THE EFFECT OF SOME NITROGEN-CONTAINING BASES ON THE EXTRACTION OF COBALT WITH α-FURILMONOXIME

F.VLÁČIL and A.JEHLIČKOVÁ

Department of Analytical Chemistry,
Institute of Chemical Technology, 166 28 Prague 6

The effect of pyridine and α- and β-picoline (B) on the rate of formation of the extractable complex of α-furilmonoxime (HL) with cobalt(II) salts and on the rate of transfer of this complex into benzene was followed. Although the above nitrogen-containing compounds do affect the rate of complex formation and its extraction, only the CoL_3 complex and no $CoL_3.B_x$ adducts were found in the extract. The optimum values of the reagent and base concentrations for the extraction-photometric determination of cobalt were found.

Methods in which a stable, inner-orbital chelate of tervalent cobalt is formed (*e.g.* the acetylacetonate, 1-nitroso-2-naphtholate or 2-nitroso-1-naphtholate) are very often employed for the photometric determination of cobalt. The chelates formed resist media of rather concentrated mineral acids or hydroxides, thus differing from the complexes of numerous other metals, which decompose in these media.

α-Furilmonoxime (HL) reacts this way with cobalt(II) salts. This reaction, which was elucidated[1] as early as 1956, has so far received little attention[2]. The reaction takes place in neutral, weakly acid or weakly alkaline media, preferably in the presence of pyridine, and can be utilized for the extraction-photometric determination of cobalt.

We have studied the reaction in detail and some results have already been published[3,4]. In the present paper, the effect of pyridine and some of its homologues on the course of the complexation reaction and on the extraction of the product formed was studied.

EXPERIMENTAL

Chemicals and Instrumentation

Pyridine and α- and β-picoline were obtained from the commercial substances (p.a.) by drying over potassium hydroxide and distillation. Cobalt(II) perchlorate was prepared from p.a. cobalt(II) acetate by evaporating several times with perchloric acid and recrystallizing from water. The other chemicals employed were of p.a. purity; α-furilmonoxime was the commercial p.a. product from Lachema, Brno.

The OP-205 pH-meter (Radelkis, Budapest) with a glass electrode from the same firm and a saturated calomel electrode (Radiometer, Copenhagen) was used for the pH measurement. Spectro-

photometric measurements were performed using the Spekol instrument with an auxiliary amplifier (Zeiss, Jena) in the visible spectral region and with the Perkin-Elmer instrument (Bodensee, FRG) in the infrared region. The Varian-Techtron instrument, model AA 4 (USA) was employed for atomic absorption spectrophotometry.

The effect of additions of pyridine, α-picoline or β-picoline on the rate of complex-formation in the aqueous phase was studied in solutions containing a cobalt(II) salt, α-furilmonoxime and pyridine or a picoline. The increase in the absorbance was monitored at λ_{max} 410 nm in dependence on time; the λ_{max} value is the same in the presence of pyridine and both picolines. The HL solubility in water increases in the presence of pyridine: the solubility is 0·106 g/100 ml water[5], 0·308 g/100 ml 1M pyridine, 0·800 g/100 ml 2M pyridine and 2·275 g/100 ml 3M pyridine.

The effect of the presence of pyridine, α-picoline and β-picoline on the rate of equilibration during the extraction of the cobalt complex with HL was followed at constant concentrations of cobalt(II) perchlorate ($1 . 10^{-5}$M) and HL ($2·5 . 10^{-3}$M) and at varying concentrations of pyridine, α-picoline or β-picoline ($0-3$M) in the aqueous phase. After standing 20 min the aqueous solutions were extracted with benzene until equilibrium was established. The volume of each of the two phases was 10 ml before the extraction. The pH value of the aqueous phase varied from 8·02 to 9·33 after the extraction.

The surface tensions of the aqueous and benzene phases were determined stalagmometrically at various concentrations of pyridine and α- and β-picoline, the initial concentrations of the compounds in the aqueous phase being 0·5, 1 and 2M.

The cobalt content in the organic phase was determined spectrophotometrically from the absorbance values in the organic phase at λ_{max} 410 nm. The results obtained were verified as follows: an aliquot of the organic phase was evaporated, the residue was dissolved in methylisobutyl ketone and the content of cobalt was determined by atomic absorption spectrophotometry (an acetylene-air flame, 2407·3 Å, a spectral interval of 2 Å). The cobalt concentration was determined from a calibration graph. The validity of the Lambert–Beer law was verified in the studied concentration range.

The dependence of the logarithm of the cobalt distribution ratio on the pH during the extraction of the cobalt(II) salt into benzene in the presence of α-furilmonoxime and pyridine was determined as follows: Aqueous solutions with a constant concentration of $Co(ClO_4)_2$, $1 . 10^{-5}$M, $1 . 10^{-3} - 5 . 10^{-2}$M in HL and $1-4$M in pyridine were extracted into benzene ($V_{aq} = V_{org} = 10$ ml). The pH of the aqueous phase was adjusted before the extraction, using 0·1M-NaOH or 0·1M-HClO$_4$. After attainment of extraction equilibrium, the cobalt concentration was determined in the organic phase and the pH measured in the aqueous phase. Volume changes of the two phases, measured by separate experiments in a Bunte burette, were considered for calculation of the cobalt distribution ratio.

RESULTS AND DISCUSSION

It has been found during monitoring of the rate of the cobalt(II) salt reaction with α-furilmonoxime in the presence and absence of pyridine and during measurement of time required for establishment of extraction equilibrium that pyridine increases the reaction rate (Table I) and shortens the equilibration time (Fig. 1). Some homologues of pyridine (α- and β-picoline were tested) have a similar effect. The equilibration time in the extraction is independent of the pH in the studied range and of the time of standing before extraction, but depends on the concentration of pyridine or its homologue.

Spectrophotometry in the visible and infrared regions was employed to study the complex compositions in the given system. Measurements in the IR region were performed in chloroform and in the visible region in benzene. The infrared spectrum of an extract containing CoL_3 and HL (ref.[3]) differs from that containing HL alone. New bands appeared in the spectrum (860, 960, 1430 and 1510 cm^{-1}) and the intensity of the C=O band in the HL spectrum is very small in the spectrum of CoL_3 - containing extract compared to the other HL bands. The bands at 3300 and 3500 cm^{-1}, corresponding to the OH group, disappeared almost entirely. From these changes it can be concluded that the central atom is bound in a chelate ring through C=O and OH groups and consequently it can be assumed that the extract contains the complex with the formula

I
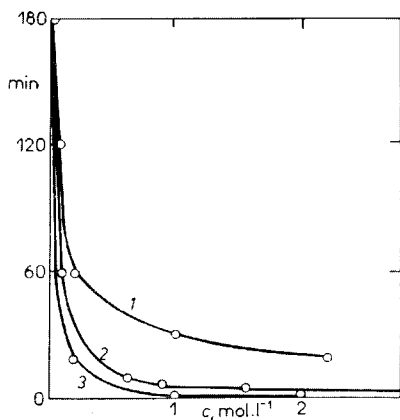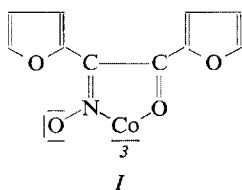
FIG. 1

The Dependence of the Time Required for Establishment of Extraction Equilibrium on the Base Concentration

1 α-Picoline, 2 pyridine, 3 β-picoline. $c(Co) = 1 . 10^{-5}$M, $c(HL) = 2.5 . 10^{-3}$M, pH 8·02—9·33; extracted with benzene.
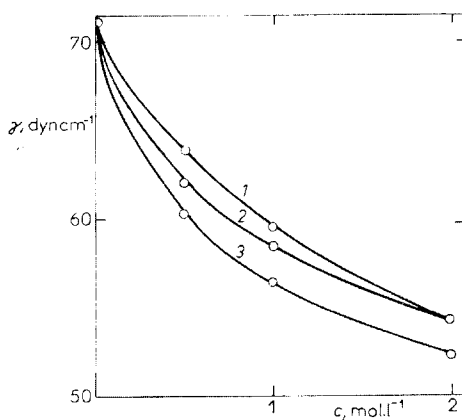
FIG. 2

The Dependence of the Aqueous Phase Surface Tension on the Initial Base Concentration

1 Pyridine, 2 α-picoline, 3 β-picoline.

The visible and IR spectra of the complex obtained by the extraction of the aqueous phase containing cobalt(II) perchlorate, HL and pyridine were measured. In addition to the complex, the extract contained free HL and pyridine. These spectra were compared with those for the extract obtained in the absence of pyridine. The two absorption curves are identical in the region from 370 to 750 nm. The IR spectra taken in the presence of pyridine differ from those obtained in its absence in the absorption bands corresponding to free pyridine. However, the band shift from 1578 cm^{-1} to 1600 cm^{-1} for coordinated pyridine[6] should be readily perceptible even in this rather complex spectrum. This shift was not observed in the spectrum. Therefore, the results of the spectral measurements in the visible and IR regions indicate that an extractable ternary complex with pyridine coordinated to the central atom (CoL_3B_x) is not formed and that the same complex, CoL_3, is extracted both in the presence and in the absence of pyridine.

However, the physical properties of the two phases between which the nitrogen-containing bases are distributed are affected by the presence of pyridine, α- and β-picoline. The dependence between the shortening of the equilibration time in the extraction and the dipole moments of pyridine, α- and β-picoline is interesting. The extraction equilibration time shortens in the order: water > α-picoline > pyridine > > β-picoline. The dipole moment increases in the same order: water < α-picoline < < pyridine < β-picoline. The highest acceleration of the extraction was achieved in the presence of β-picoline, where the equilibrium established 90 times faster than

TABLE I

The Time Required for Attainment of the Maximum Colouration of the Solutions (t)
$c(Co(ClO_4)_2) = 1 . 10^{-5} M$, $c(HL) = 2.5 . 10^{-3} M$.

$c(B)$, M	pH	t, min	$c(B)$, M	pH	t, min
	pyridine			α-picoline	
1	8·58	22	1	8·20	22
1	8·59	25	2	8·15	20
2	8·86	22		β-picoline	
2	8·05	21			
3	7·52	20	0·5	8·65	10
3	8·04	12[a]	1	8·90	12
3	8·69	11[a]		no base added	
			—	9·07	180

[a] $c(HL) = 2.5 . 10^{-2} M$.

in water (Table II). However, nitrogen-containing substances do not hasten the extraction due to the effect of their dipole moment alone, since a similar acceleration was not observed during extraction from aqueous media containing acetone ($p = 2\cdot74$) or ethanol ($p = 1\cdot70$).

On addition of pyridine, α- and β-picoline, the surface tension of the aqueous phase decreases. Although the shapes of the curves representing the dependence between the initial concentration of the bases in the aqueous phase (before extraction) and the surface tension of the phase (Fig. 2) resemble the curves of the extraction equilibration time dependence on the base concentration (Fig. 1), a different order of surface tension magnitudes (pyridine > α-piccline > β-picoline) was found from the extraction rate order (β-picoline > pyridine > α-picoline) at the given organic base concentration. Hence the surface tension of the aqueous phase is also not the decisive factor for the extraction equilibrium rate.

The dependences of log D on pH were also determined for various concentrations of pyridine and HL. The number of protons liberated during the reaction cannot be assessed from the ascending parts of the extraction curves at low pH values, since pH variations are buffered in the aqueous phase by the pyridine present. It is evident from comparison of the extraction curves that the D_{nax} value decreases with increasing pyridine concentration and thus that it is always smaller than for the extraction in the absence of pyridine[3]. The distribution ratio remains, in a wider or narrower pH interval depending on the concentrations, at a maximum value and then decreases (Figs 3 and 4).

From analysis of the experimental log $D = f(pH)$ curves, obtained during the extraction of cobalt into benzene in the presence of HL and pyridine, suitable conditions for the extraction-photometric determination of cobalt can be derived, i.e. the widest possible pH range in which the D value is constant can be found. This range widens

TABLE II

The Time Required for the Establishment of Extraction Equilibrium (t)
$c(B)_{aq} = 0\cdot5M$.

B	t, min	Dipole moment, p
—	180	$1\cdot84^{a}$
α-Picoline	43	$1\cdot97$
Pyridine	13	$2\cdot20$
β-Picoline	2	$2\cdot40$

^{a} Dipole moment of water.

with increasing HL concentration (Fig. 3) and depends on the pyridine concentration (Fig. 4). The D_{max} value is attained in a narrow pH range (about 0·5 unit) at an HL concentration of $5 . 10^{-3}$M and pyridine concentration of 1M and this interval is perceptibly wider at a pyridine concentration of 2M (one unit). A wider interval in which D is practically independent of the pH is advantageous in the extraction-photometric determination of cobalt with this reagent, since the error of the determination arising from incorrect pH adjustment of the analyzed solution is thus decreased. On an increase in the pyridine concentration, the extraction recovery decreases, which can partially be compensated for by increasing the HL concentration.

In order to attain a suitable extraction recovery with a cobalt distribution ratio which is not too dependent on the pH, the concentrations employed should be $c(HL)_{aq} \geqq 3 . 10^{-2}$M and c (pyridine)$_{aq} = 2-3$M. The recommended reagent concentration is substantially lower than used previously[1]. Although a decrease in the concentration leads to a lower recovery for the cobalt extraction at a certain pH, the limit of determination of the extraction-photometric determination of cobalt with this reagent is as low as 0·1 p.p.m. with a single extraction[7].

FIG. 3
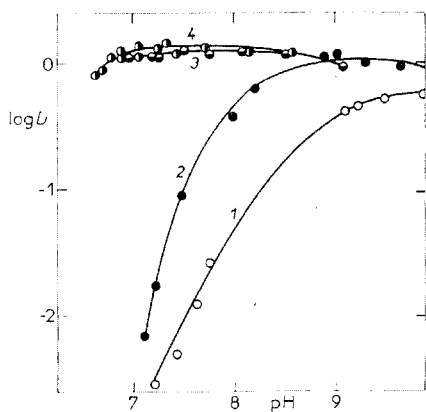
The log D vs pH Dependence for the Cobalt Extraction into Benzene, in the Presence of α-Furilmonoxime and Pyridine

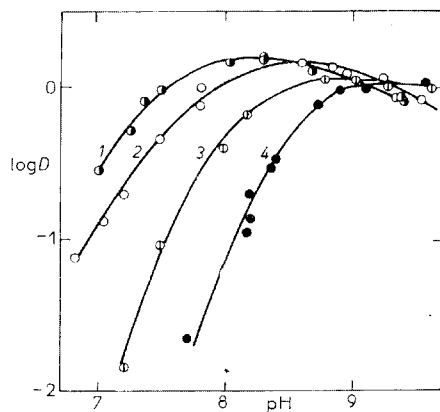$c(Co) = 1 . 10^{-5}$M, c(pyridine) $= 2$M, c(HL): 1 $1 . 10^{-3}$M, 2 $5 . 10^{-3}$M, 3 $3 . 10^{-2}$ M, 4 $5 . 10^{-2}$M.

FIG. 4

The log D vs pH Dependence for the Cobalt Extraction into Benzene, in the Presence of α-Furilmonoxime and Pyridine

$c(Co) = 1 . 10^{-5}$M, c(HL) $= 5 . 10^{-3}$M, c(pyridine): 1 1M, 2 1·5M, 3 2M, 4 3M.

REFERENCES

1. Martínek J., Hovorka V.: Chem. listy *50*, 1450 (1956).
2. Džafar A. R., Astachova E. K., Peškova V. M.: Vestn. Mosk. Univ. *1*, 65 (1966).
3. Jehličková A., Vláčil F.: This Journal *38*, 1027 (1973).
4. Jehličková A., Vláčil F.: This Journal *38*, 3395 (1973).
5. Šlenskaja V. I., Birjukov A. A., Tichuinskaja T. J., Voronina L. N.: Ž. Neorg. Chim *14*, 3331 (1969).
6. Gill N. S., Nutall R. H., Scaife D. E., Sharp D. W. A.: J. Inorg. Nucl. Chem. *18*, 79 (1961).
7. Vláčil F., Jehličková A.: Unpublished results.

Translated by M. Štulíková.