissue and its bathing medium remained uncertain.

Solvent composition and temperature can have a marked effect upon the value and measurement of the hydrogen ion activity of a solution (*2*, *6*, *26*) and although Khoo (*20*, *21*) has measured the standard electromotive forces of hydrogen–silver halide cells containing mixtures of $\mathrm{Me_2SO}$ and water at 25 °C, little work has been done to establish pH scales in aqueous mixed solvents at low temperatures.

The pH-dependent recovery of smooth muscles from storage at –13 °C in unfrozen solutions containing 30% $\mathrm{Me_2SO}$ (*31*, *32*) has defined one set of conditions under which reliable electrochemical measurements of hydrogen ion activity would be useful. This paper describes the determination of standard molal emf's in mixtures of dimethyl sulfoxide and water at temperatures between +25 and –12 °C, thereby providing a basis for the application of the hydrogen–silver, silver chloride

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cell, which is without liquid junction, to pH standardization in mixed solvents at normal and subzero temperatures.

Experimental Section

Cell emf's were measured with a Vibron electrometer (Model 33B), and a dc millivolt calibrator (type 2003, Time Electronics Ltd) was used for standardization of potentials. The cell potential was recorded to within ±0.05 mV on a millivolt chart recorder (Rikadenki). The experimental cell was a Metrohm universal titration vessel provided with a water jacket for temperature control. Control was achieved by immersing the cell in a mixture of methanol and water contained in a refrigerated bath (Grant LB4) maintained at a constant temperature (±0.1 °C). Temperature measurements were made with a calibrated platinum resistance thermometer (*29*). Hydrogen gas (British Oxygen Co.) of the high purity grade (99.99%) was passed through purifying agents and supplied to the cell through a jacketed presaturator containing the same solution as within the cell and maintained at the same temperature.

Electrodes

1. Hydrogen Gas Electrodes. Platinum–hydrogen electrodes were constructed from platinum foil squares (1 cm^2 by 0.015 cm) spot-welded to a length of platinum wire (standard wire gauge 26) and sealed into a soft glass mounting tube. Electrical contact was completed by silver soldering a length of tinned copper wire (s.w. gauge 22) to the platinum wire and finally soft-soldering a length of flexible multistranded, copper-core wire to the tinned copper for connection to the electrometer.

Platinization. Before platinization, the electrode bases were cleaned and prepared by the method of Hills and Ives (*16*). The surfaces of the hydrogen electrode bases were activated by platinization in the following way. The platinum foil bases were cathodized in lead-free chloroplatinic acid solution contained in a "U"-tube electrolysis cell (*18*). The platizing solution was 2% (w/w) chloroplatinic acid in 2 N hydrochloric acid and the process was carried out for 2 min at a current density of 100 mA cm^{-2}.

2. Silver–Silver Chloride Electrodes. Silver–silver chloride electrodes of the thermal-electrolytic type (*18*, *19*, *22*) were used throughout this work. The base of each electrode consisted of a helix of platinum wire (s.w. gauge 26) about 0.8 cm in length and 0.25 cm in diameter, sealed into a tube of soft glass (15 cm × 0.7 cm). Electrical connection to the platinum spiral was achieved in the same way as described for the platinum–hydrogen electrodes. Each base was cleaned in warm 6 M nitric acid, rinsed thoroughly several times in deionized water, and finally washed in boiling water before application of the silver–silver chloride complex.

Silver oxide used for the formation of a silver mass on the base of each electrode was prepared in the following way. Silver nitrate (84.5 g, British Drug Houses Analar Grade) was dissolved in 750 cm^3 of deionized water (conductivity $< 1.00 \times 10^{-6}$ ohm^{-1} cm^{-1}). An approximately 2 M solution of sodium hydroxide (100 cm^3) was then added, with vigorous stirring, to the solution of silver nitrate. The precipitated silver oxide was washed about 30 times by shaking vigorously with deionized water in a tall stoppered cylinder in accordance with the recommendations of Bates (*2*) and Janz (*18*).

A thick paste of the well-washed silver oxide was applied to the helical base of each electrode with a small spatula. A batch of six electrodes supported on an asbestos rack was then placed in an electric muffle furnace and heated to just below 100 °C for 30 min to allow superficial drying. This prevented sputtering by the rapid formation of steam when the temperature of the furnace was raised uniformly to 500 °C for the thermal decomposition of the silver oxide to silver. The latter process was completed within 30 min, producing a white porous mass of silver adherent to each platinum helix. A second and third layer of silver was formed in a similar manner with a progressively thinner paste of silver oxide to produce a smooth surface. Finally each silver electrode was made the anode in a cell of U-tube design and chloridized by electrolysis in a 1 M solution of double-distilled hydrochloric acid for 50 min at a current of 10 mA. A platinum spiral electrode served as the cathode in this process which was completed at least 24 h before the use of each electrode. Silver–silver chloride electrodes prepared in this way were stored in 0.05 *m* hydrochloric acid solution overnight and finally transferred to deionized water for use within a few days. Used electrodes (1–2 weeks old) were recycled by chipping-off the old AgCl–Ag mass from the platinum helix and using the electrode bases in repeated processes.

Standard Hydrochloric Acid Solutions

Solutions of hydrochloric acid for the determination of standard cell potentials were prepared by weight dilution to stock solutions of "constant-boiling" hydrochloric acid (*34*). The constant-boiling mixture is neither hygroscopic nor appreciably volatile, and its concentration remains unchanged if kept in a well-stoppered vessel out of direct sunlight.

The concentration of the stock constant-boiling hydrochloric acid was determined gravimetrically by precipitation of the chloride as silver chloride. Solutions of HCl in the concentration range 0.1–0.005 *m* were prepared in 100-cm^3 volumetric flasks with preboiled, deionized water using a top-loading torsion balance (Torbal Model ET-1). All solutions of concentration equal to or greater than 0.02 *m* were prepared by weight dilution of the stock constant-boiling HCl. More dilute cell solutions were prepared using a stock solution having one-tenth the acid concentration of the constant-boiling mixture.

Mixed-solvent solutions containing dimethyl sulfoxide were prepared by incorporating the correct weight to Me_2SO during the dilution.

For each emf measurement, 15 cm^3 of solution was poured into the cell and equilibrated with purified hydrogen bubbling at a rate of about 2 bubbles/s. Constancy of the emf readings to 0.1 mV for at least 30 min was in general taken to be criterion for equilibration.

Either two hydrogen or two reference electrodes were mounted in the cell for each measurement as this permitted an intercomparison of potentials between electrodes prepared in the same way. A freshly platinized hydrogen electrode was used for each new measurement in solutions containing dimethyl sulfoxide because it was noticed during initial experiments that the platinized electrodes became sluggish after prolonged or repeated use in the presence of Me_2SO.

Barometric pressure was recorded at regular intervals and particularly when the cell had reached equilibrium in order that emf values could be corrected to a partial pressure of hydrogen of 1 atm, which is the reference pressure. These corrections were permitted by the relationship for the change of potential of the hydrogen electrode, *E*, with pressure (*10*)

$$\Delta E = \frac{RT}{2F} \ln \frac{760}{p_{H_2}} \quad (1)$$

where the partial pressure of hydrogen gas, p_{H_2}, at the electrode surface may be obtained by subtracting the tension of water vapor, p_{H_2O}, from the barometric pressure (*2*)

$$p_{H2} = P - p_{H_2O} \quad (2)$$

At temperatures above 0 °C hydrogen electrode corrections for barometric pressures from 720 to 775 mmHg were taken from tables given by Bates (*2*), while at temperatures below zero, emf corrections were calculated from eq 1 and 2 using extrapolated values of water vapor pressures.

Evaluations of the standard potential of the cell $Pt;H_{2(g,1\ atm)},HCl_{(m)},AgCl;Ag$ were made in water at 25 and 0

°C, in 20% (w/w) Me_2SO-H_2O at +25, 0, and -5.5 °C, and in 30% (w/w) Me_2SO-H_2O at +25, 0, and -12.0 °C.

Theoretical Section

The standard electrode potential for the silver, silver chloride electrode is obtained from emf measurements for the cell without liquid junction.

$$Pt;H_{2(g,1\ atm)},HCl_{(m)},AgCl_{(s)};Ag_{(s)} \quad (3)$$

Applying the Nernst equation (see ref 27) to the cell reaction gives an expression for the emf, E, of the cell

$$E = E^\circ - (2RT/F)\ln a_\pm \quad (4)$$

where E° is the standard molal cell potential, R is the universal gas constant, F the Faraday constant, T is the absolute temperature in Kelvins, and $a_\pm$ is the mean ion activity.

Since HCl is a strong 1 to 1 electrolyte its mean ion activity may be written in terms of the molal concentration and its mean ion activity coefficient, whereby

$$E = E^\circ - 2k\log(m\gamma_\pm) \quad (5)$$

where $k = 2.3026RT/F$.

An expression for the activity coefficient of the electrolyte at moderate ionic strengths (up to 1 m) is given by the theory of Debye and Hückel (*5*)

$$\log\gamma_\pm = -\frac{AZ^2I^{1/2}}{1 + Ba^\circ I^{1/2}} + bI \quad (6)$$

where A and B are constants dependent upon the dielectric constant of the solvent and the temperature, a° is the ion size parameter, b is an empirical constant, I is the ionic strength, and Z is the ionic valence. Hence expression 5 can be rewritten as

$$E + 2k\log m - \frac{2kAm^{1/2}}{1 + Ba^\circ m^{1/2}} = E^\circ - 2kbm \quad (7)$$

where the ionic strength for the 1 to 1 electrolyte has been written as the molal concentration, m. Expressing the three terms on the left-hand side of eq 7 as E_0' we have

$$E_0' = E^\circ - 2kbm \quad (8)$$

A plot of E_0' against molality (m) would be expected to give a straight line of slope = $-2kb$ and intercept E° (*13*, *17*).

In mixed solvent systems the mean ion activity coefficient of hydrochloric acid is given (*8*, *9*, *13*) by the extended Debye-Hückel law as

$$\log\gamma_\pm = \frac{-Am^{1/2}}{1 + Ba^\circ m^{1/2}} + bm - \log(1 + 0.002M_{xy}m) \quad (9)$$

where M_{xy} is the mean molecular weight of the solvent given by

$$M_{xy} = \frac{100}{X/M_x + (100 - X)/M_y} \quad (10)$$

X is the weight percent of Me_2SO and M_x and M_y are the molecular weights of Me_2SO and water, respectively.

Hence in Me_2SO-H_2O mixed solvent

$$E + 2k\log m - \frac{2kAm^{1/2}}{1 + Ba^\circ m^{1/2}} - 2k\log(1 + 0.002M_{xy}m) = E^\circ - 2kbm \quad (11)$$

The four terms on the left-hand side of eq 11 may be denoted by E_0' in which case

$$E_0' = E^\circ - 2kbm \quad (8)$$

and again, a plot of E_0' against m should give a straight line, the extrapolation of which to infinite dilution ($m = 0$) gives the value for E°.

Table I. Dielectric Constants (ϵ) and Debye-Hückel Constants Used in the Determination of Standard Cell Potentials at Temperatures between +25 and -12 °C

Temp	constants[a]	solvent H_2O	solvent 20% (w/w) Me_2SO-H_2O	solvent 30% (w/w) Me_2SO-H_2O
25 °C	ϵ	78.30	77.90	77.40
298.16 K	A	0.5116	0.5159	0.5205
	B	0.3291	0.3301	0.3310
0 °C	ϵ	87.74	87.34	86.84
273.16 K	A	0.4918	0.4956	0.4994
	B	0.3249	0.3257	0.3265
-5.5 °C	ϵ		89.30	
267.66 K	A		0.4938	
	B		0.3253	
-12.0 °C	ϵ			91.73
261.16 K	A			0.4921
	B			0.3249

[a] The constants A and B were derived from the expressions given by Robinson and Stokes (*30*): $A = (1.825 \times 10^6)/(\epsilon T)^{3/2}$ mol$^{-1/2}$ L$^{1/2}$ K$^{3/2}$, $B = 50.29/(\epsilon T)^{1/2}$ mol$^{-1/2}$ L$^{1/2}$ K$^{1/2}$.

Results and Discussion

Electromotive forces, corrected to 1 atm pressure, for each molal concentration of hydrochloric acid in cell 3 were used to calculate values for E_0' according to the theory outlined above.

When cell 3 contained a purely aqueous solvent, it has been shown that E_0' is given by the three terms on the left-hand side of eq 7, i.e.

$$E_0' = E + 2k\log m - \frac{2kAm^{1/2}}{1 + Ba^\circ m^{1/2}} \quad (12)$$

and when the cell contains a mixed solvent then E_0' is given by

$$E_0' = E + 2k\log m - \frac{2kAm^{1/2}}{1 + Ba^\circ m^{1/2}} - 2k\log(1 + 0.002M_{xy}m) \quad (13)$$

Values of the Debye-Hückel constants A and B for different solvents over the range of temperatures at which estimations were carried out are given in Table I. The "ion-size" parameter, a°, has been assigned the widely used value of 4.4 Å for HCl.

Calculated values of E_0' at temperatures between +25 and -12 °C for water, 20% (w/w) Me_2SO-H_2O, and 30% (w/w) Me_2SO-H_2O are given in Tables II-IV. Estimations of the standard electrode potentials by extrapolation of the E_0' values to zero ionic strength using the method of least squares are also given in Tables II-IV.

Corrections of the cell electromotive forces to the reference pressure of 1 atm were achieved, as described, using eq 1 and 2. The pressure of water vapor over aqueous solutions of low and moderate concentration can be assumed, for all practical purposes, to be the same as the vapor pressure of water at the appropriate temperature (*2*) and, at low concentrations of Me_2SO, vapor pressures do not differ greatly from aqueous solutions (*20*). Pressure corrections to the hydrogen electrode potential at subzero temperatures were calculated using extrapolated values of the water pressure. This was considered to be reasonable since an uncertainty in the vapor pressure of 1 mmHg leads to an error in the emf of only 0.02 mV (*20*).

Dielectric constants (ϵ), necessary for the calculation of Debye-Hückel constants, for solvents containing Me_2SO were not available in the literature for temperatures other than 25 °C (*20*, *21*, *23*). However, it was observed from the data of Åkerlöf

Table II. E_0' Values Calculated from Equation 12 Using Measured Emf's of the Cell Pt;H_2,$HCl_{(m)}$, AgCl;Ag Containing Water at 25 and 0 °C[a]

25 °C			0 °C		
molality of HCl, m	cell potential corrected to 1 atm E, V	E_0'	molality of HCl, m	cell potential corrected to 1 atm E, V	E_0'
0.1002	0.352 40	0.221 10	0.1002	0.355 35	0.235 45
0.0499	0.385 65	0.221 45	0.0500	0.386 85	0.236 85
0.0296	0.411 10	0.221 90	0.0299	0.408 80	0.236 20
0.0204	0.428 95	0.222 95	0.0200	0.426 65	0.236 18
0.0150	0.443 95	0.221 85	0.0150	0.440 05	0.236 65
0.0100	0.463 85	0.222 05	0.0100	0.457 95	0.236 65
0.0070	0.481 70	0.222 30	0.0070	0.474 20	0.236 60
0.0050	0.497 95	0.221 85			

$E° = 0.222\ 27 \pm 0.000\ 02$ V $E° = 0.236\ 74 \pm 0.000\ 01$ V

[a] m is the molal concentration of hydrochloric acid. $E°$ (±1 standard error) is the standard potential derived from the extrapolation of E_0' values to zero ionic strength (eq 8).

(*1*) that the relationship between the log of the dielectric constant and temperature is linear and that the gradients of the lines for various organic solvents and their aqueous mixtures are essentially parallel as shown in Figure 1. This provided an acceptable method of extrapolating the measured dielectric constants for Me_2SO-H_2O mixtures at 25 °C (*20*, *21*, *23*) to subzero temperatures. An equation for the least-squares regression line for the relationship between log ϵ_{H_2O} and temperature was derived from the data given by Hamer (*11*)

$$\log \epsilon = -0.00197t + 1.9431 \qquad (14)$$

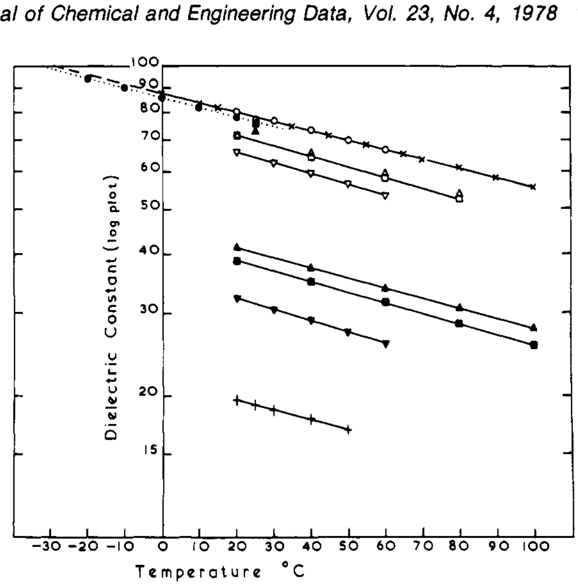

Figure 1. Logarthmic plots of the dielectric constant of some organic solvent–water mixtures against temperature. The dotted line represents the extrapolated line for 30% w/w Me_2SO-H_2O used in this work to estimate dielectric constant values at subzero temperatures. Symbol identification (symbol, solvent, reference): ×, water (*11*); ○, water (*1*); ◑, 20% w/w Me_2SO-H_2O (*20*); ●, 30% v/v Me_2SO-H_2O (*33*); ◪, 40% w/w Me_2SO-H_2O (*20*); ▲, 60% w/w Me_2SO-H_2O (*21*); □, 30% w/w ethylene glycol–H_2O (*1*); ■, 100% ethylene glycol (*1*); △, 30% w/w glycerol–H_2O (*1*); ▲, 100% glycerol (*1*); ▽, 30% w/w methanol–H_2O (*1*); ▼, 100% methanol (*1*); +, 100% acetone (*1*).

The Debye–Hückel constants given in Table I for Me_2SO-H_2O mixtures at temperatures other than 25 °C were calculated using dielectric constants estimated from the known difference between ϵ_{H_2O} and the dielectric constant for the mixed solvent at

Table III. E_0' Values Calculated (Equation 13) from Measured Emf's of the Cell, Pt;H_2,$HCl_{(m)}$,AgCl;Ag Containing 20% (w/w) Me_2SO-H_2O at Various Temperatures[a]

+25 °C			0 °C			-5.5 °C		
molality of HCl, m	cell potential corrected to 1 atm E, V	E_0'	molality of HCl, m	cell potential corrected to 1 atm E, V	E_0'	molality of HCl, m	cell potential corrected to 1 atm E, V	E_0'
0.0998	0.350 35	0.218 55	0.1003	0.353 65	0.233 55	0.099 75	0.353 35	0.235 40
0.0502	0.382 50	0.218 40	0.0504	0.383 95	0.234 20	0.050 28	0.382 95	0.236 00
0.0305	0.407 10	0.219 25	0.0323	0.403 70	0.234 50	0.020 67	0.421 50	0.236 25
0.0250	0.416 30	0.218 90	0.0195	0.426 20	0.234 65	0.014 99	0.436 05	0.236 80
0.0221	0.421 80	0.218 45	0.0150	0.438 15	0.234 90	0.009 98	0.454 00	0.236 85
0.0150	0.441 65	0.219 50	0.0100	0.455 75	0.234 40	0.004 98	0.484 25	0.236 30
0.0100	0.461 65	0.219 70	0.0070	0.472 10	0.234 65			
0.0071	0.478 45	0.219 65						
0.0053	0.492 35	0.219 15						

$E° = 0.219\ 38 \pm 0.000\ 02$ V $E° = 0.234\ 82 \pm 0.000\ 01$ V $E° = 0.236\ 71 \pm 0.000\ 01$ V

[a] m is the molal concentration of hydrochloric acid and $E°$ (±1 standard error) is the standard cell potential derived by the extrapolation of E_0' values to zero ionic strength.

Table IV. E_0' Values (from Equation 13) Calculated Using Measured Emf's of the Cell Pt;H_2,$HCl_{(m)}$,AgCl;Ag Containing 30% (w/w) Me_2SO-H_2O at Various Temperatures[a]

+25 °C			0 °C			-12 °C		
molality of HCl, m	cell potential corrected to 1 atm E, V	E_0'	molality of HCl, m	cell potential corrected to 1 atm E, V	E_0'	molality of HCl, m	cell potential corrected to 1 atm E, V	E_0'
0.100 80	0.348 00	0.216 50	0.100 80	0.351 75	0.231 90	0.100 57	0.353 15	0.238 40
0.070 61	0.365 75	0.217 60	0.070 61	0.367 35	0.232 15	0.051 23	0.381 15	0.238 60
0.049 89	0.381 40	0.216 90	0.049 89	0.382 00	0.231 70	0.029 91	0.403 50	0.238 45
0.030 46	0.406 00	0.218 00	0.030 46	0.404 35	0.232 50	0.019 86	0.421 25	0.238 80
0.020 47	0.424 50	0.217 35	0.020 47	0.422 35	0.232 85	0.015 00	0.433 75	0.239 35
0.015 05	0.440 45	0.218 40	0.015 05	0.435 25	0.232 05	0.010 00	0.450 15	0.238 40
0.010 04	0.459 75	0.217 95	0.006 96	0.470 95	0.233 10	0.007 00	0.466 30	0.239 15
0.006 96	0.478 65	0.218 85	0.004 98	0.486 65	0.233 60	0.005 08	0.479 70	0.238 65

$E° = 0.218\ 39 \pm 0.000\ 02$ V $E° = 0.232\ 99 \pm 0.000\ 02$ V $E° = 0.238\ 88 \pm 0.000\ 01$ V

[a] The standard potential $E°$ (±1 standard error), derived by extrapolation of the E_0' values to zero ionic strength ($m = 0$), is given for measurements at +25, 0, and -12 °C.

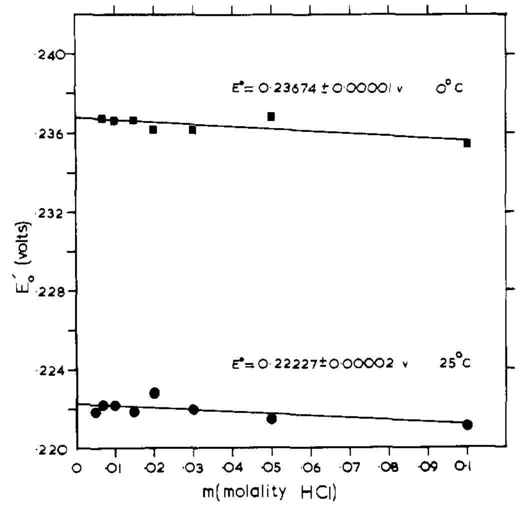

Figure 2. Plots of E_0' (eq 12) against molal concentration of hydrochloric acid to show the distribution of experimental points about the least-squares regression lines. $E°$ values (±1 standard error) for water at 25 and 0 °C were obtained by extrapolation of the regression lines to zero ionic strength (m = 0).

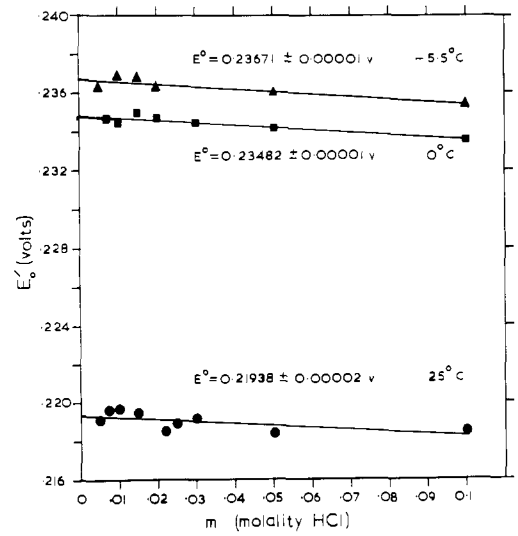

Figure 3. Least-squares regression lines for plots of E_0' (eq 13) against the molal concentrations of hydrochloric acid in 20% (w/w) Me_2SO-H_2O at +25, 0, and −5.5 °C. Standard cell potentials ($E°$, ±1 standard error) are given by the intercepts at zero ionic strength (m = 0).

25 °C by extrapolating the difference to lower temperatures. At low ionic strengths (m = 0.005) an uncertainty in the dielectric constant for 1 unit results in an uncertainty in the value of E_0' of only 0.05 mV (0.02% error).

In 1974, Travers and Douzou (*33*) published values for the dielectric constants of some mixed solvents, including Me_2SO-H_2O mixtures, at low temperatures. The values for 30% Me_2SO-H_2O at temperatures between +20 and −20 °C have been included in Figure 1. The agreement between the experimental values of Travers and Douzou and the estimated line is seen to be excellent.

Graphical plots of E_0' against the molal concentration of hydrochloric acid contained in the cell $Pt;H_{2(1\ atm)}HCl_{(m)},AgCl;Ag$ containing the solvents H_2O and 20% and 30% (w/w) Me_2SO-H_2O are shown in Figures 2, 3, and 4. The plots are seen in each case to be linear within the limits of experimental error, and the lines drawn are the least-squares regression lines. Each line has been extrapolated to zero ionic strength (m = 0), in accordance with eq 8, to give values for the standard electrode potential of each solvent system at different temperatures.

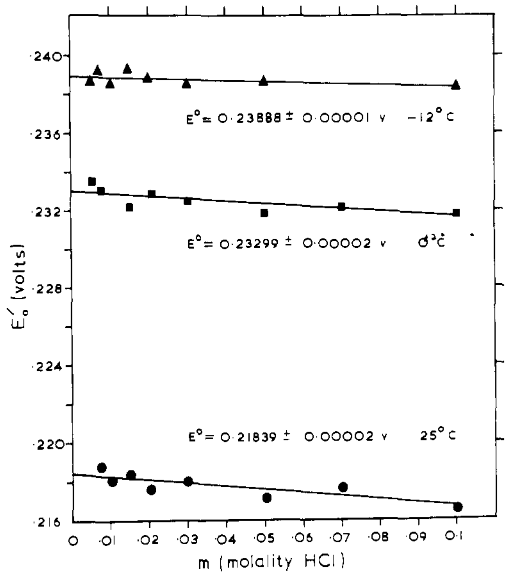

Figure 4. Linear regression lines for plots of E_0' (eq 13) against molality of HCl in 30% (w/w) Me_2SO-H_2O at +25, 0, and −12 °C, and the standard cell potentials ($E°$, ±1 standard error) given by the intercepts when m = 0.

Table V. Standard Electrode Potentials Determined in This Work for the Silver, Silver Chloride Electrode in Water and 20% (w/w) and 30% (w/w) Me_2SO-H_2O at Temperatures between +25 and −12.0 °C[a]

solvent	temp, °C	$E°$, V	Ref
H_2O	25	0.222 27 ± 0.000 02	present work
H_2O	25	0.222 22	*4*
H_2O	25	0.222 39	*12*
H_2O	25	0.222 30	*15*
H_2O	25	0.222 40	*14*
H_2O	25	0.222 34	*3*
H_2O	0	0.236 74 ± 0.000 01	present work
H_2O	0	0.236 52	*14*
H_2O	0	0.236 55	*3*
20% (w/w) Me_2SO-H_2O	25	0.219 38 ± 0.000 02	present work
20% (w/w) Me_2SO-H_2O	25	0.219 92 ± 0.000 04	*20*
20% (w/w) Me_2SO-H_2O	0	0.234 82 ± 0.000 01	present work
20% (w/w) Me_2SO-H_2O	−5.5	0.236 71 ± 0.000 01	present work
30% (w/w) Me_2SO-H_2O	25	0.218 39 ± 0.000 02	present work
30% (w/w) Me_2SO-H_2O	0	0.232 99 ± 0.000 02	present work
30% (w/w) Me_2SO-H_2O	−12.0	0.238 88 ± 0.000 01	present work

[a] Comparative values from those available in the literature are also given.

The standard electrode potentials determined in this work are given in Table V where those of H_2O and 20% Me_2SO-H_2O can be seen to be in good agreement with those available in the literature. In addition the table shows that the range of standard potentials for the silver, silver chloride electrode has been extended, in the present work, to −5.5 °C in 20% (w/w) Me_2SO-H_2O and to −12.0 °C in 30% (w/w) Me_2SO-H_2O. These standard potentials provide the basis for the establishment of pH scales under the same conditions, so that the effect of pH changes on the viability of biological systems after low-temperature storage can be investigated more fully.

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Received for review January 24, 1978. Accepted June 26, 1978.

Conductance of Lithium Tetrafluoroborate Solutions in Tetrahydrofuran

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Conductivities are presented for 19 solutions of lithium tetrafluoroborate in tetrahydrofuran at 25 °C between 0.0015 and 3.2 mol kg^{-1} (0.0013–2.6 mol dm^{-3}). Solution conductance is unaffected by small amounts of water. Equivalent conductances are quite low and display a distinct minimum at about 0.03 mol kg^{-1}.

In connection with the study of an experimental battery, we needed to select as electrolyte a suitably conducting solution of $LiBF_4$ in tetrahydrofuran (THF). However, a literature search failed to reveal any account of conductance vs. concentration for this couple. Thus, we undertook the following short study.

Experimental Section

Tetrahydrofuran was secured from Fisher Scientific Co. "Cat. No. T-397, Water Content 0.01%". One batch of this THF was used as received; a second batch was dried over pellets of Linde molecular sieve, Type X. Lithium fluoroborate from two sources was used: Cat. No. LX342 from Matheson Coleman and Bell and lot no. 101-1 from Foote Mineral Co. Both of the chemicals were nominally 98% pure so a factor of 0.98 was used in converting mass of salt to mass of $LiBF_4$. The Matheson Coleman Bell salt was used as received whereas the Foote material was first dried to constant weight over magnesium perchlorate.

The conductivity cell vessel was a 140 × 41 mm Pyrex test tube closed by a silicone rubber stopper. Through holes in this stopper were pushed a mercury thermometer and the conductivity cell, a Beckman, dip-type cell, Model CEL-KO1. The Pt electrodes of this cell were platinized, and its cell constant was determined as 0.0985 cm^{-1}. A Teflon-covered stirring bar provided magnetic stirring. Solution resistance was measured with a General Radio, Type 1650-A, impedance bridge at 1000 Hz. Capacitative balance was provided to ensure sharp null points at all measured resistances. This bridge measures resistance with an accuracy of ±1.0%.

Table I. Conductance of $LiBF_4$ Solutions in THF at 25.0 °C

molal concn m, mol kg^{-1}	molar concn C, mol dm^{-3}	Conductance: specific Ω^{-1} cm^{-1} × 10^3 κ	Conductance: equivalent, Ω^{-1} cm^2 equiv^{-1} λ
Dried Solutions			
0.00153	0.00134	0.000370	0.275
0.00353	0.00310	0.000604	0.195
0.00995	0.00874	0.00122	0.140
0.0310	0.0272	0.00353	0.130
0.0916	0.0803	0.0157	0.195
0.345	0.301	0.198	0.659
Undried Solutions			
0.00155	0.00136	0.000390	0.287
0.344	0.300	0.200	0.667
0.460	0.400	0.353	0.883
0.574	0.497	0.544	1.095
0.689	0.595	0.770	1.29
0.809	0.696	1.027	1.48
1.050	0.898	1.57	1.74
1.292	1.097	2.16	1.96
1.534	1.294	2.67	2.06
1.895	1.583	3.27	2.07
2.257	1.867	3.69	1.98
2.736	2.234	3.97	1.78
3.218	2.595	3.89	1.50

Solution preparation (by weight) and bridge measurements were done in a dry room at 2–3% relative humidity. We measured resistance over a range of about 5 °C around ambient temperature. This enabled us to correct figures to 25 °C for tabulation. The procedure was to begin with a weighed amount of THF (about 60 cm^3) in the test tube. A weighed amount of salt was added and stirred to effect dissolution and the resistance measured (while adding salt the dip cell was inserted in a dummy test tube containing a little anhydrous calcium sulfate to minimize evaporation and humidification of solution clinging to it). This

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