

A Novel Use of Electrode Sensitivity for Ion-Selective Electrodes in Determining the Amounts of Water in Nonaqueous Systems

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Received: 28/5/2009 ; Accepted: 16/1/2010

Abstract:

Electrode sensitivity (ES), the change in cell potential for a given change in water concentration using proton-isoconcentration technique (PICT), remains constant under comparable experimental conditions. This permits a direct potentiometry of water by single dilution in a sample of water-organic solvent mixture using a micro pH-glass and ordinary reference electrodes or two ion-selective electrodes (i.e. a micro pH-glass electrodes and Radiometer Chloride Selectrode). The method is simple, rapid and accurate compared with the use of calibration graphs. Results obtained on selected important solvents demonstrate a satisfactory performance of ES using PICT.

Keywords: *Electrode sensitivity; Amounts of water determination; Nonaqueous Systems; cell without liquid junction; Ion isoconcentration technique*

الاستعمال الجديد لحساسية القطب للأقطاب الانتقائية الأيونية في
تقدير كمية الماء في المنظومات اللامائية

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ملخص البحث:

تم في هذا البحث استخدام حساسية القطب (ES) في تطبيقات تقدير كمية الماء في المذيبات العضوية، وهو التغيير في جهد الخلية إلى التغيير الحاصل في تركيز الماء المعطاة باستعمال تقنية البروتون ذات التركيز المتساوي (PICT)، والتي تبقى ثابتة تحت المتغيرات التي يمكن مقارنتها تجريبياً، تُجيز هذه التقنية، تطبيق طريقة الجهدية المباشرة لتقدير الماء بطريقة الازاحة المنفردة في نموذج مزيج ماء-مذيب عضوي وباستعمال قطب زجاجي (مايكرو) مع

قطب مرجع من نوع مألوف أو باستعمال أثنين من الأقطاب الانتقائية الأيونية (مثل: قطب زجاجي، مايكرو pH، وقطب الكلوريد الانتقائي، نوع رايوميتير). هذه الطريقة سهلة وسريعة ودقيقة مقارنة مع طرائق التي تحتاج إلى رسومات المعايرة، لتقدير كمية الماء في المذيبات العضوية أي إنها لا تتطلب معايرة تمهيدية والنتائج التي حصلت على المذيبات المألوفة يبين مدى كفاءة حساسية القطب (ES) المرضية باستخدام تقنية البروتون ذات التركيز المتساوي (PICT).

Introduction

Electroanalytical applications of direct potentiometry have been largely confined to the aqueous system; potentiometric aquametry with a glass electrode is a variant of ionometry since in this case the change in the activity of hydrogen ions is measured from the change in water content in the organic solvent^[1-3]. The analysis involves measuring the electromotive force (emf) of the electroanalytical cells with and without liquid junction, and determining the concentration of the water from a calibration curve. In cells with a liquid junction, it is possible to change the diffusion potential by changing the penetration of the solution in the liquid bridge. This change is reflected in the position of the calibration curve, which is prepared in advance. Thus, the calibration curve requires periodic correction. The presence of a liquid junction reference electrode can give rise to blocking of the liquid bridge and liquid junction leak, which is detrimental at lower detection limits of water in solvents^[4, 5, 7]. These problems can be avoided by using two ion-selective electrodes. Kakabadse et al.^[4,6] established that replacement of the liquid junction reference electrode with a solid-state chloride electrode improved the stability and reproducibility of cell potential when determining residual water in organic solvents under proton isoconcentration technique (PICT), this required the use of a differential electrometer amplifier.

Methods currently used for determination of moisture contents of organic solvents include colorimetry, gas chromatography, mass spectrometry and near infra-red^[8-12].

PICT, based on a calibration procedure, require two or more standard solutions (for straight-line and curved calibration graphs, respectively). In the proposed method (ES/PICT), using a known electrode sensitivity (ES), the residual water concentration of a sample can be determined by single dilution ion isoconcentration conditions, rendering the analytical procedure simpler and faster compared with the use of calibration graphs. Possibility of applying the method (ES) is demonstrated, its advantages and limitations, are discussed.

Experiment

Reagents and Chemicals

All chemicals were of analytical reagent grade. A hydrochloric acid 5×10^{-3} M in absolute methanol and ethanol were prepared using a concentrated aqueous HCl solution. A desired amount of an electrolyte tetramethyl ammonium chloride (TMAC) and tetraethyl ammonium chloride (TEAC) was added to the acid solutions of methanol and ethanol, respectively to give a buffer solution of 5×10^{-3} M.

10^{-1} M perchloric acid in solvent were prepared freshly from 70% m/m perchloric acid (sp. gr. 1.70), and employed for the preparation of 10^{-3} M perchloric acid in normal-propanol and iso-propanol-water mixtures.

A solution of 10^{-3} M p-toluene sulphonic acid (PTSA) in a mixture of 20% methanol/ 80% acetone v/v, (prepared from a stock solution 0.1 M PTSA in methanol).

For potential measurements in acetonitrile (AN) 10^{-3} M HClO_4 in acetonitrile was used, the stock solution was 10^{-1} M HClO_4 in glacial acetic acid prepared by accurate dilution from a concentrated aqueous solution of perchloric acid (ca. 9 M).

Apparatus

Two cells were employed, one containing a micro pH glass electrode (Radiometer G-202 C) and a micro-Metrohm, Ag-AgCl 6.1225.030, with a ceramic diaphragm (filling solution sat. LiCl in ethanol) reference electrode. The other, containing a micro pH glass electrode (Radiometer G-202 C) and Radiometer Chloride Selectrode (F 1012 C). The usage of a couple ion-selective electrodes were required differential electrometer amplifier (DEA)^[6].

Glass electrodes were kept in pH7 solution, whereas, Radiometer Chloride Selectrode and metrohm reference electrode were kept dry.

Measurements were made with solutions stirred magnetically, using a Corning 150 digital pH/millivolt meter (potential range ± 1000 mV ± 0.1 mV). A temperature compensation probe (ATC) was used to determine the absolute temperature in the electrode cell, which is compared with a datum temperature of 25°C.

A 10-50 μ l, micro syringe, grade "A" was used to introduce a small amount of water into the cell.

Procedure

Samples and diluents (usually organic solvents) had an identical concentration in indicator ion. In the normal procedure (table 1), a known volume of the sample solution (V_o) was dispensed into flask equipped in thermostated water bath (at 25°C) as well as ATC probe. The cell potential was measured after 2 min under constant stirring. Then, a known amount of diluent (ΔV) at 25°C was added with a pipette, or a burette, and the change in cell potential (ΔE) noted. In the reverse procedure, a known volume of sample was added to a known amount of diluent (ΔV) in the flask, of the same temperature.

Results and Discussion

Calculating water content:

The amount of water content of the sample was calculated using the following equation^[18]:

$$C_s = \frac{\Delta E \times (V_o \times \Delta V)}{ES \times \Delta V} \quad (\text{eq. 1})$$

Where:

C_s = concentration of water (% v/v) in the sample; ΔE = change in cell potential (mV) on dilution; V_o = initial sample volume (cm^3); ΔV = volume of added diluent (cm^3) and ES = electrode sensitivity (mV/% water).

Determining electrode sensitivity of a standard solution:

A known volume of diluent was added to a desired volume of water-solvent mixture of known water concentration, C .

Fig. 1. shows ES for the system water-ethanol mixture, an increase in water concentration, ΔC , was accompanied by an observed change in cell potential, ΔE .

Hence^[18]:

$$ES = \frac{\Delta E}{\Delta C} \quad (\text{eq. 2})$$

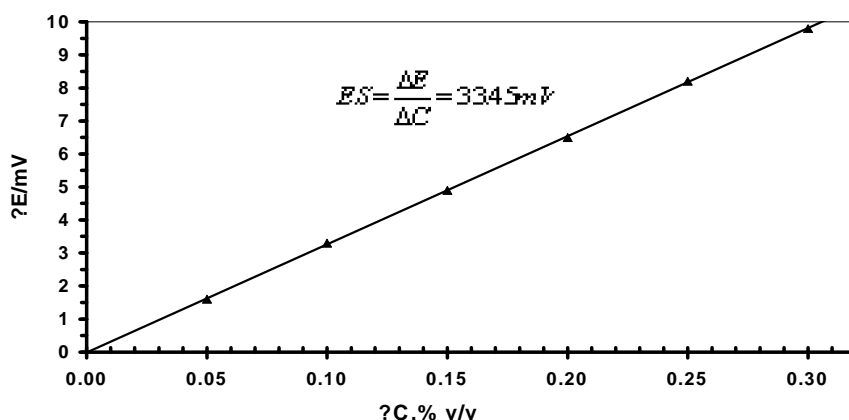


Fig. 1. Electrode sensitivity (ES) for the system water-ethanol mixture using PICT cell without liquid-junction.

An experimental tests of the glass electrodes used reflect the true activity of the hydrogen ions (protons) in nonaqueous solvents. Clearly, under this condition the slope of the potential versus water concentration will be of greatest importance. There may be several reasons for the hypersensitivity of cell potential, at high solvent concentration, to small changes in water content, e.g., the chemical composition of the glass, medium effects, the gradual dehydration of the gel layer at the outer surface of the glass electrode or an increase in proton activity in the outer swelling layer of the glass electrode^[7, 13-19].

The following requirements must be considered if the solvent effect on the cell potential is to be useful analytically: (i) the measure of sensitivity to water, there must be a large change of potential (ΔE) per unit of water concentration; (ii) the change in potential must be systematic, stable and reproducible; and (iii) a rapid electrode response.

The selection of a micro pH glass (Radiometer G-202 C) electrode shows a good sensitivity to water content of solvents cells with and without a liquid-junction.

Table 1 demonstrates a practical application of the concept of electrode sensitivity in batch analysis to the determination of water in water-organic solvent (methanol, ethanol, n-propanol, iso-propanol, propanone and acetonitrile) mixtures under proton isoconcentration techniques (PICT).

Water values found by ES (Table 1) are compared and in a good agreement with those obtained by accurate dilution of pure organic solvent, and by Karl Fischer titration.

Table 1. Direct potentiometry of water in water-organic solvents mixtures using the method of electrode sensitivity (ES) under proton isoconcentration conditions

No	Reference Electrode	[Acid]/M	ES/mV	Proced-ure ⁺	C _s , water % (v/v) found by		
					Accu. dilution	ES	Karl Fischer
		(a) water-methanol mixtures.....					
1	MET [*]	5×10 ⁻³ M HCl/TMAC	17.5	N	1.16	1.17	1.16
2	MET	5×10 ⁻³ M HCl/TMAC	17.6	R	1.16	1.17	1.16
3	R Cl ^{-**}	10 ⁻³ M HCl	23.5	N	1.16	1.16	1.16
		(b) water-ethanol mixtures.....					
4	MET	5×10 ⁻³ M HCl/TEAC	24.3	N	1.17	1.16	1.17
5	MET	5×10 ⁻³ M HCl/TEAC	24.5	R	1.17	1.18	1.17
6	R Cl ^{-**}	10 ⁻³ M HCl	33.5	N	1.17	1.17	1.18
		(c) water-n-propanol mixtures.....					
7	MET	10 ⁻³ M HClO ₄	28.5	N	1.14	1.14	1.14
8	MET	10 ⁻³ M HClO ₄	28.4	R	1.14	1.15	1.14
9	R Cl ^{-**}	10 ⁻³ M HCl	46.6	N	1.14	1.14	1.14
		(d) water-isopropanol mixtures.....					
10	MET	10 ⁻³ M HClO ₄	29.9	N	1.17	1.16	1.17
11	MET	10 ⁻³ M HClO ₄	29.8	R	1.17	1.17	1.17
12	R Cl ^{-**}	10 ⁻³ M HCl	48.4	N	1.17	1.17	1.17
		(e) water-propanone mixtures.....					
13	MET	10 ⁻³ M PTSA	14.0	N	1.16	1.16	1.16
14	MET	10 ⁻³ M PTSA	13.9	R	1.16	1.17	1.16
		(f) water-acetonitrile mixtures.....					
15	MET	10 ⁻³ M HClO ₄	80.1	N	1.18	1.18	1.18
16	MET	10 ⁻³ M HClO ₄	80.4	R	1.18	1.17	1.18

⁺N = Normal Procedure, R = Reverse Procedure.

*MET = Metrohm reference electrode.

** R Cl = Radiometer Chloride Selectrode.

Data pertaining to the reproducibility of electrode sensitivity (ES) values are presented in Table 2, as recording to standard deviation (σ) and standard error of mean (s.e.m.), the results are better to cells without a liquid-junction that is may be due to elimination of a liquid-junction potential^[6].

Table 2. Reproducibility of electrode sensitivity (ES) under proton isoconcentration techniques (PICT) for water-organic solvents mixtures using cells with and without liquid-junction (l-j)

No	Solution	Cells/l-j	H ₂ O, $\Delta C\%$	Mean $\Delta E/mV$	Mean ES/mV	σ^*/mV	s.e.m. ^{**} /mV
1	H ₂ O-MeOH	With	1.16	20.36	17.55	0.15	0.11
2	H ₂ O-MeOH	Without	1.16	27.26	23.50	0.09	0.07
3	H ₂ O-EtOH	With	0.55	13.42	24.40	0.13	0.10
4	H ₂ O-EtOH	without	0.55	18.43	33.5	0.07	0.05
5	H ₂ O-n-PrOH	with	0.75	21.34	28.45	0.14	0.11
6	H ₂ O-n-PrOH	without	0.75	34.95	46.6	0.09	0.07
7	H ₂ O-iso-PrOH	with	1.17	34.92	29.85	0.13	0.10
8	H ₂ O-iso-PrOH	without	1.17	56.63	48.40	0.08	0.06
9	H ₂ O-acetone	with	0.45	06.28	13.96	0.16	0.12
10	H ₂ O-AN	with	0.45	36.11	80.24	0.15	0.11

* Standard deviation for (7) measurements (n).

** Standard error of mean (s.e.m.) = $\pm 2\sigma/\sqrt{n}$ (representing 95% confidence limits).

The experiments, involving "narrow" range water-solvent mixtures in batch measurements, were carried out under comparable analytical conditions using proton isoconcentration technique (PICT).

These results show (i) a satisfactory reproducibility of ES values for each experiment and (ii) identical ES values for water-solvent (for a certain solvent) mixtures in batch analysis.

Conclusions

The following comments can be made about the electrode sensitivity (ES) technique:

- (a) Water values found by ES are in good agreement with those obtained by accurate dilution and Karl Fischer titration method. The method is simple and rapid, steady potentials being reached within 2-3 min.
- (b) ES values, representing in batch analysis differences of potential (eq.2), are not affected by potential drift^[6,20] and remain constant over a reasonably wide margin of analytical conditions, requiring only infrequent recalibration.
- (c) Economically, ES/PICT has the edge on the more important methods currently used, since practically all modern laboratories have a pH/mV meter and also use a pH glass electrode, determination of trace amount of water in solvents can be carried out with existing equipment.

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