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THERMODYNAMIC ACID DISSOCIATION CONSTANTS FOR PROTON-IONIZABLE CROWN COMPOUNDS IN AQUEOUS DIOXANE

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ABSTRACT

Thermodynamic acid dissociation constants (${}^{T}pK_a$) have been determined in 70% dioxane–water (v/v) for eleven macrocyclic polyether (crown ether) compounds which have pendant proton-ionizable groups, and for three crown compounds in which the ionizable group is part of the ring structure itself. The influence of structural variation within the proton-ionizable macrocyclic compounds upon the thermodynamic acid dissociation constant is assessed.

INTRODUCTION

Lipophilic macrocyclic polyether (crown ether) compounds with pendant carboxylic acid and phosphonic acid monoester groups are novel ligands for the solvent extraction and transport of alkali metal and alkaline earth cations across liquid membranes [1–9]. Compared with their neutral analogs, these proton-ionizable crown ethers have the important advantage that extraction of a metal cation into the organic medium does not require concomitant transfer of an aqueous phase anion [1]. For potential practical applications of crown ether ligands in which such highly hydrophilic common anions as chloride, nitrate and sulfate would be involved, this factor is of immense importance.

Previously we have reported [10] thermodynamic acid dissociation constants ${}^{T}pK_a$ in 70% dioxane–water (by volume) for nine crown ether carboxylic acids including **I**–**VI** (Fig. 1). Since compounds such as **V** and **VI**

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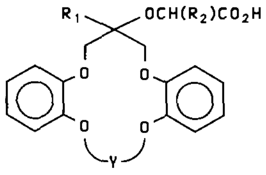
are designed to have very low water solubility, an aqueous dioxane system was utilized for the measurements. Acidities of the crown ether carboxylic acids were found to vary depending upon the crown ether ring size (variation of Y) and the attachment of an alkyl group to the central carbon of the three carbon bridge (variation of R_1).

To enhance our understanding of how structural variations within proton-ionizable crown compounds influence their acidities, thermodynamic acid dissociation constants have now been determined in 70% dioxane–water for fourteen additional compounds. These include **VII–XII** which are closely related to the previously-examined compounds plus the additional crown ether carboxylic acid **XV** in which the ionizable group is attached to a polyether ring substituent (an aromatic group) rather than directly to polyether ring. Compounds **XVI** and **XVII** are crown amino acids. In **XIII** and **XIV**, the ionizable group has been changed from a carboxylic acid function to a phosphonic acid monoethyl ester unit. Finally in crown compounds **XVIII–XX**, the ionizable group becomes part of the macrocyclic ring itself rather than being attached via a side arm.



	R_1	R_2	Y
I	H	H	$CH_2CH_2CH_2$
II	H	H	$CH_2CH_2OCH_2CH_2$
III	H	H	$CH_2CH_2(OCH_2CH_2)_2$
IV	H	C_2H_5	$CH_2CH_2OCH_2CH_2$
V	$C_{10}H_{21}$	H	$CH_2CH_2OCH_2CH_2$
VI	$C_{14}H_{21}$	H	$CH_2CH_2OCH_2CH_2$
VII	$C_{10}H_{21}$	H	$CH_2CH_2CH_2$
VIII	H	C_8H_{17}	$CH_2CH_2OCH_2CH_2$
IX	C_4H_9	H	$CH_2CH_2OCH_2CH_2$
X	C_8H_{17}	H	$CH_2CH_2OCH_2CH_2$
XI	H	C_8H_{17}	$CH_2CH_2(OCH_2CH_2)_2$

Fig. 1. Structures of proton-ionizable crown compounds.

EXPERIMENTAL

Materials

Syntheses of crown ether carboxylic acids **VIII–XII** and **XV**, crown ether phosphonic acid monoethyl esters **XIII** and **XIV**, and proton-ionizable crown compounds **XVIII–XX** have been reported [2,8,11–15].

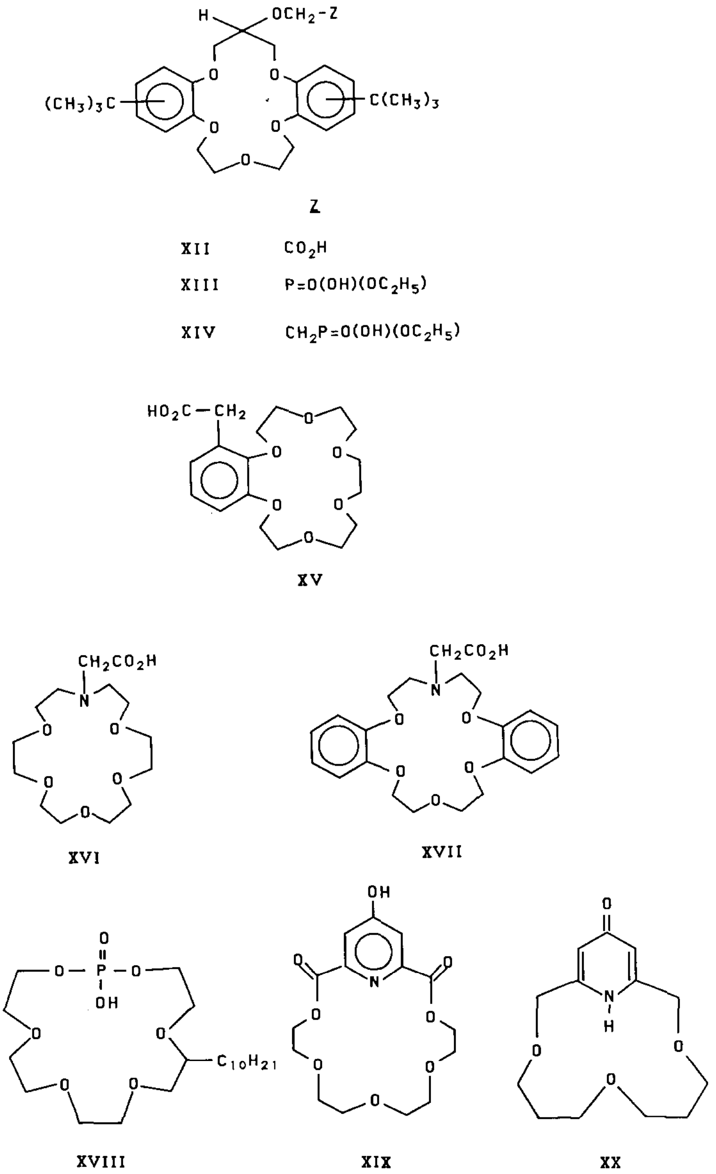


Fig. 1 (continued).

For synthesis of **XVI**, 5.00 g (19.0 mmol) of monoaza-18-crown-6 [16] and 15 g of anhydrous potassium carbonate were stirred in acetonitrile (100 ml) for 2 h. A solution of chloroacetic acid (2.00 g, 20.3 mmol) in acetonitrile (25 ml) was added dropwise and the reaction mixture was refluxed for 5 h. The solvent was evaporated in vacuo, water (100 ml) was added, and the pH was adjusted to 7 with 6N HCl. Extraction with dichloromethane (3 × 100 ml), followed by drying of the combined extracts over magnesium sulfate and evaporation in vacuo gave a crude product which was purified by column chromatography twice on silica gel with dichloromethane–methanol (97 : 3) as eluent to give 4.09 g (63%) of **XVI** as a white solid with a melting point of 88–89 °C. IR (neat, cm^{-1}): 3507 (OH), 1746 (C=O), 1630 (CO_2^-), 1110 (CO). ^1H NMR ($CDCl_3$, δ): 8.60 (br s, 1H), 4.05–3.10 (m, 26H). Analysis calculated for $C_{14}H_{27}NO_7 \cdot 2.0H_2O$: C, 47.25; H, 8.74. Found: C, 47.56; H, 8.63.

For the preparation of **XVII**, 2.50 g (6.96 mmol) of symmetrical monoazadibenzo-18-crown-6 [17], 1.19 g (7.75 mmol) of methyl bromoacetate and 1.40 g (13.9 mmol) of triethylamine were refluxed in 30 ml of ethanol–dioxane (1 : 1) for 3 days. After addition of another 1.0 g of methyl bromoacetate, the reaction mixture was refluxed for 4 days. The solvents were evaporated in vacuo, water (100 ml) and dichloromethane (80 ml) were added, and the mixture was filtered. The organic layer was separated, washed with brine (2 × 50 ml), dried over magnesium sulfate, and evaporated in vacuo. The resulting solid was washed with pentane and dried under vacuum at 60 °C to give 2.35 (78%) of the hygroscopic methyl ester of **XVII** with a melting point of 114–115 °C. IR (KBr, cm^{-1}): 1740 (C=O), 1253, 1122 (CO). ^1H NMR ($CDCl_3$, δ): 6.97 (s, 8H), 4.40–3.05 (m, 21H). Analysis calculated for $C_{23}H_{29}NO_7 \cdot O.5H_2O$: C, 62.71; H, 6.86. Found: C, 62.60; H, 6.78. A solution of 2.20 g of the methyl ester was refluxed in a solution of ethanol (45 ml) and 10% aqueous sodium hydroxide (95 ml) for 14 h. After filtration, the pH was adjusted to 7 with concentrated hydrochloric acid and the solvents were evaporated in vacuo. The residue was stirred with dichloromethane (100 ml) for 10 h. The filtered organic solution was dried over magnesium sulfate and the solvent was evaporated to give 2.10 g (98%) of hygroscopic **XVII** with a melting point of 194–196 °C. IR (KBr, cm^{-1}): 3475 (OH), 1730 (C–O), 1629 (CO_2^-), 1253, 1122 (CO). Analysis calculated for $C_{22}H_{27}NO_7 \cdot O.3H_2O$: C, 62.49; H, 6.58. Found: C, 62.47; H, 6.53.

All other chemicals were reagent grade unless stated otherwise. *p*-Dioxane was purified by the recommended method [18]. Demineralized water was prepared by passing distilled water through three Barnstead D8992 combination cartridges in series. A 10% aqueous solution of tetramethylammonium hydroxide (TMAH) was standardized against potassium hydrogen phthalate and used to prepare a 0.10 M solution of TMAH in 70% dioxane-water (by volume).

Ionization constant determination

The titration procedure for determination of ionization constants was essentially that of Albert and Serjeant [19]. A. 0.01-M reagent solution was titrated in the absence of inert salt. Measurements of pH were made with a Fisher Accument pH meter which could be read to 0.001 pH units. The pH meter was standardized against phthalate and borate buffers both before and after each titration.

Into a thermostated (25.0 or 35.0 ± 0.1° C) titration vessel equipped with a magnetic stirring bar, a glass combination electrode, and microburet of 5.0 ml capacity, 0.50 mmole of the carboxylic acid in 4.75 ml of 70% dioxane–water (v/v) was introduced. This initial volume was taken to allow for the change in total volume of the solution on titrant addition [19]. For practical purposes, the error caused by volume correction is nearly negligible (less than 0.01 pH unit for the central five readings of titration set), with a maximum error of 0.018 pH unit [20]. After 10 min, the titration was initiated by addition of a 0.50-ml aliquot of 0.10-M TMAH and recording the highest stable pH value. Further titrant additions were made in the same fashion. Titrations were conducted in duplicate and values were reproducible within ± 0.01 pH unit.

The relationship of Van Uitert and Haas [21] was utilized to evaluate the hydrogen ion concentration from the pH meter value (B)

$$-\log[\mathrm{H}^+] = B + \log U_{\mathrm{H}}^{\ominus} + \log \gamma \pm \qquad (1)$$

Values of the correction factor $\log U_{\mathrm{H}}^{\ominus}$ have been determined experimentally [22] and mean activity coefficients $\gamma \pm$ were calculated by interpolation from the data of Harned and Owen [23] assuming that the mean activity coefficients are the same on both molal and molar scales.

Ionization of a proton-ionizable crown compound (HA) in an aqueous medium gives hydrogen ion (H^+) and the anion A^-. The equilibrium constant is given by

$${}^{T}K_a(\mathrm{aq}) = ([\mathrm{H}^+][\mathrm{A}^-]/[\mathrm{HA}])(\gamma_{\mathrm{H}} + \gamma_{\mathrm{A}}^{-}/\gamma_{\mathrm{HA}}) \qquad (2)$$

which is readily transformed into

$${}^{T}\mathrm{p}K_a(\mathrm{aq}) = -\log[\mathrm{H}^+] + \log([\mathrm{HA}]/[\mathrm{A}^-]) + 2\log 1/\gamma \pm \qquad (3)$$

Assuming that γ_{HA}, the mean activity coefficient of the un-ionized acid, is unity, the final equation for computing ${}^{T}\mathrm{p}K_a$ in the dioxane–water mixture is obtained by combination of eqns. (1) and (3)

$${}^{T}\mathrm{p}K_a = B + \log U_{\mathrm{H}}^{\ominus} + \log([\mathrm{HA}]/[\mathrm{A}^-]) + \log 1/\gamma \pm \qquad (4)$$

The thermodynamic functions ($\Delta G^{\ominus}$, $\Delta H^{\ominus}$, $\Delta S^{\ominus}$) associated with the ionization were calculated employing the standard equations

$$\Delta G^{\ominus}(25\,^{\circ}\mathrm{C}) = 1.3646\ {}^{T}\mathrm{p}K_a(25\,^{\circ}\mathrm{C}) \qquad \text{(kcal)} \tag{5}$$

$$\Delta G^{\ominus}(35\,^{\circ}\mathrm{C}) = 1.4103\ {}^{T}\mathrm{p}K_a(35\,^{\circ}\mathrm{C}) \qquad \text{(kcal)} \tag{6}$$

$$\Delta H^{\ominus} = 42.06\ \left[{}^{T}\mathrm{p}K_a(25\,^{\circ}\mathrm{C}) - {}^{T}\mathrm{p}K_a(35\,^{\circ}\mathrm{C})\right. \qquad \text{(kcal)} \tag{7}$$

$$-\Delta S^{\ominus}(25\,^{\circ}\mathrm{C}) = 3.353\ \left[\Delta G^{\ominus}(25\,^{\circ}\mathrm{C}) - \Delta H^{\ominus}\right] \qquad \text{(cal)} \tag{8}$$

$$-\Delta S^{\ominus}(35\,^{\circ}\mathrm{C}) = 3.2446\ \left[\Delta G^{\ominus}(35\,^{\circ}\mathrm{C}) - \Delta H^{\ominus}\right] \qquad \text{(cal)} \tag{9}$$

RESULTS

Thermodynamic acid dissociation constants, ${}^{T}\mathrm{p}K_a$, for proton-ionizable crown compounds **VII**–**XX** in 70% dioxane–water (v/v) at 25 and 35 °C are summarized in Table 1. A ${}^{T}\mathrm{p}K_a$ value of 11.16 ± 0.02 at 25 °C in 70% dioxane–water was determined for the model compound *N,N*-dimethylglycine. Within experimental error, the ${}^{T}\mathrm{p}K_a$ values for **XIII** were the same at 25 and 35 °C. On the other hand, the ${}^{T}\mathrm{p}K_a$ values for **VIII**–**XII** were slightly larger at the higher temperature. Insufficient amounts of **VII** and **XIV**–**XX** were available to conduct the ${}^{T}\mathrm{p}K_a$ determinations at the higher

TABLE 1

Thermodynamic acid dissociation constants, ${}^{T}\mathrm{p}K_a$, for proton-ionizable crown compounds in 70% dioxane–water (v/v)

Acid	${}^{T}\mathrm{p}K_a$ [a]	
	25.0 °C	35.0 °C
VII	8.44 ± 0.21	ND [b]
VIII	8.66 ± 0.02	8.74 ± 0.04
IX	8.40 ± 0.01	8.48 ± 0.02
X	8.47 ± 0.02	8.56 ± 0.04
XI	8.87 ± 0.11	8.98 ± 0.23
XII	8.05 ± 0.02	8.19 ± 0.21
XIII	5.41 ± 0.15	5.42 ± 0.16
XIV	6.19 ± 0.20	ND [b]
XV	7.30 ± 0.03	ND [b]
XVI	10.20 ± 0.06	ND [b]
XVII	10.83 ± 0.28	ND [b]
XVIII	4.43 ± 0.04	ND [b]
XIX	9.83 ± 0.03	ND [b]
XX	13.71 ± 0.11	ND [b]

[a] Obtained using a set of at least seven determinations.

[b] Not determined.

TABLE 2

Thermodynamic parameters for acid dissociation of proton-ionizable crown compounds in 70% dioxane–water (v/v)

Acid	Thermodynamic function				
	$\Delta G^{\ominus}$ (kcal mol^{-1})		$-\Delta H^{\ominus}$ (kcal mol^{-1})	$-\Delta S^{\ominus}$ (cal mol^{-1} K^{-1})	
	25 °C	35 °C		25 °C	35 °C
VIII	11.8	12.3	3.4	51	51
IX	11.5	12.0	3.4	50	50
X	11.6	12.1	3.8	52	52
XI	12.1	12.7	4.6	56	56
XII	11.0	11.6	5.9	57	57
XIII	7.4	7.6	0.4	26	26

temperature. Thermodynamic funtions, $\Delta G^{\ominus}$, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$, associated with the ionization of the proton-ionizable crown ethers **VIII–XIII** are recorded in Table 2.

DISCUSSION

When taken together with the previously-examined **I–VI** [10], compounds **VII–XII** (Fig. 1) provide a large series of closely-related dibenzo crown ether carboxylic acids from which the effect of systematic structural variation upon acidity may be deduced. Variations include the crown ether ring size (Y variation, Fig. 1) and the introduction of an alkyl group attached directly to the crown ether ring, to the side arm which bears the ionizable group, and to the aromatic rings.

For **XII–XIV** the crown ether ring size and the alkyl groups and their attachment sites remain constant, but the ionizable group is changed from a carboxylic acid to a phosphonic acid monoester followed by insertion of a methylene group into the side arm which connects the crown ether ring and the ionizable group. Compounds **XV–XVII** are substituted acetic acids which are linked to an aromatic group substituent of a crown ether ring or to the nitrogen atom of a monoaza crown ether. Finally, in **XVIII–XX** the ionizable unit becomes part of the crown ring itself.

Influence of structural variation upon $^{T}p\mathrm{K}_a$

For crown ether carboxylic acids **I–III** the $^{T}\mathrm{p}K_a$ values at 25 °C in 70% dioxane–water (v/v) are 7.80, 7.98 and 8.34, respectively [10]. The decrease in acidity which accompanies expansion of the crown ether ring size has been attributed to enhanced hydrogen bonding of the pendant carboxylic acid group with the transannular dialkyl ether oxygen [10]. Pairs of crown ether carboxylic acids **VII**, **V** and **VIII**, **XI** differ only by the presence of an additional ethyleneoxy unit in the latter compound of each pair. With the former pair, the $^{T}\mathrm{p}K_a$ values at 25 °C in 70% dioxane–water increase slightly from 8.44 for **VII** (Table 1) to 8.53 [10] for **V**; with the latter pair, there is a more substantial enhancement from 8.66 for **VIII** to 8.87 for **XI**. Such diminished acidity with expansion of the crown ether rings is in agreement with the previous findings.

Compound groupings of **II**, **IX**, **X**, **V**, **VI** and **II**, **IV**, **VIII** and **II**, **XII** show the effect of alkyl group attachment to carbon atoms of the macrocyclic ring, the side arm, and benzo group substituents of the crown ether ring, respectively. For the first two groupings, the length of the alkyl group chain is also varied. The $^{T}\mathrm{p}K_a$ values at 25 °C in 70% dioxane–water for **II**, **IX**, **X**, **V** and **VI** are 7.98 [10], 8.40, 8.47, 8.53 [10] and 8.71 [10], respectively. Hence replacement of the hydrogen in the three-carbon bridge of **II** with a butyl group in **IX** (variation of R_1, Fig. 1) produces a substantial diminution of acidity. Then as the alkyl group is lengthened from butyl to octyl to decyl to tetradecyl, the acidity continues to decrease in a regular fashion. Since the introduction and variation of alkyl groups at a site so distant from the carboxylic acid function should exert a negligible inductive effect, the decreases in acidity just noted must arise from a different interaction. Examination of Corey-Pauling-Kortun (CPK) space-filling models shows that when the alkyl groups extend away from the hydrophilic polyether ring, the ionizable group is constrained to the region directly over the crown ether cavity. This should enhance the transannular hydrogen bonding of the carboxylic acid groups in **IX**, **X**, **V** and **VI** with their dialky ether oxygens compared with **II** and produce the observed decrease in acidity. The regular decrease in acidity as the alkyl group is lengthened suggests that enhanced alkyl group lipophilicity favors conformations in which the carboxylic acid group is correctly positioned for hydrogen bonding interactions.

For the series of **II**, **IV**, **VIII**, the structural variation is attachment of an alkyl group to the side arm (R_2 variation, Fig. 1). The $^{T}\mathrm{pK}_a$ values at 25 °C in 70% dioxane–water are 7.98 [10], 8.45 [10] and 8.66 for **II**, **IV** and **VIII**, respectively. The acidity decrease for **IV** compared with **II** undoubtedly arises from replacement of an alpha-hydrogen on the latter with an acid-weakening alkyl gorup. In terms of an inductive effect, replacement of the ethyl group in **IV** with an octyl group in **VIII** should have a negligible influence upon the acidity of the ionizable group. It is proposed that once again the tendency of a lipophilic alkyl group to extend away from the polar polyether cavity favors conformations in which the carboxylic acid group can hydrogen bond with an oxygen atom of the crown ether ring.

Compounds **II** and **XII** differ by the replacement of one hydrogen on each benzo group of **II** with a tert-butyl group in **XII**. Since this substitution is too remote from the carboxylic acid group to exert either an inductive effect or influence its positioning with respect to the polyether ring oxygens, it is not surprising that the ${}^{T}\mathrm{p}K_a$ values at 25 °C in 70% dioxane–water for **II** (7.98 [10]) and **XII** (8.05) are very nearly the same.

The alkyl-group substituted dibenzo crown ether carboxylic acids **X** and **XII** are structural isomers which have ${}^{T}\mathrm{p}K_a$ values of 8.47 and 8.05, respectively, at 25 °C in 70% dioxane–water. The lower acidity of **X** indicates a closer proximity of the carboxylic acid group to the polyether ring than in **XII**. Such preorganization of the binding site [24] might be expected to influence the metal ion complexation selectivity of the ionized ligands. Indeed, **X** has been found to be considerably more selective than **XII** in competitive transport of alkali metal cations across liquid membranes [7].

Compound **XV**, in which the carboxylic acid function is attached to a benzo group substituent of a crown ether ring, is the most acidic crown ether carboxylic acid examined. The observed ${}^{T}\mathrm{p}K_a$ value of 7.30 at 25 °C in 70% dioxane–water is considerably lower than the value of 8.32 reported [10] for acetic acid under the same conditions. Since the $\mathrm{p}K_a$ of phenylacetic acid in water is 0.5 units lower than that for acetic acid [25], it appears that the enhanced acidity of **XV** relative to acetic acid in 70% dioxane–water may be attributed primarily to an inductive effect. Examination of CPK models indicates a preferred conformation in which the carboxylic acid group is directed away from the polyether portion of the molecule.

Compounds **XVI** and **XVII** are crown amino acids with ${}^{T}\mathrm{p}K_a$ values of 10.20 and 10.83, respectively, at 25 °C in 70% dioxane–water. This compares with a value of 11.16 determined for the model compound *N*,*N*-dimethylglycine under the same conditions. The much lower acidities of **XVI** and **XVII** relative to the crown ether carboxylic acids **I**–**XII** and **XV** strongly indicates that ionization of the crown amino acids involve deprotonation at nitrogen in the zwitterion form. Compared with **XVI**, the two benzo groups in **XVII** introduce considerable rigidity into the crown ring which may be responsible for the differing acidities of these two crown amino acids.

In compound **XIII**, the carboxylic acid group in **XII** has been replaced with a phosphonic acid monoethyl ester group which lowers the ${}^{T}\mathrm{p}K_a$ value from 8.05 to 5.41. The crown phosphonic esters **XIII** and **XIV** are identical except for the insertion of an extra methylene group into the side arm which joins the crown ether ring and ionizable group in the latter. This structural modification raises the ${}^{T}\mathrm{p}K_a$ value to 6.19. Examination of CPK models reveals that the longer side arm in **XIV** allows the phosphonic ester group to be better positioned for transannular hydrogen bonding with the dialkyl ether oxygen of the crown ether ring. It is interesting to note that **XIV** is more selective than **XIII** in competitive solvent extraction of alkali metal cations [8].

Proton-ionizable crown compounds **XVIII**–**XX** differ from the previously-discussed macrocycles in that the ionizable group is part of the crown ring itself. Variation of the ionizable group type produces compounds whose ${}^{T}\mathrm{p}K_a$ values vary from 4.43 for the crown dialkyl phosphate **XVIII** to 13.70 for crown pyridone **XX**.

Thermodynamic functions for ionization

The temperature variation method utilized for the computation of $\Delta H^{\ominus}$ is subject to some error because (i) the enthalpy change associated with acid dissociation is relatively small, and (ii) values of ${}^{T}\mathrm{p}K_a$ have not been obtained at several temperatures which would allow use of a more accurate graphical method. Errors of 0.01 in the ${}^{T}\mathrm{p}K_a$ determinations at the two temperatures employed in this study could produce a maximal error of 0.42 kcal mol $^{-1}$ in the $\Delta H^{\ominus}$ value.

Although the present temperature variation method affords $\Delta H^{\ominus}$ values which contain relatively large errors, the calculated thermodynamic functions (Table 2) are still of considerable utility. Proton ionization of crown ether carboxylic acids **VIII–XII** in 70% dioxane–water is clearly exothermic. The fairly large negative values of $\Delta S^{\ominus}$ for these compounds may be rationalized as arising from requisite additional solvation of the carboxylate anion by water molecules. On the other hand, for the crown ether phosphonic acid monoethyl ester **XIII** proton ionization is only weakly exothermic and the negative $\Delta S^{\ominus}$ value is only half as large as those for the crown ether carboxylic acids. Such results suggest a considerable influence of the ionizable group identity upon the thermodynamic parameters for proton ionization.

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