RECENT ADVANCES IN DIRECT POTENTIOMETRY IN ORGANIC AND MIXED SOLVENTS*

G. J. Kakabadse, M. Al-Aziz, N. F. N. Al-Yawer,
P. Kaklugin, M. R. O. Karim, R. Perry, A. E. Tipping, P. Wake

Department of Chemistry, University of Manchester
Institute of Science & Technology, Manchester, M60 1QD, England

SUMMARY

The behaviour of ions in organic and mixed solvents is illustrated by a number of examples. Systematic study of the effect of solvent on potentials of cells with ion-selective electrodes led to the development by Kakabadse and co-workers of a new technique in direct potentiometry, viz. the ion isoconcentration technique (IICT). In IICT, concentration of solvent is varied and that of indicator ion is kept constant. Many simple mixtures show under ion isoconcentration conditions a systematic change of cell potential with variation in the concentration of organic solvent, providing a graphical method for the rapid determination of, (a) individual organic solvents in simple mixtures, and (b) residual water in organic solvents.

A laboratory prototype monitor for the continuous determination of ethanol in cider and sherry, using the fluoride isoconcentration technique (FICT), is described.

---

* Plenary lecture given by G. J. Kakabadse at the second meeting of the Portuguese Electrochemical Society, Ofir, April, 1986.

Portugaliæ Electrochimica Acta, 6 (1988) 5-25

1. INTRODUCTION

Electroanalytical applications of direct potentiometry, dating back to the late 19th century, have been largely confined to the aqueous system. In the late 1960's and early 1970's, there has been an unprecedented expansion of direct potentiometry due to the development of 'modern' ion-selective electrodes. This also brought about a renewed interest in the behaviour of ions in nonaqueous and partially aqueous media, resulting in the publication of three reviews[1-3]. The reasons for the relatively slow progress in this field are manifold and include the following: difficulty of achieving ionic dissociation, especially in solvents of low dielectric constants; not infrequently, sluggish response resulting in long equilibration; uncertainty in the liquid-junction potential at the reference electrode; possible solvent attack on membrane seal and electrode body; a less well-defined theoretical picture compared with that of the aqueous system.

The following examples illustrate some useful aspects of the use of ion-selective electrodes in organic solvents.

1.1 Cleavage of aromatic disulphides with alkali metal sulphides in methanolic solution[4]

Aromatic disulphides have a sulphur-sulphur bond, cleavage of which is an equilibrium reduction reaction, this cleavage is brought about by nucleophilic displacement of mercaptide ion from one sulphur atom which serves as an electrophilic centre. The generally accepted view of this cleavage[5,6] is that it proceeds by a bimolecular mechanism, not unlike S_N2 reactions at carbon atoms, although the detailed path by which the products are formed is often not clear.

Kakabadse and Tyas[2,7] studied the reaction of diphenyl disulphide with sodium sulphide in methanolic potassium hydroxide solution (99.98% methanol) using an Orion sulphide electrode:

$$C_6H_5S\text{-}SC_6H_5+S^{2-} = C_6H_5S^- + C_6H_5S_2^- \qquad (1)$$

Cleavage of the S-S bond can be monitored by the decrease of sulphide ion concentration. At $pH^*(S)$[8] 11.5, a systematic increase in potential over a period of time indicated that reaction (1) was more than 99 percent complete. Kinetic (potentiometric) study at 20±0.1°C of equimolar proportions of sodium sulphide and diphenyl disulphide (over a wide concentration range) showed the reaction to be first order with respect to sulphide ion.

Measurements, conducted in an enclosed system under hydrogen, were characterised by good reproducibility.

1.2 Lower limit of linear response (LLLR)*

As the lower limit of detection of a solid-state electrode is a function of membrane solubility, addition of organic solvent decreases this limit and thus offers possibilities for extending the lower detection limit of electrodes based on insoluble inorganic salts.

This was shown by Pungor and co-workers[1], who studied the behaviour of silicone-rubber halide ion-selective electrodes in mixed solvents: alcohols, propanone, dimethylformamide, acetonitrile and a mixture of benzene and methanol. They found the LLLR of the iodide electrode in a 90:10 methanol-water mixture to lie at 10^{-9} mol dm^{-3}

---

* The lower concentration of primary ion at which the electrode calibration graph begins to depart from linearity.

iodide, i.e. considerably lower than LLLR in an aqueous solution (5×10^{-8} mol dm^{-3} iodide).

Using solid-state silver chloride and silver bromide electrodes, Kakabadse and Khayat[7,14] obtained LLLR values of 1.5×10^{-5} mol dm^{-3} chloride and 4×10^{-7} mol dm^{-3} bromide in 80:20 methanol-water mixture, compared with the corresponding LLLR values of 5×10^{-5}(Cl^-) and 5×10^{-6} (Br^-) in aqueous solutions.

By contrast, organic solvents seem to be less effective with a fluoride electrode[2]. Using alcohols, acetonitrile and propene carbonate, Coetzee and Martin[9] observed that the sensitivity of the fluoride electrode can be improved by only up to one decade which ruled out the solubility of the lanthanum fluoride crystals as the controlling factor.

1.3 Effect of solvent on cell potential

Practically every solvent has a pronounced effect on potentials of cells with ion-selective electrodes (ISE), which must be borne in mind when working in nonaqueous and mixed solvents. For example, measurements of pH, using a glass electrode, can be seriously at fault if the effect of solvent is neglected[8].

One can expect a distinct solvent effect on the following e.m.f. terms related to indicator electrode, reference electrode (RE) and indicator ion, A[2]: (i) the asymmetry potential (E_a) across the membrane of the indicator electrode arising from different solvents on either side of it; (ii) the liquid-junction potential (E_j) at the reference electrode due to the difference in mobilities of the anions and cations in organic solvents; (iii) the potential term associated with single-ion activity coefficients (E_y); (iv) the transfer potential (ΔE_t) associated with the free energy of transfer of A(ΔG_t(A)) from water into mixtures of water with various co-solvents[*].

Systematic study of the effect of solvent on potentials of cells with ion-selective electrodes, using various solvents and ion-selective electrodes led to the development at UMIST by Kakabadse[2,7,11-13] and co-workers[14-19] of a new technique in direct potentiometry, the ION ISOCONCENTRATION TECHNIQUE[2] (IICT), discussed in detail below.

2 ION ISOCONCENTRATION TECHNIQUE

2.1 General aspects

In conventional direct potentiometry, the concentration of indicator ion, A, is varied and that of solvent is kept constant, permitting the determination of ion concentrations (strictly speaking, activities). In the ion isoconcentration technique, the reverse procedure is applied: concentration of solvent is varied and that of ion, A, is kept constant.

In practice, many simple mixtures show under ion isoconcentration conditions a systematic change of cell potential with variation in the concentration of organic solvent, OS, thus providing a new graphical method for the rapid determination of (a) OS in OS-water, or OS(1)-OS(2)[**] mixtures (Fig. 1)[2], and (b) residual water in organic solvents (Fig. 2)[18].

---

[*] For cells without liquid junction, $\Delta G^o_t(A) = F\Delta E^o_t(A)$, where F is a Faraday and $\Delta E^o_t = E^o(\text{water}) - E^o(\text{mixture})$[10]

[**] OS(2) is another organic solvent

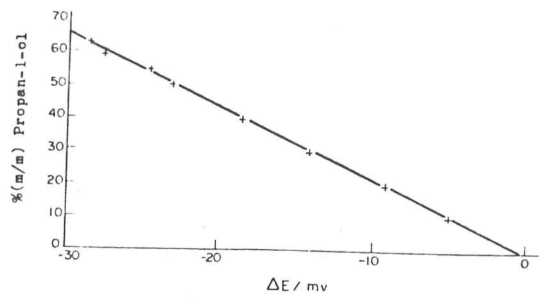

Fig. 1: Change in potential in the system, 10^{-3}mol dm^{-3} sodium sulphide plus 5% SAOB (sulphide anti-oxidant buffer) - (0-65% m/m) propan-1-ol-water, measured by using a sulphide electrode (sulphide isoconcentration technique)

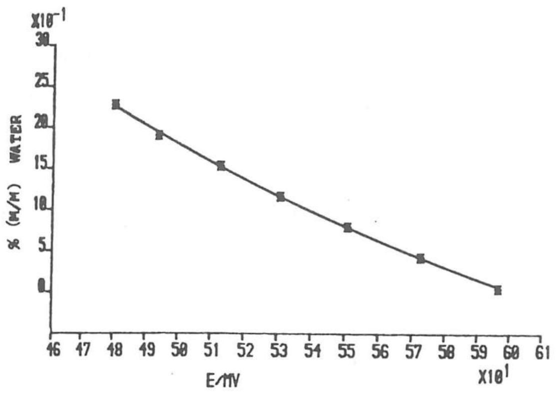

Fig. 2: Change in potential in the system, 10^{-3} mol dm^{-3} para-toluenesulphonic acid - (0.05-2.28% m/m) water-butan-2-one, measured by using a pH glass electrode (proton isoconcentration technique)

In the system, ISE/A, 0-100% OS/RE, for a given concentration of ion A, and a given reference electrode, RE, the cell potential decreases systematically with an increases in the concentration of organic solvent, OS, when A is an anion (Fig. 1, $A = S^{2-}$)[2] and the reverse is observed when A is a cation (Fig. 3, $A = Ag^{+}$)[15].

The following organic solvents, ion-selective electrodes and indicator ions, A, have been studied:

OS = methanol, ethanol, propan-1-ol, propan-2-ol, 2-methylpropan-2-ol, ethanediol, glycerol, ethanoic acid, ethanal, propanone, butan-2-one, 1,4-dioxan, formamide, acetonitrile, dimethylsulphoxide, sulpholane or propylene carbonate (including OS-water, OS-methanol and OS-propanone combinations).

ISE = solid-state, F^-, Cl^-, Br^-, I^-, S^{2-}; Ag^+, Pb^{2+}; Selectrodes, Ag^+, Cl^-; glass, pH or sodium ion.

A = F^-, Cl^-, Br^-, I^-, OH^-, S^{2-}; Ag^+, Na^+, H^+ or Pb^{2+}.

IICT stems from the observation that electrode calibration graphs show parallel displacement in proportion to the solvent content of a binary mixture, as illustrated in Fig. 4[2] for the system, potassium fluoride-ethanol-methanol. IICT, first reported by Kakabadse[7] in 1974* for the determination of methanol[7,12] and ethanol, respectively, in their aqueous mixtures under chloride, bromide and iodide isoconcentration conditions[14], was extended in April 1977[11] to the determination of residual water in methanol, ethanol, propan-1-ol, propan-2-ol and tert-butanol under proton and hydroxide isoconcentration conditions, respectively[15].

---

* At the Autumn meeting of the British Chemical Society in Leicester

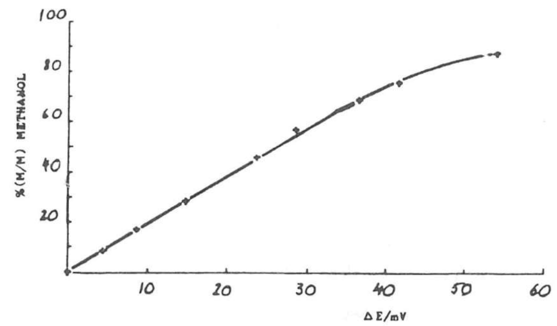

Fig. 3: Change in potential in the system, 10^{-4} mol dm^{-3} silver nitrate (plus 10^{-1} mol dm^{-3} sodium nitrate) - (0-83% m/m) methanol-water, measured by using a silver sulphide electrode (silver ion isoconcentration technique)

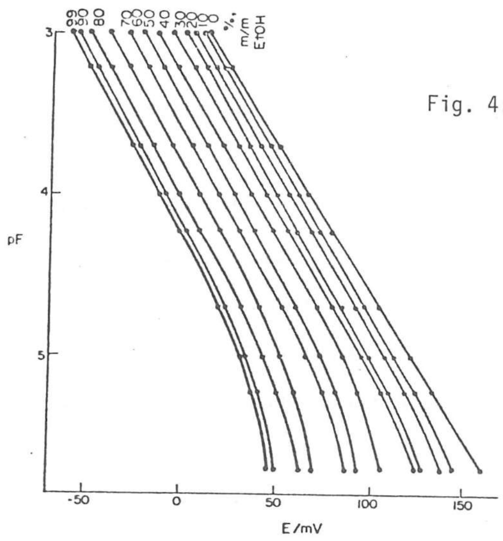

Fig. 4: Electrode calibration graphs for the system, potassium fluoride-ethanol-methanol, in solutions of constant ethanol (methanol) concentrations and various potassium fluoride concentrations (measured by using a fluoride electrode)

Interestingly, in a paper published in August 1977, Schwabe and Queck[20] suggested independently the use of a pH glass electrode for the determination of trace water in methanol under constant acid concentration (0.01 mHCl) using a cell without liquid junction.

Findings about the effect of solvent on the potentials of ion-selective electrodes have been widely reported[1-3] but, apart from Schwabe and Queck[20], only Chaudhari and Cheng[21], who studied the system, $Pb(ClO_4)_2$-(0-40%) dimethylsulphoxide-water, using a lead ion electrode, suggested in 1979 the possibility of estimating DMSO under conditions of constant lead ion concentration.

Of the many ion-selective electrodes studied by Kakabadse and co-workers, the following two proved best: (1) the fluoride electrode for the determination of solvent in largely aqueous solvent-water mixtures using the fluoride isoconcentration technique (FICT) and, (2) the pH glass electrode for the determination of residual water in organic solvents using the proton isoconcentration technique (PICT).

2.2 Continuous Monitoring of (a) Solvent in simple mixtures, and (b) Ethanol in cider and sherry using the fluoride isoconcentration technique*

A laboratory prototype monitor has been built at UMIST in which a sample is bled off and mixed with a suitable buffer before passing through a cell containing fluoride and reference electrodes.

---

* U.K. Patent Application No. 8709514, 1987

2.2.1 Experimental

(i) The Apparatus

The apparatus used is shown in Fig. 5. Multi-way selector valve 1 is connected to sample stream 2, from which the product to be analysed is sampled and is also connected to reservoirs 3-5 containing calibration solutions. Liquid from sample stream 2 or any one of the reservoirs 3-5 is supplied via valve 1 to inlet (a) of mixing chamber 6 (containing magnetic follower 7). Inlet (b) of chamber 6 is connected to reservoir 8 of buffer solution. The solutions from sample stream 2 or reservoirs 3-5 and buffer from reservoir 8 are supplied by a peristaltic pump (not shown). From chamber 6, the mixed solutions pass through outlet (c) to tube (d) of electrode cell 9 and successively through tubes (d), (e) and (f) before passing to waste through outlet (g). Tube (d) has an air vent 10 to assist debubbling and depulsing. Fluoride electrode 11 and reference electrode 12 are connected to a pH/millivolt meter 14 associated with recorder 15. Tube (f) of electrode cell 9 contains thermometer 13.

The electrode cell is held in a liquid paraffin bath (not shown) to minimise temperature fluctuations.

(ii) Ultrasonic degasser (Fig. 6)

When monitoring ethanol in carbonated drinks, e.g. cider, their high carbon dioxide content gives rise to unstable potential readings. It is therefore necessary to degass the carbonated drink prior to its entry into the mixing chamber. This is done by passing the sample through an ultrasonic degasser (Fig. 6), developed at UMIST, without interrupting the continuous flow.

The carbonated drink is pumped through a glass coil 1 (Fig. 6) immersed in ultrasonic bath 2. The liberated carbon dioxide is released to the atmosphere via vent 3, after passing through water-cooled condenser 4 to prevent the escape of ethanol vapour. Degassed drink 5 is collected in cylindrical glass vessel 6 from which it is supplied by a peristaltic pump to the mixing chamber (see Fig. 5). Copper cooling coil 7 prevents a rise in bath temperature.

(iii) Electrodes

Orion fluoride electrode and silver-silver chloride double-junction reference electrode were used.

(iv) Buffer solution

TISAB II* and TISAB IV* buffer solutions, containing 2×10^{-4} mol dm^{-3} sodium fluoride, were used for sherry and cider, respectively.

(v) Flow rate and response time

A flow rate of 10cc/min was found satisfactory, steady potentials being attained within 7-10 minutes.

2.2.2 Results

The reproducibility of FICT results (Table 1) is expressed as the standard error of the mean, s.e.m. = $\pm 2\sigma/\sqrt{n}$ (representing 95% confidence limits), where σ is standard deviation and n is sample size, viz. number of repeat runs. Unless otherwise stated, $n = 7$.

---

* Orion Research Inc., Instruction Manual for Fluoride Electrode, 1983

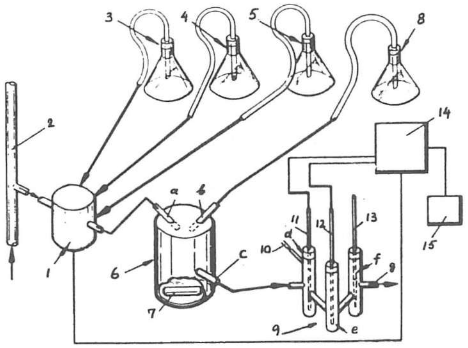

Fig. 5: Apparatus

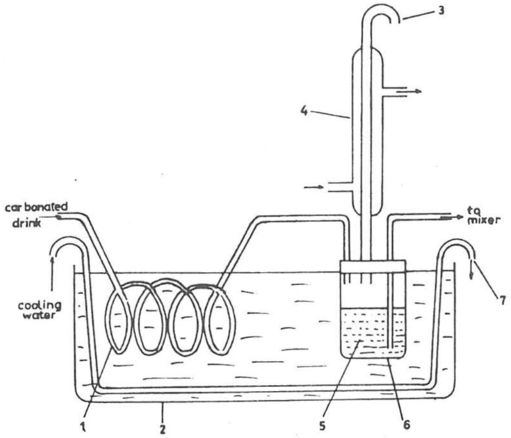

Fig. 6: Ultrasonic degasser

In Table 1(a), the solvent-water mixtures prepared by accurate dilution had a standard deviation, $\sigma \leqslant 0.1$.

2.2.3 Discussion of results

The results in Table 1 demonstrate a satisfactory performance of FICT in continuous monitoring, showing it to be accurate, reproducible and sensitive. This is reflected in low standard deviation and small absolute error (%). Composition of buffer, degree of mixing and especially choice of 'matching' standards (i.e. matching the sample composition) play a key role in this technique.

The finding that FICT performs better in on-line monitoring than in batch analysis is probably due to the fact that the electroanalytical sensors are less 'disturbed' in continuous analysis.

There is a shortage of automatic methods for on-line monitoring of ethanol in drinks. The techniques most widely used, gas chromatography and distillation/density measurement of distillate, are batch methods. FICT has therefore a great deal to offer to the drinks industry.

2.3 Direct Potentiometry of Residual Water in Organic Solvents by the Proton Isoconcentration Technique using the Batch Method

Under conditions of constant acid concentration, the 'hypersensitivity' of potential in organic solvents with a low water content forms the basis for the potentiometric determination of residual water in nonaqueous solvents[2,11-13,15-20]. There may be several reasons

TABLE 1: Monitoring of solvent by fluoride-isoconcentration technique (FICT)

(a) Determination of solvent in solvent-water mixtures by accurate dilution and by FICT

Solvent	%(v/v) solvent found			% Error (abs)
	by accurate dilution	by FICT	$2\sigma/\sqrt{n}$	
Methanol	10.5	10.75	±0.1	0.25
	20.0	20.3	±0.1	0.3
Ethanol	5.8	5.7	±0.1	-0.1
	17.5	17.3	±0.1	-0.2
	21.0	21.1	±0.1	0.1
Propan-2-ol	5.8	5.7	±0.04	-0.1
	11.3	11.3	±0.1	0
	19.7	19.6	±0.1	-0.1
	29.6	29.5	±0.2	-0.1

(b) Determination of ethanol in sherry by distillation/density measurement (DD) and by FICT

Sherry	%(v/v) Ethanol found			% Error (abs)
	by DD	by FICT	$2\sigma/\sqrt{n}$	
Luncheon Dry	17.1 ± 0.3*	17.2	± 0.2	0.1
Amontillado	17.4 ± 0.1*	17.4	± 0.2	0
Bristol Cream	17.3 ± 0.1	17.3	± 0.2*	0

* Average of three determinations

(c) Determination of ethanol in cider by GLC and by FICT

Cider	%(v/v) Ethanol found			% Error (abs)
	by GLC	by FICT	$2\sigma/\sqrt{n}$	
Woodpecker	3.5**	3.4	± 0.1	-0.1
Strongbow	5.3**	5.2	± 0.1	-0.1

** By courtesy of H. P. Bulmer Ltd.

for this behaviour[2,11,12], including the medium effect*, liquid-junction potential at the reference electrode, gradual dehydration of the gel layer on the outer surface of the glass electrode, glass composition of the pH electrode.

2.3.1 Effect of acid on the system, butan-2-one-residual water[18]

A study of the system, butan-2-one-residual water-acid (Fig. 2), showed that acid nature and acid concentration have a pronounced effect on the sensitivity of potential response, as shown by the magnitude of ΔE in Table 2.

While readings of potential in perchloric acid showed maximum sensitivity, they were also accompanied by a drift of potential due to ketone-acid interaction[2]. The latter was much less pronounced in 10^{-3} mol dm^{-3} paratoluenesulphonic acid which gave also the best reproducibility of potential of the three acids studied.

2.3.2 Comparison of the accuracy of water determination in organic solvents by the Karl Fischer method, gas chromatography and proton isoconcentration technique[17]

Table 3 shows the results of a comparative study of water analysis in methanol, ethanol, propan-1-ol, propan-2-ol and propanone.

In the case of propanone, Karl Fischer data were omitted as this method does not perform well in carbonyl compounds. In general,

---

* A measure of the difference between the free energy of a solute in its nonaqueous and its aqueous standard states.

TABLE 2: Change in potential, ΔE, for the system, butan-2-one-water-acid, in solutions of constant acid concentration and various water concentrations using pH glass electrode and calomel (lithium chloride) reference electrode

Acid	mol dm^{-3}	ΔE/mV	Water range, % m/m
$HClO_4$	10^{-2}	199	0.12 - 2.35
	10^{-3}	321	0.05 - 2.27
	10^{-4}	200	0.04 - 2.26
PTSA*	10^{-2}	121	0.26 - 2.48
	10^{-3}	117	0.05 - 2.28
	10^{-4}	108	0.03 - 2.26
HCl	10^{-2}	111	0.12 - 2.34
	10^{-3}	72	0.01 - 2.24

*para-Toluenesulphonic acid

results obtained with gas chromatography show a positive relative error due to absorption of atmospheric moisture on the needle of the microsyringe[22]. Solutions for gas chromatography (Table 3) were prepared separately, as this method cannot cope with acidic solutions.

Bearing in mind the limited data for gas chromatography, Table 3 conveys the impression that the three methods are reasonably comparable as regards quality of performance. While it is possible to place them in the following sequence of decreasing accuracy (increasing relative error), viz. Karl Fischer > gas chromatography > proton isoconcentration technique, the difference in accuracy, especially between GC and PICT, is relatively small.

A comparison of reproducibility data (standard deviations) in Table 3 shows the three methods to be roughly equal.

An added advantage of the Karl Fischer method is that it provides absolute water values.

Recent studies by Karim[19] on the determination of residual water by PICT in sulpholane, propylene carbonate and acetonitrile, respectively, have produced impressive results as regards sensitivity of potential response, accuracy of water determination and the lower limit of detection of water in these solvents. To prevent the absorption of atmospheric moisture, potentials were measured in an enclosed system in a dry-box under dry nitrogen. Karim's use of perchloric acid in glacial acetic acid proved beneficial to the stability of potential and resulted in improved standard deviation.

TABLE 3: Comparison of accuracy of water analysis by the Karl Fischer method (KF), gas chromatography (GC), and proton isoconcentration technique (PICT)

Solvent	Water % m/m	Relative error			Standard deviation		
		KF	GC	PICT**	KF	GC	PICT**
Methanol	1.870	+8.55		-0.10			
	1.610	+3.72		-1.46			
	1.360	+8.82		-1.62			
	1.110	0		+0.09			0.023
	1.008		+2.40				
	0.886		-0.90				
	0.860	0		+3.49	0.016		
	0.610	+1.63		-5.41			
	0.501		+1.69			0.008	
	0.374		+1.07				
	0.350	+1.14		+4.00			
	0.230	-0.87		-6.08			
	0.100	+1.20		+13.00			
					0.007 (0.041)*	0.006 (0.001)*	0.013 (0.140)*
Ethanol	1.870	-1.60		+2.35			
	1.620	+1.85		+2.09			
	1.360	+0.73		+1.39			
	1.130		-2.43				
	1.100	+2.72		+0.45			
	0.870	+3.70		-0.58	0.016	0.019	0.010
	0.610	+3.10		+4.90			
	0.505		+0.95				
	0.350	0		+2.20			
	0.226	-5.75		-5.50			
	0.124		+3.63				
	0.100	0		+5.45			
					0.008 (0.042)*	0.005 (0.020)*	0.008 (0.020)*
Propan-1-ol	2.319	-0.26		-3.32			
	1.825	+6.30		+1.53			
	1.575	+1.08		+2.73			
	1.330	-0.90		-1.73			
	1.083	-1.29	+2.27				
	0.835	+0.60		-2.95	0.019	0.007	0.006
	0.750			-0.72			
	0.587	+1.70		-0.68			
	0.338	-4.43		-2.07			
	0.214	-1.42		-1.87			
	0.090	+11.10		+11.10			

TABLE 3 (continued)

Solvent	Water % m/m	Relative error			Standard deviation		
		KF	GC	PICT**	KF	GC	PICT**
Propan-2-ol	1.880	+1.06		-4.40			
	1.620	+2.47		-4.50			
	1.400	+1.43		-2.70			
	1.200						0.027
	1.140	+3.50		-0.88			
	0.900	+4.44		-1.44	0.023		
	0.380	-2.63		+0.26			
	0.250	-4.00		-8.88			
	0.100	+20.00		+23.00			
Propanone	1.817			-1.49			
	1.310			+0.08			
	0.813			-2.30			0.005
	0.512		+4.34			0.005	
	0.380		+1.37				
	0.249			+1.36			
	0.138		+19.01				
	0.040			+20.00			0.006

* Figures in parenthesis denote percent m/m water

** Perchloric acid was used throughout except for prop-2-ol- water mixtures when p-toluenesulphonic acid was employed instead

ACKNOWLEDGEMENTS

Support by the following is gratefully acknowledged:

The Wolfson Foundation for a research grant; Professor J. Cabral (University of Oporto), Dr. J. R. P. Clarke (ICI plc) and Dr. J. Lee (UMIST) for advice; John Harvey & Sons Ltd. for supply of sherry, H. P. Bulmer Ltd. for supply of cider.

REFERENCES

1 Pungor, E. and To'th, K. in Lagowski, J. J. (Editor), "The Chemistry of Nonaqueous Solvents", Vol. 5A, Academic Press, New York, 1978, page 145.

2 Kakabadse, G. J., "Effect of Solvent on Potentials of Cells with Ion-Selective Electrodes" in Ion-Selective Electrode Rev., 1981, 3, 127.

3 Pungor, E.,To'th, K., Klatsmányi, P. G., and Izutsu, K., "Applications of Ion-Selective Electrodes in Nonaqueous and Mixed Solvents", in Internat. Union of Pure and Applied Chemistry, 1983, 55, 2029.

4 Lukashevich, V. O. and Sergeeva, M. M.,Doklady Akad. Nauk SSSR, 1949, 67. 1041.

5 Prior, W. A., "Mechanisms of Sulphur Reactions", Chapters 3 and 4, McGraw-Hill, N.Y., 1962.

6 Parker, A. J. and Kharash, N., J.Am.Chem.Soc., 1960, 82, 307.

7 Elbakai, A. M., Kakabadse, G. J., Khayat, M. N. and Tyas, D., Proceedings Anal.Div.Chem.Soc., 1975, 12, 83.

8 Bates, R. G., Analyt.Chem., 1968, 40, 28A.

9 Coetzee, J. F. and Martin, M. W., Analyt.Chem., 1980, 52, 2412.

10 Wells, C. F., J.Chem.Soc. Faraday I, 1976, 72, 601.

11 Kakabadse, G. J. (Editor), "Solvents - The Neglected Parameter", UMIST publication, Manchester, UK, April 1977, page 178.

12 Kakabadse, G. J., Abdulahed Malella, H., Khayat, M. N., Tassopoulos, G. and Vahdati, A., Analyst, 1978, 103, 1046.

13 Kakabadse, George (Editor), "Solvent Problems in Industry", Elsevier Applied Science Publishers, London, 1984, p.129.

14 Khayat, M. N., PhD Thesis, University of Manchester, 1974.

15 Abdulahed Malella, H., MSc.Thesis, University of Manchester, 1977.

16 Ake, H. A., PhD Thesis, University of Manchester, 1979.

17 Karim, M. R. O., PhD Thesis, University of Manchester, 1980.

18 Al-Yawer, N. F. N., PhD Thesis, University of Manchester, 1986.

19 Karim, M. R. O., Analyst, 1986, 111, 1211; 1987, 112, 163 & 1369.

20 Schwabe, K. and Queck, C., Z.Chem., 1977, 17(8), 304.

21 Chaudhari, S. N. K. and Cheng, K. L., Mikrochim.Acta, 1979, 2, 411.

22 Sakano, T., Hori, Y. and Tomari, Y., J.Chromat.Science, 1976, 14, 50.