DETERMINATION OF TRACE AMOUNTS OF ACETIC ACID IN ETHYL AND METHYL ACETATES BY FLUORIDE ISOCONCENTRATION USING THE METHOD OF STANDARD ADDITION.

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SUMMARY

The large and systematic change in cell potential(ΔE) resulting from the addition of 0-1%m/m acetic acid to a mixture of ethyl or methyl acetates -20%v/v ethanol, or methanol, containing $1x10^{-3}$M tetraethylammonium fluoride (TEAF) as background electrolyte, using fluoride electrode and calomel reference electrode filled with lithium chloride, provides a new graphical method for the rapid determination of acetic acid in ethyl or methyl acetates. Reading obtained by direct potentiometry show good reproducibility. The method is characterised by accuracy and simpilicity of operation and compares favourably with the gas chromatographic method.

Portugaliæ Electrochimica Acta, 8 (1990) 5-16

INTRODUCTION

In cells having ion-selective electrodes, many aqueous solvent mixtures show a systematic change in cell potential with variation in the concentration of organic solvent under ion isoconcentration conditions[1,2]. The use of this effect for the determination of solvents in binary solvent-water mixture, first reported in 1975[1], has been applied to the direct potentiometry of methanol-water mixtures[2]. Ethanol was determined in spirits by the fluoride isoconcentration technique(FICT) using a fluoride electrode and a reference electrode[3]. A study of binary acetic acid-water and acetic acid-methanol mixture under FICT, undertaken by Kakabadse and Ake, revealed a hypersensitivity of the fluoride electrode towards small changes in the acetic acid concentration at high methanol concentrations[4]. They proposed the use of the fluoride electrode for monitoring the production of vinegar from ethanol by FICT[5]. Recently,Karim reported the standard addition method under FICT for the determination of trace amounts of acetic acid in ethanol[6]. In the present work, the addition method based on FICT was applied to the determination of trace amounts of acetic acid in ethyl and methyl acetates which is a logical impurity in these solvents due to their hydrolysis[7].

EXPERIMENTAL

Reagents

The organic solvents were obtained from Fluka and purified as described elsewhere[8]. A stock solution of $5x10^{-3}$M tetraethylammonium fluoride (TEAF) in methanol, or ethanol, was prepared.

Apparatus

Measurements were made on magnetically stirred solutions at 25±0.1°C using a philips PW 9409 digital pH meter with a potential range of ±1000mV and a discrimination of ±0.1mV.A Hewlett Packard 9862A calculator-plotter was used and Philips model 1S 550-F^- fluoride electrode and Radiometer calomel(K 701) or silver-silver chloride K 801 reference electrodes were used. A Schott Gerate TR 156 automatic titrator was employed for the addition of acetic acid. For comparison,Pye Unicam model 28852GCD chromatograph (column packing porapak Q) was also used for the determination of acetic acid in ethyl and methyl acetates using nitrogen as a carrier gas at a flow rate of 50ml.min^{-1}.

Preparation Of Calibration Graphs

The cell consisted of a 100ml,three neck,round bottom flask fitted with a rubber stopper in which holes were bored for the insertion of the electrodes and the titrator tip. The cell was charged with 50ml of a mixture consisting of 40ml of ethyl or methyl acetates and 10ml ethanol or methanol,respectively,containing $5x10^{-3}$M TEAF[9]. Known increments(0-0.5ml)of acetic acid were added using the automatic titrator and potentials were measured immediately after each addition.Potentials

were plotted against percentage of acetic acid (Fig.1). For the determination of acetic acid in ethyl or methyl acetates, 10ml of $5x10^{-3}$M TEAF in ethanol or methanol were pipetted into a 50ml volumetric flask and the solution was diluted to the mark with 40ml of the sample. The potential of this solution was measured after washing the surface of the electrode with ethanol[6]. The percentage of acetic acid in the sample was then obtained directly from the calibration graphs.

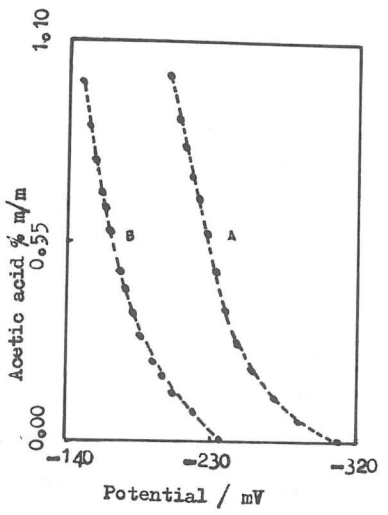

Fig.1 Calibration graphs showing the variation in potential with the addition of 0-1%m/m acetic acid to (A) ethyl acetate+20%w/v ethanol and (B) methyl acetate+20v/v methanol,mixtures containing $1x10^{-3}$mol.dm^{-3} tetraethyl ammonium fluoride,Philips fluoride electrode and calomel (LiCl) reference electrode were used.

RESULTS AND DISCUSSION

There might be several reasons for the large and systematic change in cell potential with the addition of 0-1%m/m acetic acid to a mixture of ethyl or methyl acetates and 20%v/v ethanol or methanol,respectively, in the presence of $1x10^{-3}$M TEAF as background electrolyte[6,9](Fig.1). Such reasons might include the change in the activity of the fluoride ions,the formation HF_2^- on the surface film of the electrode[9] and liquid junction potential changes at the reference electrode[2].

The following requirements must be met if the solvent effect on the cell potential is to be useful analytically: a large change of potential(ΔE) for a given change in the acetic acid concentration; a systematic and reproducible change in a potential, which must be stable , and a rapid electrode response[3].The relevant experimental parameters in this work are the nature of solvent, nature of background electrolyte and its concentration and type of reference electrode.

Effect Of Solvent

Potential measurements were unstable in pure ethyl or methyl acetates and in ethyl or methyl acetates+10%v/v ethanol or methanol mixtures,all being $1x10^{-3}$M in TEAF. This may be due to incomplete dissociation of this salt in the above solvents or to both having low permitivity(6.02 and 6.68, respectively)[8].

However stable potentials were obtained when ethyl and methyl acetates were added 20%v/v ethanol or methanol, both mixtures containing $1x10^{-3}$M TEAF. It can be seen from Table 1 that ΔE values for the addition of o-1%m/m acetic acid into ethyl acetate +20%v/v ethanol mixtures were higher than those for the methyl acetate+20%v/v methanol mixture; those values decreased when the percentage of ethanol or methanol increased in either of the solvents(ethyl or methyl acetates,respectively) .

Effect Of Fluoride Ions

Potassium,ammonium,and TEA fluorides($1x10^{-3}$M) in ethyl and methyl acetates+20%v/v ethanol and methanol mixtures, were examined. Potentials were not reproducible when potassium and ammonium fluorides were used, but potentials were very stable when $1x10^{-3}$M TEAF was used (Table 1)[6,9].Potentials were more reproducible at the higher acetic acid concentrations. This may be due to the ionising power of acetic acid in ethyl or methyl acetates-alcohol mixtures[10] .

Effect Of Reference Electrode

Calomel reference electrodes with saturated lithium or potassium chloride as the filling electrolyte were used in the present work. White crystals were formed in the ground glass junction and in the electrode filling solution when potassium chloride was used;also the potential measurements were less

reproducible with potassium chloride than with lithium chloride (Table 1) .

Accuracy Of Acetic Acid Determination

The results obtained for samples of acetic acid in ethyl or methyl acetates-mixed with 20%v/v ethanol or methanol(prepared by accurate weighing)are shown in table 2. In general, accuracy is satisfactory and comp ares favourably with that achieved by the gas chromatography .The interference of water in the acetic acid determination (0-2%m/m water) was studied by adding 0.5 or 1ml of water to 50ml of ethyl or methyl acetates+20%v/v ethanol or methanol mixtures,in the presence $1x10^{-3}$M TEAF. No significant change in cell potential was observed (it was less than 0.5mV,which is within the range of reproducibility for potential measurements) .

Limit Of Detection Of The Method($mg.Kg^{-1}$).

The sensitivity of the fluoride electrode towards changes in the acetic acid concentration in ethyl or methyl acetates+20%v/v ethanol or methanol mixtures depends on the amount of residual acetic acid present in the above mixtures and type of organic solvent (Table 3). The limit of detection of acetic acid is the amount of acetic acid($mg.Kg^{-1}$) added to ethyl or methyl acetates-20%v/v ethanol or methanol,respectively,in the presence of $1x10^{-3}$M TEAF,which produces a change in

Table 1: Change in cell potential, ΔE, standard deviation and coefficient of variation, with addition of 0-1%m/m acetic acid to ethyl or methyl acetates-ethanol or methanol mixtures, respectively, containing different concentrations of tetraethylammonium fluoride, using Philips fluoride electrode and calomel reference electrode.

Organic solvent	Reference electrode	$[F^-]$	Mean ΔE/mV	σ/mV*	Acetic acid %m/m	δ
Ethyl Acetate+	Calomel	$1x10^{-2}$	100.6	0.67	1.00	1.11
20%v/v ethanol	(LiCl)			0.89	0.05	
Ethyl acetate+	Calomel	$1x10^{-3}$	110.5	0.72	1.00	1.01_5
20%v/v ethanol	(LiCl)			0.86	0.05	
Ethyl acetate+	Calomel	$1x10^{-4}$	108.2	1.20	1.00	2.40
20%v/v ethanol	(LiCl)			2.30	0.05	
Ethyl acetate+	Calomel	$1x10^{-3}$	102.2	0.75	1.00	1.10
30%v/v ethanol	(LiCl)			0.84	0.05	
Ethyl acetate+	Calomel	$1x10^{-3}$	1o6.2	0.97	1.00	1.45
20%v/v ethanol	(KCl)			1.20	0.05	
Methyl acetate+	Calomel	$1x10^{-3}$	95.2	0.75	1.00	1.21
20%v/v methanol	(LiCl)			0.88	0.05	
Methyl acetate+	Calomel	$1x10^{-3}$	97.1	0.68	1.00	1.35
30%v/v methanol	(LiCl)			0.82	0.05	
Methyl acetate+	Calomel	$1x10^{-3}$	90.6	0.85	1.00	1.42
20%v/v methanol	(KCl)			0.97	0.05	

σ = Standard deviation for seven measurements of potential.

$\delta = 100\sqrt{\sigma_1^2 + \sigma_2^2}/\Delta E$.

σ_1 and σ_2 are the standard deviation (square root of sum square deviation divided by number of measurements minus one) for seven(n=7) measurements of potential in solution containing 1% and 0.05%m/m acetic acid, respectively .

Table 2: Accuracy expressed by the relative error* of the determination of acetic acid by direct potentiometry through the addition of 0-1%m/m acetic acid to ethyl or methyl acetates-20%v/v in ethanol or methanol mixtures, in the presence of $1x10^{-3}$M TEAF. Philips fluoride electrode and calomel (LiCl) reference electrode were used.

Solvent	Acetic acid, m/m			Relative error%	
	Prepared by accurate weighing	Found by standard addition	standard deviation for 7 determination.	Standard addition technique	Gas chromatography
Ethyl	0.90	0.92	0.05	+2.22	+1.20
acetate	0.64	0.66	0.06	+3.12	+2.83
	0.24	0.23	0.03	-4.17	-3.21
	0.10	0.10	0.02	0.00	+1.32
Methyl	0.93	0.94	0.04	+1.07	+1.80
acetate	0.57	0.56	0.04	-1.75	-2.31
	0.20	0.21	0.03	+5.00	+5.10
	0.08	0.08	0.02	0.00	+3.20

* Relative error is defined as the percentage of the accepted value

$$R.E. = \frac{x_i - x_t}{x_t} \times 100$$

x_i = observed value & x_t = accepted value

Table 3: Limit of detection of acetic acid in ethyl or methyl acetates +20%v/v in ethanol or methanol mixtures , containing $1x10^{-3}$M tetraethylammonium fluoride,using Philips fluoride electrode and calomel reference electrode with saturated lithium chloride as the filling solution.

Solvent	Acetic acid present	Sensitivity $mg.Kg^{-1}.2mV^{-1}$
Ethyl acetate	0.0	30
	0.5	64
	1.0	90
Methyl acetate	0.0	38
	0.5	70
	1.0	95

the cell potential of 2mV,corresponding to twice the value of the standard deviation[6].

Conclusion

The proposed method can be used for the determination of acetic acid in ethyl or methyl acetates. It is simple and has adequate accuracy and precision. Work is in progress for achieving continuous monitoring of acetic acid in ethyl or methyl acetates .

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(Received 11 October 1989;
Revised form 5 March 1990)

THE ELECTRODE/ELECTROLYTE INTERFACE IN NON-AQUEOUS SOLVENTS: GLASSY CARBON/TETRABUTYLAMMONIUM ELECTROLYTE IN N,N-DIMETHYLFORMAMIDE

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ABSTRACT

The interfacial region between a glassy carbon electrode and tetrabutylammonium electrolytes (halide, perchlorate and tetrafluoroborate) in N,N-dimethylformamide has been studied using impedance techniques at varying electrolyte concentration (0.01M → 0.20M) in the potential range 0.0 → -2.0V vs. SCE. The spectra can be divided into a concentration independent low frequency part (<100Hz) which is the same for all these electrolytes and a high frequency part depending on electrolyte and its concentration but not dc potential. Comparison is made with spectra obtained in aqueous solution. The results are discussed in terms of the physical properties of the solvent, electrolyte, glassy carbon, and the structure of the interfacial region. The low frequency feature is ascribed to electrolyte/electrode interactions and electrode porosity, and the high frequency feature to processes involving the electrolyte anion.

KEYWORDS: glassy carbon electrode, electrode/electrolyte interface, DMF, impedance, tetrabutylammonium salts.

INTRODUCTION

Many electrode reactions in non-aqueous media are carried out using alkylammonium salts as supporting electrolytes [1]. The large negative potential range on mercury electrodes can be increased in the positive direction by the use of solid electrodes such as glassy carbon. As in