

## ACIDOBASIC EQUILIBRIA IN 9-(3'-PYRIDYL)-2,6,7-TRIHYDROXY-3H-XANTHENE-3-ONE SOLUTIONS IN THE PRESENCE OF SURFACTANTS

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The effects of the cationic tenside Septonex and the non-ionic tenside polyvinylpyrrolidone on the acidobasic and spectral properties of 3-pyridylfluorone have been studied. Data for the dependence  $A = f(\text{pH}^*)$  were used to calculate protonization constants and molar absorption coefficients of the various acidobasic forms of 3-pyridylfluorone in solution with  $c(\text{Septonex}) = 5 \text{ mmol l}^{-1}$  or  $\rho(\text{polyvinylpyrrolidone}) = 1 \text{ g l}^{-1}$  in 10% (v/v) methanol adjusted by sodium chloride to an ionic strength 1.0. The results are compared with protonization constants of the reagent in solutions of the same ionic strengths and methanol concentrations but without a surfactant. The effects of the tensides on the shape of absorption spectra of the various acidobasic forms of the reagent are also discussed.

9-(3'-Pyridyl)-2,6,7-trihydroxy-3H-xanthene-3-one (3-pyridylfluorone) is one of the fluorone derivatives which are used in determinations of many ions<sup>1</sup>. Since the reagents and their colour complexes are sparingly soluble in water, mixed solvents (most frequently water-alcohol) are used. In most cases, the solution must be stabilized by the addition of a solubilizing agent such as polyvinylpyrrolidone, polyvinyl alcohol, gelatine, sodium n-dodecyl sulphate, and hexadecyltrimethylammonium bromide<sup>1-3</sup>. Spectral studies of these solutions have shown that surfactants frequently affect not only the intensity of absorption bands, but also cause shifts in absorption maxima of the reagents and their complexes. These phenomena enhance the sensitivity of spectrophotometric methods and improve their limits of detection<sup>2,4</sup>.

The synthesis<sup>5</sup> and purification<sup>6</sup> of 3-pyridylfluorone have been described elsewhere. Fogl and Vrbský<sup>7</sup> have studied acidobasic properties of all the three pyridylfluorone isomers in 10% (v/v) methanol solutions with 1.0 (NaCl) in the absence of any surfactant. They proposed<sup>8</sup> to stabilize the complex formed in the determination of cupric ions by 2-pyridylfluorone with polyvinylpyrrolidone, a high-molecular non-ionic tenside, in a concentration of  $1 \text{ g l}^{-1}$ . Solutions of polyvinylpyrrolidone ( $\rho = 1$  to  $2.5 \text{ g l}^{-1}$ ) have also been used in studies of the complexing reactions of 3-pyridylfluorone with some lanthanoids<sup>9,10</sup>. Small changes in the tenside con-

centration were found to have virtually no effect on the formation of the lanthanoid complexes.

Nazarenko and his co-workers<sup>1</sup> have studied complexing reactions of fluorones with metal ions and found that an  $H^+$  ion is liberated from the fluorone molecule, so that the first anionic form of the reagent is the complexing species. Multivalent metal ions bind more ligands, according to the coordination number of the central ion. The ligands may be additional fluorone molecules,  $OH^-$ ,  $Cl^-$  or molecules with a lone electron pair such as antipyrine and phenanthroline. No evidence has so far been found for the formation of mixed ligand complexes of the type fluorone–metal ion–tenside. One must also take into consideration that an increase in the tenside concentration may result in increased reflection and scattering of the radiation on the colloid particles. It has been observed that the addition of a tenside to an already formed complex does not prevent rapid precipitation of the complex from the solution<sup>11</sup>, even if the tenside is added immediately after the complex formation, i.e. to the still clear solution. The tenside must be present in the solution before the complex is formed, and it must be there in sufficient concentration for the mixed ligand complex fluorone–metal ion–tenside to be formed. A further increase in the tenside concentration may affect the stepwise formation of the ternary complexes or may lead to a change in the character of the colloid particles revealed by a change in the spectral properties of the resulting isotropic solution.

To explain – at least partly – the above phenomena, we need to know acidobasic equilibria of the reagent in a solution of precisely defined composition. The surfactants most frequently used (gelatine, polyvinyl alcohol) do not meet this requirement. Therefore, we have chosen Septonex (1-ethoxycarbonylpentadecyltrimethylammonium bromide), a cationic tenside available in sufficient purity, whose concentration can be expressed precisely. For comparison, the acidobasic equilibria have also been studied in a solution containing a non-ionic tenside, polyvinylpyrrolidone, of known relative molecular weight.

The critical micellar concentration of Septonex has been quoted<sup>12,13</sup> as ranging between  $0.77$  and  $1.6 \text{ mmol l}^{-1}$  ( $I \approx 0$ ), and as  $c_k \approx 0.1 \text{ mmol l}^{-1}$  in  $0.1$  to  $0.3M$ - $NaCl$ . In the present work, we used  $c_T = 5 \text{ mmol l}^{-1}$ , i.e.  $c_T \gg c_k$ , in order to ensure the existence of micelles in solution and to prevent association between the reagent and the tenside resulting in the formation of sparingly soluble ionic species<sup>14</sup>. Polyvinylpyrrolidone was added to the concentration  $1 \text{ g l}^{-1}$  commonly used to stabilize metal complexes of fluorone in solution.

The aim of the present work was to investigate the effects of Septonex and polyvinylpyrrolidone on acidobasic equilibria and spectral properties of 3-pyridylfluorone solutions, and the effect of the ionic strength of the solution on the properties of the reagent. The kind of strong electrolyte and its concentration were the same as in a previous work<sup>7</sup>, as were the conditions of the measurements and the method of determining the protonization constants.

## EXPERIMENTAL

## Chemicals and Instruments

A solution of 3-pyridylfluorone (3-PF) of a concentration of  $1 \text{ mmol l}^{-1}$  was prepared by dissolving 0.3213 g of 3-PF in 200 ml of methanol (analytical grade), adding 4 ml of 5M-HCl, and making up to 1 l with methanol. Solutions of lower concentrations were obtained by diluting this solution with methanol. When stored in the dark, the stock solution is stable for several months. A 0.05M-Septonex (SPX) solution was prepared by dissolving 2.1125 g of the substance (Slovakofarma Hlohovec, ČSL 3, Czechoslovakia) in 100 ml of deionized water. The solution was stable for two to three days. A polyvinylpyrrolidone (PVP) solution of a concentration of  $10 \text{ g l}^{-1}$  was prepared by dissolving Luviskol K 90 (BASF, F.R.G.;  $M_r$  36 000) in deionized water. The solution was prepared fresh every day. A 5M-NaCl aqueous solution was used to adjust the ionic strength. The pH was adjusted by 1 to 10M-HCl or 0.01 to 1M-NaOH carbonate-free solutions. In taking the spectra, the solution was buffered at  $\text{pH} \approx 7$  by adding 10 ml mixture of 0.2M-hexamethylenetetramine + 0.2M-HCl to 25 ml of the solution. Unless otherwise indicated, the chemicals used were of analytical grade (Lachema Brno).

Absorption spectra were recorded on a Specord UV-VIS instrument, and absorbances were measured using a Spekol instrument with a Spekol zv amplifier, an EK 5 cell adapter, and a TEC 1 extinction converter (Zeiss Jena, G.D.R.).

The pH was measured by means of an OP-205 pH-meter with an OP-8071-1/A combined glass electrode (Radelkis Budapest, Hungary) calibrated for the given medium by potentiometric titration of 0.1M-HCl with 0.1M-NaOH carbonate-free solution for 10% (v/v)  $\text{CH}_3\text{OH}$ , 0.2M-NaCl, and  $c(\text{SPX}) = 5 \text{ mmol l}^{-1}$  or  $\rho(\text{PVP}) = 1 \text{ g l}^{-1}$ . The pH values measured with this electrode are denoted as  $\text{pH}^*$ , and were obtained in the same way as in a previous work<sup>9</sup>. The  $\text{pK}(\text{H}_2\text{O})$  value at  $20 \pm 1^\circ\text{C}$  was calculated as 13.76 for the solution containing SPX and as 13.77 for the solution containing PVP.

## Absorption Spectra of 3-Pyridylfluorone

Absorption spectra of solutions containing 3-PF in a concentration of  $10 \mu\text{mol l}^{-1}$  with  $I \approx 0$  and  $I 0.2$  and  $c(\text{SPX}) = 5 \text{ mmol l}^{-1}$  or  $\rho(\text{PVP}) = 1 \text{ g l}^{-1}$  were recorded at various  $\text{pH}^*$ s in such a way as to terminate the recording within 2.5 min after making up and mixing the solutions, since above  $\text{pH}^* 7$  a decrease in the absorbance by 10 to 30% was observed after 5 to 10 min. The  $\text{pH}^*$  values within the range 2 to 12 were checked by measuring with the calibrated glass electrode. Lower and higher  $\text{pH}^*$  values were calculated from known concentrations of HCl and NaOH, respectively.

Figs 1 and 2 show examples of absorption spectra of the acidobasic forms of 3-PF taken in cells of 2 cm thickness with water as the reference medium. The characteristic values of the absorption spectra are given in Table I.

## Protonization Constants

Protonization constants were determined for solutions with  $10 \mu\text{mol l}^{-1}$  3-PF, 10% (v/v)  $\text{CH}_3\text{OH}$ ,  $I 0.2$  (NaCl), and  $c(\text{SPX}) = 5 \text{ mmol l}^{-1}$  or  $\rho(\text{PVP}) = 1 \text{ g l}^{-1}$ . Values of  $\text{pH}^*$  were adjusted in the same way as in measuring the absorption spectra. Absorbances were measured within 1 min after mixing the solutions.

The data for  $A$  as a function of  $\text{pH}^*$  (see Figs 3 and 4) were used to calculate protonization constants and molar absorption coefficients of the acidobasic forms of the reagent. The calcula-

tion was performed on an ICL 4-72 computer using a SPEFOT program, whose basic version has been described previously<sup>15</sup>.

The calculated protonization constants and molar absorption coefficients are listed in Tables II and III, respectively.

Average values of the logarithms of the protonization constants were used to calculate the distribution coefficients of the acidobasic forms of the reagent at various pH\* values, and a complete distribution diagram for the system with SPX was constructed. The diagram is shown in Fig. 5, which also includes, for comparison, a previously determined distribution diagram for 3-pyridylfluorone in the absence of a tenside<sup>7</sup>. The protonization constants for the latter system with 1.0·2 (NaCl) and 10% (v/v) CH<sub>3</sub>OH are as follows<sup>7</sup>: log  $K_{H1}$  = 11·4, log  $K_{H2}$  = 8·9, log  $K_{H3}$  = 5·8, log  $K_{H4}$  = 2·4, and log  $K_{H5}$  = 1·7.

The distribution diagram of the system with PVP is similar to that for the system with SPX.

## RESULTS AND DISCUSSION

As indicated by Figs 1 and 2 and Table I, SPX and PVP affect the spectral properties of each acidobasic form of 3-PF differently. In some cases, changes in the spectra are observed even in the presence of a strong electrolyte.

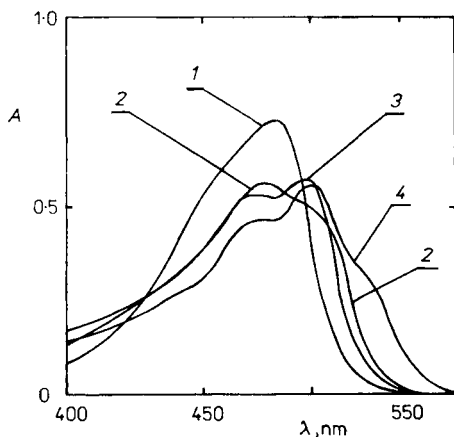


FIG. 1

Absorption spectra of the  $H_5L^{2+}$ ,  $H_4L^+$ , and  $H_3L$  forms.  $c(3\text{-PF}) = 10 \mu\text{mol l}^{-1}$ , 10% (v/v) CH<sub>3</sub>OH,  $I \approx 0$ ; pH\*, tenside concentration: 1 0·2, no tenside; 2 2·3, no tenside; 3 3·8, no tenside, 4 3·8,  $c(\text{SPX}) = 5 \text{ mmol l}^{-1}$

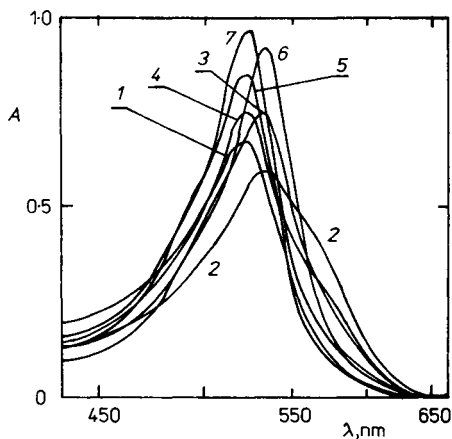


FIG. 2

Absorption spectra of the  $H_2L^-$  and  $HL^{2-}$  forms.  $c(3\text{-PF}) = 10 \mu\text{mol l}^{-1}$ , 10% (v/v) CH<sub>3</sub>OH; pH\*, ionic strength, tenside concentration: 1 7·4,  $I \approx 0$ , no tenside; 2 7·4,  $I \approx 0$ ,  $c(\text{SPX}) = 5 \text{ mmol l}^{-1}$ ; 3 7·4, 1.0·2 (NaCl),  $c(\text{SPX}) = 5 \text{ mmol l}^{-1}$ ; 4 7·4,  $I \approx 0$ ,  $\rho(\text{PVP}) = 1 \text{ g l}^{-1}$ ; 5 10·3,  $I \approx 0$ , no tenside; 6 10·3,  $I \approx 0$ ,  $c(\text{SPX}) = 5 \text{ mmol l}^{-1}$ ; 7 10·3,  $I \approx 0$ ,  $\rho(\text{PVP}) = 1 \text{ g l}^{-1}$

TABLE I  
 Characteristic values ( $\lambda_{\max}$  in nm,  $\epsilon_{\max}$  in  $l \text{ mol}^{-1} \text{ cm}^{-1}$ ) of the absorption spectra of 3-pyridylfluorone in 10% (v/v) methanol solution

pH*	Predominant form	$c(\text{SPX}) = 5 \text{ mmol l}^{-1}$						$c(\text{PVP}) = 1 \text{ g l}^{-1}$								
		No tenside			$I 0 \cdot 2(\text{NaCl})$			$I \approx 0$			$I \approx 0$			$I 0 \cdot 2(\text{NaCl})$		
		$\lambda_{\max}$	$\epsilon_{\max} \cdot 10^{-3}$	$I \approx 0$	$\lambda_{\max}$	$\epsilon_{\max} \cdot 10^{-3}$	$I \approx 0$	$\lambda_{\max}$	$\epsilon_{\max} \cdot 10^{-3}$	$I \approx 0$	$\lambda_{\max}$	$\epsilon_{\max} \cdot 10^{-3}$	$I \approx 0$	$\lambda_{\max}$	$\epsilon_{\max} \cdot 10^{-3}$	$I 0 \cdot 2(\text{NaCl})$
0.2	$\text{H}_5\text{L}^{2+}$	478	36.3	477	37.0	477	37.0	477	37.0	477	37.0	477	37.5	477	37.5	37.5
2.3	$\text{H}_4\text{L}^+$	474	28.0	474	27.9	474	28.8	474	28.8	474	28.8	474	28.0	474	29.5	29.5
3.8	$\text{H}_3\text{L}$	495	28.5	498	27.8	498	27.8	498	27.8	495	27.8	495	29.0	495	28.9	28.9
7.4 <sup>a</sup>	$\text{H}_2\text{L}^-$	468	26.3	468	23.0	468	25.8	468	25.8	468	25.8	468	26.8	468	26.5	26.5
10.3	$\text{HL}^{2-}$	517	43	529	46	528	47	528	47	517	49	518	48	518	48	48
13.5	$\text{L}^{3-}$	519	34	533	30	528	38	528	38	519	38	519	38	519	38	38
		562	46	562	36	562	29	562	29	562	28	562	28	562	34	34

<sup>a</sup> The values of  $\epsilon_{\max}$  at  $\text{pH}^* > 7$  are rounded to two significant figures because of low stability of the solutions.

Fig. 1 illustrates the absorption spectra of both the protonated and neutral forms of the reagent. It has been found that both tensides have practically no effect on the absorbance of the  $H_5L^{2+}$  and  $H_4L^+$  forms and that the absorption spectra of both forms remain practically unchanged even in the presence of a strong electrolyte. For the neutral form  $H_3L$ , SPX causes a small bathochromic shift of the maximum of the absorption band at 495 nm to 498 nm. In the absence of NaCl, the spectrum shows a band due to the first anionic form  $H_2L^-$ , whose formation is suppressed in 0.2M-NaCl, and the absorbance at 468 nm increases. The effect of PVP for both  $I \approx 0$  and  $I 0.2$  is slight, and the absorption spectra have practically the same features as in the absence of the tenside.

It is not until the first anionic form  $H_2L^-$  that a more pronounced effect of SPX is observed. For this form, SPX causes a bathochromic shift of  $\lambda_{max}$  from 517 nm to 529 nm and a hyperchromic shift by about 9% (for  $I 0.2$ ). The effect of PVP is merely a hyperchromic shift (an increase in the absorbance by 14.5% in the absence of NaCl and by 11.6% of the initial value in NaCl solution, see Fig. 2).

For the second anionic form  $HL^{2-}$ , the presence of SPX causes a bathochromic shift from 519 to 533 nm and a hypochromic shift by  $-10\%$   $A$ . In the presence of 0.2M-NaCl, there is a smaller bathochromic shift (from 519 to 528 nm), but a considerable hyperchromic shift (by 12.4%). PVP causes only a hyperchromic shift

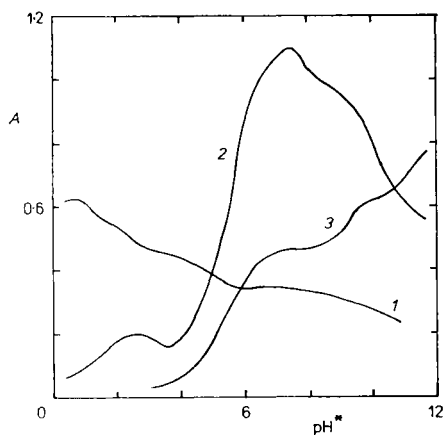


FIG. 3

A plot of  $A$  as a function of  $pH^*$  for 3-pyridylfluorone in the presence of SPX.  $c(\text{SPX}) = 5 \text{ mmol l}^{-1}$ ,  $c(3\text{-PF}) = 10 \text{ } \mu\text{mol l}^{-1}$ , 10% (v/v)  $\text{CH}_3\text{OH}$ ,  $I 0.2(\text{NaCl})$ ,  $d = 2 \text{ cm}$ ; wavelength: 1 480 nm; 2 520 nm; 3 550 nm

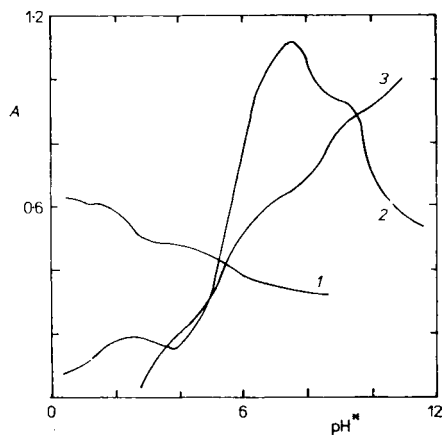


FIG. 4

A plot of  $A$  as a function of  $pH^*$  for 3-pyridylfluorone in the presence of PVP.  $\rho(\text{PVP}) = 1 \text{ g l}^{-1}$ ,  $c(3\text{-PF}) = 10 \text{ } \mu\text{mol l}^{-1}$ , 10% (v/v)  $\text{CH}_3\text{OH}$ ,  $I 0.2(\text{NaCl})$ ,  $d = 2 \text{ cm}$  (for  $\lambda = 470$  and 520 nm),  $d = 3 \text{ cm}$  (for  $\lambda = 550 \text{ nm}$ ); wavelength: 1 470 nm; 2 520 nm; 3 550 nm

TABLE II

Protonization constants of 3-pyridylfluorone. Conditions: 10% (v/v) CH<sub>3</sub>OH, *I* 0.2 (NaCl), 20 ± 1°C

$\lambda$ nm	$\log K_{H1}^a$	$\log K_{H2}$	$\log K_{H3}$	$\log K_{H4}$	$\log K_{H5}$
SPX <sup>b</sup>					
480	11.30	9.20	5.40	2.92	1.48
520	10.90	9.30	5.42	2.98	1.63
550	11.30	9.10	5.50	—	—
Average values	11.2	9.2	5.4	3.0	1.6
PVP <sup>c</sup>					
470	—	—	—	2.89	1.50
520	11.10	9.50	5.69	2.94	1.58
550	11.82	8.87	5.40	—	—
Average values	11.5	9.2	5.5	2.9	1.5

<sup>a</sup> Definition of the constants:  $K_{Hi} = [H_iL]/[H_{i-1}L][H^+]$ ; <sup>b</sup>  $c(\text{SPX}) = 5 \text{ mmol l}^{-1}$ ; <sup>c</sup>  $\rho(\text{PVP}) = 1 \text{ g l}^{-1}$ .

TABLE III

Molar absorption coefficients (in  $\text{l mol}^{-1} \text{ cm}^{-1}$ ) of acidobasic forms of 3-pyridylfluorone. Conditions: 10% (v/v) CH<sub>3</sub>OH, *I* 0.2 (NaCl), 20 ± 1°C

$\lambda$ , nm	$\epsilon_L$	$\epsilon_{HL}$	$\epsilon_{H2L}$	$\epsilon_{H3L}$	$\epsilon_{H4L}$	$\epsilon_{H5L}$
SPX <sup>a</sup>						
480	5 400	13 800	15 000	22 600	25 200	32 750
520	23 000	41 000	52 550	7 900	11 000	3 500
550	42 500	29 600	24 300	3 350	—	—
PVP <sup>a</sup>						
470	—	—	—	23 600	29 300	31 000
520	23 400	33 000	53 250	6 900	10 100	3 750
550	66 700	50 000	13 400	3 200	—	—

<sup>a</sup> The tenside concentrations are the same as in Table II.

(by 12.4%), while the maximum of the absorption band remains the same as for 3-PF alone. The presence of a strong electrolyte (0.2M-NaCl) has almost no effect on the spectrum of the system  $HL^{2-}$ -PVP.

The form  $L^{3-}$ , which prevails above  $pH^* 13.5$ , is very unstable, making it difficult to record the spectrum. Neither tenside caused any change in the wavelength of the absorption maximum of this form. The absorbance was highest for the solution of the reagent alone, and was reduced on addition of either tenside. For the solution with SPX and  $I 0.2$ , there was a further hypochromic shift of the absorption band, whereas in the case of PVP the strong electrolyte had the opposite effect.

The changes in the spectra of the various acidobasic forms of the reagent were generally more pronounced in the presence of the cationic tenside SPX, especially for the neutral molecule and the anionic forms  $H_2L^-$  and  $HL^{2-}$ . The bathochromic shifts of the absorption maxima indicate a lowering of the electron transition energies of the respective chromophores. The protonated forms of the reagent are very little affected by SPX. This is probably due to the identical charge of the reagent and the tenside, which prevents a direct chemical interaction between the two substances. No such phenomena have been observed for PVP (non-ionic tenside), indicating that in this case there is no change in the electron transition energies of the acidobasic forms of the reagent.

However, both tensides probably affect the probability of  $\pi$ -electron transitions in the chromophores, as indicated by changes in the molar absorption coefficients of the acidobasic forms. This effect is least for the cationic forms  $H_5L^{2+}$  and  $H_4L^+$ , and fairly small for the neutral form. Both tensides give rise to increases in the

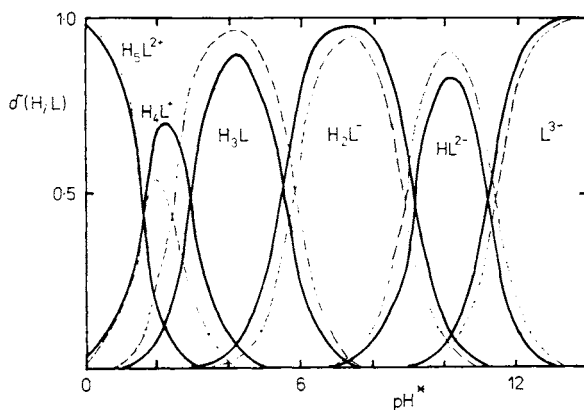


FIG. 5

Distribution diagram of 3-pyridylfluorone in the presence of SPX. 10% (v/v)  $CH_3OH$ ,  $I 0.2$  (NaCl); ———  $c(SPX) = 5 \text{ mmol l}^{-1}$ ; - - - - - no tenside



absorbance of the first anionic form  $H_2L^-$ , and SPX additionally to a bathochromic shift of the maximum. In the case of the second anionic form  $HL^{2-}$ , SPX — besides causing a bathochromic shift — markedly decreases the absorbance, whereas PVP produces a slight increase. Here, a strong electrolyte (NaCl) also has quite a pronounced effect. The chloride ion is bound to the SPX micelles probably more firmly than the fluorone anion, and this leads to a change in the interaction between the colloid particles and the reagent, resulting in a reduction of the bathochromic shift and an increase in the absorbance. With PVP, which has no electric charge, no such phenomena have been observed.

Comparison of the protonization constants with published values<sup>7</sup> obtained in the absence of a tenside at the same methanol content and ionic strength shows that SPX and PVP have practically no effect on the protonization constants  $K_{H1}$  and  $K_{H5}$ . Both tensides cause a slight increase in  $K_{H2}$  and  $K_{H4}$ , and a decrease in  $K_{H3}$ . On the whole, the changes in the protonization constants due to the presence of the tensides are small.

Fig. 5 compares a distribution diagram for the various acidobasic forms of 3-PF with that obtained in the presence of SPX. As seen, SPX at the given concentration depresses mildly the formation of  $H_3L$  and  $HL^{2-}$  while extending slightly the region of  $pH^*$  in which the predominating forms are  $H_4L^+$ ,  $H_2L^-$ , and  $L^{3-}$ . The formation of  $H_5L^{2+}$  is practically unaffected by SPX.

It has also been found that the effect of PVP on the formation of individual acidobasic forms of the reagent is very similar to that of SPX. The only difference is that PVP has no influence on the range of  $pH^*$  over which the deprotonated ligand predominates in the solution.

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