

Generalization of Acid-Base Diagrams Based on the Unified pH-Scale

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So far, pH- $\lg c_i$ diagrams have been exclusively used for the theoretical description of acid-base equilibria in aqueous solutions. Here, this approach is extended to include acid-base equilibria in nonaqueous non-hydrogen-bond-donor (non-HBD) solvents following the acid-base theory of Brønsted and Lowry, and using a unified pH scale (pH_{abs} scale). This way, it is possible to estimate the approximate concentrations of all the species involved in acid-base equilibria in a solution at any solution

acidity $\text{pH}(\text{HS})$, and vice versa. The diagrams are excellent to illustrate the differences in behavior of species involved in the solution equilibria in different solvents, for example, an aqueous solution of acetic acid is an acidic solution; however, the same concentration of acetic acid in DMSO has a $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$ value of about 10.6, that is, it is a basic solution with reference to the aqueous pH scale.

1. Introduction

Proton-transfer reactions belong to the most abundant reactions in nature. Thus it is of utmost importance to evaluate either the concentrations of the species involved in proton-transfer equilibria depending on the acid strength of a given acid in a solvent HS, expressed by the solvent-dependent acidity constant of the acid (K_a , $\text{p}K_a$), or the solution acidity expressed by the negative decadic logarithm of the activity of solvated protons ($\text{pH}(\text{HS})$). Exact mathematical calculations can be rather complicated even for simple chemical systems. pH- $\lg c_i$ diagrams, often called acid-base diagrams, or Hägg diagrams, or Sillén diagrams are a versatile tool to present the interrelations between the logarithm of equilibrium concentrations of species existing in aqueous solutions, and the pH value of the specific solutions.^[1] They have hitherto been limited to aqueous systems, most likely because the pH in most nonaqueous solvents has not been defined consistently so far. However, following the concept of the unified acidity scale developed by Himmel et al.^[2] it can be extended to nonaqueous systems, although one has to keep in mind that additional equilibria can play a role in nonaqueous solutions.

2. Acid-Base Diagrams for Aqueous Solutions

The construction and use of acid-base diagrams for aqueous solutions has been described in detail in^[1] and is outlined here only briefly. The purpose of the diagrams is to display the decadic logarithm of the *equilibrium concentrations* of chemical species present in a solution (y axis) as a function of pH (x axis) (for the sake of simplicity, acid-base diagrams display the logarithm of concentrations instead of activities of species present in solutions, and concentrations will also be used in this manuscript throughout). Figure 1 depicts an acid-base diagram

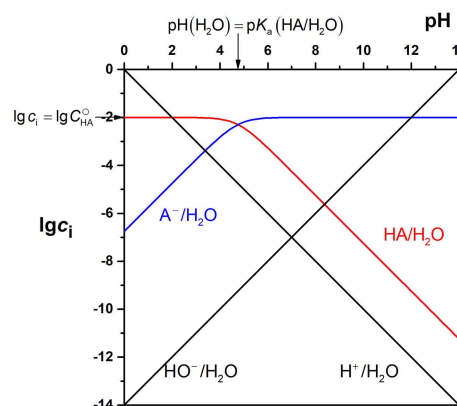


Figure 1. The pH- $\lg c_i$ diagram with the lines of $\text{H}^+/\text{H}_2\text{O}$, $\text{HO}^-/\text{H}_2\text{O}$, $\text{HA}/\text{H}_2\text{O}$ and $\text{A}^-/\text{H}_2\text{O}$ for an aqueous solution of acetic acid with $C_{\text{HA}}^0 = 0.01 \text{ mol L}^{-1}$ and $\text{p}K_a(\text{HA}/\text{H}_2\text{O}) = 4.75$.

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for an acid-base system HA/A^- , and the acid-base systems of the solvent water, i.e., $\text{H}^+/\text{H}_2\text{O}$ and $\text{H}_2\text{O}/\text{HO}^-$. The quantities $\lg c(\text{H}^+/\text{H}_2\text{O})$, $\lg c(\text{HO}^-/\text{H}_2\text{O})$, $\lg c(\text{HA}/\text{H}_2\text{O})$, and $\lg c(\text{A}^-/\text{H}_2\text{O})$ are plotted as functions of the solution pH according to (with C_{HA}^0 being the analytical concentration of the acid HA, and $\text{p}K_w$ the negative decadic logarithm of the ion product of water) [Eqs. (1)–(4)]:

$$\lg c(\text{H}^+/\text{H}_2\text{O}) = -\text{pH}(\text{H}_2\text{O}) \quad (1)$$

$$\lg c(\text{HO}^-/\text{H}_2\text{O}) = \text{pH}(\text{H}_2\text{O}) - \text{p}K_{\text{w}} \quad (2)$$

$$\lg c(\text{HA}/\text{H}_2\text{O}) = \lg C_{\text{HA}}^{\circ} - \lg(1 + 10^{\text{pH}(\text{H}_2\text{O}) - \text{p}K_{\text{a}}(\text{HA}/\text{H}_2\text{O})}) \quad (3)$$

$$\lg c(\text{A}^-/\text{H}_2\text{O}) = \lg C_{\text{HA}}^{\circ} - \lg(1 + 10^{-\text{pH}(\text{H}_2\text{O}) + \text{p}K_{\text{a}}(\text{HA}/\text{H}_2\text{O})}) \quad (4)$$

Acid-base diagrams display the equilibria of the solvent and solute (here HA) independently of each other.

As mentioned before, such diagrams can be used to (i) find the approximate equilibrium concentrations of all species involved in the chemical equilibria at any pH, and (ii) read the approximate pH of solutions having distinct equilibrium concentrations of certain species. In Figure 1 it is to be seen that in very acidic solutions (e.g. $\text{pH}=1$) the species $\text{HA}/\text{H}_2\text{O}$ dominates ($\lg C_{\text{HA}}^{\circ} \approx \lg c(\text{HA}/\text{H}_2\text{O}) = -2$) and the equilibrium concentration of the conjugated base $\text{A}^-/\text{H}_2\text{O}$ is comparable small ($\lg c(\text{A}^-/\text{H}_2\text{O}) = -5.7$). In alkaline solutions, e.g. $\text{pH}=12$, $\text{A}^-/\text{H}_2\text{O}$ is the dominating species ($\lg C_{\text{HA}}^{\circ} \approx \lg c(\text{A}^-/\text{H}_2\text{O}) = -2$), and the equilibrium concentration of the acid $\text{HA}/\text{H}_2\text{O}$ is very small ($\lg c(\text{HA}/\text{H}_2\text{O}) = -9.2$). If the acid is dissolved in water, the pH of such a solution can be read on the pH scale of the intersection point of the $\text{A}^-/\text{H}_2\text{O}$ line and the $\text{H}^+/\text{H}_2\text{O}$ line. This means, a solution of acetic acid with a concentration $C_{\text{HA}}^{\circ} = 0.01 \text{ mol L}^{-1}$ has a pH value of 3.4 (cf. Figure 1). If the salt of the conjugated base is dissolved and provided, that the cation is a very weak acid (e.g. sodium acetate), the pH is obtained at that intersection point of the $\text{HA}/\text{H}_2\text{O}$ line and the $\text{HO}^-/\text{H}_2\text{O}$ line. Hence, a solution of 0.01 mol L^{-1} sodium acetate in water has a pH of 8.4.

3. Acid-Base Diagrams for Nonaqueous Solutions

For nonaqueous solvents equations analogous to Equations (1) to (4) can be derived. For an acid HA dissolved in the solvent HS the equilibria are [Eqs. (5) and (6)]:



The only requirement is that the solvent HS has to exhibit at least some proton-donating behavior. The laws of mass action of the two equilibria are [Eqs. (7) and (8)]:

$$K_{\text{a}}(\text{HS}) = a^{\text{c}}(\text{H}^+/\text{HS})a^{\text{c}}(\text{S}^-/\text{HS}) \approx c(\text{H}^+/\text{HS})c(\text{S}^-/\text{HS}) \quad (7)$$

$$K_{\text{a}}(\text{HA}/\text{HS}) = \frac{c(\text{A}^-/\text{HS})c(\text{H}^+/\text{HS})}{c(\text{HA}/\text{HS})} \quad (8)$$

It is of utmost importance to emphasize, that acidity constants strongly depend on the given solvent.^[3] $K_{\text{a}}(\text{HA}/\text{HS})$ is first of all dependent on the capacity of the acid to provide

protons but very importantly also on the ability of the solvent to solvate HA, H^+ and A^- .

In analogy to aqueous solutions, solution acidity can be approximately expressed by $\text{pH}(\text{HS})$ as follows [Eq. (9)]:

$$\text{pH}(\text{HS}) = -\lg a^{\text{c}}(\text{H}^+/\text{HS}) \approx -\lg c(\text{H}^+/\text{HS}) \quad (9)$$

For the solvent anion S^- the following equation can be derived in analogy to OH^- [Eq. (10)]:

$$\begin{aligned} \text{pS}^-(\text{HS}) &= \\ &= -\lg a(\text{S}^-/\text{HS}) \approx -\lg c(\text{S}^-/\text{HS}) = \text{p}K_{\text{a}}(\text{HS}) - \text{pH}(\text{HS}) \end{aligned} \quad (10)$$

Equations (9) and (10) give straight lines in a diagram in which the $\text{pH}(\text{HS})$ is plotted on the x axis and $\lg c_i(\text{HS})$ on the y axis.

With the overall concentration of the acid HA in the solvent HS [Eq. (11)]:

$$C_{\text{HA}}^{\circ} = c(\text{HA}/\text{HS}) + c(\text{A}^-/\text{HS}) \quad (11)$$

the functions $\lg c(\text{HA}/\text{HS}) = f(\text{pH}(\text{HS}))$ and $\lg c(\text{A}^-/\text{HS}) = f(\text{pH}(\text{HS}))$ can be derived [Eqs. (12) and (13)]:

$$\lg c(\text{HA}/\text{HS}) = \lg C_{\text{HA}}^{\circ} - \lg(1 + 10^{\text{pH}(\text{HS}) - \text{p}K_{\text{a}}(\text{HA}/\text{HS})}) \quad (12)$$

$$\lg c(\text{A}^-/\text{HS}) = \lg C_{\text{HA}}^{\circ} - \lg(1 + 10^{\text{p}K_{\text{a}}(\text{HA}/\text{HS}) - \text{pH}(\text{HS})}) \quad (13)$$

We have chosen DMSO as the exemplary solvent in this paper. The important properties of DMSO for this study are:

- 1) Out of the commonly used nonaqueous solvents it is one of the most polar with relative permittivity $\epsilon = 46$.^[4]
- 2) DMSO is a markedly basic version of a typical solvent. The transfer free energy of H^+ from water to DMSO is $\Delta G_{\text{trans}}^{\circ}(\text{H}^+, \text{H}_2\text{O} \rightarrow \text{DMSO}) = -19 \text{ kJ mol}^{-1}$ (using the TATB assumption).^[5]
- 3) DMSO molecules efficiently solvate cations (transfer free energies of most cations from water to DMSO are negative^[5]). At the same time, its ability to solvate anions is limited. This is caused first of all by its non-HBD nature. Exemplary free energies of transfer from water to DMSO can be seen in Ref. [5].
- 4) By being markedly basic, DMSO supports ionization of acids. Its high polarity together with ion solvation ability supports dissociation of ion pairs into free ions in dilute solutions, eliminating the need to consider ion pairing, which significantly simplifies the equations.
- 5) Although appreciably basic, DMSO is a very weak acid. Its autoprotolysis constant is still measurable, but is very low: $\text{p}K_{\text{a}}(\text{DMSO}) = 34$.^[6] Therefore very wide range of acid strengths can be experimentally investigated in DMSO.
- 6) The limited anion solvating ability leads to the phenomenon called homoconjugation,^[3] whereby in a solution containing both the anion and its conjugate acid the anion forms hydrogen bond with the conjugate acid molecule, thereby receiving the stabilization that the solvent molecules are unable to provide. The extent of homoconjugation

differs widely between acids. Homoconjugation occurs first of all with acids that are strong hydrogen bond donors and form upon dissociation small anions with localized charge. Carboxylic acids are a typical example.

(7) A very large body of $pK_a(\text{HA}/\text{DMSO})$ data is available, to a large extent thanks to the monumental effort of the Bordwell group.^[6]

As the first example we will look at pentaphenylcyclopentadiene (PPCP) dissolved in DMSO. The acidity constant of PPCP in DMSO is: $pK_a(\text{PPCP}/\text{DMSO}) = 12.5$.^[6] Upon ionization PPCP gives an anion with highly delocalized charge and is therefore among those acids that do not undergo homoconjugation. The resulting acid-base diagram for an overall concentration of 0.01 mol L^{-1} is given in Figure 2.

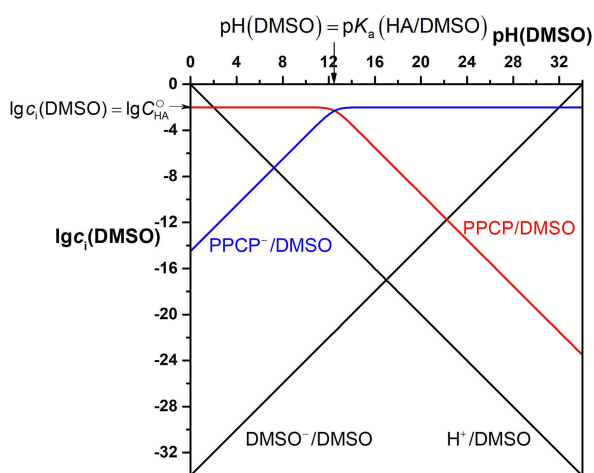


Figure 2. The $\text{pH}(\text{DMSO})\text{-lg}c_i$ diagram with the lines of H^+/DMSO , $\text{DMSO}^-/\text{DMSO}$, PPCP/DMSO and $\text{PPCP}^-/\text{DMSO}$ for a solution of pentaphenylcyclopentadiene (PPCP) in DMSO with $C_{\text{HA}} = 0.01 \text{ mol L}^{-1}$ and $pK_a(\text{PPCP}/\text{DMSO}) = 12.5$.

As for conventional $\text{pH}\text{-lg}c_i$ diagrams (see discussion above), at any given $\text{pH}(\text{DMSO})$ value the logarithms of the concentrations of H^+/DMSO , $\text{DMSO}^-/\text{DMSO}$, PPCP/DMSO and $\text{PPCP}^-/\text{DMSO}$ are obtainable. On the other hand, e.g., the $\text{pH}(\text{DMSO})$ value for a solution of pentaphenylcyclopentadiene (PPCP) in DMSO with $C_{\text{HA}} = 0.01 \text{ mol L}^{-1}$ is obtainable at the point where lines of H^+/DMSO and $\text{PPCP}^-/\text{DMSO}$ intersect (from Figure 2a value of $\text{pH}(\text{DMSO}) = 7.3$ can be read for such a solution).

4. Acid-Base Diagrams Based on the Unified pH-Scale

The acid-base diagrams discussed above are very useful if only one solvent is considered. The question now is how one can compare one and the same acid in different media. In 2010, Himmel et al.^[7] have developed a unified Brønsted acidity based on the absolute chemical potential of protons in a solvent. The

key factor was to unify the reference state for different media. The authors have used the ideal proton gas under standard conditions (1 bar pressure and 298.15 K) as the reference state. The absolute chemical potential of this reference state $\mu_{\text{abs}}^{\ominus}(\text{H}^+/\text{g})$ is defined as 0 kJ mol^{-1} (zero point for the absolute chemical potential of the proton). The absolute chemical potential is connected with the absolute activity of the proton according to:

$$a_{\text{abs}}(\text{H}^+) = \exp \frac{\mu_{\text{abs}}^{\ominus}(\text{H}^+/\text{g})}{RT} \quad (14)$$

and a modified Sørensen equation can be obtained:

$$\text{pH}_{\text{abs}} = -\lg a_{\text{abs}}(\text{H}^+) = -\frac{\mu_{\text{abs}}^{\ominus}(\text{H}^+/\text{g})}{RT \ln 10} \quad (15)$$

Thus, the zero point of the absolute pH scale is $\text{pH}_{\text{abs}} = 0$.

Upon interaction of protons with the molecules of any phase (gaseous, liquid, or solid), the chemical potential and hence the acidity of the proton will be lowered. The decrease is expressed by the standard Gibbs solvation free energy $\Delta_{\text{solv}}G^{\ominus}(\text{H}^+/\text{HS})$ (proton transfer from the ideal proton gas at 1 bar and 298.15 K creating an ideal 1 M solution). This value equates to the standard potential of the proton in the solvent [Eq. (16)]:

$$\Delta_{\text{solv}}G^{\ominus}(\text{H}^+/\text{S}) = \mu_{\text{abs}}^{\ominus}(\text{H}^+/\text{HS}) \quad (16)$$

Several standard Gibbs solvation free energies have been established, e.g. $\Delta_{\text{solv}}G^{\ominus}(\text{H}^+/\text{H}_2\text{O}) = -1104.5 \text{ kJ mol}^{-1}$ and $\Delta_{\text{solv}}G^{\ominus}(\text{H}^+/\text{DMSO}) = -1123.9 \text{ kJ mol}^{-1}$.^[8] A change of one pH unit yields in a change of the chemical potential of 5.71 kJ mol^{-1} ($RT \Delta \ln a(\text{H}^+) = 2.303RT \lg 0.1 = -5.71 \text{ kJ mol}^{-1}$ at 25°C). This allows the calculation of the chemical potential of the proton $\mu_{\text{abs}}(\text{H}^+/\text{HS})$ at any $\text{pH}(\text{HS})$ and in any solvent [Eq. (17)]:

$$\mu_{\text{abs}}(\text{H}^+/\text{HS}) = \Delta_{\text{solv}}G^{\ominus}(\text{H}^+/\text{HS}) - (\text{pH}(\text{HS}) \times 5.71 \text{ kJ mol}^{-1}) \quad (17)$$

and thus pH_{abs} according to [Eq. (18)]:

$$\text{pH}_{\text{abs}} = -\frac{\Delta_{\text{solv}}G^{\ominus}(\text{H}^+/\text{S})}{5.71 \text{ kJ mol}^{-1}} + \text{pH}(\text{HS}) \quad (18)$$

provided that $\Delta_{\text{solv}}G^{\ominus}(\text{H}^+/\text{HS})$ is known for the solvent. Since the aqueous pH scale is the most prominent, it is desirable to be able to directly compare absolute pH values with the conventional aqueous pH values (i.e. if the chemical potential of the solvated proton in a solvent equals the chemical potential of an aqueous solution with conventional $\text{pH}(\text{H}_2\text{O}) = 7.00$, the pH_{abs} value of the solvent should also be given with 7.00). To do so, $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$ values are defined to align the zero values of the pH_{abs} and the conventional $\text{pH}(\text{H}_2\text{O})$ scale [Eq. (19)].^[9]

$$\begin{aligned} \text{pH}_{\text{abs}}^{\text{H}_2\text{O}} &= \text{pH}_{\text{abs}} + \frac{\Delta_{\text{sol}} G^\circ(\text{H}^+/\text{H}_2\text{O})}{5.71 \text{ kJ mol}^{-1}} \\ &= \text{pH}_{\text{abs}} - 193.5 \text{ (at } 25^\circ\text{C)} \end{aligned} \quad (19)$$

The functions to draw the acid-base diagram change in the following way (again, approximately formulated with the equilibrium concentrations):

$$\begin{aligned} \lg c(\text{H}^+/\text{HS}) &= -\text{pH}(\text{HS}) = -\text{pH}_{\text{abs}} - \frac{\Delta_{\text{sol}} G^\circ(\text{H}^+/\text{HS})}{5.71 \text{ kJ mol}^{-1}} \\ &= -\text{pH}_{\text{abs}}^{\text{H}_2\text{O}} + \frac{\Delta_{\text{sol}} G^\circ(\text{H}^+/\text{H}_2\text{O}) - \Delta_{\text{sol}} G^\circ(\text{H}^+/\text{HS})}{5.71 \text{ kJ mol}^{-1}} \end{aligned} \quad (20)$$

It directly follows from Equation (20) that the $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$ in DMSO is shifted from the "native" pH scale in DMSO, $\text{pH}(\text{HS})$, by a constant increment found from the solvation free energy difference term of Equation (20), i.e. by 3.4 pH units. For the sake of simplification, the following Equations (21)–(23) are presented with the explicit value of this increment. If any other solvent than DMSO is considered, the increment can be calculated and replaced, easily.

$$\begin{aligned} \lg c(\text{S}^-/\text{HS}) &= -\text{p}K_{\text{a}}(\text{HS}) + \text{pH}(\text{HS}) \\ &= -\text{p}K_{\text{a}}(\text{HS}) + \text{pH}_{\text{abs}}^{\text{H}_2\text{O}} - 3.4 \end{aligned} \quad (21)$$

$$\lg c(\text{HA}/\text{HS}) = \lg C_{\text{HA}}^\circ - \lg \left(1 + 10^{\text{pH}_{\text{abs}}^{\text{H}_2\text{O}} - 3.4 - \text{p}K_{\text{a}}(\text{HA}/\text{HS})} \right) \quad (22)$$

$$\lg c(\text{A}^-/\text{HS}) = \lg C_{\text{HA}}^\circ - \lg \left(1 + 10^{\text{p}K_{\text{a}}(\text{HA}/\text{HS}) - \text{pH}_{\text{abs}}^{\text{H}_2\text{O}} + 3.4} \right) \quad (23)$$

Figure 3 shows the $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}} - \lg c_i$ diagram for a solution of pentaphenylcyclopentadiene (PPCP) in DMSO with $C_{\text{HA}}^\circ = 0.01 \text{ mol L}^{-1}$ and $\text{p}K_{\text{a}}(\text{PPCP}/\text{DMSO}) = 12.5$. Again, at any given $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$ value the logarithms of the concentrations of all

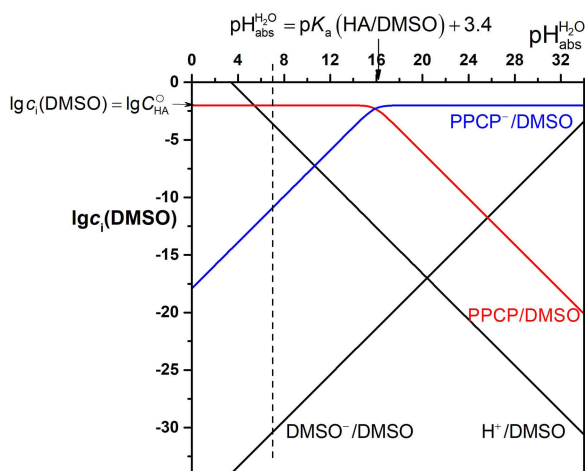
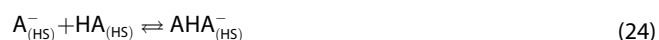


Figure 3. The $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}} - \lg c_i$ diagram with the lines of H^+/DMSO , $\text{DMSO}^-/\text{DMSO}$, PPCP/DMSO and $\text{PPCP}^-/\text{DMSO}$ for a solution of pentaphenylcyclopentadiene (PPCP) in DMSO with $C_{\text{HA}}^\circ = 0.01 \text{ mol L}^{-1}$ and $\text{p}K_{\text{a}}(\text{PPCP}/\text{DMSO}) = 12.5$.

species are obtainable, e.g. in a solution having a $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$ value of 7.00 (intersection points with the dotted auxiliary line) the undissociated acid would dominate ($\lg c(\text{PPCP}/\text{DMSO}) \approx \lg C_{\text{PPCP}}^\circ = -2$), and the concentration of the conjugated anion is comparable low under these conditions ($\lg c(\text{PPCP}^-/\text{DMSO}) = -10.8$). On the other hand, the solution of 0.01 mol L^{-1} PPCP in DMSO has a $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$ value of 10.7 (intersection point of the H^+/DMSO line and the $\text{PPCP}^-/\text{DMSO}$ line). A solution of 0.01 mol L^{-1} of an alkali metal salt of PPCP^- would have a $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$ value of 25.6 (intersection point of the PPCP/DMSO line and the $\text{DMSO}^-/\text{DMSO}$ line).

The situation is more complicated when additional equilibria have to be considered. As was explained above, carboxylic acids in polar non-HBD solvents can undergo homoconjugation [Eq. (24)]:



The species $\text{AHA}_{(\text{HS})}^-$ is termed homoconjugate. The homoconjugation constant can be formulated as follows [Eq. (25)]:

$$K_{\text{f}}(\text{AHA}^-/\text{HS}) = \frac{a(\text{AHA}^-/\text{HS})}{a(\text{A}^-/\text{HS})a(\text{HA}/\text{HS})} \approx \frac{c(\text{AHA}^-/\text{HS})}{c(\text{A}^-/\text{HS})c(\text{HA}/\text{HS})} \quad (25)$$

This means, that in solutions the species HA/HS , A^-/HS , and AHA^-/HS can be present, and the amount balance must be written as [Eq. (26)]:

$$C_{\text{HA}}^\circ = c(\text{HA}/\text{HS}) + c(\text{A}^-/\text{HS}) + c(\text{AHA}^-/\text{HS}) \quad (26)$$

The functions $\lg c(\text{HA}/\text{HS}) = f(\text{pH}_{\text{abs}}^{\text{H}_2\text{O}})$, $\lg c(\text{A}^-/\text{HS}) = f(\text{pH}_{\text{abs}}^{\text{H}_2\text{O}})$, and $\lg c(\text{AHA}^-/\text{HS}) = f(\text{pH}_{\text{abs}}^{\text{H}_2\text{O}})$ can now be derived:

$$\text{(i) } \lg c(\text{HA}/\text{HS}) = f(\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}):$$

Rearranging Equation (8) gives:

$$c(\text{A}^-/\text{HS}) = \frac{K_{\text{a}}(\text{HA}/\text{HS})c(\text{HA}/\text{HS})}{c(\text{H}^+/\text{HS})} \quad (27)$$

Rearranging Equation (25) and replacing $c(\text{A}^-/\text{HS})$ with Equation (27) gives:

$$\begin{aligned} c(\text{AHA}^-/\text{HS}) &= K_{\text{f}}(\text{AHA}^-/\text{HS})c(\text{A}^-/\text{HS})c(\text{HA}/\text{HS}) \\ &= \frac{K_{\text{f}}(\text{AHA}^-/\text{HS})K_{\text{a}}(\text{HA}/\text{HS})}{c(\text{H}^+/\text{HS})} c^2(\text{HA}/\text{HS}) \end{aligned} \quad (28)$$

Inserting Equations (27) and (28) in Equation (26) leads to [Eq. (29)]:

$$\begin{aligned} C_{\text{HA}}^\circ &= c(\text{HA}/\text{HS}) + \frac{K_{\text{a}}(\text{HA}/\text{HS})}{c(\text{H}^+/\text{HS})} c(\text{HA}/\text{HS}) \\ &+ \frac{K_{\text{f}}(\text{AHA}^-/\text{HS})K_{\text{a}}(\text{HA}/\text{HS})}{c(\text{H}^+/\text{HS})} c^2(\text{HA}/\text{HS}) \end{aligned} \quad (29)$$

and it follows:

$$0 = c^2(\text{HA}/\text{HS}) + \left(\frac{c(\text{H}^+/\text{HS}) + K_a(\text{HA}/\text{HS})}{K_f(\text{AHA}^-/\text{HS})K_a(\text{HA}/\text{HS})} \right) c(\text{HA}/\text{HS}) - \frac{c(\text{H}^+/\text{HS})}{K_f(\text{AHA}^-/\text{HS})K_a(\text{HA}/\text{HS})} C_{\text{HA}}^{\circ} \quad (30)$$

Equation (30) is a quadratic equation. This results in the following Equations (31) and (32) (taking into consideration, that only the mathematical solution with the plus sign in front of the square root term gives a real concentration):

$$c(\text{HA}/\text{HS}) = -\frac{c(\text{H}^+/\text{HS}) + K_a(\text{HA}/\text{HS})}{2K_f(\text{AHA}^-/\text{HS})K_a(\text{HA}/\text{HS})} + \sqrt{\left(\frac{c(\text{H}^+/\text{HS}) + K_a(\text{HA}/\text{HS})}{2K_f(\text{AHA}^-/\text{HS})K_a(\text{HA}/\text{HS})} \right)^2 + \frac{c(\text{H}^+/\text{HS})}{K_f(\text{AHA}^-/\text{HS})K_a(\text{HA}/\text{HS})} C_{\text{HA}}^{\circ}} \quad (31)$$

$$\begin{aligned} \lg c(\text{HA}/\text{HS}) &= \lg \left(-\frac{c(\text{H}^+/\text{HS}) + K_a(\text{HA}/\text{HS})}{2K_f(\text{AHA}^-/\text{HS})K_a(\text{HA}/\text{HS})} + \sqrt{\left(\frac{c(\text{H}^+/\text{HS}) + K_a(\text{HA}/\text{HS})}{2K_f(\text{AHA}^-/\text{HS})K_a(\text{HA}/\text{HS})} \right)^2 + \frac{c(\text{H}^+/\text{HS})}{K_f(\text{AHA}^-/\text{HS})K_a(\text{HA}/\text{HS})} C_{\text{HA}}^{\circ}} \right) \\ &= \lg \left(-\frac{10^{-\text{pH}(\text{HS})} + 10^{-\text{p}K_a(\text{HA}/\text{HS})}}{2 \cdot 10^{-\text{p}K_f(\text{AHA}^-/\text{HS}) - \text{p}K_a(\text{HA}/\text{HS})}} + \sqrt{\left(\frac{10^{-\text{pH}(\text{HS})} + 10^{-\text{p}K_a(\text{HA}/\text{HS})}}{2 \cdot 10^{-\text{p}K_f(\text{AHA}^-/\text{HS}) - \text{p}K_a(\text{HA}/\text{HS})}} \right)^2 + \frac{10^{-\text{pH}(\text{HS})}}{10^{-\text{p}K_f(\text{AHA}^-/\text{HS}) - \text{p}K_a(\text{HA}/\text{HS})}} C_{\text{HA}}^{\circ}} \right) \end{aligned} \quad (32)$$

Replacing $\text{pH}(\text{HS})$ in DMSO by [Eq. (33)]

$$\begin{aligned} \text{pH}(\text{HS}) &= \text{pH}_{\text{abs}}^{\text{H}_2\text{O}} - \frac{\Delta_{\text{solv}} G^{\ominus}(\text{H}^+/\text{H}_2\text{O}) - \Delta_{\text{solv}} G^{\ominus}(\text{H}^+/\text{HS})}{5.71 \text{ kJ mol}^{-1}} \\ &= \text{pH}_{\text{abs}}^{\text{H}_2\text{O}} - 3.4 \end{aligned} \quad (33)$$

leads to [Eq. (34)]:

$$\lg c(\text{HA}/\text{HS}) = \lg \left(-\frac{10^{-\text{pH}_{\text{abs}}^{\text{H}_2\text{O}} + 3.4} + 10^{-\text{p}K_a(\text{HA}/\text{HS})}}{2 \cdot 10^{-\text{p}K_f(\text{AHA}^-/\text{HS}) - \text{p}K_a(\text{HA}/\text{HS})}} + \sqrt{\left(\frac{10^{-\text{pH}_{\text{abs}}^{\text{H}_2\text{O}} + 3.4} + 10^{-\text{p}K_a(\text{HA}/\text{HS})}}{2 \cdot 10^{-\text{p}K_f(\text{AHA}^-/\text{HS}) - \text{p}K_a(\text{HA}/\text{HS})}} \right)^2 + \frac{10^{-\text{pH}_{\text{abs}}^{\text{H}_2\text{O}} + 3.4}}{10^{-\text{p}K_f(\text{AHA}^-/\text{HS}) - \text{p}K_a(\text{HA}/\text{HS})}} C_{\text{HA}}^{\circ}} \right) \quad (34)$$

(ii) $\lg c(\text{A}^-/\text{HS}) = f(\text{pH}_{\text{abs}}^{\text{H}_2\text{O}})$

Rearranging Equation (8) gives:

$$c(\text{HA}/\text{HS}) = \frac{c(\text{A}^-/\text{HS})c(\text{H}^+/\text{HS})}{K_a(\text{HA}/\text{HS})} \quad (35)$$

Rearranging Equation (25) and replacing $c(\text{HA}/\text{HS})$ by Equation (35) gives:

$$\begin{aligned} c(\text{AHA}^-/\text{HS}) &= K_f(\text{AHA}^-/\text{HS})c(\text{A}^-/\text{HS})c(\text{HA}/\text{HS}) \\ &= \frac{K_f(\text{AHA}^-/\text{HS})c(\text{H}^+/\text{HS})}{K_a(\text{HA}/\text{HS})} c^2(\text{A}^-/\text{HS}) \end{aligned} \quad (36)$$

Inserting Equations (35) and (36) in Equation (26) leads to [Eq. (37)]:

$$\begin{aligned} C_{\text{HA}}^{\circ} &= \frac{c(\text{H}^+/\text{HS})}{K_a(\text{HA}/\text{HS})} c(\text{A}^-/\text{HS}) + c(\text{A}^-/\text{HS}) \\ &+ \frac{K_f(\text{AHA}^-/\text{HS})c(\text{H}^+/\text{HS})}{K_a(\text{HA}/\text{HS})} c^2(\text{A}^-/\text{HS}) \end{aligned} \quad (37)$$

and it follows [Eqs. (38)–(40)]:

$$0 = c^2(\text{A}^-/\text{HS}) + \left(\frac{K_a(\text{HA}/\text{HS}) + c(\text{H}^+/\text{HS})}{K_f(\text{AHA}^-/\text{HS})c(\text{H}^+/\text{HS})} \right) c(\text{A}^-/\text{HS}) - \frac{K_a(\text{HA}/\text{HS})}{K_f(\text{AHA}^-/\text{HS})c(\text{H}^+/\text{HS})} C_{\text{HA}}^{\circ} \quad (38)$$

$$\begin{aligned} c(\text{A}^-/\text{HS}) &= -\frac{K_a(\text{HA}/\text{HS}) + c(\text{H}^+/\text{HS})}{2K_f(\text{AHA}^-/\text{HS})c(\text{H}^+/\text{HS})} + \sqrt{\left(\frac{K_a(\text{HA}/\text{HS}) + c(\text{H}^+/\text{HS})}{2K_f(\text{AHA}^-/\text{HS})c(\text{H}^+/\text{HS})} \right)^2 + \frac{K_a(\text{HA}/\text{HS})}{K_f(\text{AHA}^-/\text{HS})c(\text{H}^+/\text{HS})} C_{\text{HA}}^{\circ}} \end{aligned} \quad (39)$$

$$\begin{aligned} \lg c(\text{A}^-/\text{HS}) &= \lg \left(-\frac{K_a(\text{HA}/\text{HS}) + c(\text{H}^+/\text{HS})}{2K_f(\text{AHA}^-/\text{HS})c(\text{H}^+/\text{HS})} + \sqrt{\left(\frac{K_a(\text{HA}/\text{HS}) + c(\text{H}^+/\text{HS})}{2K_f(\text{AHA}^-/\text{HS})c(\text{H}^+/\text{HS})} \right)^2 + \frac{K_a(\text{HA}/\text{HS})}{K_f(\text{AHA}^-/\text{HS})c(\text{H}^+/\text{HS})} C_{\text{HA}}^{\circ}} \right) \\ &= \lg \left(-\frac{10^{-\text{pH}(\text{HS})} + 10^{-\text{p}K_a(\text{HA}/\text{HS})}}{2 \cdot 10^{-\text{p}K_f(\text{AHA}^-/\text{HS}) - \text{pH}(\text{HS})}} + \sqrt{\left(\frac{10^{-\text{pH}(\text{HS})} + 10^{-\text{p}K_a(\text{HA}/\text{HS})}}{2 \cdot 10^{-\text{p}K_f(\text{AHA}^-/\text{HS}) - \text{pH}(\text{HS})}} \right)^2 + \frac{10^{-\text{p}K_a(\text{HA}/\text{HS})}}{10^{-\text{p}K_f(\text{AHA}^-/\text{HS}) - \text{pH}(\text{HS})}} C_{\text{HA}}^{\circ}} \right) \end{aligned} \quad (40)$$

Replacing $\text{pH}(\text{HS})$ in DMSO by Equation (33) leads to [Eq. (41)]:

$$\begin{aligned} \lg c(\text{A}^-/\text{HS}) &= \lg \left(-\frac{10^{-\text{pH}_{\text{abs}}^{\text{H}_2\text{O}} + 3.4} + 10^{-\text{p}K_a(\text{HA}/\text{HS})}}{2 \cdot 10^{-\text{p}K_f(\text{AHA}^-/\text{HS}) - \text{pH}_{\text{abs}}^{\text{H}_2\text{O}} + 3.4}} + \sqrt{\left(\frac{10^{-\text{pH}_{\text{abs}}^{\text{H}_2\text{O}} + 3.4} + 10^{-\text{p}K_a(\text{HA}/\text{HS})}}{2 \cdot 10^{-\text{p}K_f(\text{AHA}^-/\text{HS}) - \text{pH}_{\text{abs}}^{\text{H}_2\text{O}} + 3.4}} \right)^2 + \frac{10^{-\text{p}K_a(\text{HA}/\text{HS})}}{10^{-\text{p}K_f(\text{AHA}^-/\text{HS}) - \text{pH}_{\text{abs}}^{\text{H}_2\text{O}} + 3.4}} C_{\text{HA}}^{\circ}} \right) \end{aligned} \quad (41)$$

(iii) $\lg c(\text{AHA}^-/\text{HS}) = f(\text{pH}_{\text{abs}}^{\text{H}_2\text{O}})$:

Rearranging Equation (25) and substituting $c(\text{HA}/\text{HS})$ by Equation (35) gives [Eqs. (42)–(44)]:

$$c(\text{A}^-/\text{HS}) = \frac{K_a(\text{HA}/\text{HS})c(\text{AHA}^-/\text{HS})}{K_f(\text{AHA}^-/\text{HS})c(\text{A}^-/\text{HS})c(\text{H}^+/\text{HS})} \quad (42)$$

$$c^2(\text{A}^-/\text{HS}) = \frac{K_a(\text{HA}/\text{HS})c(\text{AHA}^-/\text{HS})}{K_f(\text{AHA}^-/\text{HS})c(\text{H}^+/\text{HS})} \quad (43)$$

$$c(\text{A}^-/\text{HS}) = \sqrt{\frac{K_a(\text{HA}/\text{HS})c(\text{AHA}^-/\text{HS})}{K_f(\text{AHA}^-/\text{HS})c(\text{H}^+/\text{HS})}} \quad (44)$$

Rearranging Equation (8) and substituting $c(A^-/HS)$ by Equation (44) gives:

$$c(HA/HS) = \frac{c(A^-/HS)c(H^+/HS)}{K_a(HA/HS)} = \sqrt{\frac{c(AHA^-/HS)c(H^+/HS)}{K_f(AHA^-/HS)K_a(HA/HS)}} \quad (45)$$

Inserting these two Equations (44) and (45) in Equation (26) leads to [Eqs. (46) and (47)]:

$$C_{HA}^{\circ} = \sqrt{\frac{c(AHA^-/HS)K_a(HA/HS)}{K_f(AHA^-/HS)c(H^+/HS)}} + \sqrt{\frac{c(H^+/HS)c(AHA^-/HS)}{K_a(HA/HS)K_f(AHA^-/HS)}} + c(AHA^-/HS) = c(AHA^-/HS) + \sqrt{c(AHA^-/HS)} \left(\sqrt{\frac{K_a(HA/HS)}{K_f(AHA^-/HS)c(H^+/HS)}} + \sqrt{\frac{c(H^+/HS)}{K_f(AHA^-/HS)K_a(HA/HS)}} \right) \quad (46)$$

$$c(AHA^-/HS) = \left(\frac{-\left(\sqrt{\frac{K_a(HA/HS)}{c(H^+/HS)K_f(AHA^-/HS)}} + \sqrt{\frac{c(H^+/HS)}{K_f(AHA^-/HS)K_a(HA/HS)}} \right)}{+ \sqrt{\frac{K_a(HA/HS)}{c(H^+/HS)K_f(AHA^-/HS)}} + \sqrt{\frac{c(H^+/HS)}{K_f(AHA^-/HS)K_a(HA/HS)}} + C_{HA}^{\circ}} \right)^2 = \left(\frac{-\left(\frac{\sqrt{10^{-pK_a(HA/HS)+pH(HS)+pK_f(AHA^-/HS)} + \sqrt{10^{-pH(HS)+pK_f(AHA^-/HS)+pK_a(HA/HS)}}}{2} \right)}{+ \sqrt{\frac{10^{-pK_a(HA/HS)+pH(HS)+pK_f(AHA^-/HS)} + \sqrt{10^{-pH(HS)+pK_f(AHA^-/HS)+pK_a(HA/HS)}}}{4}} + C_{HA}^{\circ}} \right)^2 \quad (47)$$

Replacing $pH(HS)$ in DMSO by Eq. 33 leads to [Eq. (48)]:

$$2 \lg c(AHA^-/HS) = \left(\frac{-\left(\frac{\sqrt{10^{-pK_a(HA/HS)+pH_{abs}^{H_2O}-3.4+pK_f(AHA^-/HS)} + \sqrt{10^{-pH_{abs}^{H_2O}+3.4+pK_f(AHA^-/HS)+pK_a(HA/HS)}}}{2} \right)}{+ \sqrt{\frac{\left(\frac{\sqrt{10^{-pK_a(HA/HS)+pH_{abs}^{H_2O}-3.4+pK_f(AHA^-/HS)} + \sqrt{10^{-pH_{abs}^{H_2O}+3.4+pK_f(AHA^-/HS)+pK_a(HA/HS)}}}{2} \right)^2}{4}} + C_{HA}^{\circ}} \right)^2 \quad (48)$$

As an important example, acetic acid, with $pK_a(HAc/DMSO) = 12.6$ and $pK_f(AcHAc^-/DMSO) = -1.48$,^[10] is depicted in Figure 4 with $C_{HA}^{\circ} = 0.01 \text{ mol L}^{-1}$. Presenting the diagram in the $pH_{abs}^{H_2O}$ scale gives interesting possibilities to compare the acidities of acetic acid solutions, acetate buffer solutions, and acetate solutions in water and DMSO. For simplicity we look first at the 1:1 buffer, i.e. the concentrations of the acid and the salt are the same. In water the pH (and

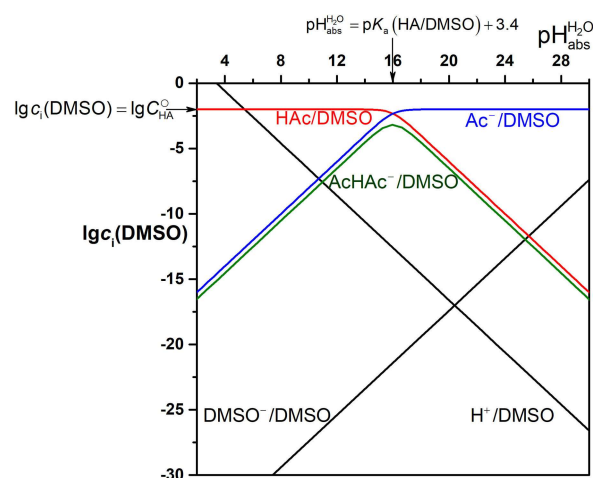


Figure 4. The $pH_{abs}^{H_2O} - \lg c_i$ diagram with the lines of $H^+/DMSO$, $DMSO^-/DMSO$, $HAc/DMSO$, $AcHAc^-/DMSO$ and $Ac^-/DMSO$ for a solution of acetic acid (HAc) in DMSO with $C_{HA}^{\circ} = 0.01 \text{ mol L}^{-1}$ and $pK_a(HAc/DMSO) = 12.6$ and $pK_f(AcHAc^-/DMSO) = -1.48$.

identically $pH_{abs}^{H_2O}$) of such solution is 4.75 (cf. Figure 1), which is mildly acidic. The same buffer solution in DMSO has $pH_{abs}^{H_2O}$ of 16.0, which means that with reference to the aqueous pH scale it is a highly basic solution. A second example is the solution of 0.01 mol L^{-1} acetic acid in water or in DMSO, respectively. From diagram in Figure 1 the pH ($pH_{abs}^{H_2O}$) of such solution in water is 3.4 (see discussion above). To obtain the $pH_{abs}^{H_2O}$ in DMSO the following charge balance holds [Eq. (49)]:

$$c(H^+/DMSO) = c(Ac^-/DMSO) + c(AcHAc^-/DMSO) + c(DMSO^-/DMSO) \quad (49)$$

The real $pH_{abs}^{H_2O}$ can hence be found on the left side of the point where the $Ac^-/DMSO$ line and the $H^+/DMSO$ line intersect (cf. Figure 4). The concentration of $DMSO^-/DMSO$ is at most $2 \cdot 10^{-27} \text{ mol L}^{-1}$ and negligible compared to $c(Ac^-/DMSO) = 5.5 \cdot 10^{-8} \text{ mol L}^{-1}$ and $c(AcHAc^-/DMSO) = 1.6 \cdot 10^{-8} \text{ mol L}^{-1}$. The concentration of the homoconjugate is, however, in the same order of magnitude to acetate anion under these conditions. Therefore, the real $pH_{abs}^{H_2O}$ is slightly left from the $pH_{abs}^{H_2O}$ taken from the intersection point of the $Ac^-/DMSO$ line and the $H^+/DMSO$ line, i.e., $pH_{abs}^{H_2O} = 10.6$ can be taken as a good approximation, which means that with reference to the aqueous pH scale it is an basic solution! At lower concentrations of acetic acid in DMSO, the influence of the homoconjugation decreases as it can be seen in Figure 5.

The $pH_{abs}^{H_2O}$ values for sodium acetate solutions in water and DMSO can be compared in the same way.

5. Conclusions

We have demonstrated that using the acid-base diagrams it is possible to create a simple, yet universal scheme for evaluating the equilibrium composition of a solution of any acid at any pH

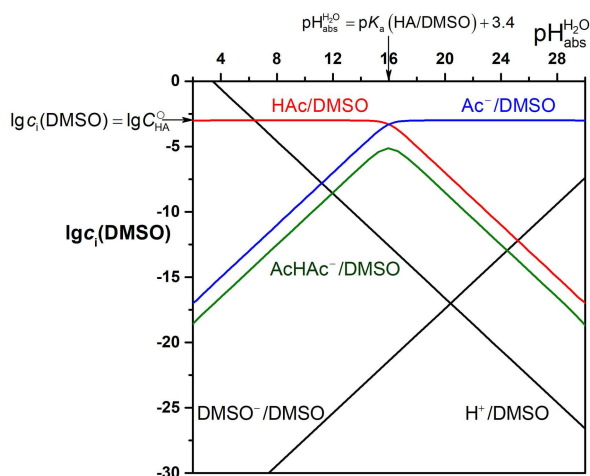


Figure 5. The $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}} - \lg c_i$ diagram with the lines of H^+/DMSO , $\text{DMSO}^-/\text{DMSO}$, HAc/DMSO , $\text{AcHAc}^-/\text{DMSO}$ and Ac^-/DMSO for a solution of acetic acid (HAc) in DMSO with $c_{\text{HA}} = 0.001 \text{ mol L}^{-1}$ and $\text{p}K_{\text{a}}(\text{HAc}/\text{DMSO}) = 12.6$ and $\text{p}K_{\text{f}}(\text{AcHAc}^-/\text{DMSO}) = -1.48$.

(HS) in an arbitrary solvent. The necessary data are the solvent autoprotolysis constant, dissociation constant (and homoconjugation constant, if applicable) of the acid and its concentration. The approach is easily extendable to $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$ if the proton solvation free energy is known in the respective solvent.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: electrochemistry · nonaqueous solvents · $\text{pH} - \lg c_i$ diagrams · proton transfer reactions · unified pH scale

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