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Standard Potential of the Silver–Silver Chloride Electrode and Mean Activity Coefficient of Hydrochloric Acid in 10 Wt% Sucrose/Water from 0 to 25°C

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ABSTRACT

As part of a study in which electromotive force (emf) measurements are used to determine thermodynamic properties of sucrose solutions approximating fruit juice, it was necessary to determine the standard potential of the silver–silver chloride electrode in this medium. Emf measurements of cells of the type: $Pt;\ H_2\ (g,\ 1\ atm)\,|\,HCl\ (m)$ *in 10 wt%* $sucrose/H_2O\,|\,AgCl;\ Ag$*, where molality = 0·005 to 0·05 over the temperature range 0 to 25°C, allowed the calculation of the molal standard potential,* E_m^0*, of the Ag–AgCl electrode in the dilute sucrose mixture. Values obtained were fitted to an equation second-order in temperature,* $E_m^0 = 0{\cdot}231\,62 - 4{\cdot}9204 \times 10^{-4}\,t - 3{\cdot}0500 \times 10^{-6}\,t^2$ *(t = temperature (°C), sd = 0·02 mV). The mean activity coefficient of HCl,* $\gamma_{\pm}$*, in the sucrose–water mixture can be described within the experimental precision of the data to 0·10 m at 25°C using a simple Debye–Hückel model which incorporates an ion-size parameter of 7·8 Å. The results provide a basis for precision emf measurements in dilute sucrose–water mixtures.*

INTRODUCTION

Aqueous solutions containing sucrose have been the subject of much attention within the realm of solution chemistry. By way of example are early attempts to clarify the molecularity and kinetics of sucrose inversion and the catalytic role of acid in this process (Jones & Lewis, 1920; Scatchard,

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1921; Pennycuick, 1926). Related work has continued to the present day (Wienen & Shallenberger, 1988). Also, studies of the effects of sucrose on the physical properties of dilute sucrose solutions (Åkerlöf, 1923; Scatchard *et al.*, 1938) have provided a wealth of physical data often cited in more recent communications (Chen, 1989). Early studies (Corran & Lewis, 1922; Corran, 1923; Scatchard, 1926) which involved electromotive force measurements (emf) to investigate the effect of sucrose on the activities of potassium, hydrogen, and chloride ions, as well as other thermodynamic properties, are of fundamental interest since most chemical reactions in solution are ultimately tied to the chemical potential or thermodynamic activity of the reacting species (Jones & Lewis, 1920; Lewis & Randall, 1921). This fact is generally applicable to food systems as well (Rockland & Beuchat, 1987; Petriella *et al.*, 1988).

The measurement of emf in galvanic cells without a liquid junction is a technique unsurpassed for obtaining reliable thermodynamic data, and can provide precise information related to the activities of chemical species involved in the cell reactions (Bates, 1978). For example, emf measurements of cells of the type,

$$\text{Pt; } H_2 \text{ (g, 1 atm)} | \text{HCl (m) in Solvent } X | \text{AgCl; Ag} \qquad \text{(A)}$$

lead to the molal standard potential, E^0_m, of the silver–silver chloride electrode and the subsequent calculation of the mean activity coefficient of HCl, $\gamma_\pm$, at molalities (m) in the solvent X, without the uncertainties of liquid-junction potentials. Once armed with E^0_m and a reasonable estimate of $\gamma_\pm$, emf measurements of Cell B,

$$\text{Pt; } H_2 \text{ (g, 1 atm)} | \text{Buffer} + \text{Cl}^- \text{ in Solvent } X | \text{AgCl; Ag} \qquad \text{(B)}$$

in which HCl is replaced by a dilute buffer solution plus a small amount of added chloride, permit the determination of the dissociation constant (pK value) of the buffer acid. Extensive measurements of cells of type B have been made by the National Institute of Standards and Technology (formerly National Bureau of Standards) for the assignment of standard pH(S) values to several aqueous buffer solutions spanning the pH range 1 to 14; numbers which are indispensable for the calibration of conventional pH meter assemblies.

Standard potential and activity coefficient data provide a basis for other emf applications in the particular solvent, such as the calibration and use of ion-selective electrodes (Durst, 1969), which can measure ionic activity in food products (Hsieh & Harris, 1987), potentiometric titrations (Kolthoff & Furman, 1931) which have been used for the estimation of buffer capacity and total acidity of fruit juices (Sinclair & Eny, 1946), as well as the precise determination of pH (Bates, 1973), a quantity of particular importance to the citrus industry where it is an indicator of fruit maturity or Brix/acid ratio (Kilburn, 1958), and plays an important role in the color and flavor stability of juices (Handwerk & Coleman, 1988). In addition, solubility (Kimball, 1985) and metal complexation (Weber, 1987) are dependent on the thermodynamic activity of the proton. When combined with a known pK, accurate pH numbers permit the calculation of the equilibrium concentrations of acid-base forms, quantities often of significance for a complete understanding of food systems (Wedzicha & Goddard, 1988).

Emf measurements have been made using cells analogous to A and B in a variety of aqueous, non-aqueous, and mixed solvents (Harned, 1959; Strehlow, 1966). Studies in sucrose–water mixtures are limited (Scatchard, 1926), yet they are a logical extension of other work dealing with the effect of hydroxyorganic compounds in water (Knight *et al.*, 1946; Harned & Nestler, 1946), and would contribute further to the understanding of the thermodynamic state of foods and beverages where sucrose is an ingredient. The results obtained could provide a starting point for further studies, by emf methods, such as the dissociation equilibria of weak acids and bases in sucrose–water mixtures. One application might be the assignment of meaningful pH values to dilute buffers in this medium, permitting the standardization of pH meter assemblies for routine use in similar media such as fruit juices. This would minimize residual liquid-junction errors, and erratic or otherwise irreproducible behavior which occurs when calibrating the glass || reference electrode assembly in purely aqueous buffer solution, then transferring to a sugar–water environment for measurement. Analytical techniques which require careful pH adjustment could thus be improved.

The primary objectives of this work were to make emf measurements of cells of the type,

$$\text{Pt; } H_2 \text{ (g, 1 atm)} \mid \text{HCl (m) in 10wt\% sucrose/}H_2O \mid \text{AgCl; Ag} \qquad \text{(C)}$$

to determine the molal standard potential of the Ag; AgCl electrode over a wide temperature range in dilute sucrose media, and to shed some light on the mean activity coefficient behavior of a strong electrolyte (HCl) in this solvent mixture.

MATERIALS AND METHODS

Reagents

A.C.S. Certified sucrose obtained from Fisher Scientific Co. was powdered and dried at 105°C overnight before use. Reagent grade (Mallinckrodt) HCl was diluted to ~6 M and distilled twice, retaining the middle 'constant boiling' fraction each time; its concentration was determined gravimetrically by weighing silver chloride. Reagent grade sodium chloride used to prepare a storage solution for the silver–silver chloride electrodes was recrystallized twice from water to remove bromide. Water which had been deionized was distilled once in an all-glass still.

Apparatus

The electrodes were prepared as described elsewhere (Bates, 1973). Both platinized and palladized hydrogen electrodes were prepared and tested for stability in the cells, and were found to behave identically. Platinized electrodes were used in all subsequent experiments. The silver–silver chloride electrodes were of the thermal-electrolytic type and were stored in 0·01 M NaCl until use. Bias potentials among electrodes never exceeded 0·02 mV. The cells were of all-glass construction with a triple-saturator for entering hydrogen gas. Hydrogen was purified with a De-oxo (Engelhard) catalytic purifier. Constant temperature was maintained by immersion of the cells in an insulated circulating bath equipped with a refrigeration unit and a proportional heater/controller. The bath solution was 50% propylene glycol/water.

Procedure

A stock HCl solution (1·06657 m) for preparation of the cell solutions was obtained by dilution of the 'constant boiling' fraction described previously. All cell solutions were prepared by weight and brought to 5°C immediately after preparation to minimize inversion of sucrose. Solutions were saturated

TABLE 1
Corrected EMF (Volts) Values for the Cell: Pt; H_2 (g, 1 atm)|HCl (m) in 10 wt% Sucrose/H_2O|AgCl; Ag from 0 to 25°C

Molality (mol kg^{-1})	*Temperature (°C)*					
	0	*5*	*10*	*15*	*20*	*25*
0·005 0	0·484 43	0·486 52	0·488 47	0·490 21	0·491 80	0·493 18
0·010 0	0·453 24	0·454 75	0·456 11	0·457 48	0·458 54	0·459 38
0·020 0	0·421 88	0·422 84	0·423 60	0·424 26	0·424 80	0·424 86
0·030 0	0·403 76	0·404 28	0·404 84	0·405 13	0·405 26	0·405 22
0·040 0	0·391 14	0·391 55	0·391 78	0·391 81	0·391 65	0·391 35
0·050 0	0·381 11	0·381 34	0·381 37	0·381 25	0·380 94	0·380 36
0·101 2						0·346 10[a]

[a] Data from Scatchard (1926).

with hydrogen by bubbling for 30 min, then transferred into the cells taking care to exclude oxygen. The emf was stable within 2 h of filling. Measurements were made of cells of type C at 5-degree intervals over the temperature range 0 to 25°C. The molality of HCl was varied from 0·005 to 0·05 mol kg^{-1}. All emf measurements were run in duplicate and the results averaged. Measurements were made initially at 5°C, then cycled to 0°C, after which readings were made at 5-deg intervals to 25°C, followed by a final reading again at 5°C. The cells displayed good stability, differences in the 5° readings being less than 0·1 mV on the average. A glucose oxidase test at the conclusion of the experiments showed the presence of invert at less than 1% of the original sucrose concentration.

RESULTS AND DISCUSSION

The emf data (Table 1) were corrected to 1 atm (101·325 kPa, 760 mm Hg) partial pressure of hydrogen by adding the quantity,

$$\Delta E = RT/2F \ln [760/(bp - p_{\mathrm{solv}})] \qquad (1)$$

where bp and p_{solv} are the corrected barometric pressure and vapor pressure of the solvent, respectively (in mm Hg). The vapor pressure for 10 wt% sucrose/H_2O at 25°C was taken from the water activity data of Scatchard (1926) to be 23·62 mm. Values used at the other temperatures were calculated by:

$$(p_{\mathrm{solv}})_t = (a_{\mathrm{w}})_{25}(p_{\mathrm{H2O}})_t \qquad (2)$$

and are listed in Table 2. The activity of water $(a_{\mathrm{w}})_{25}$ in 10 wt% sucrose at

TABLE 2

Properties of 10 wt% Sucrose/Water Solvent from 273·15 to 298·15 K

T(K)	p_{solv} *(mm Hg)*[a]	ε[b]	*Density (g/ml)*	*Debye–Hückel constants*[c]	
				A	*B*
273·15	4·5	85·0	1·0415	0·5265	0·3368
278·15	6·5	83·2	1·0410	0·5289	0·3372
283·15	9·2	81·5	1·0402	0·5310	0·3376
288·15	12·7	79·9	1·0393	0·5326	0·3379
293·15	17·4	78·0	1·0382	0·5378	0·3389
298·15	23·6	76·3	1·0369	0·5416	0·3395

[a] Vapor pressure of 10 wt% sucrose/H_2O (eqn (2)).

[b] Dielectric constant (Åkerlöf, 1932).

[c] For use in eqns (4) and (5).

25°C is 0·9943. Vapor pressure values for water at other temperatures $(p_{\mathrm{H_2O}})_t$ were taken from the International Critical Tables of Numerical Data (Washburn, 1928).

The emf of Cell C is dependent on the activities of hydrogen and chloride ion according to Nernst equation (Lewis & Randall, 1921),

$$E = E^0 - k \log a_{\mathrm{H}} a_{\mathrm{Cl}} = E^0 - k \log m_{\mathrm{HCl}}^2 \gamma_{\pm}^2 \tag{3}$$

where k is written for $(RT \ln 10)/nF$ and $\gamma_{\pm}$ is the mean activity coefficient (molal scale) of HCl. The quantities R and F are the universal gas constant (8·31433 J mol^{-1} K^{-1}) and the faraday (96 487 C mol^{-1}), respectively. The standard potential was obtained by extrapolation of the function, $E^{0'}$, of the emf, E, to $m = 0$:

$$E^{0'} \equiv E^0 - bm = E + 2k \log m - 2kAm^{1/2}/(1 + B\mathring{a}m^{1/2}) \tag{4}$$

This function is derived from rearrangement of eqn (3); a Debye–Hückel expression (Debye & Hückel, 1923) is included to approximate $\log \gamma_{\pm}$ at finite molalities of HCl, m,

$$\log \gamma_{\pm} = -Am^{1/2}/(1 + B\mathring{a}m^{1/2}) \tag{5}$$

The Debye–Hückel constants A and B are functions of the solvent density, dielectric constant (ε), thermodynamic temperature, and were calculated by the usual equations (Bates, 1973). The density of 10 wt% sucrose/H_2O at 25°C was taken from Scatchard (1926) and those at the other temperatures calculated from the volume correction factors given in the literature (Bates, 1942). Dielectric constants were interpolated from the data of Åkerlöf

TABLE 3
Standard Potential (E_m^0) of the Ag; AgCl Electrode in 10 wt% Sucrose/Water from 0 to 25°C

T (°C)	E_m^0 (V)	$\mathring{a}$(Å)[a]	s(mV)[b]
0	0·231 63	6·7	0·09
5	0·229 06	6·7	0·11
10	0·226 37	6·7	0·09
15	0·223 59	7·0	0·14
20	0·220 57	7·2	0·14
25	0·217 29	7·3	0·17
	0·217 40	7·8	0·12[c]

[a] Best-fit ion-size parameter from eqn (4).
[b] Standard deviation of the intercept (E_m^0).
[c] Results of regression with Scatchard's (1926) datapoint (Table 1) included.

(1932). The physical data used and the calculated values of A and B at all temperatures are given in Table 2.

The ion-size parameter, $\mathring{a}$, in eqn (4) was treated as an adjustable term and varied until the function $E^{0\prime}$ versus m yielded a line with the minimum regression standard deviation, as has been done earlier (White & Warner, 1988). However, within the precision of the data, this minimum standard deviation criterion resulted in a range of possible $\mathring{a}$ values at each temperature. To further narrow this down to a single 'best' value, it was decided to choose $\mathring{a}$ for which the slope was also minimized. This resulted in self-consistent values ranging from 6·7 Å to 7·8 Å at the six temperatures. Although higher than the 4–4·6 Å generally found and recommended for aqueous solutions (Harned & Owen, 1958; Bates & Guggenheim, 1960), similarly high results have been found in glucose and fructose solutions, where $\mathring{a} = 6{\cdot}6$ Å (Williams *et al.*, 1950; Crockford & Sakhnovsky, 1951). It should be noted that E_m^0 is not very sensitive to the choice of $\mathring{a}$, the change being less than 0·20 mV over the range, $\mathring{a} = 4$–8 Å.

Plots of $E^{0\prime}$ versus m at the six temperatures are shown in Fig. 1. Included at 25° is a point ($m = 0{\cdot}1$) calculated from Scatchard's data (1926) for comparison. The E_m^0 values at all temperatures, as well as the 'best' values for $\mathring{a}$ and the standard deviations are given in Table 3.

The E_m^0 data were fitted to an equation second-order in temperature using a least-squares method,

$$E_m^0 = 0{\cdot}23162 - 4{\cdot}9204 \times 10^{-4}t - 3{\cdot}0500 \times 10^{-6}t^2 \qquad (6)$$

where t = °C, with a standard deviation of 0·02 mV. Once E_m^0 values were obtained, the mean activity coefficients of HCl were computed from the emfs, molalities, and a rearrangement of eqn (3):

$$\log \gamma_{\pm} = (E_m^0 - E)/2k - \log m \qquad (7)$$

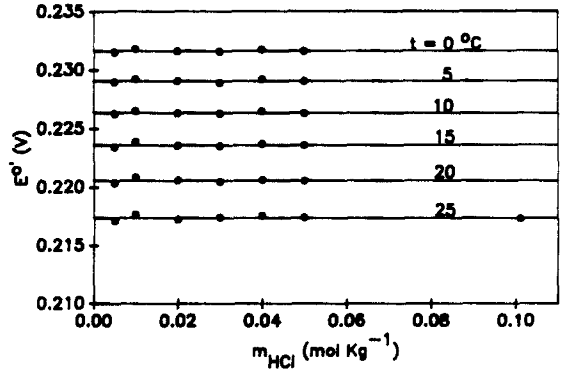

Fig. 1. Plot of $E^{0\prime}$ (eqn (4)) versus m at 0, 5, 10, 15, 20 and 25°C.

TABLE 4
Mean Activity Coefficient of HCl in 10 wt% Sucrose/Water (${}_s\gamma_\pm$) and in Water (${}_w\gamma_\pm$) at 25°C

mol kg^{-1}	${}_s\gamma_\pm$	${}_w\gamma_\pm$
0·005	0·933	0·928
0·010	0·901	0·904
0·020	0·882	0·876
0·030	0·862	0·856
0·040	0·847	0·842
0·050	0·839	0·830
0·101	0·807	0·796

Results at 25°C are listed in Table 4, along with some values in pure water. It should be emphasized at this point that the activity coefficient calculated in this manner is referred to a standard state such that it approaches unity at infinite dilution in the sucrose–water mixture. In this respect, it essentially characterizes the interionic forces (solute–solute interactions) in sucrose–water medium. It is interesting that at molalities greater than 0·01 m, the activity coefficients in the mixture are somewhat higher than the corresponding values in water; this in spite of the fact that the dielectric constant of 10% sucrose is slightly less than that of water at the same temperature. Similar behavior has been observed in 5% glucose and fructose solutions (Williams *et al.*, 1950; Crockford & Sakhnovsky, 1951); perhaps

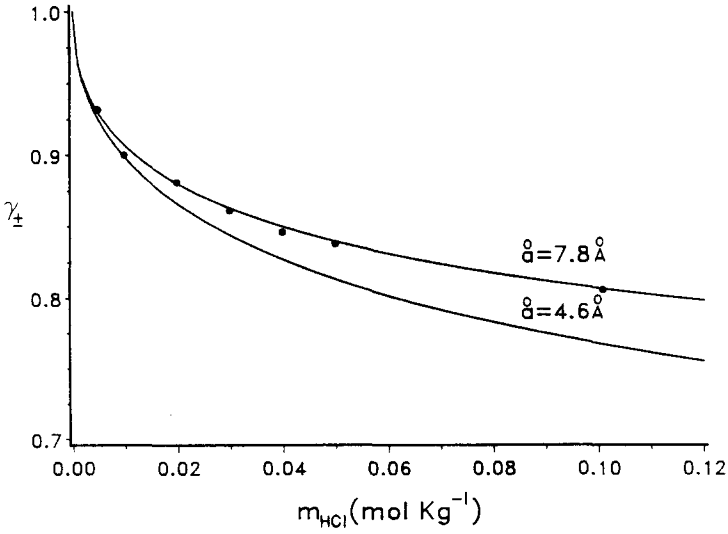

Fig. 2. Variation of the mean activity coefficient of HCl with molality in 10 wt% sucrose/water at 25°C.

hydration of the sugar molecules is a more important influence on the activity coefficient than is the dielectric constant in these dilute mixtures.

The adequacy of the simple Debye–Hückel model in describing the mean activity coefficient over the molality range is demonstrated in Fig. 2 for 25°C, where the theoretical curve ($\mathring{a} = 7{\cdot}8$ Å) is superimposed on the points derived from the experimental data using eqn (7). Also illustrated is the curve obtained with $\mathring{a} = 4{\cdot}6$ Å. One can readily see the superior fit obtained with the higher value for $\mathring{a}$. Thus, it appears that the simple Debye-Hückel equation (eqn (5), $\mathring{a} = 7{\cdot}8$ Å) can be used to approximate the activity coefficient of strong univalent electrolytes up to $m = 0{\cdot}1\ \mathrm{mol\,kg^{-1}}$ in this solvent mixture.

Although the experimental results in this study are not of the precision attained in purely aqueous and certain alcohol–water solvents (White & Warner, 1988), it is estimated that the E_m^0 data are generally reliable to within 0·20 mV, or 0·003 units in the activity coefficient. None of the difficulties with cell stability as described by Scatchard (1926) using the bubbling hydrogen electrode in the presence of sucrose were observed. These results should prove useful for further emf studies in this solvent medium.

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REFERENCES

Äkerlöf, G. (1932). Dielectric constants of some organic solvent–water mixtures at various temperatures. *J. Am. Chem. Soc.*, **54**, 4125.

Bates, F. J. (1942) (ed.). *Polarimetry, Saccharimetry, and the Sugars*. NBS circular. US Government Printing Office, Washington, DC.

Bates, R. G. (1973). *Determination of pH: Theory and Practice* (2nd edn). John Wiley & Sons, Inc., New York.

Bates, R. G. (1978). Electrode potentials. In *Treatise on Analytical Chemistry* (2nd edn), ed. I. M. Kolthoff & P. J. Elving. John Wiley & Sons, Inc., New York, Ch. 13.

Bates, R. G. & Guggenheim, E. A. (1960). Report on the standardization of pH and related terminology. *Pure Appl. Chem.*, **1**, 163.

Chen, C. S. (1989). Water activity—Concentration models in solutions of sugars, salts and acids. *J. Food Sci.*, **54**, 1318.

Corran, J. W. (1923). The effect of sucrose on the activities of certain ions. *J. Am. Chem. Soc.*, **45**, 1627.

Corran, J. W. & Lewis, W. C. M. (1922). The effect of sucrose on the activities of the chloride and hydrogen ions. *J. Am. Chem. Soc.*, **44**, 1673.

Crockford, H. D. & Sakhnovsky, A. A. (1951). Electromotive force studies in aqueous solutions of hydrochloric acid and *d*-fructose. *J. Am. Chem. Soc.*, **73**, 4177.

Debye, P. & Hückel, E. (1923). The theory of electrolytes. I. Lowering of freezing point and related phenomena. *Physik. Z.*, **24**, 185.

Durst, R. A. (ed.) (1969). *Ion-Selective Electrodes.* NBS Special Publication 314, Washington, DC.

Handwerk, R. L. & Coleman, R. L. (1988). Approaches to the citrus browning problem. A review. *J. Agric. Food Chem.*, **36**, 231.

Harned, H. S. (1959). The thermodynamic properties of the system: hydrochloric acid, sodium chloride and water from 0 to 50°C. *J. Phys. Chem.*, **63**, 1299.

Harned, H. S. & Nestler, F. H. M. (1946). The standard potential of the cell, H_2 | HCl (m) | AgCl-Ag in 50% glycerol–water solution from 0 to 90°. *J. Am. Chem. Soc.*, **68**, 665.

Harned, H. S. & Owen, B. B. (1958). *The Physical Chemistry of Electrolytic Solutions*, 3rd edn. Reinhold, New York.

Hsieh, Y. P. & Harris, N. D. (1987). Copper activity in sucrose solutions. *J. Food Sci.*, **52**, 498.

Jones, C. M. & Lewis, W. C. (1920). Catalysis, XIV. The mechanism of the inversion of sucrose. *J. Chem. Soc.*, **117**, 1120.

Kilburn, R. W. (1958). The taste of citrus juice. Relationship between Brix, acid, and pH. *Proc. Fla. St. Hort. Soc.*, **71**, 251.

Kimball, D. A. (1985). Crystallization of potassium citrate salts in citrus concentrates. *Food Tech.*, **39**, 76.

Knight, S. B., Masi, J. F. & Roesel, D. (1946). Standard potentials of hydrogen–silver–silver chloride cells in ethylene glycol solutions at 25°C. *J. Am. Chem. Soc.*, **68**, 661.

Kolthoff, I. M. & Furman, N. H. (1931). *Potentiometric Titrations* (2nd edn). John Wiley & Sons, Inc., New York.

Lewis, G. N. & Randall, M. (1921). The activity coefficient of strong electrolytes. *J. Am. Chem. Soc.*, **43**, 1112.

Pennycuick, S. W. (1926). The unimolecularity of the inversion process. *J. Am. Chem. Soc.*, **48**, 6.

Petriella, C., Chirife, J., Resnik, S. L. & Lozano, R. D. (1988). Solute effects at high water activity on nonenzymatic browning of glucose–lysine solutions. *J. Food Sci.*, **53**, 987.

Rockland, L. B. & Beuchat, L. R. (eds) (1987). *Water Activity: Theory and Applications to Food.* Marcel-Dekker, Inc., New York.

Scatchard, G. (1921). The speed of reaction in concentrated solutions and the mechanism of the inversion of sucrose. *J. Am. Chem. Soc.*, **43**, 2387.

Scatchard, G. (1926). Electromotive force measurements in aqueous solutions of hydrochloric acid containing sucrose. *J. Am. Chem. Soc.*, **48**, 2026.

Scatchard, G., Hamer, W. J. & Wood, S. E. (1938). Isotonic solutions. I. The chemical potential of water in aqueous solutions of sodium chloride, potassium chloride, sulfuric acid, sucrose, urea, and glycerol at 25°. *J. Am. Chem. Soc.*, **60**, 3061.

Sinclair, W. B. & Eny, D. M. (1946). Stability of the buffer system of lemon juice. *Plant Physio.*, **21**, 522.

Strehlow, H. (1966). Electrode potentials in non-aqueous solvents. In *The Chemistry of Non-Aqueous Solvents, Vol. 1.* Academic Press, New York, Ch. 4.

Washburn, E. W. (ed.) (1928). *International Critical Tables of Numerical Data.* Nat. Res. Council, McGraw-Hill, New York.

Weber, G. (1987). Speciation of tin in lemon juice: An example of trace metal speciation in food. *Analytica Chimica Acta*, **200**, 79.

Wedzicha, B. L. & Goddard, S. J. (1988). The dissociation constant of hydrogen sulphite ion at high ionic strength. *Food Chemistry*, **30**, 67.

White, D. R. & Warner, P. (1988). Standard potential of the Ag/AgCl electrode and dissociation constant of protonated tris(hydroxylmethyl)aminomethane in 50 wt% ethanol/water from 25 to −10°C. *J. Chem. Eng. Data*, **33**, 174.

Wienen, W. J. & Shallenberger, R. S. (1988). Influence of acid and temperature on the rate of inversion of sucrose. *Food Chemistry*, **29**, 51.

Williams, J. P., Knight, S. B. & Crockford, H. D. (1950). Potential studies of the silver–silver chloride electrode in aqueous solutions of hydrochloric acid and *d*-glucose at 25°. *J. Am. Chem. Soc.*, **72**, 1277.