

## INFLUENCE OF EXTRACTION PROPERTIES OF PVC PLASTICIZER MEMBRANE ON THE RESPONSE OF COATED WIRE TYPE ION SELECTIVE ELECTRODE

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The authors studied the influence of the extraction properties of a PVC membrane plasticizer of a coated-wire type ion-selective electrode on its response in titrations of brucine and atropine with sodium tetraphenyl borate, as well as in potentiometric determinations of these compounds. The highest attainable value of the ion pair concentration in the plasticizer, which is limited by the distribution coefficient of the ion pair, determines the interval in which the electrode potential can be changed; and a linear dependence of the potential range of the titration curves on the logarithm of the ion-pair distribution coefficient was found. The slope of the dependence of the electrode potential on the logarithm of the ion concentration to be determined, found in potentiometric measurements, is proportional to the distribution coefficient of the ion which forms a pair with the ion to be determined and in whose solution the electrode membrane is activated between the measurements. The dependence of the slope of the electrode function on the logarithm of the product of the mentioned distribution coefficients is linear.

Ion selective electrodes (ISE) of the coated wire type are electrodes with a plastic membrane without an inner solution, the membrane covering directly the central conductor. They found application mainly in the potentiometric indication of ion-pair formation titrations. Ion pairs are formed in aqueous phase during reactions of various cations or anions with oppositely charged agents of a lipophilic character; and in contrast to common inorganic precipitates they are extracted into organic solvents. The method has found wide application thanks to the development of ISE and is suitable for the determination of a number of inorganic cations and anions and various organic compounds, mainly quaternary bases and compounds with protonated aminic or heterocyclic tertiary nitrogen (alkaloids, medicals, surface active substances, dye products or intermediates, etc.)<sup>1</sup>.

A detailed study of coated wire ISE (ref.<sup>2</sup>) showed that the material of the central conductor has practically no influence on the electrode properties, unless it reacts with the membrane plasticizer or ion exchanger, and that the manufacture of the electrodes can be simplified by preparing empty membranes without the ion exchanger and allowing the membrane plasticizer to become saturated with the ion pairs during the first several titrations. An ordinary aluminium lead was therefore recommended

for the preparation of the electrodes; this is covered with the membrane simply by repeated immersion in a solution of PVC and a plasticizer<sup>3</sup>.

The plasticizer strongly influences the properties of ISE with a plastic membrane. Of a large series of compounds, 2,4-dinitrophenyl-n-octyl ether proved best in titrations based on the formation of ion pairs. Most authors dealing with the influence of plasticizer on the form of the titration curves attribute the height of the potential step at the equivalence point to the distribution coefficient of the ion pair<sup>2,4,5</sup>, which however was not checked quantitatively.

The study of extraction parameters of ion pairs has hitherto been aimed mainly at elucidating the selectivity of some ISE with a PVC membrane and an inner solution from the point of view of the distribution coefficients of ion pairs involving the analysed and interfering ions<sup>6-9</sup>. Less attention has been paid to the influence of the membrane plasticizer on the potential response in the potentiometric determination of ions. Many ISE's do not give a Nernstian response and their potential is for a cation  $Q^+$  in the absence of interfering ions given, e.g., by the equation

$$E = E_0 + k \frac{RT}{F} \ln a_Q. \quad (1)$$

Here,  $k$  denotes the correction factor for non-Nernstian response, which depends on the quality of the plasticizer<sup>1</sup>.

Coated-wire ISE's were from this point of view practically not studied; they are not suitable for direct potentiometric measurements since the measured standard potential is not stable, however they can be used for direct measurements<sup>10,11</sup> if they are activated between the measurements in a solution of a substance forming an ion pair with the ion to be determined, and if they are often calibrated.

To obtain more information about the influence of the extraction properties of the PVC membrane plasticizer on the response of the coated-wire ISE, we studied the relations between the response of electrodes with membranes treated by various plasticizers and the distribution coefficients of ion pairs and other participating substances. To this purpose, the electrodes were used in titrations of brucine and atropine with sodium tetraphenylborate ( $\text{NaBPh}_4$ ).

## EXPERIMENTAL

### Preparation of Solutions and Electrodes

Aqueous brucine solutions (pure, Lachema) and atropine (atropinium sulfuricum monohydrate, ČSL 3, VLP Prague) were prepared in a concentration of  $0.01 \text{ mol dm}^{-3}$ . A stock solution of  $0.05 \text{ mol dm}^{-3}$  sodium tetraphenylborate (reagent grade, Laborchemie Apolda, G.D.R.) was diluted five times before use in titrations. It was standardized by using  $0.01 \text{ mol dm}^{-3}$   $\text{TINO}_3$ .

(reagent grade, Fluka, Switzerland) in potentiometric titration with a coated-wire ISE. The pH values of the solutions were adjusted by Britton-Robinson buffers<sup>12</sup> prepared by mixing a solution of  $0.40 \text{ mol dm}^{-3} \text{ H}_3\text{BO}_3$ ,  $0.40 \text{ mol dm}^{-3} \text{ CH}_3\text{COOH}$ , and  $0.40 \text{ mol dm}^{-3} \text{ H}_3\text{PO}_4$  with a solution of  $2.0 \text{ mol dm}^{-3} \text{ NaOH}$ . All chemicals were of reagent grade (Lachema, Brno).

To prepare a coated-wire ISE, a 10 cm long aluminium wire of 4 mm diameter with a PVC insulation was used, 1 cm of the insulation on each end was removed, and the ends were ground. One end was wetted with a solution of 0.09 g powdered PVC (Neralit, Spolana Neratovice) and  $0.02 \text{ cm}^3$  of a plasticizer in  $3 \text{ cm}^3$  of tetrahydrofuran (pure, Laborchemie Apolda, G.D.R.). After drying, the procedure was repeated until the solution was consumed. The membrane thickness was finally 0.32 mm on the average. Di-n-butyl phthalate, di-n-nonyl phthalate, di-n-decyl phthalate, tricresyl phosphate, xylenyl phosphate (pure, Lachema), diamyl phthalate, bis(2-ethylhexyl)phthalate (for GC, T. Schuchardt, G.F.R.), di-n-butyl maleinate (pure, Urx Works, Val. Mezifíř), and 2,4-dinitrophenyl-n-octyl ether were used as plasticizers. The latter compound was synthesized from 2,4-dinitrochlorobenzene (reagent grade, Lachema) and sodium octanolate, prepared by dissolving sodium (pure, Lachema) in n-octanol (pure, Lachema). The product was washed with soda lye, hydrochloric acid, and water, the remainder of octanol was distilled off, and after double crystallization from hot ethanol the melting point was measured as  $19-20^\circ\text{C}$ . The purity of the product was checked by chromatography on Silufol UV 366.

#### Potentiometric Titrations

A solution (5 ml) of  $0.01 \text{ mol dm}^{-3}$  brucine or atropine was pipetted into a laboratory vessel of 100 ml holding capacity, and 5 ml of the buffer and 50 ml of distilled water were added. A measuring cell consisting of a coated-wire ISE and SCE (OP-0830 P, Radelkis, Hungary) filled with a saturated NaCl solution (reagent grade, Lachema) was dipped into the solution, which was titrated under stirring with  $0.01 \text{ mol dm}^{-3} \text{ NaBPh}_4$ . The cell electromotive force was measured with an OP-208/1 type apparatus (Radelkis). The third and following titrations of a given substance were recorded.

#### Direct Potentiometric Measurements

A set of 13 solutions of brucine and atropine in the concentration range from  $9 \cdot 10^{-3}$  to  $1 \cdot 10^{-6} \text{ mol dm}^{-3}$  was prepared by mixing the required quantity of the stock solution with 5 ml of the buffer of pH 5 and making up to 60 ml with water. The above-mentioned measuring cell was dipped into the stirred solution and the electromotive force measured after equilibration was recorded. The indicator electrode was immersed into a stirred solution of  $0.01 \text{ mol dm}^{-3} \text{ NaBPh}_4$  for 3 min between the measurements.

#### Preparation of Saturated Ion Pair Solution

A solution (200 ml) of  $0.01 \text{ mol dm}^{-3}$  brucine or atropine was mixed with 200 ml of  $0.01 \text{ mol} \cdot \text{dm}^{-3} \text{ NaBPh}_4$  and 34 ml of buffer of pH 5. The precipitate was filtered off and washed several times with distilled water to remove any excess of free alkaloid or  $\text{NaBPh}_4$ . The precipitate was then transferred into 550 ml of distilled water and 50 ml of a buffer of pH 5 was added, whereby the ionic strength was adjusted approximately on the same value as in the titrations and potentiometric measurements. The mixture was heated to  $80^\circ\text{C}$ , after 24 h of standing tempered to  $20^\circ\text{C}$ , and the precipitate again filtered off. The filtrate was hence an ion pair solution saturated at  $20^\circ\text{C}$ .

## Determination of Distribution Coefficients

The saturated ion pair solution (6 ml) and 0.1 ml of plasticizer were pipetted into a glass probe with a thick wall of an inner diameter 18 mm. The mixture was stirred with a glass stirrer (diameter 8 mm, span of the blades 14 mm) at a frequency of 10 Hz for 10 min, which was found sufficient for the attainment of the distribution equilibrium. The ion pair concentration in the aqueous phase was determined before and after the extraction spectrophotometrically in the UV region on a Specord UV VIS apparatus (Carl Zeiss, Jena) using a 1 cm thick cuvette. The two substances gave several absorption bands; brucine was determined at a wavelength of 302.7 nm (molar absorption coefficient  $\epsilon = 8.83 \cdot 10^4 \text{ dm}^2 \text{ mol}^{-1}$ ) and atropine at 257.8 nm ( $\epsilon = 2.03 \cdot 10^3 \text{ dm}^2 \text{ mol}^{-1}$ ). Since the organic compounds used are somewhat soluble in water and show absorption in the UV region (typical for aromatic compounds), we made blank experiments by mixing 0.1 ml of the plasticizer, 5.5 ml of water, and 0.5 ml of the buffer of pH 5, extracting as indicated, and measuring the absorption in the aqueous phase at the given wavelengths. The values of the distribution coefficients of the ion pairs were calculated from the decrease of brucine or atropine in the aqueous phase.

Extractions of brucine and atropine were carried out in the same way: 5.5 ml of their  $0.01 \text{ mol} \cdot \text{dm}^{-3}$  solution was mixed with 0.5 ml of the buffer of pH 5 and 10 ml of the plasticizer; after the extraction had been finished, 5 ml of the aqueous phase was taken and the content of the compound was determined by titration with  $0.01 \text{ mol dm}^{-3} \text{ NaBPh}_4$  using potentiometry with a coated-wire ISE. To determine the distribution coefficient of  $\text{NaBPh}_4$ , 5.5 ml of  $0.05 \text{ mol dm}^{-3} \text{ NaBPh}_4$  were mixed with 0.5 ml of the buffer of pH 5 and 2 ml of the plasticizer. The content of  $\text{NaBPh}_4$  after extraction was determined in the aqueous phase by potentiometric titration with  $0.01 \text{ mol dm}^{-3} \text{ TiNO}_3$  using a coated-wire ISE. Extractions of ion pairs, alkaloids, and  $\text{NaBPh}_4$  were carried out in a thermostat at 20°C.

## RESULTS AND DISCUSSION

To determine the effect of pH of the titrated solution on the form of the titration curves, the pH values were varied from 1 to 7 at unit steps and the slope of each titration curve,  $\Delta E/\Delta V$  (mV/0.1 ml), was evaluated as the change of the ISE potential at the equivalence point due to addition of 0.1 ml of the titrating solution of  $\text{NaBPh}_4$ . Further we evaluated the potential range,  $\Delta E$  (mV), of the titration curve as the difference between the cell electromotive force at the beginning of titration and after addition of a two-fold equivalent quantity of the titrating solution. Since the conditions of the titrations were kept constant, the mentioned characteristics give an information about the suitability of a particular ISE for a given titration, or about the effect of pH, and they can be compared with one another. With the two alkaloids, the highest slopes of the titration curves with the widest potential range are attained at pH 5. This was therefore chosen for further measurements.

The characteristics of the titration curves of brucine and atropine with  $\text{NaBPh}_4$  and a coated-wire ISE provided with PVC membranes softened by various plasticizers are given in Table I. It follows that the best results were obtained with 2,4-dinitrophenyl-n-octyl ether as plasticizer; the corresponding titration curves are shown in Fig. 1. With dibutyl maleinate, xylenyl phosphate, and higher dialkyl phthalates

the curves have a low slope and a narrow potential range, whereby the accuracy of the determination is impaired. In the dialkyl phthalate series, the potential range of the curves decreases with decreasing number of C atoms in the alkyl chain.

In direct potentiometric measurements, the slope of the dependence of the cell electromotive force on the logarithm of the concentration of the analysed substance

TABLE I

Mean values of the potential range  $\Delta E$  (mV) and slope  $\Delta E/\Delta V$  (mV/0.1 ml) of the titration curves at the equivalence point. A solution (5 ml) of  $0.01 \text{ mol dm}^{-3}$  brucine or atropine was titrated with  $0.01 \text{ mol dm}^{-3}$   $\text{NaBPh}_4$  at pH 5; the measuring cell consisted of a coated-wire ISE and SCE at  $20^\circ\text{C}$ ; the values are averages from 10 measurements

Plasticizer	Brucine		Atropine	
	$\Delta E$	$\Delta E/\Delta V$	$\Delta E$	$\Delta E/\Delta V$
Dibutyl phthalate	114.4	21.8	112.8	7.5
Diamyl phthalate	106.8	15.9	101.0	6.7
Bis(ethylhexyl) phthalate	100.7	12.0	91.0	5.0
Dinonyl phthalate	90.3	12.8	83.4	6.1
Didecyl phthalate	86.4	13.1	80.3	4.4
Dinitrophenyl octyl ether	157.4	33.7	128.0	11.3
Dibutyl maleinate	77.9	6.0	72.3	3.9
Tricresyl phosphate	115.5	10.1	118.1	5.9
Xylenyl phosphate	85.2	9.6	103.0	5.0

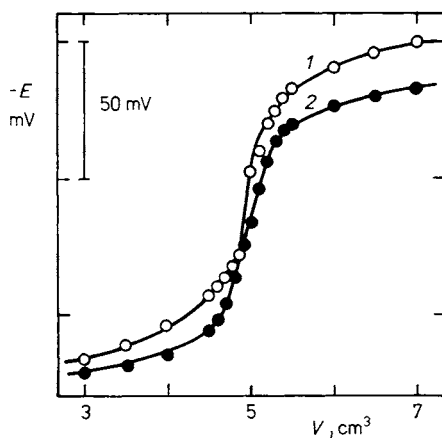


FIG. 1

Titration curves for 5 ml of  $0.01 \text{ mol dm}^{-3}$  brucine (1) and atropine (2) with  $0.01 \text{ mol dm}^{-3}$   $\text{NaBPh}_4$  at pH 5. Coated-wire ISE with PVC membrane softened with 2,4-dinitrophenyl-n-octyl ether

was determined by linear regression<sup>13</sup> together with the limits of linearity. The results are given in Table II. The highest slopes were found with the use of dibutyl phthalate

TABLE II

Mean slopes of the electrode functions,  $S$  (mV per decade), and lower limits of their linearity regions,  $c_L$  (mol dm<sup>-3</sup>), in direct potentiometry of brucine and atropine solutions at pH 5. The measuring cell consisted of a coated-wire ISE and SCE at 20°C, the ISE was activated in 0.01 mol . dm<sup>-3</sup> NaBPh<sub>4</sub> for 3 min between the measurements; the values are averages from 10 measurements

Plasticizer	Brucine		Atropine	
	$S$	$c_L \cdot 10^5$	$S$	$c_L \cdot 10^5$
Dibutyl phthalate	81.01	2.0	84.93	0.75
Diamyl phthalate	62.43	6.5	67.83	1.5
Bis(ethylhexyl) phthalate	49.05	8.5	54.56	2.5
Dinonyl phthalate	42.45	9.0	49.20	8.0
Didecyl phthalate	39.79	20	49.71	12
Dinitrophenyl octyl ether	55.29	0.70	50.51	0.50
Dibutyl maleinate	83.48	60	81.01	20
Tricresyl phosphate	66.87	3.6	69.60	0.80
Xylenyl phosphate	51.00	16	64.09	2.0

TABLE III

Distribution coefficients for brucine and atropine,  $K_D(Q)$ , ion pairs,  $K_D(Q^+BPh_4^-)$ , and sodium tetraphenyl borate,  $K_D(NaBPh_4)$ , at pH 5 from five measurements. Time of extraction 10 min, temperature 20°C

Organic phase	Brucine		Atropine		$K_D(NaBPh_4)$
	$K_D(Q)$	$K_D(Q^+BPh_4^-)$	$K_D(Q)$	$K_D(Q^+BPh_4^-)$	
Dibutyl phthalate	0.085	39.95	0.120	92.61	12.09
Diamyl phthalate	0.064	24.32	0.120	47.74	7.02
Bis(ethylhexyl)phthalate	0.051	22.43	0.094	42.85	1.30
Dinonyl phthalate	0.045	19.14	0.085	28.14	1.18
Didecyl phthalate	0.041	15.47	0.080	25.41	1.05
Dinitrophenyl octyl ether	0.067	144.31	0.110	108.43	0.50
Dibutyl maleinate	0.147	14.06	0.152	26.29	30.63
Tricresyl phosphate	0.163	35.77	0.116	73.62	3.64
Xylenyl phosphate	0.091	14.98	0.088	42.56	4.03

and dibutyl maleinate as membrane plasticizers, whereas with the use of dinitrophenyl octyl ether the slope was low, although the ISE seemed suitable for potentiometric titrations. In the dialkyl phthalate series, the slope of the electrode function is inversely proportional to the number of C atoms in the alkyl chain. The concentration range in which the electrode function is linear is narrowest for the electrode containing dibutyl maleinate and widest for dinitrophenyl octyl ether as plasticizer.

The distribution coefficients of brucine, atropine,  $\text{NaBPh}_4$  and the ion pairs in the organic phases at pH 5 are given in Table III. It can be seen that at this pH value the protonated alkaloids are very little extracted into the organic phases used, and therefore the influence of the distribution equilibrium on the response of the coated-wire ISE can be expected to be negligible. Sodium tetraphenylborate is best extracted into dibutyl maleinate and dibutyl phthalate, whereas much worse into dinitrophenyl octyl ether. The ion pairs are best extracted into the latter compound, whereas dibutyl maleinate is least suitable for this purpose. In the dialkyl phthalate series, the distribution coefficients of all the extracted substances decrease with increasing length of the alkyl chain.

Based on these findings, we can compare the extraction properties of the plasticizers with the responses of the coated-wire ISE. By comparing the data in Tables I and III it is apparent that both the potential range and slope of the titration curve are proportional to the distribution coefficient of the ion pairs formed during the titration. The dependence of the potential range of the titration curves on the logarithm of the distribution coefficient is illustrated in Fig. 2; the correlation coefficients were calculated by the method described in ref.<sup>13</sup> as 0.988 and 0.957 for brucine and atropine, respectively. Similarly, the distribution coefficient is related with the

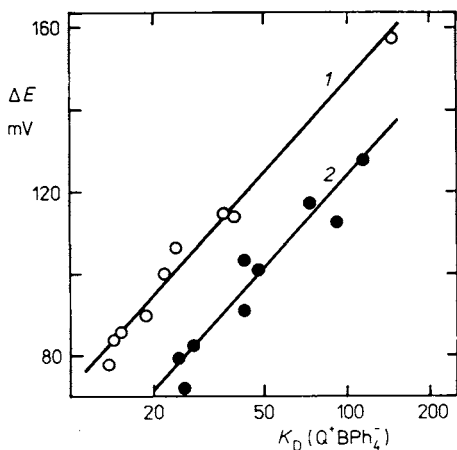


FIG. 2  
Dependence of the potential range of the titration curves for 5 ml of  $0.01 \text{ mol dm}^{-3}$  brucine (1) and atropine (2) titrated with  $0.01 \text{ mol dm}^{-3}$   $\text{NaBPh}_4$  at pH 5 on the distribution coefficient for the ion pair  $Q^+ BPh_4^-$  in the coated-wire ISE membrane plasticizer

lower limit of linearity of the electrode function: this is the lower the more ion pairs are extracted into the membrane phase. This is shown graphically in Fig. 3. Hence, it can be concluded that the distribution coefficient of the ion pairs in the membrane plasticizer is a critical quantity, which controls the width of the interval in which the coated-wire ISE is able to change its potential both in the titrations and in direct potentiometric measurements.

By comparing the data in Tables II and III it follows that the slope of the electrode function is proportional to the product of the distribution coefficients of the ion pairs and  $\text{NaBPh}_4$ . This is shown in logarithmic coordinates in Fig. 4; also here, the dependence is linear. The correlation coefficients were calculated as 0.979 and 0.987 for brucine and atropine, respectively. On this basis, the distribution coefficients characterizing the extraction properties of the membrane plasticizer can be introduced into the equation for the potential of the coated-wire ISE, whereby the correction for the non-Nernstian response of the electrode can be somewhat elucidated. From Eq. (1) follows the expression for the potential of the coated-wire ISE as function of the activity of the cation  $\text{Q}^+$  forming the ion pair  $\text{Q}^+\text{X}^-$  with the anion  $\text{X}^-$  in whose solution the ISE membrane is activated between the measurements (assuming

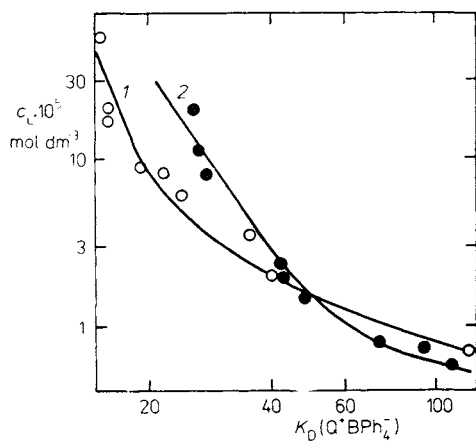


FIG. 3

Dependence of the lower limit of linearity of the ISE function on the distribution coefficient of the ion pair  $\text{Q}^+\text{BPh}_4^-$  in the coated-wire ISE membrane plasticizer. 1 Brucine; 2 atropine

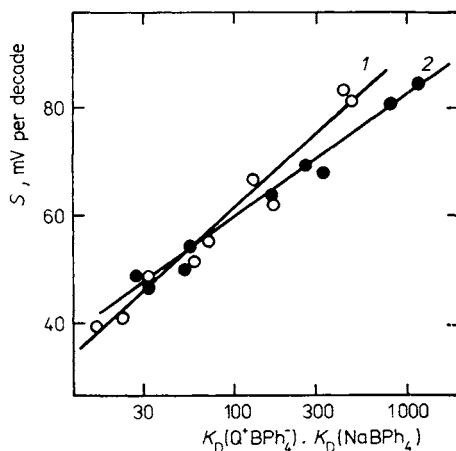


FIG. 4

Dependence of the slope of the ISE function for direct determination of brucine (1) and atropine (2) on the product of the distribution coefficients of ion pair  $\text{Q}^+\text{BPh}_4^-$  and of  $\text{NaBPh}_4$  in the coated-wire ISE membrane plasticizer



absence of interfering ions)

$$E = E_0 + b \log [K_D(Q^+X^-) K_D(X^-)] 2.303 \frac{RT}{F} \log a_Q. \quad (2)$$

For brucine,  $b = 0.523 \pm 0.0243$  and for atropine  $0.504 \pm 0.0336$  at  $20^\circ\text{C}$ . From a comparison of both these coefficients based on Student's test<sup>14</sup> follows the value of Student's criterion 0.9965 on the significance level 0.05, its critical value being 2.120. Hence, the difference between the values of  $b$  for brucine and atropine is not statistically significant.

Our results show a significant influence of the extraction properties of the PVC membrane plasticizer on the electrode response. For the use in potentiometric titrations, the plasticizer must have a high value of the distribution coefficient for the ion pair formed during the titration. This is a condition for a wide potential range of the titration curves and thus a high accuracy of the determination.

When the coated-wire ISE is used in the determination of ions by direct potentiometry, the condition of a high distribution coefficient ensuring a wide region of linearity of the electrode function must be supplemented by a high distribution coefficient of the ion forming a pair with the ion to be determined and present in the solution used for activation of the ISE membrane between the measurements. This property of the PVC membrane plasticizer ensures a high value of the slope of the electrode function, which is favourable for the accuracy of the determination.

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