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## Solvent Extraction of Vanadium (V) with *N*-Benzoyl-*N*-phenylhydroxylamine

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*N*-Benzoyl-*N*-phenylhydroxylamine is a monomeric solute in chloroform which readily extracts  $\text{VO}_2^+$  from acidic aqueous solutions. The vanadium species extracted from concentrated aqueous acid solutions have a characteristic absorption band at 450–550 m $\mu$ . Solvent extraction experiments indicate that from aqueous 1–6 *N* HCl two vanadium species are extracted into chloroform. The compositions of these species correspond to the reagent: vanadium: chloride ratios of 2:1:1 and 3:1:1.

The reaction of vanadium(V) with *N*-benzoyl-*N*-phenylhydroxylamine (BPH), firstly reported by Shome<sup>1</sup>, is interesting from many aspects. One of its peculiarities is that colored vanadium complexes are formed in very acidic aqueous solutions, up to 7 *N* HCl. The complexes are readily dissolved in organic solvents, especially in chloroform, where they show characteristic absorption spectra. This makes the basis of a highly specific method for vanadium determination<sup>2</sup>, and also serves for the separation of vanadium from diverse ions<sup>3</sup>. However, little is known about the nature of this reaction. Beside some absorption spectra in chloroform reported by Ryan<sup>2</sup> and Priyadarshini and Tandon<sup>3</sup>, the only important information seems to be that of Montequi<sup>4</sup> who isolated from an acetone solution a compound (or a mixture of compounds) containing  $\text{VO}_2^+$ , HCl and BPH in the ratio 1:1:2.

The present work investigates the reaction of vanadium with BPH by studying the distribution equilibrium between an aqueous and an organic phase, combined with the spectrophotometric study of the organic phase. The main purpose of the investigation is to obtain more information on the complex compounds formed and extracted into chloroform.

### EXPERIMENTAL

*N*-Benzoyl-*N*-phenylhydroxylamine (BPH) was a reagent grade product of Merck. It was used without further purification.

Standard vanadium solutions were made from  $\text{V}_2\text{O}_5$  obtained by calcination of reagent grade  $\text{NH}_4\text{VO}_3$  (Merck). The pentoxide was dissolved in dilute NaOH and the solution standardized against 0.1 *N*  $\text{KMnO}_4$ .

Chloroform, reagent grade (Merck), was purified by washing with dilute NaOH and  $\text{H}_2\text{SO}_4$  solutions, followed by water. (It is essential to remove the traces of alcohol.)

Vanadium was determined in aqueous solutions by the phosphotungstic spectrophotometric method<sup>5</sup>, and in organic solutions by the method of Ryan<sup>2</sup>.

Absorption spectra were recorded with a Beckman DU spectrophotometer and a Zeiss Model UR-10 infrared spectrophotometer.

The equilibration of aqueous and chloroform solutions was done in separatory funnels at room temperature. Chloroform solutions of BPH, pre-saturated with aqueous HCl solutions, were usually shaken with an aqueous solution of known vanadium and HCl concentration.

From the data of Rossotti and Rossotti<sup>6</sup> and Igrj and Brito<sup>7</sup> it was deduced that in the range of aqueous acid concentration 0.04–4 *N* (used in the present work), at total metal concentrations up to  $10^{-3}$  *M*, vanadium is mainly present in the form of monomeric  $\text{VO}_2^+$   $\times$  aq.

## RESULTS AND DISCUSSION

### *BPH in Chloroform Solution*

The characteristic behavior of BPH in chloroform was investigated spectrophotometrically in the UV and IR region. At 273  $\text{m}\mu$  a maximum in the absorption band was noticed, the molar absorption coefficient being  $7.6 \times 10^3$ . At 273  $\text{m}\mu$  Beer's law is valid. The acid dissociation constant of BPH in aqueous solution is  $8.15^8$ , and the aqueous solubility at room temperature is about  $2 \times 10^{-3}$  *M*. The distribution coefficient of BPH between a chloroform and an aqueous 2.8 *N* HCl solution is  $1.29 \times 10^2$ . BPH in chloroform does not extract HCl, although, with the vanadium complex of BPH, mineral acid is usually coextracted as will be shown later.

The BPH reagent is capable of forming hydrogen bonds which can, in principle, lead to a strong self-association in non-polar organic solvents. On the other hand, the CO–N(OH) — grouping is ideally suited to form an internal (intramolecular) hydrogen bond, in which case probably no self-association will take place. As the behavior of BPH, in this respect, is of great importance for solvent extraction of vanadium, IR absorption studies were made to solve this problem. Two absorption bands were noticed, at  $3070 \text{ cm}^{-1}$  and  $3250 \text{ cm}^{-1}$ . The former was assigned to C–H stretching, and the latter to an intramolecular hydrogen bond<sup>9</sup>. It is concluded that owing to the intramolecular hydrogen bond, BPH is monomeric in the organic solvent.

### *Absorption Spectra of BPH-Vanadium Complexes*

Vanadium is readily extracted from mineral acid solutions, but the absorption spectrum of the chloroform solution depends on the kind of acid (Fig. 1a) and its concentration in the aqueous phase<sup>3</sup>. This suggests that mineral acid is coextracted. The absorption spectra of the organic phase in dependence on the vanadium/BPH ratio is shown in Fig. 1b.

The dependence of the absorbance of the organic phase on the concentration of aqueous HCl solution is shown in Fig. 2. Between 1.5 and up to 6.5 *N* HCl, the absorbance at the 530  $\text{m}\mu$  is constant, which indicates a constant composition of the organic phase. However, at lower aqueous acidity (for example, at 0.2 *N* HCl) the absorption spectrum of the chloroform extract is rather different. This can be easily observed visually: the extract from 0.2 *N* HCl has an orange color while that from 1–5 *N* HCl is violet. Obviously, at lower acidity the vanadium species differ from those formed in the acidity range 1.5–6.5 *N*. Beer's law is valid at 530  $\text{m}\mu$  in chloroform solutions as shown in Fig. 3.

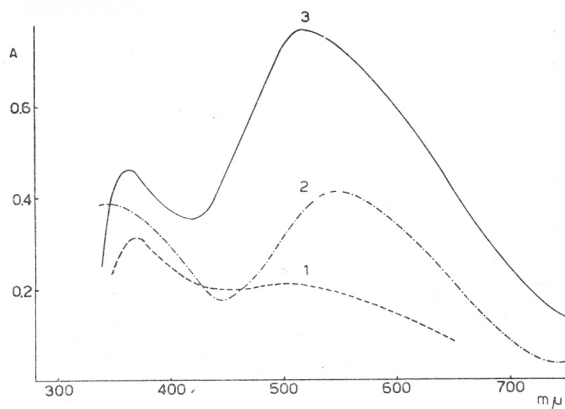


Fig. 1a. Absorption spectra of the organic phase containing 0.05 M BPH after equilibration with  $2 \times 10^{-4}$  M vanadium in 21 N  $H_2SO_4$  (curve 1) and in 1.7 N HBr (curve 2),  $5 \cdot 10^{-4}$  M vanadium in 7.5 N  $HClO_4$  (curve 3).

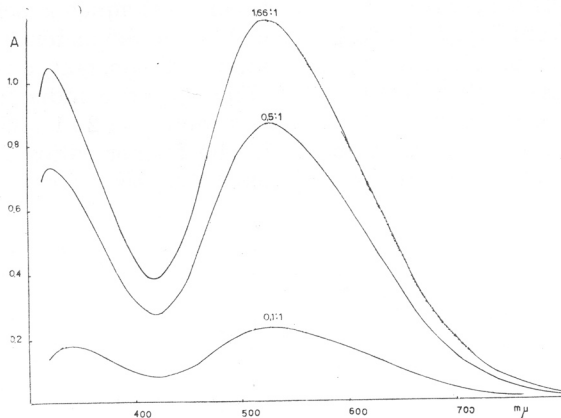


Fig. 1b. Absorption spectra of the organic solvent for various vanadium/BPH ratios in the aqueous phase. Constant aqueous HCl concentration 2.8 N.

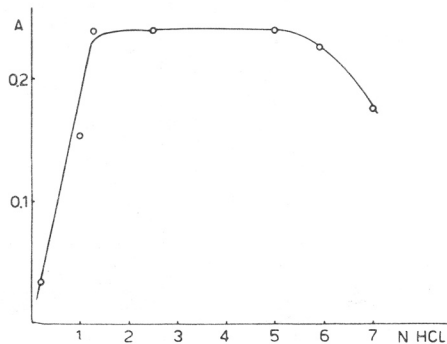


Fig. 2. Absorbance ( $530 \text{ m}\mu$ ) of the organic solvent containing  $5 \times 10^{-5}$  M  $VO_2^+$  + 0.1 M BPH as a function of aqueous HCl concentration.

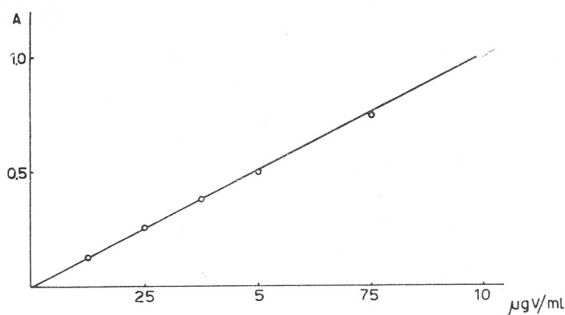


Fig. 3. Validity of Beer's law.  $5 \times 10^{-3}$  M BPH in chloroform in equilibrium with aqueous 4 N HCl solution.

### Solvent Extraction of Vanadium

Fig. 4 shows, in a log-log scale, the dependence of the extraction coefficient,  $D$ , on the free BPH concentration,  $C_{\text{BPH}}$ , at constant aqueous acidity. The slopes are above two. From Fig. 5 it can be seen that the dependence of  $\log D$  on the logarithm of aqueous chloride concentration, at constant organic BPH concentration, is linear with a slope of one. Figs. 4 and 5 indicate that the BPH:vanadium ratios in the extracted complexes might be 2:1 and 3:1, while the vanadium chloride ratio seems to be 1:1. The former ratios are supported by a two-phase method of continuous variation<sup>10-12</sup> (Job's method applied to a two

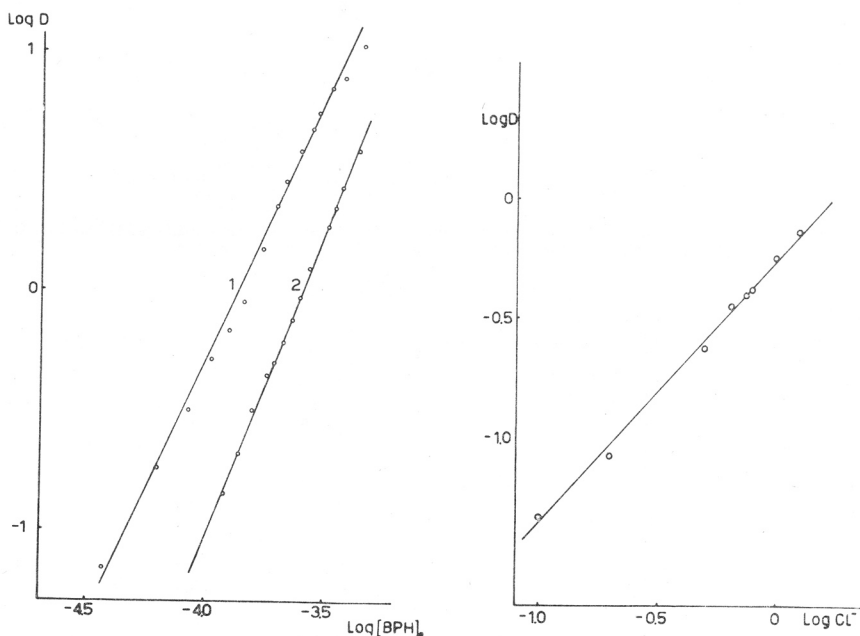


Fig. 4. Extraction coefficient ( $D$ ) vs. free BPH concentration in organic phase (log-log scale). Curve 1: 4 N HCl in aqueous phase, slope of the line: 2.2. Curve 2: 2.2 N HCl, slope 2.5.

Fig. 5. Extraction coefficient  $D$  vs. aqueous  $\text{Cl}^-$  concentration (log-log scale), at constant organic BPH conc. of  $2 \times 10^{-2}$  M. Constant ionic strength  $\mu = 3$  ( $\text{HClO}_4 + \text{HCl}$ ).

phase system), as seen in Fig. 6. Both curves in this figure have a maximum of absorption at an abscissa value between 0.27—0.35, which corresponds to BPH/vanadium ratios between 2 : 1 and 3 : 1. The two-phase method of mol-fraction, Fig. 7, also shows characteristic bendings between BPH/ $\text{VO}_2^+$  ratios of 2 : 1 and 3 : 1, in agreement with the slopes of Fig. 5 which are above two.

### Composition and Stability of the Complexes

The data given in Figs. 4, 5, 6 and 7 suggest that the basic complex extracted from 1.5—6.5 N HCl has a BPH : vanadium : HCl ratio of 2 : 1 : 1. An additional compound having a composition of 3 : 1 : 1 also seems to be present. The bluish-violet color and the shape of the spectra of the organic phase indicate a higher valency state of vanadium, but it is questionable whether vanadium in the chloroform solutions remains quinquevalent. To get more information, we have tried to extract V(IV) as  $\text{VO}(\text{SO}_4) \times \text{H}_2\text{O}$  from HCl solutions. It turned out that quadrivalent vanadium is not at all extracted

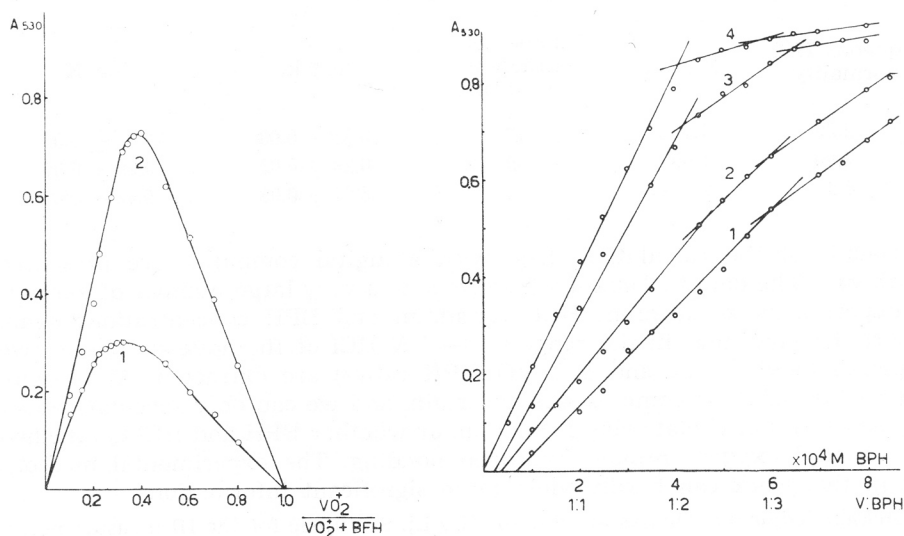


Fig. 6. Two-phase continuous variation curves. Total  $\text{VO}_2^+ + \text{BPH}$  in the two-phase system  $1 \times 10^{-3}$  M. Curve 1: 2.29 N HCl; curve 2: 6.6 N HCl.

Fig. 7. Two-phase method of mol-fractions: curve 1: 2.2 N HCl; curve 2: 2.8 N HCl; curve 3: 4.0 N HCl; curve 4: 5.3 N HCl.

except, at very high acidity, above 9 M HCl, and even then the absorption spectrum in chloroform differs from the spectra in Fig. 1. However, recently a quadrivalent complex of vanadium,  $\text{VO}(\text{BPH})_2\text{Cl}$  was isolated<sup>14</sup>, which might suggest that vanadium, at least in the organic phase, is quadrivalent.

BPH is a typical bidentate chelating agent and, in principle, may form one or two chelate rings with  $\text{VO}_2^+$ . These compounds can hardly be stable in aqueous solutions of 1—6 N HCl, but they might be stable in the chloroform extract. We have tried a quantitative treatment of the extraction data at

three constant acidities (2.20, 2.80 and 4.05 N HCl) assuming that formally the reaction



takes place. An analysis of the data has shown that such an interpretation is not satisfactory, and that in addition to the above reaction, the formation of an adduct compound must be assumed:



If the equilibrium constants for the two reactions are denoted  $k_1$  and  $k_2$ , and the over-all constant  $K = k_1 k_2$ , if the activity coefficients in the organic phase are neglected and, as a crude approximation, the mean molar activity coefficients for HCl are taken instead of the coefficients for  $\text{VO}_2\text{Cl}$ , the results presented in Table I are obtained.

TABLE I  
Equilibrium Constants

Aqueous HCl normality	$\gamma_{\pm\text{HCl}}$	Number of extraction experiments	$\log k_1$	$\log K$
2.20	1.172	17	$6.33 \pm 0.03$	$10.0 \pm 0.03$
2.80	1.407	49	$6.28 \pm 0.03$	$9.98 \pm 0.05$
4.05	2.322	21	$6.27 \pm 0.03$	$9.48 \pm 0.05$

Details of the calculation done with a digital computer, are presented elsewhere<sup>13</sup>. The data in Table I which refer to a very large number of extraction experiments at different HCl, vanadium and BPH concentrations again support the view that in the range of 1—6 N HCl of the aqueous phase, two complexes (having 1:2 and 1:3  $\text{VO}_2/\text{BPH}$  ratios) are extracted. At present, the structure of these complexes is uncertain, and we can only speculate about the possibilities of chelate ring formation, or whether BPH and HCl is attached to a vanadyl oxygen through hydrogen bonding. The experimental methods used in this work can hardly yield more significant information.

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### IZVOD

#### Ekstrakcija vanadijuma (V) *N*-benzoil-*N*-fenilhidroksilaminom

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*N*-benzoil-*N*-fenilhidroksilamin je monomerni rastvorak u hloroformu koji lako ekstrahuje  $\text{VO}_2^+$  iz kiselih vodenih rastvora. Ekstrahovane vrste vanadijuma iz jako kiselih vodenih rastvora imaju karakterističnu apsorpcionu traku na 450—550 m $\mu$ . Eksperimenti ekstrakcije rastvaračima pokazuju da se iz 1—6 *N* HCl hloroformom ekstrahuju dve vrste kompleksa vanadijuma. Sastav ovih vrsta odgovara odnosu reagens:vanadijum:hlorid 2:1:1 i 3:1:1.

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