DETERMINATION OF ORGANIC BASES BY ION-PAIR EXTRACTION POLAROGRAPHY USING ORANGE II AS COUNTER ION

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The combination of ion-pair extraction and differential pulse polarography is shown to be a method suitable for the determination of 10^{-7} mol l^{-1} concentrations of organic bases or quaternary ammonium compounds. Orange II (4-[2-hydroxy-1-naphthyl]azobenzenesulfonic acid) was found to be an appropriate polarographically active counter-ion. The proposed method was used for the determination of tetrapentylammonium bromide (as model compound), Septonex ([1-(ethoxycarbonyl)-pentadecyl]trimethylammonium bromide) and codeine.

Ion-pair extraction has become a very important and useful procedure not only for the extraction of compounds from aqueous media into a suitable organic solvent, but also for the determination of these compounds, in combination with a suitable analytical method (especially in the case of analytically inactive analytes). In such a case, an analytically active counter ion is selected and the analysis is based on the determination of the equivalent amount of this counter ion extracted together with the analyte into the organic phase, usually chloroform.

A highly coloured counter ion may be used for photometric determination of the original analyte, e.g. refs[1 - 9] (extraction photometry), a highly fluorescence counter ion enables its fluorometric determination[10 - 12] (extraction fluorometry). If a complex metal ion is used as the counter ion, atomic absorption spectrophotometry can be used as the final analytical method[13].

When no side reactions[14] occur the extraction process can be described for 1 : 1 species by the reaction scheme

$$BH^+_{aq} + A^-_{aq} \rightleftharpoons BHA_{org} , \qquad (1)$$

where aq and org mean aqueous, respectivelly organic phases. The equilibrium of this process is quantitatively characterized by the extraction constant K_{ex} defined[14] as (2)

$$K_{ex} = [BHA]_{org} / [BH^+]_{aq} [A^-]_{aq} . \qquad (2)$$

If analytical concentrations c of both, the base and the acid, are equal, an almost complete recovery by one-step extraction is achieved[15] when $K_{ex}\ c \geq 10^6$. When samples with lower extraction constants are extracted, an excess of the counter ion has to be used in order to reach the optimum recovery. Factors affecting the liquid–liquid extraction of the ion pair are: properties of the pairing ions (size, hydrophobicity, dissociation constants, concentration), properties of the extraction phase (polarity, specific solvation, presence of adduct-forming agents, volume), properties of the aqueous phase (salt concentration, pH, volume), the nature of the ion pair (size, hydrophobicity, specific solvation behaviour, dissociation), and temperature[16].

Recently, we have shown[17,18] that ion-pair extraction can be used advantageously also in combination with polarography (ion-pair extraction polarography) enabling the determination of low concentrations of electrochemically inactive analytes. The procedure is based on the formation of an ion pair of the analyte with the picrate ion as a highly electrochemically active counter ion (6-electron reduction). The procedure was used with good results for the determination of 10^{-7} mol l^{-1} concentrations of tetrabutylammonium bromide and Septonex®.

Application of this procedure for the determination of weak bases, e.g. codeine, resulted in low recoveries in the extraction step at pH 6. It was impossible to use pH 3.75 which was theoretically derived[19] as an optimum for the ion pair codeine–picric acid because of the high blank value (the extraction of free picric acid). Therefore, a new ion-pairing agent with more advantageous properties had to be found to enable successful determination of both, strong and weak bases.

EXPERIMENTAL

Reagents

Tetrapentylammonium bromide (TPABr) was obtained from Fluka (Switzerland), codeine and [1-(ethoxycarbonyl)pentadecyl]trimethylammonium bromide (Septonex®) from Slovakofarma Hlohovec (Czechoslovakia).

Azo dyes (Eriochrome Black T (C.I. 14645), Eriochrome Blue Black B (C.I. 14640), Eriochrom Red B (C.I. 18760), Metanil Yellow (C.I. 13065), Tropaeolin O (C.I. 14270), Tropaeolin OO (C.I. 13080), Nitrazine Yellow (C.I. 14890), Orange II (C.I. 15510), Methyl Orange (C.I. 13025)) and codeine dihydrogenphosphate were pure compounds from our collection of standards. All other chemicals were purchased from Lachema Brno (Czechoslovakia) and were of p.a. grade.

Chloroform was shaken with water three times to remove ethanol.

Britton–Robinson buffers 0.1 and 0.4 mol l^{-1} were prepared by combining acetic, phosphoric and boric acids at appropriate ratios[20]. Water used for preparing solutions was redistilled from potassium permanganate.

The aqueous stock solutions of analytes were prepared at the concentration of $2 \cdot 10^{-3}$ mol l^{-1} and diluted to appropriate concentrations.

Extraction Procedure

Sample solution (5 ml) was placed into glass tubes (18 × 2 cm) together with 500 ml of 0.4 mol l^{-1} Britton–Robinson buffer pH 3 for codeine, or pH 5 for quaternary ammonium compounds, the appropriate amount of the Orange II aqueous solution (500 μl of 4 . 10^{-3} mol l^{-1} solution for codeine, 500 μl of 1 . 10^{-3} mol l^{-1} solution for TPABr and 200 μl of 1 . 10^{-3} mol l^{-1} solution for Septonex). Finally, 5 ml of chloroform were added. Closed tubes were shaken on the laboratory shaker LT1 (Kavalier, Votice, Czechoslovakia) until reaching the equilibrium (10 min for codeine and 60 min for Septonex and TPABr). Then, after the phases were separated, the upper aqueous phase was sucked off carefully by a pipette connected to a vacuum pump and 4 ml of the chloroform extract were transferred by a pipette into a dry beaker. Chloroform was then evaporated and the residuum dissolved in 10 ml of the supporting electrolyte and the DPP measurement was carried out.

In order to test the necessary amount of Orange II solution, 20 . 10^{-7} mol l^{-1} concentration of the analyte solution was chosen and the same extraction procedure was carried out. An amount of 10, 20, 50, 100, 200, 500 and 1 000 μl of the 1 . 10^{-3} mol l^{-1} Orange II solution in the case of Septonex and TPABr, and 10, 20, 50, 100 μl of 1 . 10^{-3} mol l^{-1}, 50, 125, 250 μl of 4 . 10^{-3} mol l^{-1} in the case of codeine (these volumes respond to 1 : 1, 2 : 1, . . ., 50 : 1, 100 : 1 Orange II : analyte molar ratios) were used.

Polarography

DPP measurements were carried out using the polarographic analyzer PA 2 connected with the *x–y* recorder 4103 (both equipments from Laboratorní přístroje Praha, Czechoslovakia). A two-electrode configuration consisting of a dropping mercury electrode (DME) and a saturated calomel electrode (SCE) was used. The following parameters for DPP measurements were used: drop time 2 s, scan rate −2 mV s^{-1}, modulation amplitude −100 mV. The parameters of DME: the height of mercury column 50 cm, the mercury flow rate 0.79 mg s^{-1}.

Prior to the DPP scanning, the measured solution was purged with a stream of a water-saturated nitrogen for at least 5 min.

Britton–Robinson buffer 0.1 mol l^{-1} pH was chosen as the supporting electrolyte. The corresponding peak potential of Orange II in this medium is −710 mV and the calibration graph of the DPP current intensity against Orange II concentration in the polarographic cell was found to be linear with a correlation coefficient better than 0.999 in the concentration range studied. Higher current sensitivity can be achieved in a buffer of pH 6 but the shape of the peak is worse in comparison to that obtained at pH 10.

The method used for the determination of peak heights for the supporting electrolyte is shown in Fig. 1. Peak shape and height are not affected by the presence of the counter ion within the measured concentration range.

RESULTS AND DISCUSSION

Our investigations were directed to the discovery of a new ion-pairing agent with higher acidity retaining all other important properties of an ion-pairing agent. From the commonly used compounds[14] with strong acidic character, both arylsulfonic acids and aryl- respectively alkylarylsulfates were excluded due to their low polarographic activity, and an idea was accepted to choose a suitable compound from a wide range of azo dyes. These compounds have several important advantages for our purposes:

1. Many of the most common dyes are strong acids due to the presence of a sulfo group in their molecules.

2. Their polarographic activity is well-known and is fully described[21 - 24]. This activity increases with the increasing electron density at the central –N=N– linkage. This can be easily accomplished by introducing electron-releasing substituents, such as *o*-hydroxy, *p*-hydroxy, amino or dimethylamino groups into the molecule or by substituting the benzene ring with a greater aromatic system, such as naphthalene.

3. Azo compounds with the above mentioned properties e.g. Methyl Orange[1 - 3,5], Orange II[6 - 8], Tropaeolin O[5], Tropaeolin OO[2,4,5], Naphtol Orange[9], Fast Red A[9], have been already described in literature in connection with their use in extraction photometric methods.

According to these principles the sulfonated azo dyes listed in Experimental were tested. The best results were achieved with Orange II because of its high polarographic activity connected with a very good extraction ability. The polarographic method was thus modified for this azo dye. Orange II has also some other important properties necessary for its further successful use for ion-pair extraction polarography: low acidity of the hydroxy group (pK_A = 11.4, so that in the pH range studied no divalent anion of Orange II can occur)[25], high sensitivity (approximately 1 . 10^{-7} mol l^{-1} in polarographic cell), sharp and well-developed peak and linearity of the callibration graph ($r > 0.999$). Expectations of negligible amounts of the undissociated form of Orange II extracted into the organic phase was also verified. This essential conclusion followed from the extraction of the blanks at pH 2 – 6, revealing no peaks of Orange II.

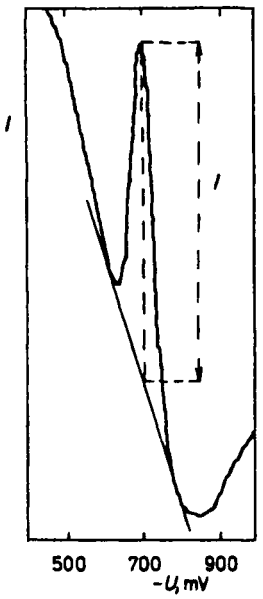

FIG. 1
Peak shape and polarographic peak height of Orange II

Three various compounds were chosen as model bases: codeine as a representative of weak bases, Septonex and TPABr. The latter two are quaternary ammonium solutions and strong electrolytes. Septonex is a cationic surfactant while TPABr has no surface-active properties.

In the first step, the time interval necessary for reaching the equilibrium state in the two-phase system for individual ion-pairs had to be determined. This interval was found to be quite short for codeine (10 min) in contrast to TPABr (45 min) and Septonex (60 min). This is in full agreement with literature data because slow extractibility of Orange II with cationic surfactants was described[7] and the same effect was also observed[26] in the case of tetraalkylammonium bases with longer chains (C_5, C_6) pairing with iodide anions. The disadvantage of time-consuming extraction is compensated by the possibility of carrying out simultaneous extractions of 20 – 40 samples on one shaker.

In the second step, the influence of the excess of Orange II towards the base was tested. The results are presented in Fig. 2. It is shown that the influence is nearly negligible for TPABr and Septonex. Almost the same current intensity corresponding to the given concentration of the ion-pair was obtained with any excess of Orange II. This fact was expected because these bases were found to have high extraction constants ($\log K_{ex} > 8$), when measured photometrically[27]. However, it is not clear why Spetonex gives only about 80% recovery. It is known that some cationactive surfactants can decrease the height of the polarographic wave of the azo dye Methyl Red[28]. When this possibility was verified in the case of Orange II, it was found that the current intensity is the same for the sample with and/or without Septonex. Side reactions in the aqueous phase that may result in turbidity of the aqueous phase at a greater excess than 20 : 1, could be a possible explanation. On the other hand, the amount of extracted codeine ($\log K_{ex}$ = 3.86, ref.[27]) increases strongly with the increasing excess of Orange II and

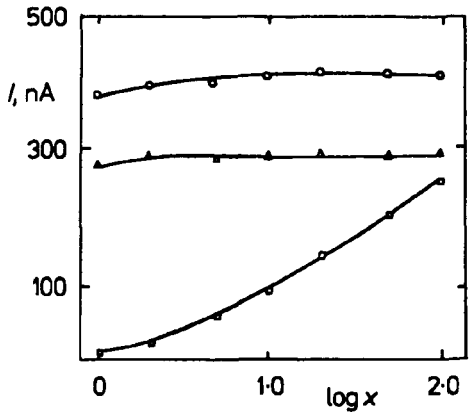

FIG. 2
Dependence of DPP current intensity I on the molar ratio of Orange II (O), $x = n_O / n_B$, where n is amount of substance. B: ○ TPABr, △ Septonex, □ codeine

therefore, the highest (100 : 1) excess of Orange II solution had to be used in further experiments.

Finally, calibration graphs were measured in the concentration range of $2.5 - 20.0 \cdot 10^{-7}$ mol l^{-1} for Septonex and TPABr, and $5.0 - 40.0 \cdot 10^{-7}$ mol l^{-1} for codeine. The results obtained are presented in Table I. The linearity of graphs is very satisfactory. Statisatical evaluation of the calibration lines determined by the least square method (L^D is the detection limit defined[29] by equation $L^D = t\,s\,/\,k$, where s is the standard deviation of the measured points from calculed regression line, k is the slope of this line and t is the Student coefficient for 99% reliability and corresponding number of degrees of freedom $\nu = 6$, r is regression coefficient):

TPABr: $I = 20.44 \cdot 10^7\, c - 9.21$, $r = 0.9995$, $s = 4.28$, $L^D = 6.6 \cdot 10^{-8}$ mol l^{-1};

Septonex: $I = 15.87 \cdot 10^7\, c + 4.14$, $r = 0.9993$, $s = 3.80$, $L^D = 7.5 \cdot 10^{-8}$ mol l^{-1};

codeine: $I = 12.38 \cdot 10^7\, c + 31.17$, $r = 0.9982$, $s = 9.73$, $L^D = 2.5 \cdot 10^{-8}$ mol l^{-1},

where I is in nA, c in mol l^{-1}.

Worse reproducibility was found in the case of the $2.5 \cdot 10^{-7}$ mol l^{-1} concentration of Septonex and TPABr. The explanation can be found in a slightly stuffing base line of the base electrolyte which influnces the peak height. This effect is the most significant

TABLE I
Dependence of mean current intensity I (nA) on the concentration c (mol l^{-1}) of base in a sample

$c \cdot 10^7$	TPABr			Septonex			Codeine		
	I	s	r	I	s	r	I	s	r
2.5	47.3	10.55	121.1	48.1	13.28	123.2	–	–	–
5.0	90.8	5.51	98.1	86.1	6.23	93.0	92.5	6.71	99.9
7.5	138.4	3.42	94.7	119.5	6.37	81.8	–	–	–
10.0	192.7	4.50	96.6	158.1	5.50	79.2	157.5	8.52	78.9
12.5	247.4	3.40	97.8	199.5	5.95	78.8	–	–	–
15.0	301.5	3.98	98.3	241.5	6.14	78.7	227.32	6.27	74.1
17.5	351.7	2.84	97.6	282.9	3.87	78.6	–	–	–
20.0	396.7	2.38	95.9	325.3	2.83	78.7	272.8	5.73	66.0
25.0	–	–	–	–	–	–	323.5	5.63	62.1
30.0	–	–	–	–	–	–	410.9	5.69	65.5
35.0	–	–	–	–	–	–	461.1	4.62	62.8
40.0	–	–	–	–	–	–	532.7	3.93	63.3

[a] s (%) relative standard deviation of repeatability, r (%) recovery calculated as r (%) = $100\, I\,/\,I_{st}$, where I_{st} is a current intensity for the known amount of Orange II corresponding to the theoretical 100% recovery of the ion pair. Number of measurements $n = 15$ for each concentration and compound.

for low peaks. The reproducibility for codeine is worse than for quarternary ammonium compounds, being probably caused by the lower extraction constant.

The proposed combination of ion-pair extraction and differential pulse polarography using Orange II as the electrochemically active counter ion enables the determination of 10^{-7} mol l^{-1} concentrations of organic bases and quarternary ammonium compounds. The advantage of the use of Orange II as the counter-ion is in its applicability in a broad range of pH (no blank in the range of pH 2 – 10). Further advantage of the procedure is that it involves also the isolation step of the analyte and is applicable to analytically inactive compounds. Applications can be expected in the field of ionogenic tenside determination in waters, sewage waters, the determination of basic drugs in biological fluids and pollutants in the enviroment.

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