

Determination of Trace Amounts of Water in Organic Solvents Using the Differential Potentiometric Method

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Abstract

A differential potentiometric method (DPM) of the system, organic solvent-(0-0.1% m/m) water- 10^{-3} M perchloric acid using two pH glass electrodes of the same type, 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 trace amounts of water in organic solvents, without preliminary calibration.

Keywords: Trace water determination; organic solvents; cell without liquid junction; differential potentiometric method

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, 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].

In this paper, the possibility of applying cells without a liquid junction by the differential potentiometric method (DPM) is demonstrated, and the potential sensitivity of the method, its advantages and limitations, are discussed.

Experimental

Reagents

All chemicals were of analytical reagent grade. Stock solutions of 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 5×10^{-3} , 10^{-3} or 10^{-4} M perchloric acid- water- solvent mixtures.

Apparatus

Measurements were made at $25 \pm 0.1^\circ\text{C}$ with solutions stirred magnetically using a Corning 150 digital pH/millivolt meter with a potential range ± 1000 mV and a discrimination of ± 0.1 mV. The pH glass electrodes were of Corning 003-11101J type. A 10 μl microsyringe

was used to introduce a small amounts of water into the cell.

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, or a series of increments of a known volume of water was added by a 10 μl microsyringe to a known volume solvent with same concentration of protons. Each solution was placed in a 100 cm^3 three-necked round-bottomed flask fitted with two pH glass electrodes and automatic temperature compensation (ATC) probe. All potentials were measured, in an enclosed system to prevent the absorption of atmospheric moisture, and recorded over periods of 4-8 min. to allow for equilibration at 25°C . The unknown water concentration is found from the calibration curve.

Results and Discussion

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 Corning 003-11101J pH glass electrodes shows a good sensitivity to water content of solvents.

The proposed method, differential potentiometric method (DPM), is preferable since it does not require preliminary calibration curve and periodic correction. The data of analysis by DPM presented in Table 1 agree well with the values obtained by accurate dilution, which confirms the suitability of the method for determining the moisture content of organic solvents, e.g., methanol, isopropanol, acetic acid, acetone, acetonitrile and cyclohexanone.

Table 1. Determination of Trace Amounts of Water in Organic Solvents by Differential Potentiometric Method (DPM) and by Karl Fischer Titration

Solvent	Water found, % m/m			Relative error, %	
	Accurate dilution	DPM	Karl Fischer	DPM	Karl Fischer
Methanol	0.0250	0.0240	0.0245	-4.0	-2.0
	0.0550	0.0540	0.0555	-1.8	+0.9
	0.1150	0.1140	0.1160	-0.9	+0.9
Isopropanol	0.0130	0.0120	0.0120	- 7.7	+7.7
	0.0620	0.0600	0.0635	-3.2	+2.4
	0.1000	0.0980	0.1020	-2.0	+2.0
Acetic acid	0.0150	0.0140	0.0160	-6.7	+6.7
	0.0500	0.0510	0.0510	+2.0	+2.0
	0.1250	0.1240	0.1250	-0.8	0.0
Acetone	0.0150	0.0140	0.0155	-6.6	+3.3
	0.0510	0.0490	0.0520	-3.9	+2.0
	0.0900	0.0870	0.0880	-3.3	-2.2
Acetonitrile	0.0130	0.0140	0.0135	+7.7	+3.3
	0.0500	0.0490	0.0490	-2.0	-2.0
	0.1050	0.1040	0.0550	-1.0	+1.0
Cyclohexanone	0.0530	0.0540	0.0545	+1.9	+2.8
	0.0420	0.0425	0.0423	+1.2	-0.7
	0.1260	0.1250	0.1270	-0.8	+0.8

In regard to accuracy, generally the relative error of the results found by DPM, shown in Table 1, does not exceed (7%) which is satisfactory and compares favorably with that achieved by Karl Fischer titration and accurate dilution.

Electrode sensitivity, the change in cell potential for a given change in water concentration, of the method

systematic for the narrow range 0.005-0.1% m/m, decreasing with the amount of trace water in the solvent from a maximum value for a water content of zero. For equal contents of water in different solvents, the electrode sensitivity (Fig. 1) depends on the nature of the solvent, i.e., ability of solvent to proton exchange.

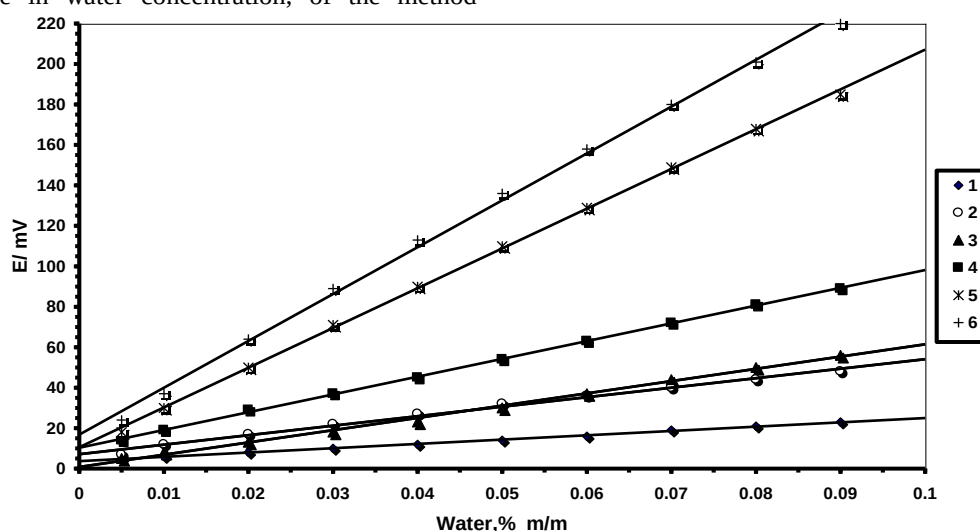
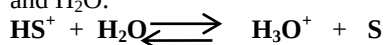


Fig. 1. The potential change of two glass electrodes as a function of residual water in solvents: (1) methanol; (2) isopropanol; (3) acetic acid; (4) acetonitrile; (5) acetone; (6) cyclohexanone

For example, on adding small quantities of water to a nonaqueous acid (HS^+) solution, there will be an equilibrium exchange process between the solvent (S) and H_2O :



The low sensitivity of some alcohols (curve 1 in Fig. 2) can be improved by adding aprotic solvents such as benzene (curve 2 in Fig. 2).

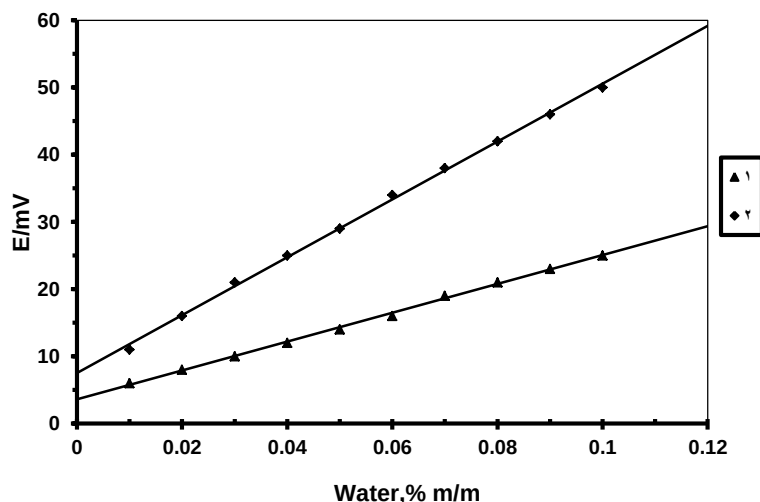


Fig. 2. Effect of benzene on the sensitivity of cell potential, for the system water-methanol mixture with benzene: (1) absent; (2) present.

The reproducibility, standard deviation (σ /mV) and standard error of the mean (SEM), and the stability of potential change (ΔE) for a given change of trace water,

Table 2, are better in the precision when using two glass electrodes owing to elimination of the liquid junction.

Table 2. Change in cell potential, ΔE , and the precision with the addition of 0.01% m/m water to solvent- 10^{-3} M HClO_4 using two glass electrodes

Solvent	Mean ΔE /mV	σ /mV*	SEM [§]
Methanol	2.1	0.31	± 0.21
Isopropanol	4.4	0.40	± 0.27
Acetic acid	6.1	0.60	± 0.40
Acetone	8.9	0.40	± 0.27
Acetonitrile	19.8	0.60	± 0.40
Cyclohexanone	20.9	0.70	± 0.47

* σ : Standard deviation for 9 measurements (n).

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

Effect of acid concentration on cell potential, the concentration of 10^{-3} M HClO_4 (Fig. 1) proved a good sensitivity and stability, a decrease in acidity to 10^{-4} M

HClO_4 (Table 3) does not change the behavior of electrodes to sensitivity. Further, decreasing in the concentration to 10^{-5} M HClO_4 leads to instability in the potential measurement due to the resistance of the electrolyte.

Table 3. Effect of acid concentration on the stability of cell potential (mean ΔE) for the system 0.01-0.1% m/m water-solvent-acid using two glass electrodes

Solvent	10^{-3} M HClO_4		10^{-4} M HClO_4		10^{-5} M HClO_4	
	$\Delta E^*/\text{mV}$	σ/mV	$\Delta E^*/\text{mV}$	σ/mV	$\Delta E^*/\text{mV}$	σ/mV
Methanol	2.1	0.31	2.2	0.33	2.0	0.51
Isopropanol	4.4	0.40	4.3	0.41	4.0	0.65
Acetic acid	6.1	0.50	6.1	0.52	6.1	0.77
Acetone	8.9	0.40	8.8	0.42	8.5	0.99
Acetonitrile	19.8	0.60	19.7	0.65	18.5	0.95
Cyclohexanone	20.9	0.70	20.6	0.72	20.0	1.10

ΔE^* : mean ΔE for nine repetition.

All potential measurements were carried out using automatic temperature compensation (ATC) probe, which adapts the temperature to $25 \pm 0.1^\circ\text{C}$, over periods

of 4-8 min. a time given to allow for equilibration and stability of the potential readings.

The potential values can be reliable if measured down to 2-3 mV, then from (Fig. 1) this corresponds to a water

value of 0.04-0.05% for acetic acid and 0.005-0.01% for a cyclohexanone. The values of the parameter for the other solvents lie between these two values. It is clear the solvent used as reference must have a lower or equal moisture content. An important advantage of the differential potentiometric method is that its possible to use it in the presence of oxidizing and reducing agents, as long as the glass electrode does not respond to them.

Conclusions

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The proposed method, DPM, 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. An added advantage of DPM is its adaptability to continuous monitoring.

تقدير الكميات الضئيلة من الماء في المذيبات العضوية باستخدام طريقة قياس الجهد التفاضلي

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الملخص

تم تطبيق طريقة قياس الجهد التفاضلي لمنظومة مذيب عضوي - (0-0.1% m/m) ماء - 10^{-3} مولاري حامض البيركلوريك باستخدام قطبين زجاجيين من نفس النوع واختبرت تجريبياً. تُظهر المنظومة تغييراً منتظماً في الجهد مع التغيير في تركيز الماء، تُجيز هذه التقنية طريقة سهلة وسريعة ودقيقة لتقدير الكميات الضئيلة من الماء في المذيبات العضوية، وكما إنها لا تتطلب معايرة تمهيدية.