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Study of the Stability of Some Ion-Pairs in Non-Aqueous Solutions by Potentiometric and Spectrophotometric Methods

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Changes in selected complexes caused by photodissociation were studied potentiometrically by measuring the time dependence of electromotive force of suitable cells and spectrophotometrically by measuring the time dependence of absorbance to evaluate the stability constants. Ion pairs labetalol (LAB)-reineckate (REINE) in nitromethane and crystal violet (CV)-tetrachloroferrate(III) ($FeCl_4$) in tetrachloroethane were used. The concentration ranges were determined, in which the EMF variations are greatest: the $4–5.5 \times 10^{-4}$ mol l^{-1} range for the LAB–REINE complex and the $0.9–3 \times 10^{-6}$ for the CV–$FeCl_4$ complex. Linear dependence of the EMF variation on the intensity of radiation, as well as a slight effect of temperature on irradiated solution were found. The stability constants of the studied complexes in chloroform, determined directly from spectrophotometric measurements are $\log\beta_{av} = 6.6$ for LAB-REINE complex and $\log\beta_{av} = 7.3$ for the CV–$FeCl_4$ complex.

Key words: stability constants, ion-pairs, non-aqueous solution, spectrophotometry, potentiometry

Using specific ion pairs it is possible to monitor the course of a chemical reaction or to determine groups of compounds or elements, what is useful in chemical analysis and in environment protection [1–3]. Most components of ion-association complexes are pharmaceuticals, used in medicine and in veterinary medicine. Ion-selective electrodes, containing ion pairs, in which a pharmaceutical is an ion [4–6], offer the prospects of a rapid and precise determination of pharmaceutical preparations. Sensitivity and selectivity of ion-selective electrodes are determined by the rate of formation and by the properties of ion pairs. The potentiometric method based on the EMF measurements in a non-aqueous solvent of a suitable cell, containing the studied ion pair, permits to study the stability of compounds, taking advantage of the photodissociation reaction. The same reaction can also be applied for stability constant determinations of complexes in the kinetic spectrophotometry method. Both methods are complementary and yield similar parameters characterizing the stability of the complex compounds studied.

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In this paper the ion-association complexes of labetalol with reineckate and of crystal violet complexes with $FeCl_4^-$ were studied. Labetalol is a drug administered in vascular hypertension, in coronary disease, in cardiac failure and in heart rhythm disorder. The reineckate is a trivalent chromium complex salt, used in biochemical analysis for precipitation of amines and in many ion-pair type complexes [6–8]. The crystal violet is an indicator commonly used in acid-base titration in non-aqueous solutions; it is applied also in the medicine as a bactricide and a fungicide. It is also used in ion-selective electrodes, *e.g.* in iron determination in blood, hematite, vitaminized soft drinks [9] and in cadmium determinations in potable water or sewage and in cadmium trace determinations in zinc [10].

EXPERIMENTAL

Reagents: The following reagents of analytical grade were used: $LiCl \cdot H_2O$, HCl, CH_3NO_2 (NM) (POCh Gliwice Poland), crystal violet (CV) (BDH Ch.Ltd.Poland), $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$ (L.P.P-H Lublin, Poland), reineckate (REINE), 1,1,2,2-tetrachloroethane (TCE) (ALDRICH), labetalolum-HCl (SIGMA), tetrabutyloammonium chloride (TBACl) (FLUKA).

Preparation of the complex compounds: A 0.1 M solution of labetalolum hydrochloride was mixed with an equimolar solution of the ion-pairing agent – REINE and the resulting precipitates were collected by centrifugation. The ion-pair complexes obtained were washed extensively with distilled water and dried at room temperature for 24 h. The CV^+–$FeCl_4^-$ complex solution was prepared as described in [9], using TCE as a solvent. Other solutions used in this work were prepared from stock solutions or from weighted samples of corresponding reagents.

Apparatus and measurements: The light from a type KB 11711 slit illuminator with a xenon source (“COBRABID” ZD, Opole) was directed to a nickel mirror and then to the vessel containing the solution of the complex, which served as a cell. The EMF variations of this cell were measured with a pH-meter (“TELEKO” N5172).

The schemes of the studied cells are given below:

a) for the LAB–REINE complex in nitromethane (NM)

		$\downarrow h\nu$		
Hg, Hg_2Cl_2	Li^+, TBA^+,	LAB^+ – $REINE^-$,	LAB^+,	Hg_2Cl_2, Hg
	Cl^-	TBACl	Cl^-	
	in H_2O	in NM	in H_2O	

b) for the CV–$FeCl_4$ complexes in tetrachloroethane (TCE)

		$\downarrow h\nu$		
Hg, Hg_2Cl_2	Li^+	CV-$FeCl_4$,	Li^+,NH_4^+,	Hg_2Cl_2, Hg
	Cl^-	Cl^-	$FeCl_4$, Cl^-	
	in H_2O	in TCE	in H_2O	

Kinetic spectrophotometric measurements were carried out by recording the time dependence of absorbance during the pumping (a type PP11305 “ZALIMP” peristaltic pump was used) with a Hewlett-Packard diode spectrophotometer 8452A, using a “HELLMA” flow cell and “COLE-PARMER” teflon hoses.

RESULTS AND DISCUSSION

Potentiometric measurements: Potentiometric measurements were carried out by recording the electromotive force (EMF) variation with time of the irradiated solution. The radiation wavelength ranges used had been determined earlier in order to find the optimal conditions. The following wavelength ranges were chosen from spectra recorded for the aqueous solution of labetalolum hydrochloride, REINE, CV and $FeCl_4^-$ ion, the solution, and the solution of complex in NM or TCE: 460–600 nm for LAB–REINE and 620–680 nm for CV–$FeCl_4$. In these ranges, the absorption by the complex is maximal and it is minimal for the compounds. The potentiometric curve is given in Fig. 1, being influenced by reactions occurring in the solutions. Like in our earlier measurements [11,12], some curves do not return to the initial potential value, *e.g.* curve II of Fig. 1, what is due to the photolysis reaction occurring during the measurement [11,12].

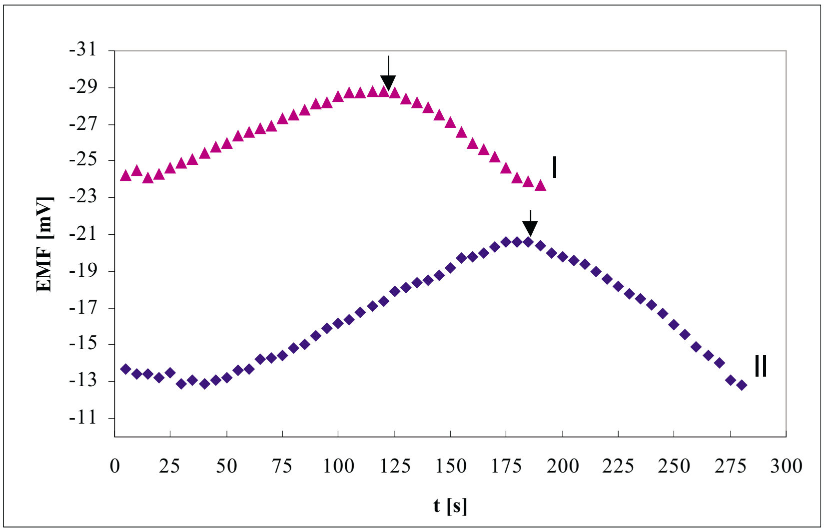

Figure 1. The changes of potential of LAB–REINE in NM with time for complex concentrations: 6×10^{-5} (I), 10^{-4} (II) mol l^{-1}. ↓ – The moment when the irradiating light was switched off.

The rate constant, τ, was determined from [13].

$$EMF = EMF_{t=0}(1 - e^{-t/\tau}) \tag{1}$$

Comparison of τ for different complexes allow to estimate their stabilities. The dependences of variations in electromotive force of the cell on the concentration of irradiated complex is illustrated in Figs 2 and 3 and in Tables 1 and 2; the curve shapes of the complexes studied are similar to those obtained earlier, both in aqueous and in organic solutions [9,10]. The optimal concentration ranges, in which the EMF variations are highest, are: 4×10^{-4}–5.5×10^{-4} mol l^{-1} for the LAB–REINE complex, 9×10^{-7}–3×10^{-6} mol l^{-1} for the CV–$FeCl_4$ complex. We have also confirmed that the variation in the EMF of the cell is directly proportional to the variations in irradiating light and that the effect of temperature is insignificant and it does not change the experimental potential values [11,12].

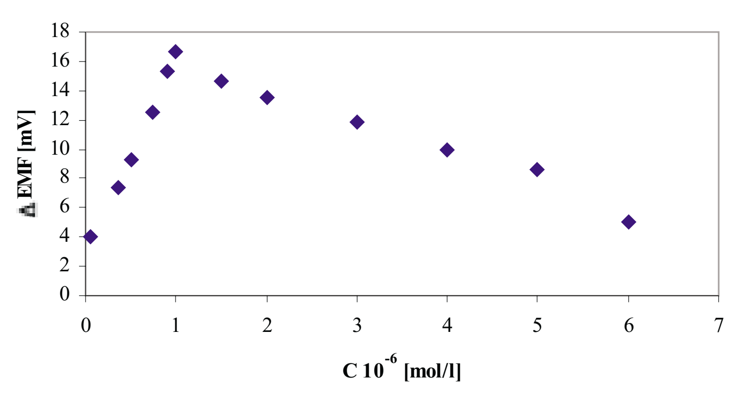

Figure 2. Dependence of potential on LAB–REINE concentration in NM.

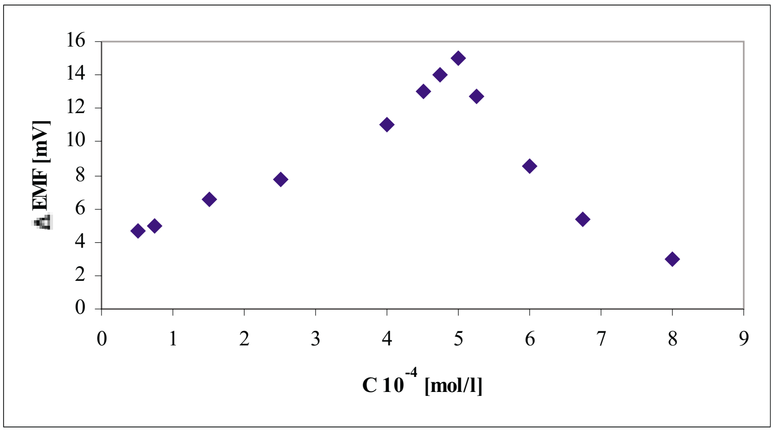

Figure 3. Dependence of potential on CV–$FeCl_4$ concentration in TCE.

The ΔEMF values, obtained for the complex at which the concentration dependence was maximal, were processed statistically to check the reproducibility. The statistical evaluation is presented in Table 3.

Spectrophotometric measurements: The spectrophotometric measurement technique and the shape of the resulting curves were the same as previously [11,12]. The measurements were made in the selected wavelength ranges, in which the absorption of the studied complex compounds was strongest; they were: 500–580 nm for

LAB–REINE complex and 620–660 nm for CV–$FeCl_4$ complex. No return to the initial absorbance value was caused by photolysis during the irradiation. The absorbance values before the irradiation and of the plateau of the curve were determined from the spectrophotometric curves and the equilibrium concentration value and the stability constants of the complexes studied were determined from these values basing on the Lambert-Beer's law. The statistical evaluation of the resulting logβ values was also done – Tables 4 and 5.

Table 1. The potentiometric results for the complex $CV^+–FeCl_4^-$ in TCE.

$C \times 10^{-6}$ [mol/l]	t_0 [s]	Δ EMF [mV]	τ [s]
6	898	4.0	92
5	878	8.5	84
4	885	10.0	73
3	845	11.3	85
2.5	948	12.0	96
2	714	13.5	92
1.5	810	14.5	86
1	888	16.9	89
0.75	894	12.5	83
0.5	742	9.2	78
0.1	856	7.4	73
0.05	872	4.0	72
			$\tau_{av} = 84$

C – initial concentration of the complex; t_0 – time of attaining of the initial potential; Δ EMF – the difference of the plateau potential and the initial potential; τ – time-constant.

Table 2. The potentiometric results for the complex $Lab^+–Rein^-$ in NM.

$C \times 10^{-4}$ [mol/l]	t_0 [s]	Δ EMF [mV]	τ [s]
0.5	388	4.8	47
0.75	330	5.3	54
1.5	345	7.0	58
2.5	378	8.0	48
4	408	11.0	52
4.5	402	13.0	62
4.75	402	14.0	64
5	396	15.1	57
5.25	400	12.8	50
6.75	420	5.2	63
8	360	3.2	67
			$\tau_{av} = 57$

Table 3. The statistic parameters of the potentiometric results of the complex Lab^+–$Rein^-$ ($C = 5 \times 10^{-4}$ mol/l).

	t_0 [s]	Δ EMF [mV]	τ [s]
1	488	14.5	57
2	372	17.5	52
3	336	11.7	56
4	402	13.5	58
5	488	13.2	52
6	402	18.0	55
7	348	16.8	58
8	360	14.3	57
9	402	15.8	55
10	450	15.6	54
		$\Delta EMF_{av} = 15.1$	$\tau_{av} = 55$
	$t_{0av} = 405$	$s = 2.01$	$s = 2.22$
		$s_{av} = 0.63$	$s_{av} = 0.70$

s – mean standard deviation of individual results; s_{av} – standard deviation of arithmetical mean.

Table 4. The results of spectrophotometric measurements for the complex Lab^+–$Rein^-$ in NM.

$C \times 10^4$ [mol/l]	A_1	ε [l cm × mol]	A_2	$[ML] \times 10^4$ [mol/l]	β	log β
7	2.413	4464	2.4	5.38	20393.84	5.309499
6	2.389	4464	2.356	5.28	101183.4	5.005109
5.5	2.324	4464	2.301	5.15	431988.4	5.635472
5	2.267	4464	2.192	4.91	6115680	6.786445
4.5	2.213	4464	2.001	4.48	147000000	8.166782
4	2.207	4464	1.768	3.96	25478926	7.406181
3.5	2.152	4464	1.547	3.47	29118772	7.464173
2.5	2.148	4464	1.108	2.48	77283000	7.888084
						$\log \beta_{av.} = 6.6$ $s = 1.43$ $s_{av} = 0.5$

C – initial concentration of the complex; A_1 – initial absorbance of the complex solution; A_2 – absorbance of the complex in equilibrium; ε – molar absorption coefficient determined as the slope of the curve $A_1 = f(C)$; [ML] – the equilibrium concentration of the complex; β – stability constant; s – mean deviation of individual results; s_{av} – standard deviation of arithmetical mean.

Table 5. The results of spectrophotometric measurements for the complex $CV^+–FeCl_4^-$ in TCE.

$C \times 10^6$ [mol/l]	A_1	ε [l/cm·mol]	A_2	$[ML] \times 10^6$ [mol/l]	$\beta \times 10^6$	log β
10	3.315	475921	3.304	6.94	0.743	5.870724
7.5	3.129	475921	3.11	6.53	7.01	6.845899
7	3.116	475921	3.08	6.47	23.2	7.365193
6	3.092	475921	2.567	5.39	14.7	7.166591
5.5	3.086	475921	2.076	4.36	3.37	6.52746
5	3.069	475921	2.056	4.32	9.34	6.970528
4.5	3.029	475921	2.015	4.23	59.8	7.776637
4	2.987	475921	1.869	3.93	739	8.868886
3.5	2.654	475921	1.62	3.40	369	8.566771
						$\log \beta_{av} = 7.3$ $s = 0.95$ $s_{av} = 0.3$

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