

SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
3 (1997)

TESTING OF SOME NITRO COMPOUNDS
AS NEW PLASTICIZERS
OF POLYMERIC MEMBRANE-BASED
ELECTRODES

Karel VYTRÁS^{a1}, Milena KADERÁBKOVÁ^a and Jaromír SOCHA^b

^aDepartment of Analytical Chemistry, ^bDepartment of Organic Chemistry
University of Pardubice, CZ-532 10 Pardubice

Received December 31, 1997

An ion-pair formation-based titration monitored by simple polymeric membrane-containing electrodes of the coated-wire type proved as a procedure suitable for quick testing of new plasticizers. In the titration of a model compound, extraction capabilities of individual plasticizers can be estimated from the magnitude of the potentiometric titration break. A proper amount of a plasticizer needed for preparation of the membrane can be evaluated graphically as a maximum value of this break. However, the lifetime of the membranes must also be taken into account. From the 15 nitro compounds under test, all 2,4-dinitrophenyl n-octyl, 2-nitrophenyl n-octyl and 2-nitrophenyl 2-ethylhexyl ethers proved to be the most suitable from both the criteria (the lifetime of the sensing electrode as well as the value of the potential break). Dialkyl 3-nitrophthalates can also be recommended giving the titration breaks equivalent to those obtained with 2-nitrophenyl alkyl ethers. With other nitro compounds tested, either the potential break is sharp enough but the lifetime of

¹ To whom correspondence should be addressed.

corresponding sensors is more or less shortened, or the break magnitude is depressed.

Introduction

The nature of organic solvent used in liquid membrane-based ion-selective electrodes determines the extraction parameters of an ion-pair involved as an ion-exchanger and, consequently, the electrode selectivity towards the ion of interest [1,2]. The role of plasticizers in plastic membrane electrodes may be considered analogous, however, special attention has to be paid to their compatibility with the polymeric matrix.

Organic solvents containing nitro groups predominate in all the liquid membrane electrodes employed in ion-pair formation-based titrations, nitrobenzene being the popular membrane mediator in home-made organic ion-selective electrodes. With regard to poly(vinyl chloride) membrane electrodes, the most frequently used plasticizers are those formed by different esters of dicarboxylic acids, namely dialkyl phthalates [3]. From among the compounds containing nitro groups, 2-nitrophenyl *n*-octyl ether has been recommended as a mediator for calcium ion-selective electrode [4], and has also been used—besides 2-nitrophenyl 2-ethylhexyl ether—in simple sensors for monitoring titrations of organic compounds of ionic character [3]. Recently, both 2,4- and 2,6-dinitrophenyl as well as 2,4,6-trinitrophenyl *n*-octyl ethers have been synthesized [5] the first one has found its application in some of the commercial Crytur polymeric membrane electrodes [5-8]. More recently, also 2-nitrophenyl phenyl ether was introduced as a membrane plasticizing solvent mediator [9].

Some other nitro compounds synthesized for this study are introduced in this paper. The first group is represented by three 3-nitrophenyl alkyl (or aryl) ethers. In the second, various dialkyl esters of both nitrophthalic and nitroisophthalic acids have been prepared to combine the properties of the commonly used phthalate mediators and solvents containing nitro groups. From among these compounds, only di-*n*-octyl 3-nitrophthalate was tested recently [10] as a mediator in electrodes for titrations of arenediazonium ions. The application of other compounds prepared has been studied and the results are presented here.

Experimental

Apparatus

Potentiometric titrations were performed using an OP-208 pH meter (Radelkis, Budapest). The simple sensing electrodes of the coated-wire type were prepared as described previously [11] using an aluminium conductor as a support for the polymeric membrane, which was obtained from a solution of poly(vinyl chloride) (0.09 g) in tetrahydrofuran (3 ml) mixed with various volumes (0–0.2 ml) of an appropriate plasticizer; no electroactive substance was added. An RCE-102 Crytur calomel electrode (Monokrystaly, Turnov) of double-junction construction, filled with saturated potassium chloride (inner compartment) and 0.01 M sodium nitrate solution (outer compartment), was used as a reference half-cell.

Table I Plasticizers of poly(vinyl chloride)-based membranes

Code	Substance	Boiling point, °C (pressure, kPa)	
I	DNPOE	2,4-dinitrophenyl <i>n</i> -octyl ether	165 (0.05)
II	NPOE	2-nitrophenyl <i>n</i> -octyl ether	116 (0.03)
III	NPEHE	2-nitrophenyl 2-ethylhexyl ether	not specified
IV	DB3NP	di- <i>n</i> -butyl 3-nitrophthalate	222–4 (1.47)
V	DB4NP	di- <i>n</i> -butyl 4-nitrophthalate	225–7 (1.33)
VI	DB5NIP	di- <i>n</i> -butyl 5-nitroisophthalate	103–5 (1.73)
VII	DO3NP	di- <i>n</i> -octyl 3-nitrophthalate	> 250 (1.07)
VIII	DO4NP	di- <i>n</i> -octyl 4-nitrophthalate	> 250 (1.07)
IX	DO5NIP	di- <i>n</i> -octyl 5-nitroisophthalate	180–2 (1.20)
X	BEH3NP	bis-(2-ethylhexyl) 3-nitrophthalate	> 250 (1.07)
XI	BEH4NP	bis-(2-ethylhexyl) 4-nitrophthalate	> 250 (1.07)
XII	BEH5NIP	bis-(2-ethylhexyl) 5-nitroisophthalate	145 (1.07)
XIII	3NPBE	3-nitrophenyl benzyl ether	not measured
XIV	3NPJAE	3-nitrophenyl isoamyl ether	not measured
XV	3NPJBE	3-nitrophenyl isobutyl ether	not measured

Plasticizers

All the compounds tested as plasticizers are listed in Table I. Compounds I and II were purchased from Monokrystal, Turnov, and compound III was synthesized in VÚOS, Pardubice-Rybitví. Other compounds (IV-XV) were synthesized at the Department of Organic Chemistry, University of Pardubice.

Titration, Model Samples and Titration Procedure

Sodium tetrphenylborate solution (0.25%, i.e. ca. 0.007 mol l^{-1}) was prepared by dissolving a weighed amount of the substance (Lachema, Brno) in water (about half of the volume desired) and shaking the cloudy solution with a small amount of alumina; after standing and filtration, the solution was adjusted to pH 9 by adding sodium hydroxide solution and diluted to the desired volume with water. The solution was standardized potentiometrically against standard 10^{-2} M thallium(I) nitrate solution [12,13].

Compounds forming univalent organic cations in aqueous medium, such as a representative of cationic surfactants (cetyltrimethylammonium bromide, CTAB), salts of alkaloids (novocain, i.e., 2-(diethylamino)ethyl 4-aminobenzoate hydrochloride), and basic dyes (Rhodamine B, an aminoxanthene dye listed under C.I. 45170, C.I. Basic Violet 10) were used as model samples; their 0.001 M stock solutions were prepared. The selection was based on our previous experience with ion-pair titrations of the above compounds [14-16].

Aliquots (50 ml) of one of the above model sample solutions were placed into a 100 ml beaker and titrated with magnetic stirring using 10 ml burettes.

Results and Discussion

As it is well known [17], the customary type of liquid membrane electrode is one in which the membrane is composed of a water-immiscible organic solvent containing the ion in question, usually in the form of an ion-pair. The membrane is interposed between a standard (internal) and the test (external) ion solution, the voltage being measured for the complete electrochemical cell which comprises the membrane separating internal and external electrolytes as well as the two (internal and external) reference electrodes. Various arrangements of liquid membrane electrodes have been constructed. In the most used assembly, the organic liquid is held within the pores of a thin disc of about 0.1 mm pore diameters. The inner chamber is filled with the internal aqueous solution in which the inner reference electrode is immersed; this avoids the use of a thick layer of the organic phase.

The role of plasticizers in polymeric membranes may be considered analogous to that of organic solvent in liquid membrane electrodes. Above all,

these determine the value of the distribution ratio of the particular ion-pair employed as an ion-exchanger. However, special attention must be paid to their compatibility with the polymeric matrix.

In ion-pair formation-based titrations using coated-wire polymeric membrane electrodes, it was shown many times that no ion-exchanger must be incorporated into the membrane during its preparation. As reported by Higuchi et al. [18], these polymeric membranes respond to concentration changes of lipophilic organic ions. Within first successive titrations (usually only two are needed), the concentration of ion-exchanging compound in the membrane increases gradually to an optimum value, which is limited by the distribution ratio of the particular ion-pair. When the titration system (titrant, determinand, or both) is changed, usually two titrations are needed again to recombine corresponding ion-pairs in the membrane [3,15]. The same effect is achieved when the freshly prepared membrane is left to be conditioned in the stirred aqueous suspension of the ion-pair requested [11].

It should be mentioned that correlations between the terms of ion-selective electrode potentiometry and the extraction parameters of the ion-pairs used as the electroactive materials in liquid and/or polymeric membrane electrodes were studied by numerous authors. Scholer and Simon [1] developed a sensor exhibiting a Nernstian response towards "onium" salts, and explained its selectivity in terms of the extraction properties; Martin and Freiser [2] showed the role of solvent extraction in determining the selectivity sequence of their dinonylnaphthalene sulfonate electrode. Although surface adsorption and coulombic effect may need to be taken into account as well, the extraction parameters seem to play a predominant role. During ion-pair titrations, both the steepness and the overall potential break at the end-point increases with increasing polarity of the plasticizer as a result of higher extractability of the ion-pair compound precipitated in aqueous solution of the sample analyzed (see, for example, Fig. 1 in Ref. [14]). To verify the role of the equilibria involved, the values of both the distribution ratios and the extraction constants as well as the solubility products of N-alkyl-N-ethylpyrrolidinium tetraphenylborates were determined recently; the value of the titration break could readily be correlated with the logarithmic values of the extraction parameters [19].

As it can be seen from Figs 1-3, similar influence of the plasticizers character on the shape of the potentiometric titration curves as described previously [14] have been observed in determinations of all cationic substances under test; some characteristic values of these titrations are given in Table II. Simultaneously, the coated-wire technique of the monitoring sensors preparation has offered an advantage of a quick and inexpensive test for which the membranes have been prepared using verified amounts [11] of both poly(vinyl chloride) and an appropriate plasticizer.

However, the polymeric matrix can be considered as a microporous frit or a close netting, resp., the vacancies of which are occupied by a plasticizer.

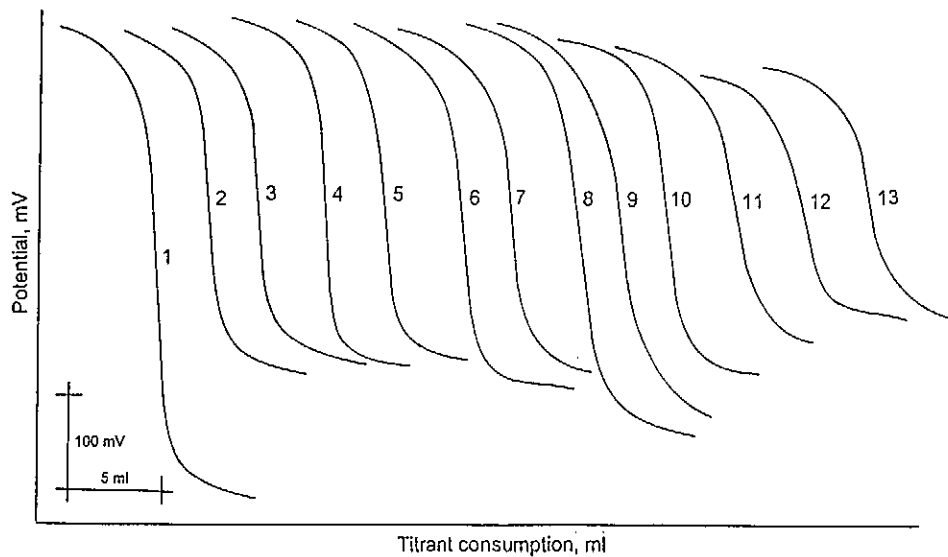


Fig. 1 Potentiometric titration curves of Rhodamine B solutions (ca. 25 mg/50 ml) using 0.25% sodium tetraphenylborate titrant. Membrane plasticizers: 1 - DNPOE, 2 - NPOE, 3 - NPEHE, 4 - DO3NP, 5 - BEH3NP, 6 - DB3NP, 7 - BEH5NIP, 8 - 3NPIBE, 9 - 3NPIAE, 10 - BEH4NP, 11 - DO5NIP, 12 - DB4NP, 13 - DO4NP

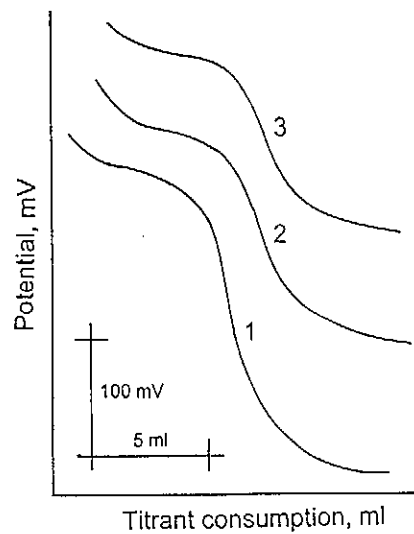


Fig. 2 Potentiometric titration curves of ca. 10^{-3} M solutions of novocain using 0.25% sodium tetraphenylborate titrant. Membrane plasticizers: 1 - NPEHE, 2 - NPOE, 3 - DB3NP

It is evident that the concentration of the electroactive substance in such a membrane depends on the amount of plasticizer, which is of course limited by its compatibility with the desired polymer (in addition in case of coated-wire sensors, it is also highly desirable to obtain a membrane with the properties of a softened polymer, not of a viscous liquid). Therefore, further experiments have been made in order to find the lowest possible content of plasticizer in the membrane: during its fabrication, the same volumes of the PVC solution in tetrahydrofuran (3 ml, corresponding to 0,09 g of solid PVC) were mixed with

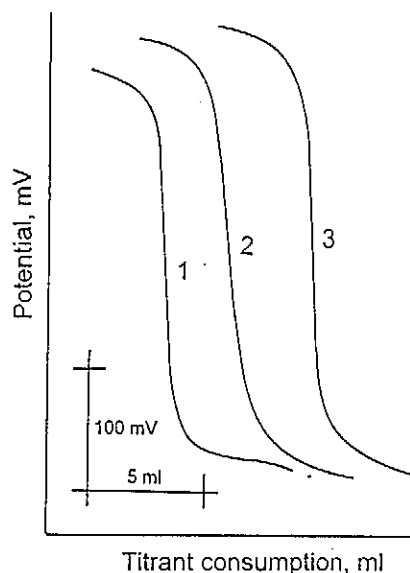


Fig. 3 Potentiometric titration curves of ca. 10^{-3} M solutions of cetyltrimethylammonium bromide using 0.25% sodium tetraphenylborate titrant. Membrane plasticizers: 1 - DB3NP, 2 - NPEHE, 3 - NPOE

changing volumes of plasticizers (max. 0.2 ml). Then the sensors were prepared by covering the aluminium wires by the membrane formed from corresponding mixtures and used to monitor the titration of Rhodamine B as a model cationic compound. As it can be seen from Fig. 4, further increase of the plasticizer content in the membrane does not bring any advantage.

With regard to the application of some new plasticizers tested, not only their extraction ability but the lifetime of corresponding sensors must mainly be taken into account. From this viewpoint, it should be stated that the longest stability was observed with electrodes whose membranes contained nitrophenyl alkyl ethers, namely, DNPOE, NPOE, or NPEHE; the electrodes prepared using these compounds could be used to monitor the ion-pair formation-based titrations for more than one year without any significant decrease of the potential

breaks (it should be mentioned that their boiling points given in Table I must not be compared with values of other compounds as they have been measured under significantly different pressures). Dialkyl 3-nitrophthalates can also be recommended for sensors preparation, the membranes containing dioctyl (both *n*-octyl and 2-ethylhexyl) derivatives offering somewhat longer lifetime. Electrode membranes softened with 4-nitrophthalates have quite good time stability but, in titrations of all model compounds, they exhibited somewhat lower potential breaks. The lifetime of membranes containing nitroisophthalates was shorter, only the di-*n*-octyl derivative could be used with some time limitation. This fully corresponds with the values of boiling points following a sequence DO5NIP > BEH5NIP > DB5NIP (see Table I). Other compounds such as 3NPBE, 3NPPIAE, and 3NPPIBE cannot be recommended for very short lifetime of the corresponding electrodes.

Table II Characteristic values^a of potentiometric titration curves using coated-wire polymeric membrane electrodes with different plasticizers

Plasticizer	Compound titrated					
	Rhodamide B		Novocain		CTAB	
	Break	Steepness	Break	Steepness	Break	Steepness
DNPOE	490-520	18-25	200-230	23-28		
NPEHE	400-480	19-22	155-180	11-14	360-380	22-35
NPOE	400-440	8-19	160-180	5-8	360-365	18-26
DB3NP	340-460	16-18	150-190	5-8	330-340	30-40
DB4NP	260-280	10-12	120-170	9-10		
DO5NIP	320-340	12-13	200-245	6-8		
BEH5NIP	380-400	20-40	160-170	8-10		
DO3NP	360-375	20-32	160-190	7-9		
BEH3NP	360-370	20-36	140-180	6-10		
DO4NP	250-270	12-18	120-130	8-10		
BEH4NP	365-380	32-35	80-120	2-6		
3NPBE	120-135	6-9				
3NPPIBE	270-430	12-14	70-110	2-7		
3NPPIAE	420-440	8-14	180-200	8-10		

^a) Given in mV for potential break, or for steepness in mV per 0.1 ml of titrant near the inflex of the potentiometric titration curve

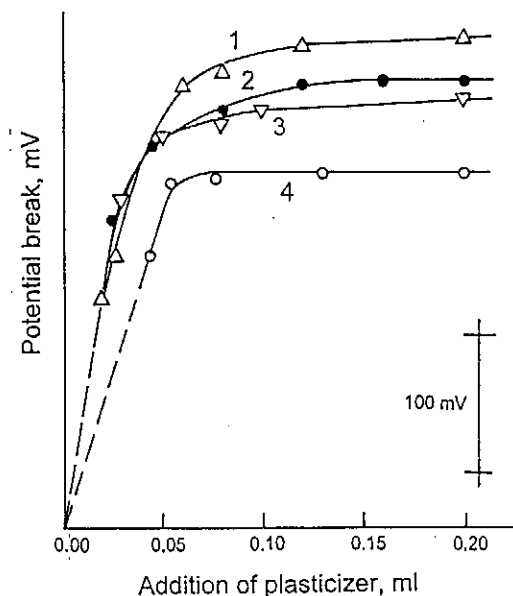


Fig. 4 Influence of the content of plasticizer in polymeric matrix (given in ml/0.09 g PVC) on the magnitude of potential break in titrations of Rhodamine B solutions (ca. 25 mg/50 ml) using 0.25% sodium tetraphenylborate titrant. Membrane plasticizers: 1 - DB3NP, 2 - NPOE, 3 - DO5NIP, 4 - DB4NP

Conclusion

The introduction of coated-wire electrodes has contributed significantly to the simplification of the measuring procedures used in various determinations based on ion-pairing principle. It should be stated that additionally, these techniques have proved competent for quick but reliable way of testing the quality of compounds newly prepared as perspective plasticizers.

Acknowledgements

The authors are indebted to Dr. Miroslav Panoch and Dr. Miroslav Remeš for their kind supplying the samples of DNPOE and NPOE, or NPEHE, respectively.

References

1. Scholer P., Simon W.: *Helv. Chim. Acta* **55**, 1801 (1972).
2. Martin C.R., Freiser H.: *Anal. Chem.* **52**, 568 (1980).
3. Vytřas K.: *Ion-Selective Electrode Rev.* **7**, 77 (1985).
4. Amman D., Guggi M., Pretsch E., Simon W.: *Anal. Lett.* **8**, 709 (1975).
5. Semler M., Panoch M.: *Czech. Pat. CS 208,880* (1983).
6. Panoch M., Semler M., Ryba O., Petránek S.: *Czech. Pat. CS 214,057* (1984).
7. Panoch M., Semler M., Dufek P.: *Czech. Pat. CS 244,919* (1984).
8. Panoch M., Semler M., Dufek P.: *Czech. Pat. CS 217,537* (1985).
9. Moody G.J., Owusu K.K., Thomas J.D.R.: *Analyst (London)*, **112**, 121 (1987).
10. Vytřas K., Latinák J., Čapoun T., Svobodová H.: *Chem Prům.* **32**, 81 (1982).
11. Vytřas K.: *Mikrochim. Acta* **1984/III**, 139.
12. Vytřas K., Říha V., Kotrlý S.: *Sb. Věd. Prací, Vys. Škola Chem. Technol., Pardubice* **35**, 41 (1976).
13. Vytřas K.: *Amer. Lab.* **11**(2), 93 (1979); *Internat. Lab.* **9**(2), 35 (1979).
14. Vytřas K., Dajková M., Mach V.: *Anal. Chim. Acta* **127**, 165 (1981).
15. Vytřas K., Dajková M., Remeš M.: *Česk. Farm.* **30**, 61 (1981).
16. Vytřas K., Kadeřábková M.: *Chem. Prům.* **36**, 137 (1986).
17. Vytřas K.: *Potentiometry*, in *Encyclopedia of Pharmaceutical Technology*, (J. Swarbrick, J.C. Boylan, Eds.), Vol. 12, p. 347, Marcel Dekker, New York 1995.
18. Higuchi T., Illian C.R., Tossounian J.L.: *Anal. Chem.* **42**, 1674 (1970).
19. Vytřas K., Čapoun T., Halánek E., Souček J., Štajerová B.: *Collect. Czech. Chem. Commun.* **55**, 941 (1990).