

The Relative Acidities of Water and Methanol

Henry I. Abrash

Department of Chemistry, California State University, Northridge, CA 91330-8262; henry.abrash@csun.edu

There is a potentially confusing disparity between the way the acidity constant of water is presented in general chemistry textbooks and in organic chemistry textbooks. Most general chemistry textbooks introduce the ion product, an approximation of the thermodynamic equilibrium constant for the autoprotolysis of water,

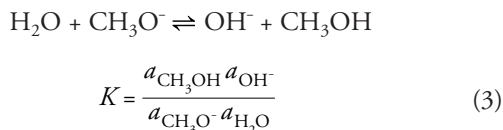
$$K_w = [\text{H}^+][\text{OH}^-] \approx a_{\text{H}_3\text{O}^+} a_{\text{OH}^-} = 10^{-14.0} \quad (1)$$

whereas most organic chemistry textbooks present a constant based on concentrations, including the concentration of water in a dilute aqueous solution (55.6 M) in the denominator, and assign a $\text{p}K_a$ value of 15.74 rather than 14.0:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = 10^{-15.74} \quad (2)$$

Earlier publications in this *Journal* have dealt with this question, some supporting the use of the ion product (1–3) and others supporting the constant that includes the water concentration (4–7). Those authors favoring concentration-based constants claim that activity-based values give water a special status and, by comparison, undervalue the acidity of alcohols such as glycerol and ethylene glycol (4, 7). None of these publications cite references providing experimental evidence concerning the relative acidities of alcohols and water, and the issue receives little or no attention other than presentation of equilibrium constant values in tables in organic chemistry texts.

One interesting feature of this debate is that the K_a value for methanol (3.2×10^{-16}) presented in many organic chemistry texts (e.g., 8) appears to be based on measurements of the activity-based equilibrium constant for the hydrogen ion transfer between water and methoxide ion in mixed solvents of water and methanol.



In the 1920s, Augusta Unmack reported detailed studies of the equilibrium of proton transfers of water and methanol, using a variety of methods and a variety of water–methanol solvents (9–11). These results may be the basis of the $\text{p}K_a$ value for methanol in current textbooks. I will review this experimental evidence, discuss some later publications, consider the structural implications of the acidity of methanol, and conclude with my views concerning the proper form for acidity constants.

Stating the Problem

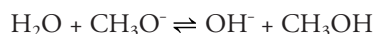
Any attempt to judge the relative acidities of two acids faces the problem of what reaction to consider and in which medium that reaction occurs. Because of solvent effects (12), the relative values of the autoprotolysis constants of water and methanol (13),

$$K_w = [\text{H}^+][\text{OH}^-] \approx a_{\text{H}_3\text{O}^+} a_{\text{OH}^-} = 10^{-14.0}$$

and

$$K_{\text{auto,Me}} = a_{\text{CH}_3\text{OH}_2^+} a_{\text{CH}_3\text{O}^-} = 10^{-16.7}$$

do not provide a valid comparison. A comparison of the acidities of water and methanol in water could provide a suitable comparison, but there is a lack of precise data because of the low degree of dissociation of methanol in dilute aqueous solutions. The most suitable basis for the comparison of acidities of methanol and water is the equilibrium constant for the reaction between methoxide ion and water to form hydroxide ion and methanol, measured over a range of concentrations of methanol–water mixed solvents.



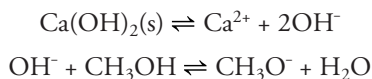
Experimental Results

As can be seen from the data in Table 1, measurements of the equilibrium constants for the transfer of a hydrogen ion from water to methanol in methanol–water solutions are quite variable and reflect differing experimental methods and different assumptions regarding activity coefficients. Unmack's

Table 1. Measured Equilibrium Constants for $\text{H}_2\text{O} + \text{CH}_3\text{O}^- \rightleftharpoons \text{OH}^- + \text{CH}_3\text{OH}$

| Author | Ref | Method | K |
|--------------------|-----|---|--|
| Unmack | 9 | Conductance | 0.37 ± 0.05 at 18 °C |
| Unmack | 9 | $\text{Ca}(\text{OH})_2$ solubility | 0.21 |
| Unmack | 9 | Methyl iodide solvolysis | 0.36 in 32 mol % methanol 1.13 in 15 mol % methanol |
| Unmack | 10 | Potentiometric | 0.47 in 8–100 mol % methanol |
| Unmack | 11 | Autoprotolysis constants and partition coefficients | ~2 |
| Koskikallio | 14 | Potentiometric | 0.13 ± 0.02 at 25 °C |
| Ballinger and Long | 15 | Conductance of 0.0375 M NaOH | 0.96 in 0–5 M aq methanol |
| Mock and Zhang | 16 | ^{13}C chemical shift | ~0.1 (recalculated) |

conductance data (9) are for the range 10 to 40 mol % water and are based on the Raoult's law activities of water and methanol and the assumption that hydroxide ion and methoxide ion have similar activity coefficients. The calcium hydroxide method is based on the observation that increasing methanol concentration (up to 1 M methanol) decreases the solubility of calcium hydroxide less than the solubility of lead chloride. This effect was ascribed to the reactions



and used to obtain the equilibrium constant for the latter reaction. The solvolysis of methyl iodide in various aqueous methanol solutions was treated as the sum of the rates of nucleophilic substitutions of hydroxide and methoxide ions and interpreted in terms of the activities of these two ions in the solutions. The potentiometric data (10) were interpreted by assuming that hydroxide ion and hydronium ion had the same partition coefficient between water and methanol and using a Debye–Hückel treatment to calculate activity coefficients. An attempt to calculate the equilibrium constant by comparing the autoprotolysis constants of water and methanol (11) foundered on the lack of reliable data for the junction potential.

In later work, Koskikallio (14) also measured hydrogen ion electrode potential in methanol–water solutions but used a cell without a liquid–liquid juncture and made assumptions different from Unmack's about activities. Ballinger and Long (15) used the conductivities of 0.0375 M NaOH in solvents ranging from 0 to 5 M aqueous methanol.

Mock and Zhang measured the dissociation of various alcohols in strongly alkaline aqueous solutions by the changes in ^{13}C chemical shifts versus H_- values (a measure of basicity in concentrated alkaline solutions) and obtained a $\text{p}K_{\text{a}}$ value for methanol at 26 °C of 14.46 ± 0.04 (16). Their definition of $\text{p}K_{\text{a}}$ is

$$\text{p}K_{\text{a}} = \text{H}_- + \log \frac{[\text{CH}_3\text{OH}]}{[\text{CH}_3\text{O}^-]} \quad (4)$$

A comparison with the earlier results requires a knowledge of the activity of water and methanol and the activity coefficient of methoxide ion. If we assume that H_- is equivalent to pH, the H_- value of 14.5 (the value at which methoxide and methanol concentrations are equal) corresponds to 2.5 M NaOH (17). Jandik et al. estimated the mean activity coefficient for NaOH in a 2.5 M solution to be approximately 0.75 (18). If we assume that this is also the activity coefficient for sodium methoxide ion and also assume that the water activity is approximately 1 and use a Raoult's law activity of methanol, we obtain a K value of approximately 0.1.

Conclusions

The difficulties in measuring activities in the various mixed solvents have resulted in varied estimates and prevented the determination of any precise value for the equilibrium constant. Nevertheless, the preponderance of evidence indicates that methanol is more acidic than water by at least a factor of approximately 2 or 3. This appears to be the source of the dissociation constant values published in organic

chemistry textbooks. For example, the concentration-based values in Wade (8) (methanol: 3.2×10^{-16} ; water: 1.8×10^{-16}) yield a ratio of 1.8.

Data relating to the acidities of higher alcohols are sparse. Mock and Zhang found that ethanol and 2-propanol in water have similar acidities and are about five times less acidic than methanol (16); in other words, approximately the same as water. These relative acidities of ethanol are consistent with the results of Ballinger and Long (15). Brauman and Blair (19) found the reverse order of alcohols acidities in the gas phase.

The relative acidities of water and methanol call for caution in invoking inductive effects on acidity. Replacement of a hydrogen atom with a methyl group does stabilize a carbocation and appears to stabilize the positive charges on ammonium ions, but the effect on destabilizing a negative charge is not as predictable. A methyl group does have a negative σ value (20), decreasing the acidity of a *p*-carboxyl group, but this effect is in conflict with the greater acidity of methanol compared to water. The possibility that the greater acidity of methanol may be due to differences in solvation enthalpies or entropies is diminished by the ion cyclotron resonance studies of Brauman and Blair (19), which showed a gas-phase proton transfer from methanol to hydroxide but found no evidence of the reverse reaction.

This apparent reversal of the inductive effect on acidity is a legitimate topic for an advanced organic chemistry course. However, most beginning organic chemistry textbooks show commendable reserve about the issue of inductive effects, and only a very few invoke the supposed inductive effect of a methyl group to explain the decreased acidity of acetic acid compared to formic acid. Indeed, the issue of the acidity of methanol and other alcohols rarely involves more than the presentation of dissociation constants in a table. This raises the point of the wisdom of presenting the dissociation constant of water in terms of concentrations ($\text{p}K_{\text{a}}$ 15.74) rather than its autoprotolysis constant. The main argument for this is that the autoprotolysis constant might mislead students regarding the relative acidities of alcohols and water. However, this issue is rendered moot by the lack of attention that this topic receives in text books.

Another argument against the autoprotolysis constant is that it grants water a special status. This is true only in aqueous systems and is due to water's role as solvent, not any inherent feature of water. The introduction of acid–base equilibria in general chemistry is restricted to aqueous solutions and is based on the Arrhenius definition of acidity, in which the behavior of a substance in water is the criterion for its acidity. According to the broader Brønsted–Lowry definition (21), water loses its special status in nonaqueous systems. However, this becomes an issue only when textbooks and instructors choose to present detailed calculations for nonaqueous systems based on the Brønsted–Lowry definitions rather than the Arrhenius definitions. Should they do so, concentration-based constants will be just as ineffective as dealing with solvent effects as constants based on activities in aqueous solutions.

The argument against a concentration-based dissociation constant for water is that it creates a discontinuity with the practice in general chemistry, physical chemistry, and analytic chemistry courses and therefore provides an added burden to the students. Furthermore, concentration based dissociation constants cannot be used to calculate Gibbs free energy changes.

Literature Cited

1. Baldwin, W.; Burchill, C. *J. Chem. Educ.* **1987**, *64*, 1067.
2. Baldwin, W.; Burchill, C. *J. Chem. Educ.* **1992**, *69*, 514.
3. Tapparo, A. *J. Chem. Educ.* **1992**, *69*, 516.
4. Starkey, R.; Norman, J.; Hintze, M. *J. Chem. Educ.* **1986**, *63*, 473.
5. Thomson, R. *J. Chem. Educ.* **1990**, *67*, 220.
6. de Lange, A.; Potgieter, J. *J. Chem. Educ.* **1991**, *68*, 304.
7. Thomson, R. *J. Chem. Educ.* **1992**, *69*, 515.
8. Wade, L. G. Jr. *Organic Chemistry*, 3rd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1995; p 26.
9. Unmack, A. *Z. Phys. Chem.* **1927**, *129*, 349.
10. Unmack, A. *Z. Phys. Chem.* **1928**, *131*, 371.
11. Unmack, A. *Z. Phys. Chem.* **1928**, *133*, 45.
12. Bates, R. G. *Determination of pH. Theory and Practice*; Wiley: New York, 1973; p 234.
13. Bjerrum, N.; Unmack, A.; Zechmeister, L. *Kgl. Dansk Videnskab Selskab, Math-fys Medd.* **1924**, *5* (11), 1.
14. Koskikallio, J. *Suomen Kemitilehti* **1957**, *30B*, 111.
15. Ballinger, P.; Long, F. A. *J. Am. Chem. Soc.* **1960**, *82*, 795.
16. Mock, W.; Zhang, J. *Tetrahedron Lett.* **1990**, *31*, 5687.
17. Yagil, G. *J. Phys. Chem.* **1967**, *71*, 1034.
18. Jandik, P.; Meites, L.; Zuman, P. *J. Phys. Chem.* **1983**, *87*, 238.
19. Brauman, J.; Blair, L. *J. Am. Chem. Soc.* **1970**, *92*, 5986.
20. March, J. *Advanced Organic Chemistry*; Wiley: New York, 1992; p 280.
21. See Kauffman, G. *J. Chem. Educ.* **1988**, *65*, 28.