

The Electrostatic Effects in the Ionization of Weak Acids in Water and Water-Dioxane Mixtures

GUNNAR AKSNES

Chemical Institute, University of Bergen, Bergen, Norway

The equation for the ionization of weak acids: $-RT\ln(K/C) = A_{\text{non}} + A_{\text{el}}$, proposed by Gurney is discussed. It is shown that when A_{el} is expressed by Ne^2/r^*D according to Born, the plot of ΔF against $1/D$ is nearly linear. The r^* -values thus obtained for various acids differ from values found earlier by Baughan. The temperatures at which the ionization constants of various acids have their maximum values are in agreement with the temperatures evaluated from the Gurney equation. The empirical equation of Harned and Embree for the temperature dependence of the ionization constants around the maximum results from the equation of Gurney as a good approximation.

The ionization of weak acids in water-dioxane is discussed.

Gurney¹, twentyfour years ago, proposed that the free energy of ionization G of acids in solution at infinite dilution of acid might be expressed as the sum of a non-electrostatic term A_{non} and an electrostatic term, A_{el} :

$$-RT\ln(K/C) = A_{\text{non}} + A_{\text{el}} \quad (1)$$

where C is a statistical factor. If the electrostatic term is expressed by Born's² formula, eqn. (1) takes the form:

$$\Delta F = -RT\ln K = \Delta F_{D=\infty} + Ne^2/r^*D \quad (2)$$

where r^* is defined as: $\frac{1}{r^*} = \frac{1}{2}\left(\frac{1}{r_+} + \frac{1}{r_-}\right)$; r_+ and r_- are the radii of the two ions. $\Delta F_{D=\infty}$ is the free energy of ionization at the hypothetical dielectric constant $D = \infty$. The factor C has been set equal to 1.

Baughan³ and later LaMer and Brescia⁴ and Magee *et al.*⁵ have discussed the equation of Gurney and tested its applicability to the ionization of weak acids in water. Upon differentiation of eqn. (2) Baughan³ derived the following expression for the enthalpy function:

$$\Delta H = \Delta H_{D=\infty} + \frac{Ne^2}{r^*} \left[\frac{1}{D} \left(1 + \frac{T}{D} \frac{dD}{dT} \right) \right] \quad (3)$$

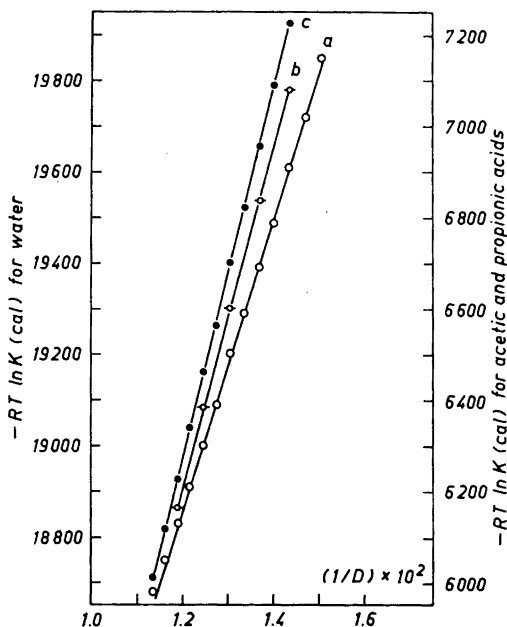


Fig. 1. Plots of $-RT \ln K$ against $1/D$ for the ionization of weak acids; a) water, b) acetic acid, c) propionic acid.

where $\Delta H_{D=\infty}$ is the enthalpy change at the hypothetical dielectric constant $D = \infty$. In Table 1 are recorded the values of r^* obtained by Baughan for several weak acids. Harned and Owen⁶ have pointed out that the plot of ΔH against $\frac{1}{D} \left(1 + \frac{T}{D} \frac{dD}{dT} \right)$ shows distinct curvature, *i.e.*, eqn. (3) seems therefore not to be strictly valid.

An examination of the available data for ionization constants at various temperatures shows that the free energy of ionization of the acids is almost linearly dependent on $1/D$. Plots of $-RT \ln K$ against $1/D$ for water and for acetic and propionic acid are shown in Fig. 1. The plot for the ionization of water shows greatest deviation from linearity; however, when a straight line is drawn through the points in the middle of the temperature interval the observed ΔF -values at 0° and 60° are only approximately 30 cal higher than the values corresponding to the linear plot. If ΔF for the ionization of acids was exactly linearly dependent on $1/D$ then ΔF extrapolated to $D = \infty$ would be temperature independent, *i.e.*, $\Delta F_{D=\infty} = \Delta H_{D=\infty}$ and $\Delta S_{D=\infty} = 0$. The assumption of Gurney¹ that the free energy of ionization can be divided into two parts — a non-electrostatic part insensitive to the environment and independent of temperature, and an electrostatic part sensitive to the environment — seems therefore to be nearly fulfilled.

Table 1 also records the values of r^* for 31 weak acids calculated from the slope of the straight line plot of $-RT \ln K$ against $1/D$. The most remarkable

Table 1. Thermodynamic functions for ionization of weak acids *.

Acid	Mean radii r^* from Baughan ³	Mean radii r^* This paper	T_{\max} exp.	T_{\max} from eqn. (8b)	T_{\max} from eqn. (8c)	Ref.
Water	0.68	1.04	—	—	—	9
Acetic	0.85	0.89	298	295	291	9
Formic	0.68	1.14	297	298	293	9
Propionic	0.78	0.87	293	295	291	9
Butyric	0.65	0.81	283	273	279	9
Oxalic(2)	—	0.80	—	—	—	9
Sulphuric(2)	—	0.75	—	—	—	9
Phosphoric(1)	—	1.27	—	—	—	9
Phosphoric(2)	0.74	0.65	—	—	—	9
Glycine(A)	—	2.90	—	—	—	9
Glycine(B)	—	1.95	—	—	—	9
Alanine(A)	—	2.30	—	—	—	9
Alanine(B)	—	1.81	—	—	—	9
Boric	0.66	0.63	—	—	—	9
Lactic	0.63	1.14	~300	306	296	9
Glycolic	0.71	1.18	~300	314	300	9
Malonic(2)	—	0.66	—	—	—	9
Iodoacetic	—	1.05	—	—	—	15
Bromoacetic	—	1.15	—	—	—	15
Chloroacetic	0.76	1.19	—	—	—	15
Fluoroacetic	—	1.22	—	—	—	15
Benzoic	—	1.00	293	294	290	16
<i>m</i> -Cyanobenzoic	—	1.23	303	309	298	16
<i>m</i> -Chlorobenzoic	—	1.19	303	317	302	16
<i>m</i> -Bromobenzoic	—	1.13	298	300	294	16
<i>p</i> -Chlorobenzoic	—	1.15	308	319	303	16
<i>p</i> -Nitrobenzoic	—	1.25	303	301	294	16
<i>p</i> -Bromobenzoic	—	1.13	310	316	301	16
<i>p</i> -Cyanobenzoic	—	1.23	298	305	296	16
<i>p</i> -Hydroxybenzoic	—	1.01	306	322	304	16
Cyanoacetic	—	1.37	—	—	—	17

* The numerical value of Ne^2/r^*D is calculated with $^{14}N = 6.0247 \times 10^{23}$, $e = 4.8029 \times 10^{-10}$ esu and $1 \text{ erg} = 2.3901 \times 10^{-8} \text{ cal}$.

feature is that the calculated r^* -values except for boric acid and dihydrogen phosphate are much larger than the values calculated by Baughan³ from the ΔH function (eqn. 3). However, the new r^* -values are of the order of magnitude to be expected from theoretical considerations. The r^* -value calculated for the ionization of water is found to be 1.04 Å. The radius of the hydroxyl ion is probably very near 1 Å; that of the hydronium ion is perhaps somewhat greater than 1 Å. We find therefore that the calculated r^* -value for the ionization of water, 1.04 Å, is close to the value expected from the ionic radii. The second step in the dissociation of sulphuric, phosphoric, malonic and oxalic acids gives very small r^* -values which is in accordance with stronger electrostatic forces during the separation of the doubly negatively charged anion and the proton. The zwitterions alanine and glycine give very large r^* -values which are in agreement with the charge neutralization effect of the dipole. In series of substituted acids, for example halogen-substituted acetic acids and various substituted benzoic acids, the r^* -values increase with increasing capacity of the substituents to withdraw electrons from the dissociating hydroxyl group. The negative charge in the anion will thus be spread more evenly throughout the ion resulting in a decreasing electrostatic interaction between the proton and the anion during the separation process.

Eqn. (2) can also be used to calculate the temperature at which the ionization constant has its maximum value. Differentiation of eqn. (2) with respect to temperature gives:

$$-R \ln K - RT \frac{d \ln K}{dT} = \frac{Ne^2}{r^*} \frac{d(1/D)}{dT} \quad (4)$$

Thus, when K has its maximum value:

$$-R \ln K_{\max} = \frac{Ne^2}{r^*} \cdot \frac{d(1/D)}{dT} \quad (5)$$

The experimental values⁷ for the dielectric constant, D , in the interval 0–60°C can be expressed as an inverse function of T^2 or T^3 with an accuracy better than ± 0.5 %:

$$D = \frac{1.013 \times 10^7}{T^2 + 4.0256 \times 10^4}, \text{ or} \quad (6)$$

$$D = \frac{4.385 \times 10^9}{T^3 + 2.928 \times 10^7} \quad (7)$$

Substitution of eqn. (6) in eqn. (5) gives:

$$-R \ln K_{\max} = \frac{2Ne^2 \cdot T_{\max}}{r^* \times 1.013 \times 10^7} \quad (8a)$$

or

$$-\log K_{\max} = \frac{1.432 \times 10^{-2}}{r^*} \cdot T_{\max} \quad (8b)$$

When the same substitution is made with D according to eqn. (7) the following expression results:

$$-\log K_{\max} = \frac{5.0 \times 10^{-5}}{r^*} \cdot T_{\max}^2 \quad (8c)$$

The values of T_{\max} calculated from the experimental values of K_{\max} using the r^* values from column 3 in Table 1 are recorded in columns 5 and 6 of the same table. It is seen that the T_{\max} -values of different acids calculated with the expression of D according to eqn. (6) and (7) show approximately the same conformity with the experimental T_{\max} -values.

According to Harned and Embree⁸ the ionization constants of various acids can approximately be expressed by the general equation:

$$\log K - \log K_{\max} = -p(T - \Theta)^2 \quad (9)$$

Here, Θ is the temperature at which the ionization constant has its maximum value and p is a general constant which has the value of approximately 5.0×10^{-5} degree⁻². This experimental value of p can be derived on the basis of the above equations, as follows.

Substitution of expression (7) for the dielectric constant into eqn. (4), introduction of the numerical values of N and e , and subtraction of eqn. (8c), gives:

$$\log K - \log K_{\max} = \frac{5.0 \times 10^{-5}}{r^*} (\Theta^2 - T^2) - T \frac{d \log K}{dT} \quad (10)$$

where T_{\max} has been put equal to Θ . The last term is, from eqn. (9), equal to:

$$d \log K / dT = 2p(\Theta - T) \quad (11)$$

so that eqn. (10) becomes:

$$\log K - \log K_{\max} = \frac{5.0 \times 10^{-5}}{r^*} (\Theta^2 - T^2) - 2p(\Theta T - T^2) \quad (12)$$

Equating the right sides of eqns. (9) and (12) now gives:

$$p = \frac{5.0 \times 10^{-5}}{r^*} \approx 5.0 \times 10^{-5} \quad (13)$$

since the values of r^* for the various acids for which eqn. (9) has been experimentally verified, according to Table 1 are of the order of 1 Å.

It might be argued that for example glycine and alanine which have r^* -values in the neighbourhood of 2 Å should not give so good agreement with the empirical eqn. (9) of Harned and Embree⁸. However, the T_{\max} values for glycine and alanine used to fit eqn. (9) are very uncertain since they are derived from measurements below T_{\max} only.

THE IONIZATION OF WEAK ACIDS IN WATER-DIOXANE MIXTURES

The ionization constants of weak acids become markedly smaller when dioxane is added to the water. Thus, K for acetic acid in pure water is 1.754×10^{-5} at 25°C as compared with 4.75×10^{-9} in 70 % dioxane-water mixture⁹ (by weight). However, according to the experimental values of K at various temperatures⁹ the temperature at which the ionization constant has its maximum value is very little different from that in pure water. If the ionization constant of weak acids in dioxane-water mixtures is expressed by eqn. (2) using the macroscopic dielectric constant of the mixture, the calculated values of r^* increase rapidly with the dioxane content. The same is true for the A_{non} term. Since the A_{non} term is the non-electrostatic contribution to the free energy of ionization one would expect this term to be relatively independent on whether the transfer of the proton from the acid to a neighbouring water molecule takes place in pure water, or in water-dioxane mixtures. Gurney¹⁰ expresses the temperature at which the ionization constant has its maximum value as follows:

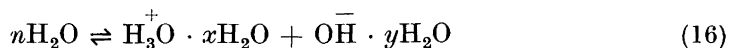
$$T_{\text{max}} = \vartheta(1 + A_{\text{non}}/A_{\text{el}}) \quad (14)$$

where ϑ is an empirical constant for expressing the temperature variation of the dielectric constant: $D = D_0 \exp(-T/\vartheta)$. Since ϑ shows only a small decrease from water to dioxane-water mixtures (approximately 15 % decrease from pure water to 70 % dioxane-water mixtures) the decrease in T_{max} which is of the same magnitude as for ϑ can be explained if the ratio $A_{\text{non}}/A_{\text{el}}$ has approximately the same value in water as in water-dioxane mixtures. If we assume that A_{non} is relatively independent of the dioxane content, as suggested above, it follows that also the electrostatic term, A_{el} , must be independent of the amount of dioxane present. We therefore tentatively conclude that A_{el} is dependent on the dielectric constant of the *water only* in the mixture. Consequently, eqn. (2) must be written:

$$-RT \ln K_c = \Delta F_{D=\infty} + Ne^2/r^*D_w \quad (15)$$

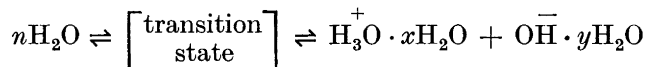
where D_w refers to the dielectric constant of the water in the mixtures.

The smaller ionization constants of weak acids in water-dioxane mixture thereby becomes a statistical effect. A statistical factor C is included in eqn. (1). Gurney¹¹ explains C as due to the difference between the number of solute molecules in reactants and products. For the ionization of water the reactant (the water) is not regarded as a solute but 2 solute species are formed, the hydronium ion and the hydroxyl ion, and Gurney, therefore, considers the difference as 2 and the statistical factor as 55.5^2 . Since the ions formed in every ionization process strongly immobilize a certain number of water molecules in their hydration sphere we assume that these immobilized water molecules should be included in the reaction products; therefore, the statistical factor must also account for the disappearance of the free water molecules which are held in the hydration shell. The ionization of water should accordingly be formulated:



where $n-2$ is the number of water molecules immobilized by the ions ($x + y = n-2$).

If the hydrated ions are regarded as separate units, then according to Gurney's view the difference between the solute particles in reactants and products is still 2. However, a statistical factor of 55.5^2 is much too small to account for the large decrease in the ionization constant of water in dioxane-water mixtures. A different approach to the problem seems possible from a reaction kinetic point of view. Suppose that a fixed relative orientation of a certain number of water molecules is necessary for the proton transfer to take place, not only of the two water molecules between which the proton is jumping but also of the water molecules which are necessary for the hydration of the proton and the hydroxyl ion formed. It seems reasonable to expect that for an exchange of the non-electrostatic energy (chiefly vibration) between the two water molecules and the two ions formed to occur, a spontaneous solvation of the ions in order to average out the energy with its environment is necessary. Since the frequency of vibration in water molecules is of the order of 10^{14} and the mean life time of hydrogen bonds¹² is of the order of 10^{-11} sec, the required configuration with closed hydrogen bonds between a certain number of water molecules should be able to exist over time intervals corresponding to a large number of vibrations. This necessary configuration may be regarded as a transition state and the number n of water molecules which is required in order to form the transition state will have to be included in the equilibrium equation:



and

$$K_c = \frac{[\text{H}_3\text{O}^+ \cdot x\text{H}_2\text{O}] \cdot [\text{OH}^- \cdot y\text{H}_2\text{O}]}{[\text{H}_2\text{O}]^n} \quad (17)$$

where K_c means the ionization constant on the concentration scale.

If the dielectric constant of water and its temperature variation were exactly the same in dioxane-water mixtures as in pure water, it would follow that:

$$\log K_{c(\text{water})} - \log K_{c(\text{mixture})} = n(\log 55.5 - \log M) \quad (18)$$

where M is the number of moles of water per liter of the mixture.

Fig. 2. Plots of $[\log K_{c(\text{water})} - \log K_{c(\text{mixture})}]$ against $[\log 55.5 - \log M]$ for different acids, a) water, b) acetic and propionic acids, c) formic acid, d) glycine.

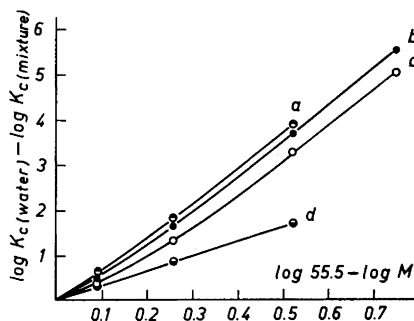


Table 2. ΔH and ΔS for the ionization of weak acids in water and water-dioxane mixtures¹³. Temp. 25°C.

Acid	Water		Formic		Acetic		Propionic		Glycine, K_A	
	ΔH kcal	ΔS e.u.	ΔH kcal	ΔS e.u.	ΔH kcal	ΔS e.u.	ΔH kcal	ΔS e.u.	ΔH kcal	ΔS e.u.
0	13.52	-18.7	-0.02	-17.6	0.09	-22.1	-0.16	-22.8	1.16	-6.9
20	13.52	-21.5	-0.36	-17.9	-0.05	-24.4	-0.05	-25.5	1.18	-8.1
45	13.19	-28.8	-1.07	-19.7	-0.44	-30.3	-0.21	-30.7	0.99	-10.9
70	12.66	-39.2	-1.47	-27.1	-0.61	-40.1	-0.20	-40.1	0.83	-15.4
82	—	—	-2.51	-31.8	-1.34	-50.8	-1.06	-51.2	—	—

Plots according to eqn. (18) are shown in Fig. 2. The curvature of the lines may indicate that D of water and its variation with temperature is not quite equal in pure water and in water-dioxane mixtures. It may also be due to an immobilization effect of the dioxane molecules upon the water in the mixture; this is easily seen to give deviation in the direction shown in Fig. 2. However, the n -values of about 5 to 7 which are calculated from the slopes of Fig. 2 for neutral acids are of the order of magnitude to be expected. Also, water has a n -value slightly higher than the fatty acids, which is in agreement with the ionization of water requiring one extra water molecule as compared with fatty acids. The average n -value for formic acid is somewhat smaller than the values for other fatty acids. This may be caused by greater conjugation in the formate ion as compared with the anions of other fatty acids; such an effect would be expected to reduce the average number of strongly immobilized water molecules. The n -value of glycine is approximately 3. Since glycine has a positively charged nitrogen atom and a zwitter ion is formed during the ionization process it is reasonable to expect that the difference between the number of strongly bonded water molecules in reactants and products will be greatly reduced as compared with neutral acids.

The experimentally evaluated ΔH - and ΔS -values for the ionization of weak acids in water-dioxane mixtures⁹ (Table 2) show that the large decrease of the ionization constant is chiefly due to a much larger negative value of the entropy of ionization. These facts are thus in accordance with the assumption that the decrease of the ionization constant in dioxane-water mixtures is chiefly due to a statistical effect.

REFERENCES

1. Gurney, R. W. *J. Chem. Phys.* **6** (1938) 499.
2. Born, M. *Z. Physik* **1** (1920) 45.
3. Baughan, E. C. *J. Chem. Phys.* **7** (1939) 951.
4. LaMer, V. K. and Brescia, F. *J. Am. Chem. Soc.* **62** (1940) 617.

5. Magee, J. L., Ri, T. and Eyring, H. *J. Chem. Phys.* **9** (1941) 419.
6. Harned, H. S. and Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*, Reinhold Publishing Corp., New York 1942, p. 531.
7. Collie, C. H., Hasted, J. B. and Ritson, D. M. *Proc. Phys. Soc. (London)* **60** (1948) 145.
8. Harned, H. S. and Embree, N. D. *J. Am. Chem. Soc.* **56** (1934) 1050.
9. Ref.⁶, p. 581.
10. Gurney, R. W. *Ionic Processes in Solution*, McGraw-Hill Book Co., New York 1953, p. 128.
11. Ref.¹⁰, p. 105.
12. Hall, L. *Phys. Rev.* **73** (1948) 775.
13. Ref.⁶, p. 514.
14. Moore, W. J. *Physical Chemistry*, Longmans, Green and Co. New York 1957, p. 441.
15. Ives, J. G. and Pryor, J. H. *J. Chem. Soc.* **1955** 2104.
16. Briegleb, G. and Bieber, A. *Z. Electrochem.* **55** (1951) 250.
17. Feates, F. S. and Ives, J. G. *J. Chem. Soc.* **1956** 2798.

Received April 25, 1962.