

## Effect of Added Macro Ions on the Apparent $pK$ & Spectral Behaviour of Crystal Violet & Malachite Green

SOLIMAN N BASAHL, MOHAMED A F Ez EL-ARAB†, ALI H ABUL GASEM & MOSTAFA M EMARA\*

Department of Chemistry, Faculty of Science, King Abdul Aziz University, Jeddah, Kingdom of Saudi Arabia

Received 26 April 1985; revised and accepted 24 October 1985

The effect of added macro ions, such as polyethylene glycols of different molecular weights, polyvinyl alcohol (PVA) and poly(sodium styrene sulphonate) (Na PSS), on the spectral behaviour and the apparent  $pK$  of the cationic  $pH$ -indicators, crystal violet (CV) and malachite green (MG), has been studied. It is found that  $\Delta pK$  of CV has negative value in the case of weak polyelectrolytes and a positive value in the case of the strong (anionic) NaPSS polyelectrolyte. Addition of similar concentrations of the weak polyelectrolytes PEG 200, 400, 600, 1000, 4000, 6000 EG and PVA does not affect the spectrum of CV. Malachite green (MG) shows two different responses toward the various polyelectrolytes.  $\Delta pK$  tends to be positive with all weak polyelectrolytes at the first equilibrium position ( $pK_1$ ); however, a negative shift occurs at ( $pK_2$ ). This can be attributed to the difference in the nature of these two equilibria. The difference in the effects of weak and strong polyelectrolytes on the indicators is discussed in the light of the electrostatic interaction theory.

Recently Prini<sup>1</sup> pointed out that the addition of polyelectrolyte to a dye solution, different in charge sign from the dye ion, could affect the  $pK$  of the dye ionization or aggregation. He showed that this phenomenon causes changes in the band positions and the extinction coefficients and a shift in the  $pK$  of the dye occurs whenever polyions and oppositely charged dye molecules coexist in solutions. It was also observed that in the case of cationic dye indicators the  $pK$  shifts were positive while in the case of anionic dye the  $pK$  was shifted to lower values by polyelectrolyte addition. This change in  $pK$  values of the dye is thought to be due to the so called polyelectrolyte effect<sup>1</sup>.

In an earlier investigation<sup>2</sup> we carried out spectral measurements on congo red  $pH$ -indicator in the presence of various polyelectrolytes to see the validity of the above theory. In this study we have extended the measurements to two other cationic  $pH$ -indicators in presence of strong and weak polyelectrolytes.

### Materials and Methods

Polyethylene glycols (PEG) of various molecular weights. PEG 200, PEG 400, PEG 600, PEG 1000, PEG 4000 and PEG 6000 were BDH reagents as was the monomer ethylene glycol (EG). Polyvinyl alcohol (PVA) was a BDH reagent.

Poly(sodium styrene sulphonate) (NaPSS) (molecular weight  $\sim 500,000$ ) was purchased from the Chemical Research Lab., U.S.A.

The indicators employed in this study were crystal violet (CV) (BDH reagent) and malachite green (MG)

(Griffin and George). Their solutions were prepared in pure deionized distilled water or in modified universal buffers.

Two spectrophotometers were used for spectral measurements in this study. Pye Unicam sp 8000 was used when scanning was needed. Zeiss PMQ-3 was used when measurements were carried out at fixed wavelengths.

The  $pH$  measurements were carried out using a TACUSSEL PHN 78  $pH$ -meter.

### Methods of calculation

Well known spectrophotometric methods<sup>4-6</sup> were used to determine the  $pK$  of various indicators.

CV exhibits two bands at 530 and 590 nm in pure aqueous solutions. These two bands have been assigned<sup>7</sup> to the dimer and monomer forms of CV. When the  $pH$  was varied from 1 to 4, it was found that the colour of CV changed from colourless to violet.

Measurements at various  $pH$  values were carried out to obtain the  $pK$  of CV. The concentration was maintained in all the measurements at  $1 \times 10^{-5} M$  unless stated otherwise.

### Results and Discussion

Well known methods of calculations<sup>4-6</sup> were used to obtain the  $pK$  value of CV in pure water at both the wavelengths, 590 and 530 nm. The average value was calculated to be 2.23. All  $pK$ s of CV with different macro-ions and at different concentrations were determined using the same procedure (Table 1). Typical absorbance vs  $pH$  plots, from which we obtained the  $pK$  values, are shown in Fig. 1.

$\Delta pK$  with weak polyelectrolytes was found to have a

†Department of Chemistry, Faculty of Science, Al-Azhar University, Nasr City, Cairo, Egypt.

Table 1—Calculated  $pK$  Values of  $1 \times 10^{-5} M$  Crystal Violet Dye in Various Solutions Measured at  $\lambda = 530$  and  $590$  nm at  $25^\circ C$ 

Added compound	Conc. of added compound	$(pK)_1$	$(pK)_2$	$pK_{(av.)}$	$\Delta(pK)_1$	$\Delta(pK)_2$	$\Delta pK_{(av.)}$
No additive	zero	2.25	2.20	2.23			
Ethylene glycol (EG)	$5 \times 10^{-6} M$	2.40	2.30	2.35	0.15	0.10	0.13
	$2 \times 10^{-5} M$	2.20	2.05	2.13	-0.05	-0.15	-0.10
	$4 \times 10^{-5} M$	2.25	2.10	2.18	0.00	-0.10	-0.05
PEG 200	$5 \times 10^{-6} M$	2.45	2.25	2.35	0.20	0.05	0.13
	$2 \times 10^{-5} M$	2.40	2.30	2.35	0.15	0.10	0.13
	$4 \times 10^{-5} M$	2.40	2.10	2.25	0.15	-0.10	0.03
PEG 400	$5 \times 10^{-6} M$	1.95	1.85	1.90	-0.30	-0.35	-0.32
	$2 \times 10^{-5} M$	2.20	2.10	2.15	-0.05	-0.10	-0.07
	$4 \times 10^{-5} M$	2.30	2.10	2.20	-0.05	-0.10	-0.02
PEG 600	$5 \times 10^{-6} M$	2.05	1.85	1.95	-0.20	-0.35	-0.27
	$2 \times 10^{-5} M$	2.15	1.95	2.05	-0.10	-0.25	-0.17
	$4 \times 10^{-5} M$	2.10	1.90	2.00	-0.15	-0.30	-0.22
PEG 1000	$5 \times 10^{-6} M$	2.15	1.95	2.05	-0.10	-0.25	-0.17
	$2 \times 10^{-5} M$	2.20	2.15	2.18	-0.05	-0.05	-0.05
	$4 \times 10^{-5} M$	2.05	1.90	1.98	-0.20	-0.30	-0.25
PEG 4000	$5 \times 10^{-6} M$	1.95	1.95	1.95	-0.30	-0.25	-0.27
	$2 \times 10^{-5} M$	2.15	2.05	2.10	-0.10	-0.15	-0.12
	$4 \times 10^{-5} M$	2.10	2.05	2.08	-0.15	-0.15	-0.15
PEG 6000	$5 \times 10^{-6} M$	2.30	2.10	2.20	0.05	-0.10	-0.02
	$2 \times 10^{-5} M$	2.25	2.10	2.18	0.00	-0.10	-0.05
	$4 \times 10^{-5} M$	2.10	1.90	2.00	-0.15	-0.30	-0.23
PVA	$5 \times 10^{-6} M$	2.30	2.15	2.23	0.05	-0.05	0.00
	$2 \times 10^{-5} M$	2.30	2.15	2.23	0.05	-0.05	0.00
	$4 \times 10^{-5} M$	2.30	2.25	2.28	0.05	-0.05	0.00
NaPSS	$5 \times 10^{-6} M$	2.25	2.20	2.23	0.00	0.00	0.00
	$2 \times 10^{-5} M$	2.35	2.20	2.28	0.10	0.00	0.05
	$4 \times 10^{-5} M$	2.45	2.20	2.33	0.20	0.00	0.10

negative value. The maximum  $\Delta pK$  is approximately  $-0.3 pK$  units. Bearing in mind that no spectral changes for all combinations of the dye with weak polyelectrolytes were observed either in different or at constant  $pH$  value, one can state that no interaction of the dye with this type of electrolytes takes place. The considerable negative deviation of the  $pK$  value observed can be interpreted as an experimental error.

The results observed with CV-NaPSS combinations show that with increasing [NaPSS], the  $pK$  value of CV increases steadily. A positive  $\Delta pK$  was observed for CV (cationic) dye and the strong (anionic) NaPSS polyelectrolyte. This result agrees completely with electrostatic theory of interaction<sup>3</sup>.

The spectrum of the dye was recorded in the presence of different concentrations of polyelectrolytes. Addition of NaPSS in concentrations ranging from  $5 \times 10^{-6} M$  to  $4 \times 10^{-5} M$ , per monomer to  $1 \times 10^{-5} M$  CV decreases the absorbance at  $\lambda = 590$  while the absorbance at  $\lambda = 530$  increases. Addition of similar concentrations of the weak polyelectrolytes did not affect the spectrum.

The spectra of  $1 \times 10^{-5} M$  CV in the presence of different concentrations of polyelectrolytes were also obtained at a constant  $pH$  of 2.6. All the polyelectrolytes and EG were added in the concentrations  $5 \times 10^{-6} M$ ,  $1 \times 10^{-5} M$ ,  $2 \times 10^{-5} M$  and  $4 \times 10^{-5} M$  per monomer. No effect of weak polyelectrolytes was seen. The effect of NaPSS concentration is very clear, as shown in Fig. 2. The same result can be stated on the basis of  $OD/OD_w$  values, which in the case of weak electrolytes approach unity at all wavelengths, but exhibit a serious drop when NaPSS is added. The drop in  $(OD/OD_w)$  value is more clear at the  $\lambda_{max} = 590$  nm reflecting the loss in absorbance due to NaPSS addition.

The behaviour of malachite green (MG) is quite similar to that of crystal violet. The maximum wavelength at which it absorbs almost approaches that of CV, namely 610 nm. The high sensitivity of MG to light was also observed, similar to that of CV. Time seriously affects the absorbance of the MG in all  $pH$  media.

The  $pK$  values of the dye with three polyelectrolytes were determined by using the well known methods of

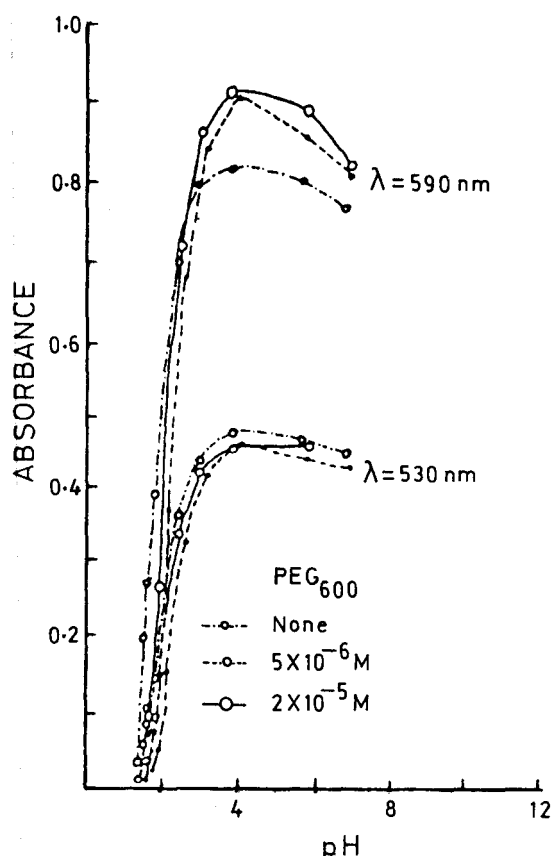


Fig. 1—Effect of PEG<sub>600</sub> on the absorbance versus pH curves of  $1 \times 10^{-5} M$  crystal violet at 25°C

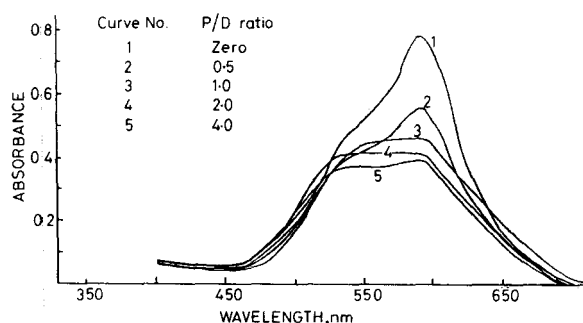


Fig. 2—Absorbance spectrum of  $1 \times 10^{-5} M$  crystal violet with NaPSS at pH = 2.6

calculations<sup>4-6</sup> (Table 2). Two  $pK$  values for MG were obtained in the two indicated transition regions.

The  $pK_1$  of the free dye was found to be 1.65 and  $pK_2$  10.75.  $pK$  values of MG with NaPSS, PVA and PEG 6000 were also obtained. The absorption spectra represented by Fig. 3 were used to obtain  $pK$  values. This was done for MG with P/D (polyelectrolyte/dye) ratios 0.5, 1, 2 and 4 with each of the three polyelectrolytes.

For MG,  $\Delta pK$  tends to be positive with all weak polyelectrolytes at the first equilibrium position  $pK_1$ ; it tends to be negative at  $pK_2$ . This can be attributed to

Table 2—Calculated  $pK$  for  $1.5 \times 10^{-5} M$  Malachite Green in Presence of Various Macroions Measured at  $\lambda = 610 \text{ nm}$  at 25°C

Added polymer	Additive concentration	$pK_1$	$pK_2$	$\Delta pK_1$	$\Delta pK_2$
No additive	—	1.65	10.75	—	—
NaPSS					
	$0.75 \times 10^{-5} M$	2.05	10.87	0.40	0.12
	$1.5 \times 10^{-5} M$	2.20	11.15	0.55	0.40
	$3.0 \times 10^{-5} M$	2.25	11.16	0.60	0.41
	$6.0 \times 10^{-5} M$	2.32	10.40	1.67	-0.35
PVA					
	$0.75 \times 10^{-5} M$	2.00	10.55	0.35	-0.20
	$1.5 \times 10^{-5} M$	2.06	9.87	0.41	-0.88
	$3.0 \times 10^{-5} M$	2.12	10.57	0.47	-0.18
	$6.0 \times 10^{-5} M$	1.90	11.02	0.25	0.27
PEG 6000					
	$0.75 \times 10^{-5} M$	2.25	10.25	0.60	-0.5
	$1.5 \times 10^{-5} M$	2.20	9.75	0.55	-1.0
	$3.0 \times 10^{-5} M$	1.70	10.52	0.05	-0.23
	$6.0 \times 10^{-5} M$	2.07	10.10	0.42	-0.65

the difference in the nature of these two equilibria.  $pK_1$  can be attributed to specific interactions taking place at low weak polyelectrolyte concentrations. The unsteadiness of  $\Delta pK$  with increasing polyelectrolyte concentration was interpreted on the basis of competitive process between monomer cation interaction and its tendency to deprotonate on further anion availability<sup>8</sup>. Thus addition of more anionic polyelectrolyte will minimize the positive  $\Delta pK_1$  through its negative effect on the tendency of protonation of MG. This interpretation is not applicable to CV as it is originally less protonated than MG in this range of pH<sup>8</sup>.

$\Delta pK_2$  tends, in general, to be negative on adding weak polyelectrolytes. On further addition of anionic weak polyelectrolytes this equilibrium state is shifted to less pH values resulting in the existence of negative  $\Delta pK$ . Contradictions between these results of MG-weak polyelectrolytes systems and the results of Prini<sup>3</sup>, are attributed to the differences between the nature of the systems studied.

The results with strong negatively charged polyelectrolyte NaPSS were indeed in agreement with the results obtained by Prini. The  $\Delta pK_1$  is positive and increases steadily with increasing concentration of NaPSS. If we take a mean value between  $\Delta pK_1$  and  $\Delta pK_2$ , the resulting  $\Delta pK$  average agrees nicely with Prini's prediction.

No changes were observed with the two weak polyelectrolytes. With NaPSS, the spectral changes are very clear, and clear shifts in the positions of the maxima and absorbance change are observed. This

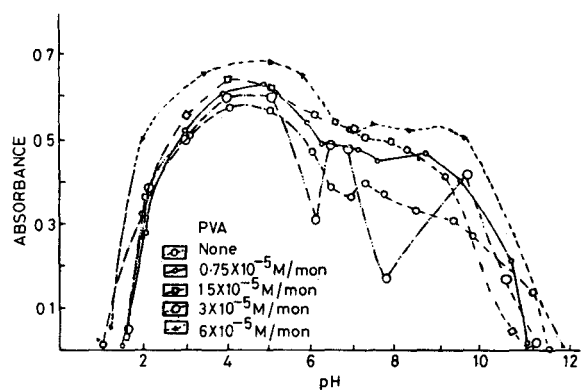


Fig. 3—Effect of PVA on the absorbance versus pH curves of  $1.5 \times 10^{-5}$  M malachite green at  $\lambda = 610$  nm

change was found to increase with increasing polyelectrolyte concentration.

Also, there was no shift in absorbance of the weak polyelectrolytes at pH 4 and the ratio  $(OD/OD_w)$

remained constant at unit value, while the ratio P/D changed.

In the case of strong polyelectrolyte (NaPSS) the  $(OD/OD_w)$  ratio decreased to less than unity gradually with increasing P/D ratio.

### References

- 1 Ferna'ndez-Prini R & Turyn D, *Chem Commun*, (1972) 1013
- 2 Ferna'ndez-Prini R & Turyn D, *J chem Soc, Faraday I*, (1973) 69, 1326.
- 3 Ueda T, Harada S & Ise N, *Polymer J*, 3 (1972) 476.
- 4 Ashy M A, Basahl S N, Emara M M & Ez El-Arab M A F, *J Indian chem Soc*, (accepted).
- 5 Baumgartner E, Fern'andez-Prini R & Turyn D, *J chem Soc, Faraday Trans, I* (1974) 70.
- 6 Issa R M, *J Chem U A R*, 14 (1971) 113.
- 7 Issa R M, Sadek H & Ezzat I I, *Z physik Chem(N F)*, 74(1971) 17.
- 8 Colleter J C, *Ann Chem*, 5 (1960) 415.
- 9 Ez El-Arab Moh, *Studies of the physicochemical properties of polyelectrolytes in presence of dyes*, Ph D Thesis, Al-Azhar University (1978).
- 10 Lamonosov S A, Sorokin G Kh, Proper E I, Shokolyukova N I & Nosova I P, *Zh analit Khim*, (28) (1973) 1877.