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Physical Properties of 2-Carbethoxy-5-hydroxy-1-(4-tolyl)-4-pyridone — a New Extractant for Metals

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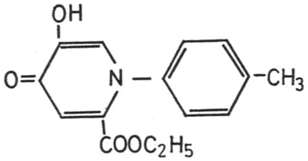
Physical properties of 2-carbethoxy-5-hydroxy-1-(4-tolyl)-4-pyridone (HA) are described and discussed. Molecular weight determination showed that this reagent is a monomer in chloroform solution. The UV absorption spectra of HA dissolved in water at various *p*H values were recorded. The ionization constant of HA was determined spectrophotometrically and by potentiometric titration. The distribution of the reagent between chloroform and 1 *M* aqueous perchlorate solution has been determined spectrophotometrically.

INTRODUCTION

It has been reported that 2-carbethoxy-5-hydroxy-1-(4-tolyl)-4-pyridone (HA) appears to be very suitable as a selective extractant for certain metals[1,2]. In order to explain the extraction mechanisms it was important to determine the physical characteristics of this reagent.



Therefore, we determined its molecular weight, ionisation constant and its distribution between $CHCl_3$ and aqueous phase.

EXPERIMENTAL

Materials and Methods

The synthesis of HA has already been described[3]. Reagent grade chemicals were used for all analytical measurements. In these studies the solutions of HA in chloroform served as the organic phase. All experimental procedures are the same as described in our previous paper[5]. A Beckman Spectrophotomer model DU-2 was used for spectrophotometric measurements.

RESULTS AND DISCUSSION

Determination of the Molecular Weight of the Reagent

The determination of molecular weight has been performed by the modified Signer's method[4]. Pentaacetyl glucose was used as a standard solute. Both pentaacetyl glucose and HA were dissolved in $CHCl_3$ and the change in volume of $CHCl_3$ was followed until equilibrium was attained. The molecular weight obtained, 276.2, is in good agreement with the formula weight, 273.3, indicating that the reagent is monomeric in chloroform solution.

Determination of the Ionisation Constant of HA

The ionisation constant of HA was determined by two methods, spectrophotometrically and by potentiometric titration.

Since the extinction of the reagent depends on the *p*H of the solution, it was possible to determine the ionisation constant of HA spectrophotometrically. The biggest difference in the extinction of the molecular and ionized form has been found at 250 nm (Fig. 1). Therefore this wavelength was chosen for maesurements. Series of solutions with various *pH* values have been prepared and the extinctions were recorded. The phosphate buffer was applied to control the *p*H. The *p*K values are presented in Table I and they were calculated according to the equation:

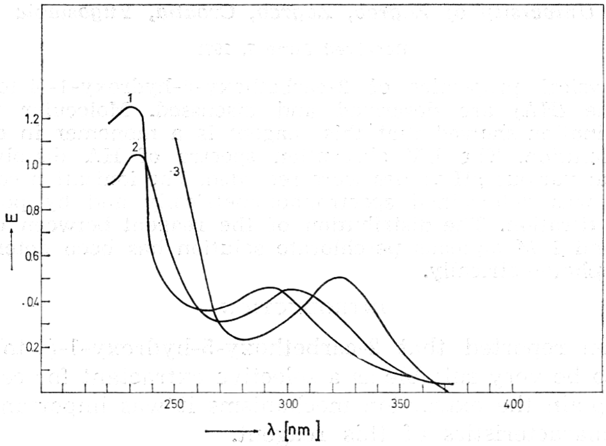


Fig. 1. Ultraviolet absorption spectra of 5×10^{-5} *M* HA solution in: 1-0.1 *M* HCl; 2-0.1 *M* NaOH and 3- in solution at *p*H = 6.9.

$$pK = pH + \log \frac{E_A - E}{E - E_M}$$

where E_A represents the extinction of the ionic form of the reagent (obtained in 0.1 *M* NaOH), E_M the extinction of the molecular form (in 0.1 *M* HCl) and E the extinction obtained at given *p*H.

The ionization constant of HA was also determined by potentiometric titration. For this measurements a 0.01 *M* solution of reagent in 50% ethanol was prepared since the solubility of the reagent in water is low. This solution was titrated with a 0.1 *M* aqueous sodium hydroxide solution. The *p*K values were calculated according to the following equation:

$$pK_{HA} = pH + \log \frac{[HA]}{[A^-]}$$

and are given in Table II.

TABLE I

Determination of pK_{HA} *by the Spectrophotometric Method*

Concn. of HA = 5×10^{-5} *M*, λ = 250 nm, $E_A = 0.900$ (in 0.1 *M* NaOH) $E_M = 0.258$ (in 0.1 *M* HCl)

pH	E	$\log \frac{E_A - E}{E - E_M}$	pK_{HA}
6.934	0.412	+ 0.501	7.44
7.237	0.507	+ 0.197	7.43
7.370	0.544	+ 0.091	7.46
7.538	0.593	— 0.039	7.49
7.652	0.642	— 0.173	7.48
7.844	0.712	— 0.384	7.46
7.901	0.729	— 0.439	7.46

Mean 7.46 ± 0.03

TABLE II

Titration of 0.01 M *HA in 50 per cent Ethanol with 0.1* M *NaOH*

ml NaOH	pH	[HA]	$[A^-]$	pK_{HA}
0.25	5.466	0.0087	0.0012	8.58
0.50	8.080	0.0075	0.0023	8.59
0.75	8.286	0.0062	0.0034	8.55
1.00	8.494	0.0050	0.0045	8.54
1.25	8.688	0.0039	0.0055	8.54
1.50	8.876	0.0027	0.0066	8.49
1.60	8.967	0.0023	0.0070	8.48
1.70	9.083	0.0018	0.0074	8.47
1.80	9.215	0.0014	0.0078	8.47

Mean 8.53 ± 0.06

The obtained value is higher by about 1 *p*K unit from the value obtained by the spectrophotometric method. It is well known that in alcoholic solution the ionisation of both acids and bases is decreased, and in 50% ethanol the *p*K of an acid will raise by roughly 1 *p*K unit[5,6]. Taking this into account the results obtained for the pK_{HA} values are in reasonable agreement.

Distribution of HA between Chloroform and 1 M *Aqueous Perchlorate Solution*

The partition K_d of the reagent between chloroform and 1 *M* aqueous perchlorate solution was determined at constant ionic strength (0.1 *M* $HClO_4$ + + 0.9 *M* $NaClO_4$). The concentration of HA in the aqueous phase was measured spectrophotometrically. The standard curve was established previously by plotting the extinction against the HA concentrations. These measurements were made at 305 nm. As the solutions of HA in the concentration range used obey the Lambert-Beer's law straight line was obtained. Prior to the distribution measurements an aqueous perchlorate solution was saturated with chloroform, and then equilibrated for 1 hr with an equal volume of the HA solution in chloroform. Three different concentrations of HA were used, and the K_d values obtained are listed in Table III. The results show that K_d does not depend on the concentration of HA in the concentration range examined.

TABLE III

The Distribution of HA between Chloroform and 1 M *Aqueous Perchlorate Solution (0.1* M *$HClO_4$ + 0.9* M *$NaClO_4$)*

Initial HA concentration in $CHCl_3$	HA found (γ/10 ml) in		K_d	log K_d
	chloroform	aqueous phase		
1×10^{-3} M	2727.2	5.7	478.45	2.68
,,	2727.2	5.7	478.45	2.68
,,	2726.9	6.0	454.48	2.66
3×10^{-3} M	8181.2	17.5	467.50	2.67
,,	8180.9	17.8	459.60	2.66
,,	8180.4	18.3	447.00	2.65
5×10^{-3} M	13635.5	29.0	470.20	2.67
,,	13636.2	28.3	481.90	2.68
,,	13635	28.7	475.07	2.68

Mean 2.67 ± 0.05

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IZVOD

Fizikalna svojstva 2-karbetoksi-5-hidroksi-1-(4-tolil)-4-piridona, novog ekstraktanta za metale

M. Janko i M. J. Herak

Opisane su neke fizikalne karakteristike novog ekstraktanta 2-karbetoksi-5-hidroksi-1-(4-tolil)-4-piridona (HA). Određivanjem molekulske težine utvrđeno je da se HA otopljen u kloroformu nalazi u monomernom obliku. Snimljeni su uv. spektri vodenih otopina reagensa pri različitim *p*H vrijednostima. Rezultati pokazuju da postoji znatna ovisnost apsorpcije svjetla o *p*H otopine. Određena je konstanta ionizacije HA spektrofotometrijski i potenciometrijskom titracijom. Određena je podjela HA između kloroforma i 1 *M* perkloratne otopine. Koncentracija HA u vodenoj fazi određena je spektrofotometrijski.

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