Direct Potentiometry of Low Levels of Water in Organic Solvents using Cells without a Liquid-junction under the Proton Isoconcentration Technique

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Abstract

Direct potentiometry of the system, non-polar organic solvent (acetonitrile)-(0-0.118 % m/m) water-10^{-3}M hydrochloric acid using a micro pH glass electrode and Radiometer chloride selectrode (cell without liquid junction), has been employed and tested experimentally. The system shows systematic change in potential with variations in water concentration. This technique allows simple, rapid and accurate determination of low levels of water in acetonitrile under Proton Isoconcentration Technique (PICT).

Keywords: *Direct Potentiometry; low levels water; acetonitrile; organic solvent; cell without liquid junction; Proton Isoconcentration Technique*

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. In conventional direct potentiometry the concentration of indicator ion, A, is varied and that of solvent is kept constant, permitting the determination of ion concentration (activities) by graphical methods. In the ion-isoconcentration technique (IICT) the reverse procedure is applied: concentration of solvent is varied and that of ion, A, is kept constant. Methods currently used for determination of moisture contents of organic solvents include colorimetry, gas chromatography, mass spectrometry, near infra-red and differential potentiometric method [8-13].

In this study, PICT has been applied to the direct potentiometry of trace amounts of water in non-polar solvent (acetonitrile)-water in presence of hydrochloric acid using glass pH electrode and the possibility of applying cells without a liquid junction (Radiometer chloride selective electrode as a reference electrode in potential measurements).

Experimental

Apparatus

All electromotive force (e.m.f) measurements were made with solutions stirred magnetically, using a Corning 150 digital pH/millivolt meter (potential range ±1000 mV and a discrimination of ±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, although a thermostatic water bath with the range temperature of 25 ± 0.1 ºC was used. The electrodes micro pH glass electrode (Radiometer G-202 C) and Radiometer Chloride Selectrode (F 1012 C) were used. The usage of a couple ion-selective electrodes were required differential electrometer amplifier (DEA) [6]. The storage of the electrodes as following: micro pH glass electrodes were kept in pH7 solution overnight, whereas, Radiometer Chloride Selectrode was kept dry. A 10-50 µl, micro syringe, grade "A" was used.

Reagents

All solvents were of Riedel-deHaen analytical-reagent grade. The water content of dry solvents was determined by the Karl Fisher titration method [7] (was 0.006 % m/m). buffer stock solutions of 1 and 10^{-1} mole dm^{-3} hydrochloric acid were prepared from BDH analytical-reagent concentrated hydrochloric acid (sp. gr. 1.18) by accurate dilution. A series of solutions (standards and sample) with different concentrations of water in the solvent under investigation were prepared by accurate weighing.

Preparation of Calibration Graphs

A series of solutions with the same concentration of protons and different concentrations of water in solvent under investigation were prepared by accurate weighing. All potentials were measured in an enclosed system (in a dry-box) to prevent the absorption of atmospheric moisture. Each solution was placed in a 100 cm³ three-necked round-bottomed flask fitted with: (i) a pH glass electrode; (ii) chloride selectrode and (iii) automatic temperature compensation (ATC) probe, and the all potential measurements were recorded over periods of 4-6 min. to allow for equilibration at 25 ± 0.1 ºC (closer to room temperature). The unknown water concentration is found from the calibration curve.

Results and Discussion

A study of the cell potentials (without liquid-junction) over a narrow range for system solvent (acetonitrile)- 0-0.1% m/m water-10^{-3} mole dm^{-3} hydrochloric acid using a micro pH glass electrode versus Radiometer Chloride Selectrode (F 1012 C) as reference electrode has shown the change in cell potential (ΔE) to be both systematic, large and stable may be due to elimination of liquid-junction potential. Acetonitrile was tested as non-polar solvent using the above mentioned system successfully.

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, 13-20].

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 electrode versus Radiometer Chloride Selectrode (F 1012 C) as reference electrode shows a good sensitivity to water content of solvents Table 1shows the reproducibility (precision) of potential measurements which proved a good stability according to standard deviation (σ) and standard error of mean (SEM).

Effect of Acid

Hydrochloric acid was the obvious choice of acid solution as it is responds reversibly to both ion-selective electrodes. Variation of the acid concentration between 10^{-4}, 10^{-3} and 10^{-2} mole dm^{-3}, in general, 10^{-3} mole dm^{-3} HCl was found to be satisfactory, data in (Table 1) shows standard deviation and standard error of mean.

Table 1. Reproducibility of potential measurements for the system HCl- acetonitrile-water using a micro pH glass electrode versus Radiometer chloride selectrode

HCl concentration	Water, % m/m	Mean, E/mV	σ^{*}(SEM)**
10^{-4} mole dm^{-3}	0.0059	812	0.40(0.11)
	0.059	818	0.32(0.09)
	0.118	824	0.31(0.09)
10^{-3} mole dm^{-3}	0.0059	809	0.21(0.06)
	0.059	814	0.15(0.04)
	0.118	819	0.09(0.03)
10^{-2} mole dm^{-3}	0.0059	804	0.30(0.09)
	0.059	809	0.28(0.08)
	0.118	814	0.29(0.08)

*Standard deviation for 7 measurements (n).

**Standard error of mean = ± 2σ/√n (representing 95% confidence limits).

Accuracy of Water Determination

The results obtained from unknown water samples are shown in Table 2. At low water (0.005-0.118 % m/m) concentration , the relative error is slightly large. This may be due to an acetonitrile acid interaction in the form of hydrolysis [21, 22]. Generally, the accuracy shown is satisfactory and a good agreement with those found by Karl Fischer titration and accurate dilution.

Table 2. Determination of Trace Amounts of Water in acetonitrile by Accurate dilution, PICT and by Karl Fischer Titration

Solvent	**Water found, % m/m**			**Relative error*, %**	
	Accurate dilution	**PICT**	**Karl Fischer**	**PICT**	**Karl Fischer**
Acetonitrile	0.0060	0.0057	0.0063	5.0	5.0
	0.0354	0.0350	0.0370	1.13	1.13
	0.0590	0.0575	0.0600	2.5	4.5
	0.0826	0.0822	0.0812	0.5	1.7
	0.0944	0.0949	0.0950	0.5	0.6
	0.1180	0.1170	0.1200	0.85	1.7

- For 7 measurements. The *relative error* is frequently amore revealing measure accuracy, is often expressed as a percentage (RE% = x_i-x_t / x_t ×100).

Limit of Detection (LD) of Water in Acetonitrile

Applying the data for the sensitivity of the potential response to the amount of water necessary to give a change in potential of 0.5/mV for 0.005% (50) ppm water, standard deviation (reproducibility of potential, SEM/mV, in Table 1). Table 3 gives the Limit of detection (LD) value (expressed in % m/m) acetonitrile (AN), 50 ppm.

Sensitivity of Potential Response

Under identical conditions, v.z., a constant concentration of hydrochloric acid and the same Radiometer micro pH glass electrode and Radiometer Chloride Selectrode the sensitivity of the potential response (ΔE/unit water concentration e.g., 0.01%) for the system, solvent-0-0.118% m/m added water-10^{-3} M HCl, depends largely on the nature of the solvent. Table 3 shows the sensitivity of potential response in acetonitrile as a rule, from ″soft″ solvents has ΔE values of (10/mV) for the given system that is higher than for ″hard″ solvents [6].

Table 3. Sensitivity of the potential response and Limit of detection of water corresponding to a change in potential of 1 mV for 0.0118% m/m water

Water amounts in acetonitrile, % m/m	Sensitivity/ mV
0.0118	1
0.059	5
0.118	10

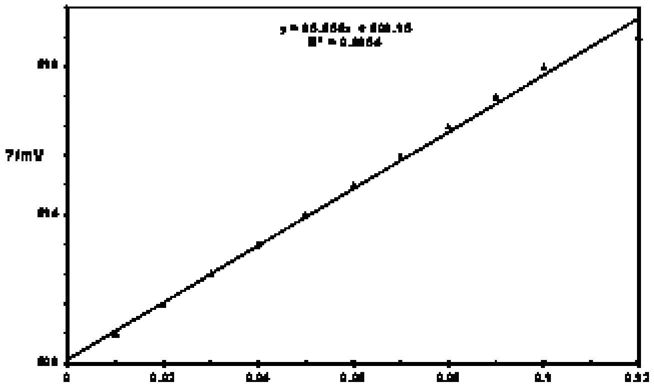

Fig. 1. Change in the potential of the system acetonitrile-0.0-0.1%m/m water-0.001M HCl using a micro pH glass electrode and Radiometer chloride selectrode (cell without liquid-junction)

Effect of the Electrodes

Radiometer micro pH glass electrode (G-202 C) and Radiometer Chloride Selectrode (F 1012 C) in the process of reference electrode were tested for ΔE in the system pH glass electrode/ 10^{-3} mole dm^{-3} HCl/ (0-0.1% m/m water)/ acetonitrile/ Radiometer Chloride Selectrode. Magnitudes of ΔE were found to be ,10.0mV for a change of (0-0.1) % v/v, this is corresponding to (0-0.118)% m/m H_2O, (Fig. 1) with high stability is probably due to usage of Radiometer Chloride Selectrode (elimination of liquid-junction). Although, ΔE value is less than when using Radiometer pH glass electrode with ordinary reference electrode and 2×10^{-3} mole dm^{-3} $HClO_4$ [20, 21]. This is belong to that the potential response of cationic electrode is in opposite direction to that for anionic electrodes.

Hence the possibility arises of enhancing the over-all effect (viz., achieving a satisfactory sensitivity) by using a cell consisting of a cation selectrode electrode (e.g. Radiometer micro pH glass electrode) and anion selective electrode (e.g. Radiometer Chloride Selectrode). The solid-state chloride electrode did not require conditioning after being kept dry overnight. A disadvantage of these electrodes is the vulnerability to solvent attack on the membrane seal and the epoxy electrode body[7].

Conclusions

The proposed method, included using of cells without a liquid junction (containing a micro pH glass and Radiometer Chloride Selectrode) in batch system can be used for the determination of trace amounts of water in organic solvents and is characterized by accuracy, simplicity of operation, and gives an improved stability of potential owing to elimination of the liquid junction. The method compared favorably with the Karl Fischer titration method (Table 2).

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الطريقة المجهادية المباشرة لتقدير الكميات الضئيلة من الماء في المذيبات العضوية باستعمال خلايا بدون سائل الالتقاء وباستخدام تقنية البروتون ذات التركيز المتسوي

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الملخص

تم في هذا البحث دراسة استخدام القطب الأنتقائي الآيوني نوع (Radiometer Chloride Selectrode) بدلا من القطب المرجع المألوف وذلك للتخلص من جهد التقاء السائل مقابل القطب الزجاجي نوع (Radiometer micro pH glass electrode) في تطبيقات تقدير الكميات الضئيلة من الماء في المذيبات العضوية (استخدم في هذه الدراسة المذيب اللاقطبي اسيتونتريل) كما في المنظومة: اسيتونتريل–(٠–٠,١١٨ % m/m) ماء–10^{-3} مولاري حامض الهيدروكلوريك، تظهر المنظومة جهداً متانسقاً منتظماً بتغيير كمية الماء المضاف وبثبوت تركيز الحامض باستعمال تقنية البروتون ذات التركيز المتساوي (PICT)، والتي تبقى ثابتة تحت المتغيرات التي يمكن مقارنتها تجريبيا، تُجيز هذه التقنية، تطبيق طريقة الجهدية المباشرة لتقدير الماء في المذيبات العضوية. هذه الطريقة سهلة وسريعة ودقيقة مقارنة مع الطرائق الأخرى إضافة انها لاتحتاج إلى أجهزة ثمينة ومكلفة. وكانت التوافقية للقراءات الجهدية والدقة لتقدير الماء جيدة ومرضية مقارنة مع الطرائق الأخرى.