

Stability of the γ -Sultone Form of Bromcresol Green in the Organic Phase from Partitioning of the Dye between Water and Benzene

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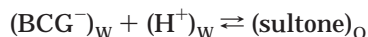
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In this study, bromcresol green, BCG, was partitioned between benzene and buffered aqueous solutions, pH 3.12 to 3.92. The colorless γ -sultone form of the dye in the organic phase was determined spectrophotometrically upon back-extracting into aqueous phosphate buffer at pH 6.7. The yellow monoanion (quinoid) form, BCG^- , in the benzene phase prior to back-extraction was found to be practically negligible ($\leq 1 \times 10^{-6} \text{ mol dm}^{-3}$). From the above, the equilibrium constant of the reaction $(\text{BCG}^-)_w + (\text{H}^+)_w \rightleftharpoons (\text{sultone})_{\text{organic}}$ is $373 \pm 42 \text{ mol}^{-1} \text{ dm}^3$. Lithium chloride and/or 18-crown-6 only slightly increased the extractability of BCG under the experimental conditions.

Introduction

It is well-known that some sulfonephthaleins are present largely as a colorless γ -sultone in acetonitrile¹ and chloroform.² In aqueous medium the sultone concentration is extremely small.¹ In the extraction of an alkali metal ion, M^+ , with a crown ether, L, and a sulfonephthalein (e.g. bromcresol green, BCG) from water into an immiscible organic solvent, the absorbance of the extracted ion pair, LM^+BCG^- , in the visible region is a measure of M^+ originally present in the aqueous phase.^{3–6} It, therefore, is of interest to estimate the sultone content of the organic phase in such extractions.

The purpose of this study is to determine the equilibrium constant, $K^{\text{dist}}(\text{sultone})$, involving the sultone form of BCG in benzene saturated with water and the yellow quinoid monoanion, BCG^- , in water saturated with benzene according to the reaction



$$K^{\text{dist}}(\text{sultone}) = [\text{sultone}]_o / [\text{BCG}^-]_w \gamma (\text{BCG}^-)_w a(\text{H}^+)_w \quad (1)$$

The subscripts O and W denote the organic and aqueous phases, respectively; γ is the solution activity coefficient, and $a(\text{H}^+)_w$ is the activity of the hydrogen ion in water.

In the present work, aqueous solutions of bromcresol green in acetic acid–lithium acetate or succinic acid–lithium bisuccinate buffers of pH 3.1 to 3.9 were extracted into benzene. Denoting with a subscript t the total concentration in both phases

$$(\text{BCG})_t = \sum [\text{BCG}]_o + \sum [\text{BCG}]_w = [\text{BCG}^-]_o + [\text{sultone}]_o + [\text{BCG}^-]_w + [\text{BCG}^{2-}]_w \quad (2)$$

To determine $\sum [\text{BCG}]_o$, the colorless benzene phase was back-extracted into an aqueous phosphate buffer at pH 6.8. This converts $(\text{BCG}^-)_o$ (mainly as ion pair) and $(\text{sultone})_o$ completely into the dianion BCG^{2-} in the aqueous extract. Using eq 2, $[\text{sultone}]_o$ was evaluated, neglecting $[\text{BCG}^-]_o$. The quantity $\sum [\text{BCG}]_w$ is the difference $(\text{BCG})_t - \sum [\text{BCG}]_o$.

Experimental Section

Benzene, Matheson, Coleman and Bell, Omni Solv spectroquality Grade, was used without further purification. **Caution: toxic.** Bromcresol green, Eastman Kodak, was recrystallized from glacial acetic acid according to Orndorff and Purdy⁷ and dried in vacuo at 340 K. Table 1 summarizes the spectral characteristics of HBCG, BCG^- , and BCG^{2-} in water.

The maximum molar absorption coefficient of BCG^{2-} at 615 nm, ϵ_{615} , is in good agreement with that reported by Franglen and Martin.⁸ In this study seven concentrations of BCG were taken. Lithium chloride (Ventron) and 18-crown-6 (Parish 97% purity) were used previously.⁹ For preparation of the aqueous buffers, glacial acetic acid (Chemical Manufacturing Co.; Spectrum Reagent Grade) was partially neutralized with lithium carbonate (Aldrich, purity 99%). Aliquots of these buffer solutions were taken for pH measurements. This avoids contamination of the solution to be extracted with K^+ arising from leakage of the saturated calomel reference electrode. A Corning Catalog No. 4-6022 pH glass electrode was standardized in a potassium biphthalate solution used in conjunction with a Corning Model 10 expanded scale pH meter.

For extraction, 20 mL of the aqueous phase containing bromcresol green, buffer, and 20 mL of benzene was stirred vigorously for 0.5 h in a 50 mL recovery flask and then allowed to stand overnight at 298 K. The benzene phase

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Table 1. Absorption Spectral Characteristics of Bromcresol Green in Three Different Water-Based Media^a

parameter	9 mol dm ⁻³ HClO ₄ in water	0.1 mol dm ⁻³ HCl in water	0.0443 mol dm ⁻³ Na ₂ HPO ₄ and 0.0572 mol dm ⁻³ NaH ₂ PO ₄ in water
pH		1.4	6.7
charge on bromcresol green	0	1-	2-
10 ⁻⁵ (conc of BCG) (mol dm ⁻³)	1.88	2.76	0.595–2.38
λ _{max} /nm	561 ^b	440 ^c	615 ^d
10 ⁻⁴ ε _{max} (dm ³ mol ⁻¹ cm ⁻¹)	4.07	1.97	4.54 ± 0.021 4.57 ^e
color of solution	violet	yellow	blue

^a pK₁(yellow → blue) = 4.35 ± 0.01.¹¹ ^b Other maximum, ε₄₃₄ = 1.43 × 10⁴ dm³ mol⁻¹ cm⁻¹. ^c Other maximum, ε₂₇₀ = 8.70 × 10³ dm³ mol⁻¹ cm⁻¹; the same spectrum occurs in aqueous 0.28 mol dm⁻³ acetic acid. Isobestic points in a mixture of BCG⁻ and BCG²⁻: ε₅₀₈ = 0.77 × 10⁴ and ε₃₂₆ = 0.69 × 10⁴ dm³ mol⁻¹ cm⁻¹. ^d Other lesser maxima: ε₃₀₇ = 1.35 × 10⁴, ε₃₉₅ = 9.78 × 10³ dm³ mol⁻¹ cm⁻¹. ^e Reference 8 ε₆₁₃.

Table 2. Partitioning of Bromcresol Green from Water into Benzene

components of buffer mol dm ⁻³	10 ⁻⁴ [BCG] _i ^a mol dm ⁻³	pH	10 ⁻⁴ Σ[BCG] _w mol dm ⁻³	γ ⁻	α ^b	10 ⁻⁴ Σ[BCG] _o ^c mol dm ⁻³	K ^{dist} (sultone) mol ⁻¹ dm ³
H ₂ SO ₄ , 0.0050	2.69	2.30	0.70		0.996	1.99	
H ₂ Suc, ^d 0.067	2.69	2.75	1.57	0.955	0.993	1.12	423
HOAc, 0.788	8.25	3.12	7.09	0.887	0.982	1.16	(248)
LiOAc, 0.0168							
H ₂ Suc, ^d 0.042	2.69	3.15	2.10	0.937	0.981	0.595	435
LiHSuc, 0.004							
H ₂ Suc, ^d 0.0315	2.69	3.90	2.60	0.890	0.898	0.0930	356
LiHSuc, 0.0165							
HOAc, 0.0881	8.25	3.90	8.00	0.887	0.890	0.248	312
LiOAc, 0.0168							
HOAc, 0.0881	2.69	3.92	2.61	0.889	0.883	0.0837	340
LiOAc, 0.0168							

^a Total concentration in both phases. ^b α = [BCG⁻]_w/([BCG⁻]_w + [BCG²⁻]_w); pK₁ = 4.95.¹¹ ^c From back-extraction of benzene phase with aqueous buffer; regarded to be sultone only. ^d H₂Suc = succinic acid.

was then isolated in a separatory funnel and the absorption spectrum from 350 to 450 nm recorded immediately versus pure benzene as reference in a Cary Model 15 spectrophotometer. Quartz glass stoppered silica cells were used with benzene as reference solvent. Duplicate runs were made of each entry and averaged; reproducibility was 1–2%. The absorbance increased irreproducibly with time when the benzene solution was removed from contact with the aqueous phase. All glassware was washed with detergent and then immersed in dilute nitric acid, washed, and then dried at 410 K overnight. Quartz cells were immersed in dilute nitric acid and washed with ethanol.

In the back-extraction, 5 mL of the benzene phase mentioned above and 10 mL of aqueous phosphate buffer (0.0554 mol dm⁻³ Na₂HPO₄, 0.0458 mol dm⁻³ NaH₂PO₄, pH 6.8) were shaken in a 50 mL separatory funnel for 1–2 min, and then allowed to stand overnight. The back-extracted BCG²⁻ was determined spectrophotometrically at 615 nm. A negligible absorbance (<0.005) was detected in a second back-extraction with another portion of aqueous phosphate buffer. Reproducibility as standard deviation was ≤1%. The absorbance of the separated aqueous phase did not change with time.

Results

Extraction of Bromcresol Green into Benzene. Results from the extraction data are presented in Table 2. The quantity Σ[BCG]_o, practically only sultone, was estimated from the absorbance at 615 nm, A₆₁₅, following back-extraction. The absorbance at 410 nm, A₄₁₀, of the benzene phase prior to back-extraction of the next to bottom entry in Table 2 is ~0.020, corresponding to [BCG⁻]_o ≤ 1 × 10⁻⁶ mol dm⁻³, which was neglected. The molar absorptivity

coefficient of 18-cr-6 K⁺BCG⁻ in CHCl₃ was reported to be 1.78 × 10⁴ dm³ mol⁻¹ cm⁻¹ by Petrosyan et al.² Activity coefficients of BCG⁻ in water were evaluated from the partially extended Debye–Hückel expression -log γ = 0.5115I^{1/2}/(1 + 3.29aI^{1/2}), taking a = 0.70 nm for BCG⁻. The value of K^{dist}(sultone) from Table 2 is 373 ± 42 mol⁻¹ dm³.

Extraction of Phenol Red (PR) into Benzene. Partitioning of an aqueous solution of 2.99 × 10⁻⁴ mol dm⁻³ PR, 4.5 × 10⁻² mol dm⁻³ (succinic acid and lithium bisuccinate), pH 4.1, and 1.0 × 10⁻³ mol dm⁻³ potassium chloride into benzene containing 6.34 × 10⁻⁴ mol dm⁻³ 18-cr-6 yielded a colorless benzene phase. No absorbance was detected (0.000) at 558 nm in the aqueous phase after back-extraction with 0.13 mol dm⁻³ ammonium hydroxide. Apparently, neither 18-cr-6 K⁺PR⁻ or the sultone was present in benzene. On the other hand, a colorless form of PR is stable in acetonitrile (colorless – yellow), pK = 13.7.¹

Discussion

Additional Equilibria Involved in Sulfonephthalein Extraction. These are discussed below and appear to have a minor effect in the extractions described above. (i) Acetic acid in the buffer is partitioned between water and benzene, with a constant of 8.2 × 10³ for the monomer.¹⁰ At high concentrations (>0.5 mol dm⁻³) acetic acid or ethanol renders the aqueous phase “organic-like”. This favors the distribution of sultone into the aqueous phase, as seen from the low value of K^{dist}(sultone) in Table 2 when C(HOAc) = 0.788 mol dm⁻³. From Table 3 the presence of 7% ethanol decreases Σ[BCG]_o and therefore the sultone content of the extracted BCG. This results in low “extraction blanks” in the extraction of alkali salts with BCG and 18-crown-6 in the presence of ethanol. Succinic acid does

Table 3. Effect of 18-Crown-6 and/or Lithium Chloride on Partitioning of 8.12×10^{-4} mol dm $^{-3}$ Bromocresol Green between Water–Ethanol Mixtures and Benzene^a

% EtOH by volume	$10^{-4}C(18\text{-cr-6})$ mol dm $^{-3}$	$C(\text{LiCl})$ mol dm $^{-3}$	$10^{-5}[\text{BCG}]_o^b$ mol dm $^{-3}$	$10^{-5}[\text{BCG}^-]_o^c$ mol dm $^{-3}$
0	0	0	2.44	≤0.1
0	6.84	0	2.65	0.36
7	0	0	1.25	0.33
7	6.84	0	1.30	0.30
7	0	0.103	1.43	
7	6.84	0.103	1.57	

^a Aqueous solution initially: 8.81×10^{-2} mol dm $^{-3}$ HOAc, 1.68×10^{-2} mol dm $^{-3}$ LiOAc; pH after extraction 3.90–3.98. ^b From absorbance at 615 nm, taking $\epsilon_{615} = 4.54 \times 10^4$ dm 3 mol $^{-1}$ cm $^{-1}$ (Table 1). ^c From absorbance at 410 nm, regarding $\epsilon_{410} = 1.78 \times 10^4$ dm 3 mol $^{-1}$ cm $^{-1}$ (ref 2).

not partition into benzene; similar values of $K^{\text{dist}}(\text{sultone})$ are obtained using its buffers compared to those of dilute acetic acid in Table 2. (ii) The presence of a large amount of lithium chloride exerts a “salting out” effect,⁹ which is expected to increase the sultone concentration in benzene. It appears, however, from Table 3 that lithium chloride, 0.1 mol dm $^{-3}$, has little effect on the bromocresol green extraction, even in the presence of 6.84×10^{-4} mol dm $^{-3}$ 18-crown-6. Under these conditions the presence of 18-cr-6 Li^+BCG^- in the organic phase appears to be minimal.

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Received for review August 28, 2000. Accepted June 14, 2001. The authors wish to thank the National Science Foundation (Grants CHE-8000243 and CHE75-22642) for financial support.

JE000285V