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A formula for correlating pK_a values determined in D_2O and H_2O

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Abstract

A linear correlation between pH-meter readings in equivalent D_2O and H_2O solutions, determined experimentally, leads to a novel equation, which allows for a direct recalculation of pK_a values measured in D_2O into a H_2O equivalent: pK^H = 0.929pK^{H*} + 0.42. The comparison of this equation with the previously used approach is discussed.
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1. Introduction

D_2O is widely used in chemistry and biochemistry as a solvent alternative to H_2O. The most popular applications, taking advantage of magnetic and isotopic effects of D/H substitution, include NMR, FTIR and MS techniques. Comparisons of H_2O/D_2O kinetics are also used in studies of reaction mechanisms and in detection of $^1O_2$. Comparisons of pK_a values for a given compound or group between H_2O and D_2O solutions are often important for such studies. The accurate pH measurements in H_2O are readily obtained using glass electrodes and appropriate calibration procedures, like usage of standard buffers – for regular pH measurements, or acid/base titrations for calibration in potentiometry [1]. The same is possible for the corresponding pD measurements in D_2O and the appropriate reference values for buffers were published and recommended by IUPAC [2,3]. In laboratory practice a related quantity is used, however, so called pH*, which is a direct reading in a D_2O solution of the H_2O-calibrated pH-meter. The conversion of pH* into pD is then accomplished by adding a constant of ca. 0.4. This is based on measurements of acids and/or bases dissolved at the same concentrations in H_2O and D_2O [4,5]. The comparisons of

pH and pD determined data are not straightforward, due to the fact that the binding affinities of protonating groups are, in general, different for D^+ and H^+. It is often simplistically assumed that the apparent pK_a values, determined in D_2O and expressed using pH*, are similar to the corresponding values, determined in H_2O and expressed in pH units. This is called a "cancel-out" approach, as the constant term of 0.4 in pH*/pD conversion is approximately canceled by a decrease of acidities of acids in D_2O, compared to H_2O. A recommendation follows, that pH* and pH can be used conversely in comparative experiments [6,7].

Below we demonstrate a formula derived experimentally from pH-meter readings of equivalent solutions in H_2O and D_2O, which provides a surprisingly accurate tool for converting the values of pK_a determined in H_2O into those valid for D_2O and vice versa. This formula also has a theoretical justification.

2. Materials and methods

D_2O (99.9%) and DCl (35% in D_2O) were purchased from Cambridge Isotope Laboratories, Inc.; NaOD (40% in D_2O), $NaH_2PO_4 \cdot H_2O$, $Na_2HPO_4 \cdot 7H_2O$, pyridine, Tris buffer (Tris[hydroxymethyl]aminomethane), L-His, L-Arg, glutathione (GSH), and glutathione glycine ethyl ester (γ-Glu-Cys-Gly-OEt, γECGOEt) were obtained from Sigma; HCl was from Roth; acetic acid

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from Riedel-de Haën. NaOH, anhydrous sodium acetate, $KH_2PO_4 \cdot 2H_2O$, K_2HPO_4, and $Na_3PO_4 \cdot 12H_2O$ were provided by POCH. 2-Mercaptoethanol, potassium hydrogen pthalate (KHP), $Na_2B_4O_7 \cdot 10H_2O$ and sodium (3-trimethylsilyl)-2,2,3,3-tetradeuteriopropionate (TSP) were purchased from Merck. The remaining GSH analogs, γ-Glu-Cys-Ala (γECA), γ-Glu-Cys-Ser (γECS), γ-Glu-Cys-Glu (γECE), and γ-Glu-Cys-Gly-amide (γECGam) were synthesized using standard solid phase methodology, as described elsewhere [8].

The pH measurements in D_2O and H_2O were done using Mettler Toledo M 220 pH-meter, and a Mettler InLab 422 combined glass/AgCl electrode, calibrated using NIST-recommended KHP and borax buffers (pH 4.008 and 9.128, respectively) as well as standard Mettler buffers, pH 4.01 and 9.21, conforming to NIST specifications. Sample manipulations and measurements were done under argon blanket, to avoid interference from ambient carbon dioxide and isotopic dilution with H_2O vapor. Triplicate readings of three independently prepared samples were used for each experimental point. Standard deviations of measurements were calculated by pooling all results together. Some of the experiments were repeated using other pH-meters, from Mettler and Beckman (Φ72), using Mettler and Russell (CMAWL) combined electrodes, with consistent results (data not shown).

In the first set of experiments, the concentrations of substances tested were 50 mM, except for L-His and L-Arg, 4 mM, AcOH, 15 mM, KH_2PO_4 and Na_2HPO_4, 10 mM, 2-mercaptoethanol, 85 mM and pyridine, 74 mM. The ionic strengths were adjusted to 0.1 M, where necessary, with KNO_3. In the second set of experiments, 5 mM sodium phosphate, borate and acetate buffers were used, with ionic strengths adjusted to 0.1 M with KNO_3. Isotopic dilutions of D_2O, due to non-deuterated solutes, resulted in errors of pH^* determinations of 0.001–0.009 pH units, well within experimental errors of determinations.

Potentiometric titrations in H_2O in the presence of 0.1 M KNO_3 were performed at 298 K, over the pH range 2.2–10.5, using Molspin automatic titrator, with 0.1 M NaOH as titrant. Changes of pH were monitored with a combined glass–Ag/AgCl electrode, calibrated daily in H^+ concentrations by HNO_3 titrations [1]. Sample volumes of 1.5–2 ml and compound concentrations of 2 mM were used. The experimental data were analyzed using the SUPERQUAD program [9]. Standard deviations computed by SUPERQUAD refer to random errors. Comparative titrations of 2 mM HCl in $H_2O/0.1$ M KNO_3 with 0.1 M NaOH and of 2 mM DCl/0.1 M KNO_3 in D_2O with 0.1 M NaOD were performed, with sample volumes of 2 ml, and analyzed using SUPERQUAD.

^{1}H NMR spectra of 5 mM samples of peptides and L-His in D_2O were recorded at 298 K, on a Bruker AMX-300 spectrometer, at 300 MHz. TSP was used as internal ^{1}H standard. The pH^* of the samples was regulated using small volumes of concentrated DCl or NaOD. The protonation macroconstants in D_2O were calculated from group constants, derived from NMR titrations, according to a method of Rabenstein and Sayer [10]. All NMR-derived constants were expressed in pH^*.

3. Results and discussion

Fig. 1(a) presents a correlation between pH-meter readings (R_{pH} and R_{pH^*}) for 16 widely used, simple chemical substances, dissolved to identical concentrations in H_2O and D_2O. The substances represent a wide range of mono- and multifunctional acids, bases and amphoteric substances, with N, O, and S as H/D-exchanging atoms, including the most common buffers. No common specific features can be assigned to this set of substances, except for the adjusted ionic strength, $I = 0.1$ M and the fact that they release or bind H^+/D^+ ions. Therefore, any differences between pH and pH^*
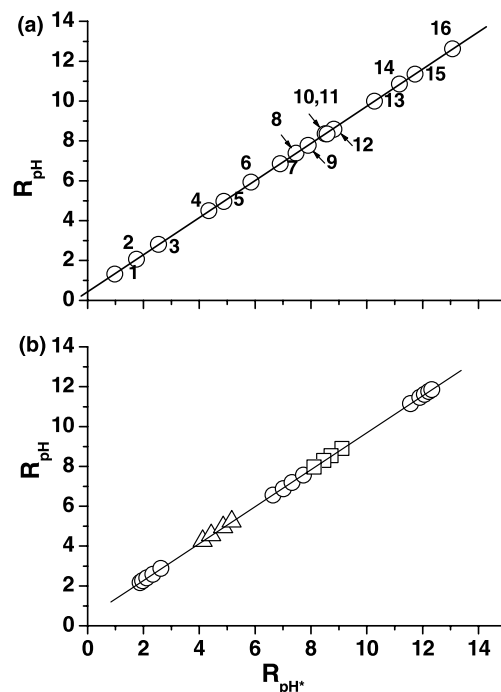

Fig. 1. (a) Experimental correlation of R_{pH} and R_{pH^*} with solutions of 16 chemical substances dissolved in H_2O and D_2O at $I = 0.1$ M (KNO_3). 1, HCl; 2, equimolar H_3PO4/NaH_2PO_4; 3, CH_3COOH; 4, equimolar CH_3COOH/CH_3COONa; 5, KH_2PO_4; 6, 2-mercaptoethanol; 7, NaH_2PO_4/Na_2HPO_4; 8, L-His; 9, CH_3COONa; 10, pyridine; 11, Tris/Tris–HCl; 12, Na_2HPO_4; 13, L-Arg; 14, Tris; 15, Na_2HPO_4/Na_3PO_4; 16, NaOH. Solid line represents the linear fit to experimental points. Experimental errors are smaller than the size of graphical symbols. (b) Experimental correlation of R_{pH} and R_{pH^*} with solutions of 22 buffers (5 mM) in H_2O and D_2O at $I = 0.1$ M (KNO_3); ○, phosphate buffers; △, acetate buffers and □, borate buffers.

readings for these substances are due solely to differences in acidities of respective solutions, combined with a differential glass electrode response to H^+ and D^+. Fig. 1(b) presents an analogous correlation, obtained using dilute phosphate, borate and acetate buffers at $I = 0.1$ M (the total of 18 data points). The linearities of these two correlations between pH-meter readings in H_2O (R_{pH}) and D_2O (R_{pH^*}) are excellent: $R > 0.999$, $p < 0.0001$. The coefficients of the corresponding equations are identical within their experimental errors. The analysis of the pooled data of both experiments (the total of 34 data points) yielded the linear equation:

$$R_{pH} = 0.929(1)R_{pH^*} + 0.42(1). \tag{1}$$

Analogous correlations, between $\Delta R = R_{pH^*} - R_{pH}$ and R_{pH^*} are shown in Fig. 2, and are expressed by a complementary equation:

$$\Delta R = 0.073(1)R_{pH^*} - 0.42(1). \tag{2}$$

The numbers in parentheses in the above equations denote standard deviations on the last significant digits of their parameters.

The slope factor in Eq. (1) is significantly different from 1, and therefore the slope factor in Eq. (2) is different from 0. As a consequence, the term for recalculation of R_{pH^*} into R_{pH} varies from ca. −0.4 pH units at pH 0 to ca. +0.5 pH units at pH 14, with the sign change at R_{pH^*} of 6.176.

The empirical equation (1) results in fact from the difference between ionic products K_w of light and heavy water. The negative logarithms of these values define the respective pH and pD scales. These values for pure solvents ($I = 0$ M) are: $pK_w^H = 13.995$, $pK_w^D = 14.951$ [11], and their ratio is 0.936. The comparison of these values for solutions with identical molar fractions of protonated and deprotonated solvent forms yields:

$$pD = pH \times 1.06831. \tag{3}$$

For ionic products established here for $I = 0.1$ M (KNO_3), $pK_w^H = 13.80$, $pK_w^D = 14.85$, an analogous Eq. (4) is valid:

$$pD = pH \times 1.076. \tag{4}$$

The relation between activities of H^+ and D^+ ions, according to Gross–Butler–Purlee theory [4,12] is expressed by Eq. (5).

$$pD = pH^* + 0.44. \tag{5}$$

Combining Eqs. (3)–(5) one obtains semiempirical Eqs. (6) and (7), for $I = 0$ M and $I = 0.1$ M, respectively:

$$pH = 0.936pH^* + 0.412, \tag{6}$$

$$pH = 0.929pH^* + 0.41. \tag{7}$$

The agreement between the empirical Eq. (1) and the independently derived, semiempirical Eq. (7) is excellent.

Fig. 3 presents titrations of the corresponding HCl/H_2O and DCl/D_2O solutions with NaOH and NaOD, respectively, measured with the same combined electrode. The inset to Fig. 3 presents the linearity of the dependence of glass electrode E^0 on the molar fraction of D_2O in H_2O. The same is true for its slope (s_L) parameter, and the above equations can be adopted for mixed H_2O/D_2O solutions. For Eq. (2) this is done simply by multiplying its coefficients by the molar fraction of D_2O. The linearity of the D/H isotope effect on pH* was also demonstrated previously for pH* measurements in mixed H_2O/D_2O solutions [5]. It should be noted that we found no influence of electrode type on the correlations presented by Eqs. (1) and (2),
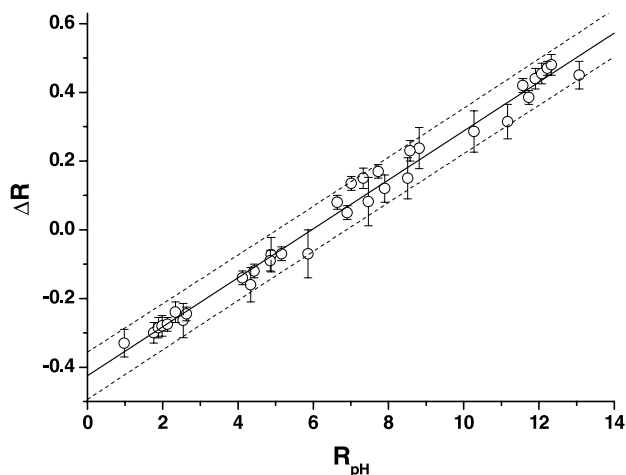

Fig. 2. Dependence of $\Delta R = R_{pH^*} - R_{pH}$ on R_{pH}, with standard errors of triple determinations. Combined data from Fig. 1. Solid line represents the linear fit to experimental points, dashed lines mark the limits of the 95% probability confidence bands.
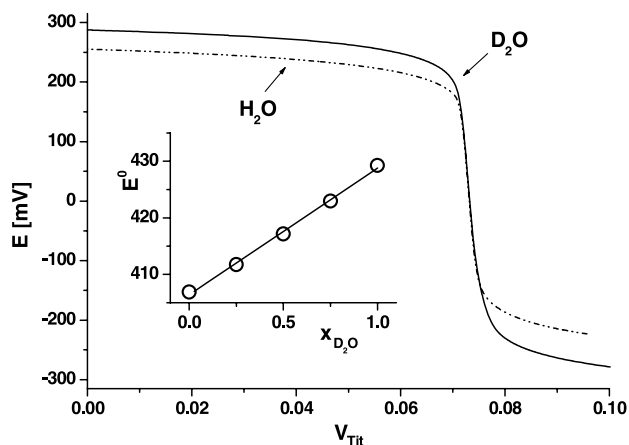

Fig. 3. Comparison of titrations of 2 mM HCl in H_2O/0.1 M KNO_3 with 0.1 M NaOH and 2 mM DCl/0.1 M KNO_3 in D_2O with 0.1 M NaOD. Inset presents linear dependence of standard potential of glass electrode, E^0 on molar fraction of D_2O.

although individual standard electrode potentials varied widely. The same was demonstrated previously for pH*/ pD conversions [4,5].

Another simple effect, which is often neglected in practice, is the influence of I on R_{pH} and R_{pH*}, due to effects on ion activities. Protonation constants are conveniently measured by potentiometry at constant I, typically 0.1 M, which is assured by additions of weakly competing salts, as NaCl, KNO_3 or $NaClO_4$. Such additions are preferably avoided in NMR or ESI MS, because the higher ionic strengths often lead to deterioration of the spectra. Therefore, it is frequently very useful to compare constants obtained under varied ionic conditions. The Debye–Hückel formula for calculating the activity coefficient γ_i of an ion carrying ionic charge z is applicable here (presented here in an approximate version for I up to 0.1 M [13]):

$$\log \gamma_i = -0.51z^2 \left[\frac{\sqrt{I}}{(\sqrt{I} + 1) - 0.33I} \right]. \tag{8}$$

This equation can be simplified further for the pH range between 3.5 and 10.5 and rearranged for the hydrogen ion. A linear equation (9) results, which deviates from the accurate, non-linear Eq. (8) by less than 0.01 pH units:

$$R_{pH,I=0.1} = 0.98189R_{pH,I=0} + 0.1245. \tag{9}$$

Corrections provided by Eqs. (1) and (3) or (4) can be applied together to correlate pK_a values determined under different conditions, e.g., by NMR at $I \sim 0$ M in D_2O and by potentiometry at $I = 0.1$ M in H_2O (pK^H). Examples of such calculations are given in Table 1, using the total of 28 protonation constants of eight different compounds, including 13 carboxylates, 7 amines,

Table 1
Application of pH/pH* and ionic corrections (Eqs. (1), (8) and (9)) to protonation macroconstants

Constant	NMR experiment at low I^a	MR + ionic correction (pK^{H*})	NMR + ionic and pH/pH* corrections	Potentiometric experiment^b (pK^H)	Deviations $\Delta pK^{Hc-H}/\Delta pK^{H*-H}$
His pK_{a1}	1.44(5)^{c,d}	1.46	1.78	1.82(4)	−0.04/−0.36(9)^e
His pK_{a2}	5.95(3)	5.97	5.97	6.036(2)	−0.07/−0.07(3)
His pK_{a3}	9.37(4)	9.32	9.08	9.136(2)	−0.06/0.18(4)
GSH pK_{a1}^f	1.94(3)	1.98	2.26	2.18(1)	0.08/−0.20(4)
GSH pK_{a2}	3.48(1)	3.54	3.71	3.512(5)	0.20/0.03(2)
GSH pK_{a3}	9.05(4)	9.01	8.79	8.736(4)	0.05/0.27(4)
GSH pK_{a4}	9.94(5)	9.88	9.60	9.655(2)	−0.06/0.22(5)
γECA pK_{a1}^f	2.10(1)	2.15	2.42	2.26(2)	0.16/−0.11(3)
γECA pK_{a2}	3.60(1)	3.66	3.82	3.63(1)	0.19/0.03(2)
γECA pK_{a3}	9.07(1)	9.03	8.81	8.723(8)	0.09/0.31(2)
γECA pK_{a4}	9.98(2)	9.92	9.64	9.670(4)	−0.03/0.25(2)
γECS pK_{a1}^f	1.83(3)	1.87	2.16	2.07(2)	0.09/−0.20(5)
γECS pK_{a2}	3.30(1)	3.35	3.53	3.43(1)	0.10/0.08(2)
γECS pK_{a3}	8.92(3)	8.88	8.70	8.643(8)	0.06/0.24(4)
γECS pK_{a4}	9.85(3)	9.80	9.55	9.638(4)	0.09/0.16(3)
γECE pK_{a1}^f	1.88(6)	1.92	2.20	2.18(2)	0.02/−0.26(8)
γECE pK_{a2}	3.27(7)	3.32	3.50	3.45(1)	0.05/−0.13(8)
γECE pK_{a3}	4.55(7)	4.59	4.68	4.76(1)	−0.08/−0.17(8)
γECE pK_{a4}	9.10(8)	9.06	8.84	8.887(8)	−0.05/0.17(9)
γECE pK_{a5}	10.10(6)	10.04	9.75	9.818(4)	−0.07/0.22(6)
GSH-am pK_{a1}^f	1.87(2)	1.91	2.19	2.15(2)	0.04/−0.24(4)
GSH-am pK_{a2}	8.51(3)	8.48	8.30	8.29(1)	0.01/0.19(4)
GSH-am pK_{a3}	9.49(3)	9.44	9.19	9.347(5)	−0.16/0.09(4)
GSH-Et pK_{a1}^f	1.89(3)	1.93	2.21	2.20(3)	0.01/−0.27(6)
GSH-Et pK_{a2}	8.76(6)	8.73	8.53	8.46(1)	0.07/0.27(7)
GSH-Et pK_{a1}	9.75(6)	9.70	9.43	9.501(6)	−0.07/0.20(7)
TCEP pK_{a3}^g	4.29(7)	4.31	4.42	4.306(3)	0.11/0.00(7)
TCEP pK_{a4}	7.8(1)	7.79	7.66	7.681(2)	−0.02/0.11(10)

^{a} Calculated from titration curves, generated from NMR spectra at 298 K, in D_2O solutions at concentrations of 5–10 mM.
^{b} Calculated from potentiometric titration curves at 298 K, in H_2O solutions containing 0.1 M KNO_3 at concentrations of 1–2 mM.
^{c} Standard errors on the last digits are given in parentheses.
^{d} Ionic corrections for acidic constants of pK_a lower than 3.5 were done using a formula derived from Eq. (3); Eq. (4) was used in all other cases.
^{e} Values of deviations and their standard errors rounded to 0.01 log units, error in parentheses common to both values.
^{f} All pK^H values for these compounds taken from [8].
^{g} All pK^{H*} and pK^H values taken from [14].

6 thiols, 1 imidazole and 1 phosphine. These compounds were studied in our laboratory recently, under identical experimental conditions. The selection is otherwise accidental. The values of interest are discussed below, using the following notation:

- pK^{H^*} (column 3 of Table 1) is the value determined by NMR in terms of pH^* and corrected for ionic strength via Eq. (8) or (9), where appropriate.
- pK^{Hc} (column 4 of Table 1) is derived from pK^{H^*} via Eq. (1).
- pK^{H} (column 5 of Table 1) is obtained experimentally by potentiometry.

The comparison of the validity of our proposed approach vs. the "cancel out" approach [6,7], on the basis of the dataset of Table 1, is obtained by calculating the differential values of deviations between the constants obtained in D_2O and H_2O, $\Delta pK^{Hc-H} = pK^{Hc} - pK^{H}$ for our approach and $\Delta pK^{H^*-H} = pK^{H^*} - pK^{H}$ for the "cancel out" approach [6,7]. These values are presented in column 6 of Table 1. They clearly demonstrate that our formula provides a better correlation between pH and pH^* constants. The average of absolute values of ΔpK^{Hc-H} deviations is 0.07, and 14 out of these 28 values are within the experimental limits of their determinations. The average of absolute values of ΔpK^{H^*-H} deviations is 0.18, and only 1 out of 28 is within the experimental error. The values of deviations are lower in our approach for 22 out of 28 data pairs.

Carboxylates comprise the biggest subgroup among constants presented in Table 1, and the average of absolute values of ΔpK^{Hc-H} over this subgroup is 0.11, higher than the overall value of 0.07 (the average of experimental errors of constant determinations is 0.05 log units in both cases). Martin analyzed the correlation between pK^{H} and pK^{D} (constants expressed in terms of pD) [15]. He gave particular attention to carboxylate constants, and provided a carboxylate-specific formula, which included an additional molecular charge term (Eq. (10) in [15]). In later papers, notably, (but not exclusively) in a series of works on acid/base properties of nucleic acid derivatives by Sigel and co-workers [16–20], the simplified version of this equation, without the molecular charge term, was used. For the purpose of compari-
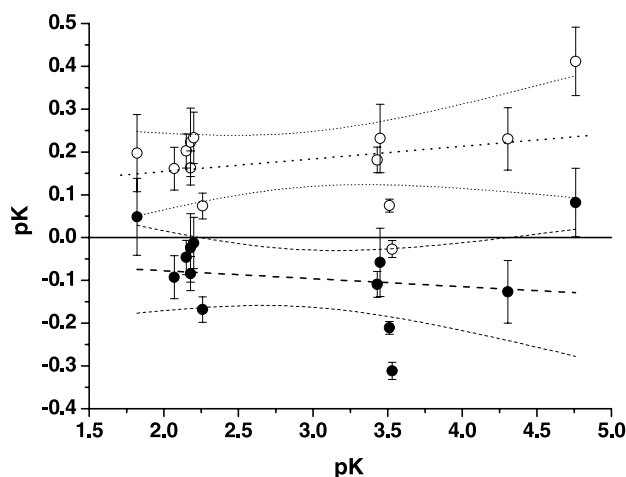

Fig. 4. Comparison of correlations between ΔpK^{D-H} and pK^{H} provided by Eq. (5) (open symbols) and [12] (solid symbols). Trend lines and 95% probability confidence bands are shown in dashed lines for Eq. (10) and in dotted lines for Eq. (10) from [14].

sons, our pK^{H^*} constants were converted into pK^{D} values by adding a common term of 0.4. Then Eq. (1) was rearranged to Eq. (10), which yielded a required correlation format:

$$\Delta pK^{D-H} = 0.076 pK^{H} - 0.05. \tag{10}$$

The corresponding equation for recalculating pK^{H^*} directly into pK^{H} stems directly from Eq. (1):

$$pK^{H} = 0.929 pK^{H^*} + 0.42. \tag{11}$$

The average of absolute values of these deviations is 0.10 for our general Eq. (10), while it is 0.19, almost twice as much, for the original Martin's formula. The graphical comparison of these two approaches is presented in Fig. 4. It can be clearly seen that there are systematic deviations from zero for both approaches, with opposite signs. On the other hand, the trends, marked with dashed and dotted lines in Fig. 4, are statistically insignificant. It should be noted here, that if the constant value of 0.45, implied by a rearranged version of Eq. (1), were used for conversion between pK^{H^*} and pK^{D}, instead of traditional 0.4 (resulting in the absence of the last term in Eq. (10)), then our formula would work even better (average of absolute

Table 2
Average discrepancies (pH units) between the experimental ΔpK^{D-H} values and the values recalculated using empirical equations

Eq. (10)	R.B. Martin, full version[a]	R.B. Martin, simplified[b]	Dataset
0.10	0.19	0.24	Acidic from Table 1
0.06	0.14	0.06	Alkaline from Table 1
0.08	0.16	0.14	All from Table 1
0.21		0.05	Refs. [16–19]
0.12		0.05	Ref. [20]

[a] Eq. (10) from [15], which includes the molecular charge term.
[b] Version of Eq. (10) from [15], without the molecular charge term, used in [16–20].

values of deviations $= 0.05$), and that proposed by Martin even worse (average of absolute values of deviations $= 0.24$). Interestingly, the simplified Martin's formula performs poorly for carboxylic constants, but it works fine for alkaline constants from Table 1 (see Table 2). Our approach gives the most accurate results for all combinations of data from Table 1. These trends change if the data from [16–20] are used for comparisons. Following these papers, only the simplified version of Martin's approach was used. This equation works better than ours for those data (Table 2). The likely reason for this effect is the presence of various strong intramolecular interactions in nucleotides, which introduce a systematic bias in the $\Delta p K^{D-H}$ values, which is intrinsically present in the simplified Martin's formula (but note that if the coefficient of 0.45 is used to convert pH^* into pD, rather than 0.4, then our approach provides a slightly better match for the data from [20]).

Summing up all the above considerations, our equations provide a method for accurate conversions of protonation constants, measured in D_2O solutions, into constants valid for H_2O solutions. Due to its general mode of derivation, which did not depend on any protonation constant, our method is reliable in the absence of specific interactions, which would exhibit strong isotopic effects, such as strong hydrogen bonds. Eq. (1) has universal applications, wherever glass electrodes are used to establish acidities of H_2O and D_2O solutions. Its usage can therefore be expected to facilitate experiment planning and data analysis, and help avoid errors and discrepancies. More studies will be required to set out specific quantitative criteria, but our approach may also provide an easy and powerful method for detecting such specific interactions. Our results also suggest that the value of 0.45 provides a better accuracy for pH^*/pD conversions than the traditional value of 0.4.

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