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First Ionization Constant of Phosphoric Acid and of Acetic Acid in H_2O and D_2O from $T = 373$ K to 573 K at $p = 11.5$ and 20 MPa by AC Conductivity Methods

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Abstract

The first ionization constants of phosphoric acid and acetic acid have been measured in H_2O and D_2O from $T = 373$ K to $T = 573$ K and $p = 11.5$ and 20 MPa to yield accurate values of the deuterium isotope effect. Sequential conductivity measurements using a unique high-precision flow-through AC conductance instrument were made on dilute ($m \leq 10^{-2}$ mol·kg^{-1}) aqueous solutions of phosphoric acid, acetic acid, potassium dihydrogenphosphate, sodium acetate, potassium hydroxide, sodium hydroxide, hydrochloric acid, potassium chloride and sodium chloride in light and heavy water under the same experimental conditions (temperature, pressure, flow-rate), so that systematic experimental errors between the two solvents would cancel. The experimental molar conductivities of potassium dihydrogenphosphate, sodium acetate, hydrochloric acid, and the corresponding chloride salts were used to calculate the molar conductivities for the fully dissociated acids [$\lambda(D^+)$, $\lambda(D_2PO_4^-)$ and $\lambda(CH_3COO^-)$]. Together with the molar conductivities measured for partially ionized acids, $\Lambda(D_3PO_4)$ and $\Lambda(CH_3COOD)$, these yielded values for the degree of dissociation, α, and the ionization constants, pK_{a1}. The iterative process was repeated at each temperature in both H_2O and D_2O where the Fuoss-Hsia-Fernández-Prini ("FHFP") and the Quint-Viallard ("QV") equations were used to correct for ionic strength. The resulting values of pK_{a1} for phosphoric acid in H_2O agree with those reported from conductivity studies by previous works over the entire temperature range and with low temperature potentiometric studies to within the combined experimental uncertainties. The results for pK_{a1} above 298.15 K in D_2O are the first to be reported in the literature. The new values for pK_a(CH_3COOD) yield more accurate values for the deuterium isotope effect on the ionization constant of acetic acid than those reported in our previous work (Erickson et al. in J. Phys. Chem. B. 123:9503–9506, 2019). The single-ion limiting conductivities for dihydrogenphosphate and acetate in D_2O, $\lambda(D_2PO_4^-)$ and $\lambda(CH_3COO^-)$, were found to be the same as those in H_2O once corrected for viscosity effects, confirming previous observations for other ions.

Keywords Deuterium isotope effect · Acetic acid · Phosphoric acid · D_2O · Heavy water · Hydrothermal solution · Ionization constant · Conductivity

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1 Introduction

An accurate understanding of the pH and chemical speciation of aqueous systems at high temperature is critical to optimise the plant chemistry regime of nuclear power plants and establish safety margins. The Canadian CANDU-PHWR (“CANada Deuterium Uranium Pressurized Heavy Water Reactor”) design is unique compared to other Pressurized Water Reactors (PWRs) in that it uses D_2O rather than H_2O in the primary coolant system as a neutron moderator and heat transport medium [1]. To optimize PHWR chemistry regimes and safety margins, experimental values for the equilibrium constants of acid ionization and metal oxide hydrolysis reactions in heavy water at high temperature and pressure are required. A few high temperature aqueous systems have been reported [2–4] with the data being much more limited for D_2O systems. Understanding the deuterium isotope effects on equilibrium constants for a variety of chemical systems over an extended temperature range will help to probe differences in the solvation behaviour of light and heavy water to develop accurate models of their reactions under CANDU primary coolant conditions.

A great deal of progress has been made towards understanding these effects at ambient temperatures [5–11]. The increase in the molar mass of heavy water causes small but detectable differences in the properties of the solvent, and as temperature increases the average number and strength of the hydrogen bonds in both H_2O and D_2O weaken, resulting in drastic changes in the physical properties of both solvents. Experimental deuterium isotope effects on ionization reactions, $\Delta pK = pK_{a,D2O} - pK_{a,H2O}$, have been reported at ambient conditions for many organic and inorganic species [5–12], where ΔpK values ranged between 0.2 and 0.7. At higher temperatures accurate measurements remain scarce, with only a few studies of acid–base ionization having been reported above 373 K [13–22].

This work adds to previous investigations carried out at the University of Guelph [16–22], aimed at measuring the small differences in equilibrium constants between light and heavy water over an extended range of temperatures and pressures with sufficient accuracy that the deuterium isotope effects can be modeled. This study reports measurements of the phosphoric acid first ionization constant in H_2O, $K_{a1,H2O}$, and D_2O, $K_{a1,D2O}$, from 298 to 571 K at 20 MPa using a unique custom-made high-temperature flow AC conductivity instrument [23, 24], where the experiments were designed to measure the *difference* in molar conductivity between solutions in D_2O and H_2O directly, so that most systematic errors would cancel. The measurements also yielded values for the single-ion limiting molar conductivities, $\lambda°$, of K^+, Cl^-, Na^+, $D_2PO_4^-/H_2PO_4^-$, CH_3COO^-, D_3O^+/H_3O^+ and OD^-/OH^- in D_2O and H_2O at temperatures up to $T = 573$ K. The additional measurements on the ionization constant of acetic acid were made to reduce the uncertainties on its deuterium isotope effect reported in our previous study [18, 19]. The conductivity data were analyzed with the Fuoss-Hsia-Fernández-Prini (“FHFP”) model [25] and the Quint-Viallard (“QV”) [26–28] equations following Conrad et al. [29].

2 Experimental

2.1 Chemicals and Solution Preparation

Aqueous stock solutions of 1.1905 $mol\cdot kg^{-1}$ H_3PO_4 in H_2O and 0.8679 $mol\cdot kg^{-1}$ D_3PO_4 in D_2O were prepared from purchased phosphoric acid aqueous solutions (Fisher Scientific,

#A242P-500, 85 wt %) and (Sigma Aldrich, #176,753, 85 wt % in D_2O, 98 atom % D), respectively. Both solutions were standardized against a standard NaOH solution at 298 K to ± 0.1%. Aqueous stock solutions of 0.1299 $mol \cdot kg^{-1}$ HCl, 0.4677 $mol \cdot kg^{-1}$ DCl, 0.2433 $mol \cdot kg^{-1}$ KOH, and 0.1355 $mol \cdot kg^{-1}$ KOD were prepared by dilution from purchased solutions (HCl, Sigma Aldrich, #318965, 0.1 N standard; DCl, Sigma Aldrich, #543047, 35 wt % in D_2O, 99 atom % D; KOH, Fisher Scientific, #SS254-4, 50 wt %; KOD, Sigma Aldrich, #176761, 40 wt % in D_2O, 98 + atom % D). The HCl and DCl solutions were standardized against a standard NaOH solution, and the KOH and KOD solutions were standardized against potassium hydrogen phthalate (KHP, $C_8H_5O_4K$, Fisher Scientific, #AC17712, 99.99%) to ± 0.1% at 298 K. Stock solutions of 0.1163 $mol \cdot kg^{-1}$ KCl (Fisher Scientific, #BP366-500, > 99%) in H_2O and 0.1134 $mol \cdot kg^{-1}$ KCl in D_2O, 0.1011 $mol \cdot kg^{-1}$ KH_2PO_4 (Sigma Aldrich, #P0662, > 99%) in H_2O, and 0.09297 $mol \cdot kg^{-1}$ KD_2PO_4 (Sigma Aldrich, #329916, 98 atom % D) in D_2O were prepared by mass from their salts using a balance accurate to ± 0.00002 g with buoyancy corrections and accuracy better than ± 0.2%. KHP, KCl, and KH_2PO_4 were dried at 403 K, 573 K, and 393 K respectively until a constant mass was achieved.

Degassed and deionized water from a Millipore Direct-Q 5 water purification system (resistivity 18.2 MΩ·cm) was used to prepare the H_2O solutions. The heavy water used in the D_2O solution preparation was donated from Ontario Power Generation Inc. and determined to be > 99.8 mol% D with ^{1}H NMR, using a standardized D_2O solution of acetic acid (CH_3COOD, Sigma Aldrich, #537020, 99.85%) as the internal proton reference. The solutions in D_2O were prepared in a glove bag purged with argon, which was continually kept under positive argon pressure. Stock solutions were diluted to a concentration of ~ 10^{-3} $mol \cdot kg^{-1}$ by mass, to a relative precision of ± 0.01%, and stored in sealed Pyrex glass or HDPE Nalgene bottles under a positive argon atmosphere to prevent contamination from atmospheric CO_2(g).

2.2 Impedance Measurements and Experimental Design

The experimental design was based on our recent acetic acid study [18, 19]; here, solutions of phosphoric acid, acetic acid, potassium dihydrogenphosphate, sodium acetate, hydrochloric acid and potassium or sodium chloride, in both light and heavy water, were injected in sequence at each temperature, pressure, and flow rate, so that systematic errors in the experimental molar conductivities of solutions in the two solvents would cancel, thus yielding more precise values of the deuterium isotope effect, $\Delta pK = pK_{a1,D2O}$—$pK_{a1,H2O}$. Experiments were performed for dilute aqueous solutions of H_3PO_4/D_3PO_4, CH_3COOH/CH_3COOD, HCl/DCl, KOH/KOD, KCl, NaCl, $NaCH_3COO$, and KH_2PO_4/KD_2PO_4 in both H_2O and D_2O (~ 10^{-4} to ~ 10^{-3} $mol \cdot kg^{-1}$) from $T = 373$ K to 573 K at a constant pressure $p \sim 11.5$ or 20 MPa with a high-temperature, high-pressure AC conductivity flow of cell used in our earlier studies [24, 30–34]. The temperature of the cell was controlled to ± 0.15 K over the several days required for conductivity measurement and recorded to ± 0.02 K. High-performance liquid chromatographic (HPLC) pumps were used to inject solutions into the flow conductivity cell, at a rate of 0.5 $cm^3 \cdot min^{-1}$. The pressure was controlled by a back-pressure regulator (Circle Seal Controls Inc. model BPR21U25512 6000 psi) located at the end of the flow line and measured to an accuracy of ± 0.01 MPa. A set of Pyrex glass bottles or high density polyethylene Nalgene bottles (for KOH, KOD, NaOH and NaOD), equipped with KIMAX GL-45 gastight tops, contained the test solutions in both light and heavy water, and the two solvents, H_2O and D_2O, for injection into the high-pressure flow AC conductivity instrument. The solutions and solvents in the flasks used for the feed system were kept under a positive argon pressure for the duration of the experimental runs.

Complex impedances, $Z(\omega)=Z_{\mathrm{Re}}(\omega)-j\cdot Z_{\mathrm{Im}}(\omega)$, of the aqueous solutions were measured as a function of concentration and the angular frequency (ω) at each temperature. Impedance spectra were collected at nine frequencies in the range 100 to 10 kHz, to yield values for both real $Z_{\mathrm{Re}}(\omega)$ and imaginary $Z_{\mathrm{Im}}(\omega)$ components. AC impedance data (at 100, 200, 500, 1000, 2000, 4000, 6000, 8000 and 10 000 Hz) were collected for the following sequence of solutions for the phosphoric acid measurements: H_2O, D_2O, NaCl/H_2O, NaCl/D_2O, KCl/H_2O, KCl/D_2O, H_3PO_4, D_3PO_4, KH_2PO_4, KD_2PO_4, HCl, DCl, KOH, KOD, NaCl/H_2O, NaCl/D_2O, D_2O and H_2O, and similarly, for the acetic acid measurements: H_2O, D_2O, NaCl/H_2O, NaCl/D_2O, CH_3COOH, CH_3COOD, CH_3COONa/H_2O, CH_3COONa/D_2O, HCl, DCl, NaOH, NaOD, NaCl/H_2O, NaCl/D_2O, D_2O and H_2O. Eighty to one hundred impedance measurements were taken with a computer over a time span of 50 min or more. Each sample injection was followed by a large injection of de-ionized water from the main reservoir, typically 80 mL, to rinse the equipment until the cell conductance had returned to its baseline value. The resistance of the solution was determined from the high frequency limit of $Z_{\mathrm{Re}}(\omega)$ using Eq. 1:

$$Z_{\mathrm{Re}}(\omega) = R_s + b_1 \cdot \omega^{-n} \tag{1}$$

where R_s is the solution resistance that we seek to measure, and b_1 and n are fitting parameters. Details on the extrapolation method and the experimental uncertainty limits in $Z_{\mathrm{Re}}(\omega)$ and $Z_{\mathrm{Im}}(\omega)$ are discussed in Ref. [35].

2.3 Experimental Conductivities and Solvent Correction

Experimental solution conductivities ($\kappa_{\mathrm{soln}}{}^{\mathrm{exp}} = R_s / k_{\mathrm{cell}}$) were determined from the resistances of the aqueous solution (R_s) after a calibration of the conductivity cell. The procedures used for calibrating the instrument and determining the cell constant (k_{cell}) have been reported in previous studies [18, 19, 24, 34, 36]. Temperature-dependent cell constants used in this work are reported in Tables 1 and 2. To check the accuracy of the calibration, two NaCl solutions (in H_2O and in D_2O) were run as internal standards before and after the series of other electrolytes at each temperature. As shown in Tables 3, 4 and 5 the values agreed with one another to within ± 1 % or better, which is considered to be the precision of our conductivity measurements. Limiting conductivity values, Λ°(NaCl), were derived from these measurements, and were found to agree with literature results [24] to within less than ± 3% which is considered to be the experimental uncertainty of our conductivity measurements. Results are shown in Figure 1.

As in our previous studies, the data treatment to extrapolate experimental conductivities to infinite dilution is based on the theoretical Fuoss–Hsia–Fernández-Prini ("FHFP") conductivity model [25]. In this work the Quint-Viallard ("QV") conductivity model [26–28] was also used to confirm the results from Conrad et al. [29]. The full details for the QV treatment are reported in Ref. [29]. Experimental solution conductivities, $\kappa_{\mathrm{soln}}^{\mathrm{exp}}$, were corrected for impurities within the solvent to yield the *true* solution conductivities, κ. The solvent correction is different if the considered electrolyte is an acid, a base, or a salt. For simple salts, experimental solution conductivities were corrected for impurities within the solvent using the expression:

Table 1 Experimental molar conductivities, Λ^{exp}, and fitted (FHFP and QV) limiting molar conductivities, $\Lambda°$, for NaCl(aq), HCl(aq), NaOH(aq), $NaCH_3COO$(aq), KCl(aq), KOH(aq), KH_2PO_4(aq), and H_3PO4(aq), in H_2O from $T=298$ K to $T=573$ K at $p=20$ MPa and $p=11.5$ MPa

Solute	$m \times 10^6$ mol·kg^{-1}	$c \times 10^6$ mol·L^{-1}	$\kappa \times 10^6$ S·cm^{-1}	Λ^{exp} S·cm^2·mol^{-1}	$\Lambda°$ (FHFP)	$\Lambda°$(QV)
$T=298.15$ K, $p=11.549$ MPa, $\rho_w=1002.2$ kg·m^{-3}, $\eta_w=0.00889$ P, $\varepsilon_w=78.91$						
$k_{\mathrm{cell}}=0.06681$ cm^{-1}, $\kappa_w^{\mathrm{exp}}=0.2180\times10^{-6}$ S·cm^{-2}, $\kappa_w^{\mathrm{pure}}=0.0579\times10^{-6}$ S·cm^{-2}						
NaCl(aq)	167.5657 ± 0.0053	167.93 ± 0.17	21.6 ± 0.2	128.6 ± 0.9	129.7 ± 0.9	129.7 ± 0.9
HCl(aq)	266.20 ± 0.20	266.79 ± 0.27	29.1 ± 0.2	417.1 ± 3.0	419.6 ± 3.0	419.6 ± 3.0
NaOH(aq)	159.707 ± 0.085	160.06 ± 0.16	14.9 ± 0.1	93.0 ± 0.7	94.0 ± 0.7	94.0 ± 0.7
$NaCH_3COO$(aq)	8293.84 ± 0.71	8309.4 ± 8.8	690.9 ± 5.0	83.1 ± 0.6	89.8 ± 0.7	89.7 ± 0.7
CH_3COOH(aq)	41.9209 ± 0.0053	42.013 ± 0.042	7.5 ± 0.1	178.4 ± 1.3	379.7 ± 2.7	379.6 ± 2.7
$T=298.17$ K, $p=20.30$ MPa, $\rho_w=1006.0$ kg·m^{-3}, $\eta_w=0.00886$ P, $\varepsilon_w=79.14$						
$k_{\mathrm{cell}}=0.06478$ cm^{-1}, $\kappa_w^{\mathrm{exp}}=1.159\times10^{-6}$ S·cm^{-2}, $\kappa_w^{\mathrm{pure}}=0.060\times10^{-6}$ S·cm^{-2}						
KCl(aq)	1269.1 ± 1.3	1276.6 ± 1.3	187.5 ± 1.3	146.9 ± 1.1	150.2 ± 1.1	150.2 ± 1.1
HCl(aq)	912.90 ± 0.91	918.33 ± 0.92	385.7 ± 2.7	419.9 ± 3.0	424.8 ± 3.1	424.8 ± 3.1
KOH(aq)	2523.3 ± 2.5	2538.3 ± 2.6	672.9 ± 4.8	265.1 ± 1.9	271.2 ± 2.0	271.1 ± 2.0
H_3PO_4(aq)	2626.8 ± 2.6	2642.2 ± 2.7	807.5 ± 5.8	305.6 ± 2.2	376.5 ± 2.7	376.4 ± 2.7
KH_2PO_4(aq)	1154.5 ± 1.1	1150.5 ± 1.2	118.9 ± 0.8	99.1 ± 0.7	101.9 ± 0.7	101.8 ± 0.7
$T=374.22$ K, $p=21.28$ MPa, $\rho_w=967.27$ kg·m^{-3}, $\eta_w=0.00284$ P, $\varepsilon_w=55.98$						
$k_{\mathrm{cell}}=0.06691$ cm^{-1}, $\kappa_w^{\mathrm{exp}}=1.981\times10^{-6}$ S·cm^{-2}, $\kappa_w^{\mathrm{pure}}=0.863\times10^{-6}$ S·cm^{-2}						
KCl(aq)	156.59 ± 0.16	151.46 ± 0.15	59.5 ± 0.4	393.0 ± 2.8	396.8 ± 2.8	396.8 ± 2.8
HCl(aq)	107.14 ± 0.11	103.63 ± 0.10	89.2 ± 0.6	860.8 ± 6.2	865.3 ± 6.2	865.3 ± 6.2
KOH(aq)	264.00 ± 0.26	255.36 ± 0.26	159.4 ± 1.1	624.3 ± 4.5	630.2 ± 4.5	630.2 ± 4.5
H_3PO_4(aq)	1061.8 ± 1.1	1027.0 ± 1.0	600.6 ± 4.3	584.8 ± 4.2	746.5 ± 5.4	746.5 ± 5.4
$T=423.35$ K, $p=11.488$ MPa, $\rho_w=922.95$ kg·m^{-3}, $\eta_w=0.00185$ P, $\varepsilon_w=44.32$						
$k_{\mathrm{cell}}=0.06672$ cm^{-1}, $\kappa_w^{\mathrm{exp}}=2.143\times10^{-6}$ S·cm^{-2}, $\kappa_w^{\mathrm{pure}}=1.926\times10^{-6}$ S·cm^{-2}						
NaCl(aq)	167.5657 ± 0.0053	154.65 ± 0.15	82.0 ± 0.6	530.2 ± 3.8	536.3 ± 3.8	536.3 ± 3.8
HCl(aq)	266.20 ± 0.20	245.69 ± 0.25	256.8 ± 1.8	1045.4 ± 7.5	1055.9 ± 7.6	1055.8 ± 7.6
NaOH(aq)	162.892 ± 0.087	150.34 ± 0.15	118.9 ± 0.8	791.1 ± 5.7	798.2 ± 5.7	798.2 ± 5.7
$NaCH_3COO$(aq)	8293.84 ± 0.71	7652.9 ± 8.1	2972 ± 22	385.4 ± 2.8	420.2 ± 3.1	420.2 ± 3.1
CH_3COOH(aq)	41.9209 ± 0.0053	38.691 ± 0.039	11.7 ± 0.1	301.9 ± 2.2	937.2 ± 6.7	937.2 ± 6.7
KCl(aq)	268.57 ± 0.01	247.88 ± 0.25	143.8 ± 1.0	580.0 ± 4.2	592.7 ± 4.2	592.3 ± 4.2
KOH(aq)	199.75 ± 0.03	184.36 ± 0.18	153.9 ± 1.1	834.7 ± 6.0	845.5 ± 6.1	845.5 ± 6.1
KH_2PO_4(aq)	5086.0 ± 0.4	4694.0 ± 4.9	1978 ± 14	419.4 ± 3.1	448.3 ± 3.3	448.2 ± 3.3
$T=423.30$ K, $p=21.31$ MPa, $\rho_w=928.25$ kg·m^{-3}, $\eta_w=0.00188$ P, $\varepsilon_w=44.76$						
$k_{\mathrm{cell}}=0.06688$ cm^{-1}, $\kappa_w^{\mathrm{exp}}=2.854\times10^{-6}$ S·cm^{-2}, $\kappa_w^{\mathrm{pure}}=2.022\times10^{-6}$ S·cm^{-2}						
KCl(aq)	156.59 ± 0.16	145.35 ± 0.15	82.4 ± 0.6	566.8 ± 4.1	572.8 ± 4.1	572.8 ± 4.1
HCl(aq)	107.14 ± 0.11	99.45 ± 0.10	107.3 ± 0.8	1078.4 ± 7.7	1085.1 ± 7.8	1085.1 ± 7.8
KOH(aq)	264.00 ± 0.26	245.06 ± 0.25	192.8 ± 1.4	786.8 ± 5.6	795.7 ± 5.7	795.7 ± 5.7
H_3PO_4(aq)	1061.8 ± 1.1	985.6 ± 1.0	620.7 ± 4.4	629.8 ± 4.5	935.3 ± 6.7	935.3 ± 6.7
$T=473.21$ K, $p=11.544$ MPa, $\rho_w=871.97$ kg·m^{-3}, $\eta_w=0.00137$ P, $\varepsilon_w=35.16$						
$k_{\mathrm{cell}}=0.06669$ cm^{-1}, $\kappa_w^{\mathrm{exp}}=3.263\times10^{-6}$ S·cm^{-2}, $\kappa_w^{\mathrm{pure}}=3.027\times10^{-6}$ S·cm^{-2}						
NaCl(aq)	167.5657 ± 0.0053	146.11 ± 0.15	101.0 ± 0.7	691.3 ± 5.0	700.1 ± 5.0	700.1 ± 5.0
HCl(aq)	266.20 ± 0.20	232.12 ± 0.23	267.4 ± 1.9	1151.8 ± 8.3	1165.8 ± 8.4	1165.7 ± 8.4
NaOH(aq)	159.707 ± 0.085	139.26 ± 0.14	136.0 ± 1.0	976.3 ± 7.0	986.3 ± 7.1	986.3 ± 7.1
$NaCH_3COO$(aq)	8293.84 ± 0.71	7230.9 ± 7.6	3719 ± 27	508.0 ± 3.7	556.8 ± 4.1	556.9 ± 4.1
CH_3COOH(aq)	41.9209 ± 0.0053	36.554 ± 0.037	9.7 ± 0.1	264.1 ± 1.9	1022.4 ± 7.3	1022.5 ± 7.3
KCl(aq)	268.57 ± 0.01	234.17 ± 0.23	175.6 ± 1.2	749.7 ± 5.4	760.0 ± 5.4	759.9 ± 5.4
KOH(aq)	199.75 ± 0.03	174.16 ± 0.17	172.9 ± 1.2	993.0 ± 7.1	1004.7 ± 7.2	1004.6 ± 7.2

Table 1 (continued)

Solute	$m \times 10^6$ mol·kg^{-1}	$c \times 10^6$ mol·L^{-1}	$\kappa \times 10^6$ S·cm^{-1}	Λ^{exp} S·cm^2·mol^{-1}	Λ° (FHFP)	Λ°(QV)
KH_2PO_4(aq)	5086.0 ± 0.4	4398.4 ± 4.5	2433 ± 18	547.2 ± 4.0	587.9 ± 4.3	587.8 ± 4.3
$T = 471.88$ K, $p = 21.30$ MPa, $\rho_w = 880.24$ kg·m^{-3}, $\eta_w = 0.00140$ P, $\varepsilon_w = 35.78$						
$k_{\text{cell}} = 0.06685$ cm^{-1}, $\kappa_w^{\text{exp}} = 3.654 \times 10^{-6}$ S·cm^{-2}, $\kappa_w^{\text{pure}} = 3.198 \times 10^{-6}$ S·cm^{-2}						
KCl(aq)	495.27 ± 0.50	435.95 ± 0.44	316.0 ± 2.2	724.9 ± 5.2	739.9 ± 5.3	739.8 ± 5.3
HCl(aq)	839.90 ± 0.84	739.31 ± 0.74	871.1 ± 6.2	1178.2 ± 8.5	1202.6 ± 8.6	1202.4 ± 8.6
KOH(aq)	1687.8 ± 1.7	1485.7 ± 1.5	1443 ± 10	971.5 ± 7.0	1002.4 ± 7.2	1002.2 ± 7.2
H_3PO_4(aq)	3620.3 ± 3.6	3186.3 ± 3.3	1233.5 ± 8.9	387.1 ± 2.8	1024.6 ± 7.4	1024.4 ± 7.4
$T = 498.22$ K, $p = 11.546$ MPa, $\rho_w = 841.69$ kg·m^{-3}, $\eta_w = 0.00121$ P, $\varepsilon_w = 31.17$						
$k_{\text{cell}} = 0.06668$ cm^{-1}, $\kappa_w^{\text{exp}} = 3.542 \times 10^{-6}$ S·cm^{-2}, $\kappa_w^{\text{pure}} = 3.389 \times 10^{-6}$ S·cm^{-2}						
NaCl(aq)	1675.657 ± 0.0053	141.04 ± 0.14	108.3 ± 0.8	767.7 ± 5.5	778.0 ± 6.1	777.9 ± 5.6
HCl(aq)	266.20 ± 0.20	224.06 ± 0.22	277.0 ± 2.0	1236.1 ± 8.9	1252.3 ± 9.5	1252.2 ± 9.0
NaOH(aq)	159.707 ± 0.085	134.42 ± 0.13	136.3 ± 1.0	1014.1 ± 7.3	1025.5 ± 7.7	1025.4 ± 7.3
$NaCH_3COO$(aq)	8293.84 ± 0.71	6980.4 ± 7.4	4012 ± 29	566.5 ± 4.2	622.6 ± 5.1	623.0 ± 4.6
CH_3COOH(aq)	41.9209 ± 0.0053	35.284 ± 0.035	8.2 ± 0.1	233.8 ± 1.7	1096.9 ± 7.9	1097.2 ± 7.9
$T = 498.02$ K, $p = 21.07$ MPa, $\rho_w = 849.85$ kg·m^{-3}, $\eta_w = 0.00123$ P, $\varepsilon_w = 31.60$						
$k_{\text{cell}} = 0.06563$ cm^{-1}, $\kappa_w^{\text{exp}} = 3.823 \times 10^{-6}$ S·cm^{-2}, $\kappa_w^{\text{pure}} = 3.644 \times 10^{-6}$ S·cm^{-2}						
KCl(aq)	747.52 ± 0.75	635.28 ± 0.64	522.70 ± 3.7	822.8 ± 5.9	844.5 ± 6.1	844.4 ± 6.1
HCl(aq)	748.10 ± 0.75	635.77 ± 0.64	794.85 ± 5.6	1250.2 ± 9.0	1276.8 ± 9.2	1276.7 ± 9.2
KOH(aq)	1338.9 ± 1.34	1137.9 ± 1.15	1251.2 ± 8.9	1099.6 ± 7.9	1132.5 ± 8.1	1132.3 ± 8.1
H_3PO_4(aq)	6136.1 ± 6.1	5213.5 ± 5.4	1435.7 ± 10.9	275.4 ± 2.0	1081.1 ± 7.9	1081.0 ± 7.9
$T = 523.19$ K, $p = 11.531$ MPa, $\rho_w = 807.32$ kg·m^{-3}, $\eta_w = 0.00108$ P, $\varepsilon_w = 27.49$						
$k_{\text{cell}} = 0.06666$ cm^{-1}, $\kappa_w^{\text{exp}} = 3.676 \times 10^{-6}$ S·cm^{-2}, $\kappa_w^{\text{pure}} = 3.482 \times 10^{-6}$ S·cm^{-2}						
NaCl(aq)	167.5657 ± 0.0053	135.28 ± 0.14	114.0 ± 0.8	842.7 ± 6.0	854.7 ± 6.1	854.6 ± 6.1
HCl(aq)	266.20 ± 0.20	214.91 ± 0.22	280.2 ± 2.0	1304.0 ± 9.3	1322.6 ± 9.5	1322.5 ± 9.5
NaOH(aq)	159.707 ± 0.085	128.94 ± 0.13	137.6 ± 1.0	1067.6 ± 7.6	1080.6 ± 7.7	1080.6 ± 7.7
$NaCH_3COO$(aq)	8293.84 ± 0.71	6696.2 ± 7.1	4262 ± 31	625.5 ± 4.6	689.5 ± 5.1	690.1 ± 5.1
CH_3COOH(aq)	41.9209 ± 0.0053	33.843 ± 0.034	6.54 ± 0.05	193.2 ± 1.4	1157.4 ± 8.3	1158.0 ± 8.3
KCl(aq)	268.57 ± 0.01	216.82 ± 0.22	193.8 ± 1.4	893.0 ± 6.4	908.6 ± 6.5	909.4 ± 6.4
KOH(aq)	217.56 ± 0.03	175.63 ± 0.18	188.3 ± 1.3	1071.9 ± 7.7	1087.1 ± 7.8	1087.0 ± 7.8
KH_2PO_4(aq)	5086.0 ± 0.4	4062.0 ± 4.2	2724 ± 20	663.5 ± 4.8	717.3 ± 5.2	717.4 ± 5.2
$T = 523.56$ K, $p = 21.14$ MPa, $\rho_w = 816.64$ kg·m^{-3}, $\eta_w = 0.00111$ P, $\varepsilon_w = 27.87$						
$k_{\text{cell}} = 0.06562$ cm^{-1}, $\kappa_w^{\text{exp}} = 3.891 \times 10^{-6}$ S·cm^{-2}, $\kappa_w^{\text{pure}} = 3.812 \times 10^{-6}$ S·cm^{-2}						
KCl(aq)	747.52 ± 0.75	610.45 ± 0.61	544.08 ± 3.9	891.3 ± 6.4	916.4 ± 6.6	916.2 ± 6.6
HCl(aq)	748.10 ± 0.75	610.93 ± 0.61	801.24 ± 5.7	1311.5 ± 9.4	1341.8 ± 9.6	1341.7 ± 9.6
KOH(aq)	1420.8 ± 1.4	1160.3 ± 1.2	1359.6 ± 9.7	1171.8 ± 8.4	1210.5 ± 8.7	1210.4 ± 8.7
H_3PO_4(aq)	6136.1 ± 6.1	5009.7 ± 5.2	1154.2 ± 8.4	230.4 ± 1.7	1143.1 ± 8.4	1142.9 ± 8.4
$T = 548.21$ K, $p = 11.531$ MPa, $\rho_w = 767.24$ kg·m^{-3}, $\eta_w = 0.000973$ P, $\varepsilon_w = 23.98$						
$k_{\text{cell}} = 0.06664$ cm^{-1}, $\kappa_w^{\text{exp}} = 4.058 \times 10^{-6}$ S·cm^{-2}, $\kappa_w^{\text{pure}} = 3.268 \times 10^{-6}$ S·cm^{-2}						
NaCl(aq)	167.5657 ± 0.0053	128.56 ± 0.13	116.6 ± 0.8	907.0 ± 6.5	921.0 ± 6.6	920.9 ± 6.6
HCl(aq)	266.20 ± 0.20	204.24 ± 0.20	274.3 ± 1.9	1343.1 ± 9.6	1364.3 ± 9.8	1364.2 ± 9.8
NaOH(aq)	159.707 ± 0.085	122.54 ± 0.12	138.0 ± 1.0	1126.4 ± 8.1	1141.5 ± 8.2	1141.4 ± 8.2
$NaCH_3COO$(aq)	8293.84 ± 0.71	6365.2 ± 6.7	4470 ± 33	686.4 ± 5.1	759.0 ± 5.6	760.1 ± 5.6
CH_3COOH(aq)	41.9209 ± 0.0053	32.163 ± 0.032	4.38 ± 0.03	136.2 ± 1.0	1203.6 ± 8.6	1204.7 ± 8.6
KCl(aq)	268.57 ± 0.01	206.06 ± 0.21	197.5 ± 1.4	958.5 ± 6.9	976.6 ± 7.0	976.5 ± 6.9
KOH(aq)	217.56 ± 0.03	166.92 ± 0.17	194.9 ± 1.4	1167.7 ± 8.4	1364.3 ± 9.8	1185.4 ± 8.4
KH_2PO_4(aq)	5086.0 ± 0.40	3860.1 ± 4.0	2794.9 ± 20	717.1 ± 5.2	778.5 ± 5.7	778.9 ± 5.7

Table 1 (continued)

Solute	$m \times 10^6$ mol·kg^{-1}	$c \times 10^6$ mol·L^{-1}	$\kappa \times 10^6$ S·cm^{-1}	Λ^{exp} S·cm^2·mol^{-1}	Λ° (FHFP)	Λ°(QV)
T = 548.63 K, p = 20.14 MPa, ρ_{w} = 778.11 kg·m^{-3}, η_{w} = 0.00100 P, ε_{w} = 24.37						
k_{cell} = 0.06560 cm^{-1}, $\kappa_{\text{w}}^{\text{exp}}$ = 3.638 × 10^{-6} S·cm^{-2}, $\kappa_{\text{w}}^{\text{pure}}$ = 3.629 × 10^{-6} S·cm^{-2}						
KCl(aq)	582.37 ± 0.58	453.15 ± 0.45	436.42 ± 3.1	963.1 ± 6.9	988.9 ± 7.1	988.7 ± 7.1
HCl(aq)	671.80 ± 0.67	522.74 ± 0.53	700.34 ± 5.0	1339.8 ± 9.6	1372.3 ± 9.8	1372.2 ± 9.8
KOH(aq)	1806.9 ± 1.8	1406.1 ± 1.4	1688 ± 12	1200.2 ± 8.6	1249.0 ± 9.0	1248.9 ± 9.0
H_3PO_4(aq)	5735.3 ± 5.7	4461.6 ± 4.6	837.79 ± 6.1	187.8 ± 1.4	1160.5 ± 8.5	1160.4 ± 8.5
T = 573.43 K, p = 11.517 MPa, ρ_{w} = 717.92 kg·m^{-3}, η_{w} = 0.000869 P, ε_{w} = 20.49						
k_{cell} = 0.06662 cm^{-1}, $\kappa_{\text{w}}^{\text{exp}}$ = 2.799 × 10^{-6} S·cm^{-2}, $\kappa_{\text{w}}^{\text{pure}}$ = 2.731 × 10^{-6} S·cm^{-2}						
NaCl(aq)	167.5657 ± 0.0053	135.28 ± 0.14	118.5 ± 0.8	985.1 ± 7.1	1001.7 ± 7.2	1001.6 ± 7.2
HCl(aq)	266.20 ± 0.20	214.91 ± 0.22	264.3 ± 1.9	1382.8 ± 9.9	1407 ± 10	1407 ± 10
NaOH(aq)	162.892 ± 0.087	128.94 ± 0.13	142.8 ± 1.0	1221.3 ± 8.7	1239.4 ± 8.9	1239.3 ± 8.9
$NaCH_3COO$(aq)	8293.84 ± 0.71	6696.2 ± 7.1	4638 ± 34	761.4 ± 5.6	844.9 ± 6.2	847.0 ± 6.2
CH_3COOH(aq)	41.9209 ± 0.0053	30.096 ± 0.030	3.62 ± 0.03	120.3 ± 0.9	1250.6 ± 9.0	1252.7 ± 9.0
KCl(aq)	268.57 ± 0.01	191.11 ± 0.19	199.8 ± 1.4	1036.1 ± 7.4	1057.5 ± 7.6	1057.3 ± 7.6 a>
KOH(aq)	199.75 ± 0.03	143.40 ± 0.14	181.3 ± 1.3	1264.4 ± 9.1	1284.6 ± 9.2	1284.5 ± 9.2
KH_2PO_4(aq)	5086.0 ± 0.4	3611.4 ± 3.7	2799 ± 20	768.0 ± 5.6	839.1 ± 6.1	840.0 ± 6.1
T = 571.91 K, p = 21.15 MPa, ρ_{w} = 739.04 kg·m^{-3}, η_{w} = 0.00091 P, ε_{w} = 21.36						
k_{cell} = 0.06558 cm^{-1}, $\kappa_{\text{w}}^{\text{exp}}$ = 3.295 × 10^{-6} S·cm^{-2}, $\kappa_{\text{w}}^{\text{pure}}$ = 3.269 × 10^{-6} S·cm^{-2}						
KCl(aq)	582.37 ± 0.58	430.41 ± 0.43	437.67 ± 3.1	1016.9 ± 7.3	1046.3 ± 7.5	1046.1 ± 7.5
HCl(aq)	671.80 ± 0.7	496.50 ± 0.50	695.86 ± 4.9	1402 ± 10	1439 ± 10	1438 ± 10
KOH(aq)	1245.4 ± 1.3	920.47 ± 0.93	1185.3 ± 8.4	1287.7 ± 9.3	1334.9 ± 9.6	1334.8 ± 9.6
H_3PO_4(aq)	5735.3 ± 5.7	4237.6 ± 4.4	636.10 ± 4.6	150.1 ± 1.1	1251.1 ± 9.1	1251.0 ± 9.1

$$\kappa = \kappa_{\text{soln}}^{\text{exp}} - \kappa_{\text{w}}^{\text{exp}} \tag{2}$$

where solution conductivities of acids and bases, $\kappa_{\text{soln}}^{\text{exp}}$, were corrected following:

$$\kappa = \kappa_{\text{soln}}^{\text{exp}} - \kappa_{\text{w}}^{\text{exp}} + \kappa_{\text{w}}^{\text{pure}} \tag{3}$$

because these chemicals shift the auto-ionization equilibrium state of the solvent, and thus affect its contribution to the solution conductivity. In Eqs. 2 and 3, $\kappa_{\text{w}}^{\text{exp}}$ is the experimental conductivity of water and $\kappa_{\text{w}}^{\text{pure}}$ is the conductivity of pure water calculated assuming the molar conductivity of H^+ (H_3O^+) and OH^- equal their limiting values. Temperature dependent values of λ°(H_3O^+) and λ°(OH^-) were calculated using the Marshall reduced density relationship [37], and for $K_{\text{w,H2O}}$ they were obtained from the equation of state (EOS) reported by Marshall and Franck [38] (using EOS from Refs [33] or [39] lead to insignificant differences in the final results). D_2O values of $\Lambda_{\text{w}}^{\circ}$[$\Lambda_{\text{w}}^{\circ}$ = λ°(D_3O^+) + λ°(OD^-)] were calculated using the Marshall reduced density relationship [37] and applying a correction for viscosity effects [34] using Walden's rule. Values of $K_{\text{w,D2O}}$ were calculated using a density model fit to the experimental data from Mesmer and Herting [15]:

$$\log_{10}K_{\text{w},D_2O} = -9.742 + \frac{168.0}{T} - \frac{417500}{T^2} + \left(12.67 - \frac{3427}{T}\right)\log_{10}\rho_{D_2O} \tag{4}$$

Table 2 Experimental molar conductivities, Λ^{exp}, and fitted (FHFP and QV) limiting molar conductivities, Λ°, for KCl(aq), D_3PO4(aq), KD_2PO_4(aq), DCl(aq), and KOD(aq) in D_2O from $T = 298$ K to $T = 573$ K at $p = 20$ MPa and $p = 11.5$ MPa

Solute	$m \times 10^6$ mol·kg^{-1}	$c \times 10^6$ mol·L^{-1}	$\kappa \times 10^6$ S·cm^{-1}	Λ^{exp} S·cm^2·mol^{-1}	Λ° (FHFP)	Λ°(QV)
$T = 298.15$ K, $p = 11.549$ MPa, $\rho_w = 1110.4$ kg·m^{-3}, $\eta_w = 0.0109$ P, $\varepsilon_w = 78.61$						
$k_{\text{cell}} = 0.06681$ cm^{-1}, $\kappa_w^{\text{exp}} = 0.5100 \times 10^{-6}$ S·cm^{-2}, $\kappa_w^{\text{pure}} = 0.0130 \times 10^{-6}$ S·cm^{-2}						
NaCl(aq)	255.617 ± 0.017	283.84 ± 0.28	29.1 ± 0.2	102.4 ± 0.7	103.6 ± 0.7	103.6 ± 0.7
DCl(aq)	238.93 ± 0.17	265.30 ± 0.27	79.8 ± 0.6	300.6 ± 2.2	302.6 ± 2.2	302.6 ± 2.2
NaOD(aq)	153.256 ± 0.017	170.18 ± 0.17	24.0 ± 0.2	141.1 ± 1.0	142.2 ± 1.0	142.2 ± 1.0
$NaCH_3COO$(aq)	8381.75 ± 0.63	9303.7 ± 9.8	636.1 ± 4.6	68.4 ± 0.5	74.1 ± 0.5	74.0 ± 0.5
CH_3COOD(aq)	48.752 ± 0.023	54.134 ± 0.054	3.68 ± 0.03	68.0 ± 0.5	273.1 ± 2.0	273.1 ± 2.0
$T = 298.17$ K, $p = 20.30$ MPa, $\rho_w = 1114.7$ kg·m^{-3}, $\eta_w = 0.0109$ P, $\varepsilon_w = 78.95$						
$k_{\text{cell}} = 0.06478$ cm^{-1}, $\kappa_w^{\text{exp}} = 1.568 \times 10^{-6}$ S·cm^{-2}, $\kappa_w^{\text{pure}} = 0.017 \times 10_{-6}$ S·cm^{-2}						
KCl(aq)	1116.4 ± 1.1	1244.5 ± 1.3	149.93 ± 1.1	120.5 ± 0.9	123.2 ± 0.9	123.1 ± 0.9
DCl(aq)	3244.1 ± 3.2	3616.0 ± 3.7	1090.7 ± 7.8	301.6 ± 2.2	308.8 ± 2.2	308.7 ± 2.2
KOD(aq)	1108.8 ± 1.1	1236.0 ± 1.3	210.70 ± 1.5	170.5 ± 1.2	173.6 ± 1.2	173.6 ± 1.2
D_3PO_4(aq)	6105.2 ± 6.1	6803.7 ± 7.1	989.42 ± 7.2	145.4 ± 1.1	272.6 ± 2.0	272.6 ± 2.0
KD_2PO_4(aq)	822.77 ± 0.82	911.24 ± 0.92	79.16 ± 0.60	85.0 ± 0.6	87.0 ± 0.6	87.0 ± 0.6
$T = 374.22$ K, $p = 21.28$ MPa, $\rho_w = 1073.3$ kg·m^{-3}, $\eta_w = 0.00333$ P, $\varepsilon_w = 55.75$						
$k_{\text{cell}} = 0.06691$ cm^{-1}, $\kappa_w^{\text{exp}} = 6.071 \times 10^{-6}$ S·cm^{-2}, $\kappa_w^{\text{pure}} = 0.290 \times 10^{-6}$ S·cm^{-2}						
KCl(aq)	125.57 ± 0.13	134.78 ± 0.13	46.03 ± 0.30	341.5 ± 2.4	344.6 ± 2.5	344.6 ± 2.5
DCl(aq)	1026.7 ± 1.0	1102.0 ± 1.1	694.7 ± 4.9	630.4 ± 4.5	641.9 ± 4.6	641.8 ± 4.6
KOD(aq)	182.78 ± 0.18	196.2 ± 0.2	77.54 ± 0.60	395.3 ± 2.8	399.2 ± 2.9	399.2 ± 2.9
D_3PO_4(aq)	823.40 ± 0.80	883.8 ± 0.9	333.5 ± 2.4	377.4 ± 2.7	552.5 ± 4.0	552.4 ± 4.0
$T = 423.35$ K, $p = 11.488$ MPa, $\rho_w = 1023.9$ kg·m^{-3}, $\eta_w = 0.00213$ P, $\varepsilon_w = 44.19$						
$k_{\text{cell}} = 0.06672$ cm^{-1}, $\kappa_w^{\text{exp}} = 1.516 \times 10^{-6}$ S·cm^{-2}, $\kappa_w{}^{\text{pure}} = 0.613 \times 10^{-6}$ S·cm^{-2}						
NaCl(aq)	255.617 ± 0.017	261.73 ± 0.26	121.9 ± 0.9	465.8 ± 3.3	472.7 ± 3.4	472.7 ± 3.4
DCl(aq)	238.93 ± 0.17	244.64 ± 0.25	201.4 ± 1.4	823.4 ± 5.9	832.0 ± 6.0	832.0 ± 6.0
NaOD(aq)	158.646 ± 0.019	162.44 ± 0.16	98.2 ± 0.7	604.8 ± 4.3	610.9 ± 4.4	610.9 ± 4.4
$NaCH_3COO$(aq)	8381.75 ± 0.63	8579.6 ± 9.1	2909 ± 21	337.7 ± 2.5	369.6 ± 2.7	369.6 ± 2.7
CH_3COOD(aq)	48.752 ± 0.023	49.917 ± 0.050	6.54 ± 0.05	131.0 ± 0.9	728.9 ± 5.2	728.9 ± 5.2
KCl(aq)	296.13 ± 0.01	303.21 ± 0.30	155.6 ± 1.1	513.0 ± 3.7	526.4 ± 3.8	526.3 ± 3.8
KOD(aq)	149.31 ± 0.08	152.88 ± 0.15	98.9 ± 0.7	647.1 ± 4.6	655.7 ± 4.7	655.7 ± 4.7
KD_2PO_4(aq)	5257.40 ± 0.40	5383.0 ± 5.6	1997 ± 14	370.3 ± 2.7	397.1 ± 2.9	397.0 ± 2.9
$T = 423.30$ K, $p = 21.31$ MPa, $\rho_w = 1029.9$ kg·m^{-3}, $\eta_w = 0.00217$ P, $\varepsilon_w = 44.56$						
$k_{\text{cell}} = 0.06688$ cm^{-1}, $\kappa_w^{\text{exp}} = 9.422 \times 10^{-6}$ S·cm^{-2}, $\kappa_w^{\text{pure}} = 0.726 \times 10^{-6}$ S·cm^{-2}						
KCl(aq)	125.57 ± 0.13	129.32 ± 0.13	63.71 ± 0.50	492.6 ± 3.5	497.6 ± 3.6	497.5 ± 3.6
DCl(aq)	1026.7 ± 1.0	1057.4 ± 1.1	850.5 ± 6.1	804.4 ± 5.8	821.7 ± 5.9	821.6 ± 5.9
KOD(aq)	182.78 ± 0.18	188.24 ± 0.19	83.95 ± 0.60	446.0 ± 3.2	451.7 ± 3.2	451.7 ± 3.2
D_3PO_4(aq)	823.40 ± 0.80	847.98 ± 0.85	340.5 ± 2.4	401.6 ± 2.9	703.2 ± 5.0	703.1 ± 5.0
$T = 473.21$ K, $p = 11.544$ MPa, $\rho_w = 966.54$ kg·m^{-3}, $\eta_w = 0.00155$ P, $\varepsilon_w = 35.00$						
$k_{\text{cell}} = 0.06669$ cm^{-1}, $\kappa_w^{\text{exp}} = 2.087 \times 10^{-6}$ S·cm^{-2}, $\kappa_w^{\text{pure}} = 1.042 \times 10^{-6}$ S·cm^{-2}						
NaCl(aq)	255.617 ± 0.017	247.04 ± 0.25	151.4 ± 1.1	612.8 ± 4.4	623.0 ± 4.5	622.9 ± 4.5
DCl(aq)	238.93 ± 0.17	230.91 ± 0.23	221.0 ± 1.6	957.2 ± 6.9	969.2 ± 6.9	969.1 ± 6.9
NaOD(aq)	153.256 ± 0.017	148.12 ± 0.15	103.3 ± 0.7	697.7 ± 5.0	706.0 ± 5.1	706.0 ± 5.1
$NaCH_3COO$(aq)	8381.75 ± 0.63	8099.2 ± 8.6	3679 ± 27	451.6 ± 3.3	497.1 ± 3.7	497.3 ± 3.7
CH_3COOD(aq)	48.752 ± 0.023	47.117 ± 0.047	5.22 ± 0.04	110.7 ± 0.8	843.3 ± 6.0	843.5 ± 6.0
KCl(aq)	296.13 ± 0.01	286.22 ± 0.29	190.3 ± 1.4	664.9 ± 4.8	676.2 ± 4.8	676.1 ± 4.8
KOD(aq)	149.31 ± 0.08	144.32 ± 0.14	108.2 ± 0.8	749.5 ± 5.4	758.0 ± 5.4	758.0 ± 5.4

Table 2 (continued)

Solute	$m \times 10^6$ mol·kg^{-1}	$c \times 10^6$ mol·L^{-1}	$\kappa \times 10^6$ S·cm^{-1}	Λ^{exp} S·cm^2·mol^{-1}	$\Lambda°$ (FHFP)	$\Lambda°$(QV)
KD_2PO_4(aq)	5257.40 ± 0.40	5034.6 ± 5.2	2477 ± 18	486.8 ± 3.6	525.1 ± 3.8	525.1 ± 3.8
T = 471.88 K, p = 21.30 MPa, ρ_w = 975.82 kg·m^{-3}, η_w = 0.00159 P, ε_w = 35.63						
k_{cell} = 0.06685 cm^{-1}, κ_w^{exp} = 13.068 × 10^{-6} S·cm^{-2}, κ_w^{pure} = 1.219 × 10^{-6} S·cm^{-2}						
KCl(aq)	824.56 ± 0.82	804.61 ± 0.81	503.9 ± 3.6	626.2 ± 4.5	644.0 ± 4.6	643.8 ± 4.6
DCl(aq)	3010.1 ± 3.0	2937.3 ± 3.0	2724 ± 20	927.4 ± 6.7	966.3 ± 7.0	966.3 ± 7.0
KOD(aq)	831.90 ± 0.83	811.79 ± 0.82	607.8 ± 4.3	748.7 ± 5.4	767.9 ± 5.5	767.8 ± 5.5
D_3PO_4(aq)	4753.5 ± 4.8	4637.5 ± 4.8	905.4 ± 6.5	195.2 ± 1.4	826.0 ± 6.0	826.0 ± 6.0
T = 498.22 K, p = 11.546 MPa, ρ_w = 932.19 kg·m^{-3}, η_w = 0.00136 P, ε_w = 31.00						
k_{cell} = 0.06668 cm^{-1}, κ_w^{exp} = 2.260 × 10^{-6} S·cm^{-2}, κ_w^{pure} = 1.177 × 10^{-6} S·cm^{-2}						
NaCl(aq)	255.617 ± 0.017	238.28 ± 0.24	162.8 ± 1.2	683.3 ± 4.9	695.3 ± 5.0	695.2 ± 5.0
DCl(aq)	238.93 ± 0.17	222.73 ± 0.22	227.4 ± 1.6	1021.1 ± 7.3	1035.1 ± 7.4	1035.0 ± 7.4
NaOD(aq)	153.256 ± 0.017	142.86 ± 0.14	106.5 ± 0.8	745.4 ± 5.3	755.0 ± 5.4	755.0 ± 5.4
$NaCH_3COO$(aq)	8381.75 ± 0.63	7812.8 ± 8.2	3974 ± 29	505.0 ± 3.7	557.7 ± 4.1	558.1 ± 4.1
CH_3COOD(aq)	48.752 ± 0.023	45.446 ± 0.045	4.25 ± 0.03	93.6 ± 0.7	897.5 ± 6.4	897.9 ± 6.4
T = 498.02 K, p = 21.07 MPa, ρ_w = 941.45 kg·m^{-3}, η_w = 0.00139 P, ε_w = 31.40						
k_{cell} = 0.06563 cm^{-1}, κ_w^{exp} = 3.097 × 10^{-6} S·cm^{-2}, κ_w^{pure} = 1.435 × 10^{-6} S·cm^{-2}						
KCl(aq)	609.67 ± 0.61	573.97 ± 0.58	406.45 ± 2.9	708.1 ± 5.1	726.4 ± 5.2	726.3 ± 5.2
DCl(aq)	2283.6 ± 2.3	2149.9 ± 2.2	2170 ± 16	1009.4 ± 7.3	1049.5 ± 7.6	1049.5 ± 7.6
KOD(aq)	661.60 ± 0.66	622.87 ± 0.63	557.1 ± 4.0	894.5 ± 6.4	915.5 ± 6.6	915.4 ± 6.6
D_3PO_4(aq)	5657.0 ± 5.7	5324.4 ± 5.5	831.9 ± 6.0	156.2 ± 1.1	902.3 ± 6.6	902.3 ± 6.6
T = 523.19 K, p = 11.531 MPa, ρ_w = 893.26 kg·m^{-3}, η_w = 0.00120 P, ε_w = 27.30						
k_{cell} = 0.06660 cm^{-1}, κ_w^{exp} = 2.372 × 10^{-6} S·cm^{-2}, κ_w^{pure} = 1.476 × 10^{-6} S·cm^{-2}						
NaCl(aq)	255.617 ± 0.017	228.34 ± 0.23	171.6 ± 1.2	751.7 ± 5.4	765.8 ± 5.5	765.7 ± 5.5
DCl(aq)	238.93 ± 0.17	213.43 ± 0.21	230.0 ± 1.6	1077.5 ± 7.7	1093.6 ± 7.8	1093.5 ± 7.8
NaOD(aq)	153.256 ± 0.017	136.90 ± 0.14	113.0 ± 0.8	825.2 ± 5.9	836.6 ± 6.0	836.5 ± 6.0
$NaCH_3COO$(aq)	8381.75 ± 0.63	7487.8 ± 7.9	4203 ± 31	555.6 ± 4.1	615.9 ± 4.5	616.7 ± 4.5
CH_3COOD(aq)	48.752 ± 0.023	43.549 ± 0.044	3.32 ± 0.02	76.2 ± 0.5	943.7 ± 6.8	944.5 ± 6.8
KCl(aq)	296.13 ± 0.01	264.52 ± 0.27	212.0 ± 1.5	801.4 ± 5.7	816.9 ± 5.9	816.8 ± 5.9
KOD(aq)	153.86 ± 0.08	137.44 ± 0.14	120.2 ± 0.9	874.4 ± 6.3	886.1 ± 6.3	886.1 ± 6.3
KD_2PO_4(aq)	5257.40 ± 0.40	4652.0 ± 4.8	2788 ± 20	593.2 ± 4.3	644.6 ± 4.7	644.8 ± 4.7
T = 523.56 K, p = 21.14 MPa, ρ_w = 903.90 kg·m^{-3}, η_w = 0.00123 P, ε_w = 27.75						
k_{cell} = 0.06562 cm^{-1}, κ_w^{exp} = 3.072 × 10^{-6} S·cm^{-2}, κ_w^{pure} = 1.546 × 10^{-6} S·cm^{-2}						
KCl(aq)	609.67 ± 0.61	551.08 ± 0.55	428.84 ± 3.0	778.2 ± 5.6	799.5 ± 5.7	799.3 ± 5.7
DCl(aq)	2283.6 ± 2.3	2064.2 ± 2.1	2193 ± 16	1062.4 ± 7.7	1108.1 ± 8.0	1108.1 ± 8.0
KOD(aq)	715.90 ± 0.72	647.11 ± 0.65	624.44 ± 4.4	965.0 ± 6.9	990.3 ± 7.1	990.2 ± 7.1
D_3PO_4(aq)	5657.0 ± 5.7	5112.0 ± 5.3	669.06 ± 4.8	130.9 ± 1.0	957.2 ± 7.0	957.1 ± 7.0
T = 548.24 K, p = 11.531 MPa, ρ_w = 847.78 kg·m^{-3}, η_w = 0.00107 P, ε_w = 23.75						
k_{cell} = 0.06658 cm^{-1}, κ_w^{exp} = 2.282 × 10^{-6} S·cm^{-2}, κ_w^{pure} = 1.434 × 10^{-6} S·cm^{-2}						
NaCl(aq)	255.617 ± 0.017	216.71 ± 0.22	177.5 ± 1.3	819.3 ± 5.9	835.8 ± 6.0	835.7 ± 6.0
DCl(aq)	238.93 ± 0.17	202.56 ± 0.20	227.8 ± 1.6	1124.5 ± 8.1	1143.1 ± 8.2	1143.0 ± 8.2
NaOD(aq)	153.256 ± 0.017	129.93 ± 0.13	119.8 ± 0.8	921.7 ± 6.6	935.3 ± 6.7	935.2 ± 6.7
$NaCH_3COO$(aq)	8381.75 ± 0.63	7108.2 ± 7.5	4353 ± 32	603.2 ± 4.5	671.7 ± 5.0	673.0 ± 5.0
CH_3COOD(aq)	48.752 ± 0.023	41.331 ± 0.041	2.37 ± 0.02	57.2 ± 0.4	979.0 ± 7.0	980.3 ± 7.0
KCl(aq)	296.13 ± 0.01	251.06 ± 0.25	217.8 ± 1.5	867.7 ± 6.2	885.9 ± 6.3	885.7 ± 6.3
KOD(aq)	153.86 ± 0.08	130.44 ± 0.13	127.1 ± 0.9	974.0 ± 7.0	987.9 ± 7.1	987.9 ± 7.1
KD_2PO_4(aq)	5257.40 ± 0.40	4415.0 ± 4.6	2861 ± 21	641.8 ± 4.7	700.8 ± 5.1	701.2 ± 5.1

Table 2 (continued)

Solute	$m \times 10^6$ mol·kg^{-1}	$c \times 10^6$ mol·L^{-1}	$\kappa \times 10^6$ S·cm^{-1}	Λ^{exp} S·cm^2·mol^{-1}	Λ° (FHFP)	Λ°(QV)
$T = 548.63$ K, $p = 20.14$ MPa, $\rho_{\mathrm{w}} = 860.27$ kg·m^{-3}, $\eta_{\mathrm{w}} = 0.00110$ P, $\varepsilon_{\mathrm{w}} = 24.27$						
$k_{\mathrm{cell}} = 0.06560$ cm^{-1}, $\kappa_{\mathrm{w}}^{\mathrm{exp}} = 2.990 \times 10^{-6}$ S·cm^{-2}, $\kappa_{\mathrm{w}}^{\mathrm{pure}} = 1.524 \times 10^{-6}$ S·cm^{-2}						
KCl(aq)	681.09 ± 0.68	585.93 ± 0.59	498.82 ± 3.5	851.3 ± 6.1	877.5 ± 6.3	877.4 ± 6.3
DCl(aq)	2405.8 ± 2.4	2069.8 ± 2.1	2244 ± 16	1084.0 ± 7.8	1136.6 ± 8.2	1136.7 ± 8.2
KOD(aq)	958.70 ± 0.96	824.78 ± 0.83	833.42 ± 5.9	1010.5 ± 7.3	1043.9 ± 7.5	1043.7 ± 7.5
D_3PO_4(aq)	3841.6 ± 3.8	3304.3 ± 3.4	412.47 ± 3.0	124.8 ± 0.9	970.9 ± 7.0	971.0 ± 7.0
$T = 573.46$ K, $p = 11.52$ MPa, $\rho_{\mathrm{w}} = 791.31$ kg·m^{-3}, $\eta_{\mathrm{w}} = 0.000949$ P, $\varepsilon_{\mathrm{w}} = 20.22$						
$k_{\mathrm{cell}} = 0.06656$ cm^{-1}, $\kappa_{\mathrm{w}}^{\mathrm{exp}} = 2.068 \times 10^{-6}$ S·cm^{-2}, $\kappa_{\mathrm{w}}^{\mathrm{pure}} = 1.248 \times 10^{-6}$ S·cm^{-2}						
NaCl(aq)	255.617 ± 0.017	202.28 ± 0.20	180.6 ± 1.3	892.7 ± 6.4	912.4 ± 6.5	912.2 ± 6.5
DCl(aq)	238.93 ± 0.17	189.07 ± 0.19	220.3 ± 1.6	1165.4 ± 8.4	1187.1 ± 8.5	1187.0 ± 8.5
NaOD(aq)	158.646 ± 0.019	125.54 ± 0.13	127.6 ± 0.9	1016.7 ± 7.3	1033.3 ± 7.4	1033.2 ± 7.4
$NaCH_3COO$(aq)	8381.75 ± 0.63	6638.3 ± 7.0	4681 ± 34	692.4 ± 5.1	772.2 ± 5.7	774.6 ± 5.7
CH_3COOD(aq)	48.752 ± 0.023	38.579 ± 0.039	1.56 ± 0.01	40.5 ± 0.3	1046.9 ± 7.5	1049.4 ± 7.5
KCl(aq)	296.13 ± 0.01	234.33 ± 0.23	220.0 ± 1.6	939.0 ± 6.7	960.6 ± 6.9	960.5 ± 6.9
KOD(aq)	149.31 ± 0.08	118.16 ± 0.12	124.9 ± 0.9	1057.4 ± 7.6	1073.8 ± 7.7	1073.7 ± 7.7
KD_2PO_4(aq)	5257.40 ± 0.40	4120.4 ± 4.3	2865 ± 21	689.2 ± 5.0	756.9 ± 5.5	758.1 ± 5.5
$T = 571.91$ K, $p = 21.15$ MPa, $\rho_{\mathrm{w}} = 815.87$ kg·m^{-3}, $\eta_{\mathrm{w}} = 0.00100$ P, $\varepsilon_{\mathrm{w}} = 21.25$						
$k_{\mathrm{cell}} = 0.06558$ cm^{-1}, $\kappa_{\mathrm{w}}^{\mathrm{exp}} = 3.062 \times 10^{-6}$ S·cm^{-2}, $\kappa_{\mathrm{w}}^{\mathrm{pure}} = 1.405 \times 10^{-6}$ S·cm^{-2}						
KCl(aq)	681.09 ± 0.68	555.70 ± 0.56	512.1 ± 3.6	921.5 ± 6.6	951.8 ± 6.8	951.7 ± 6.8
DCl(aq)	2405.8 ± 2.4	1963.0 ± 2.0	2209 ± 16	1125.1 ± 8.1	1184.3 ± 8.6	1184.5 ± 8.6
KOD(aq)	649.11 ± 0.65	529.61 ± 0.53	578.5 ± 4.1	1092.3 ± 7.8	1124.5 ± 8.1	1124.4 ± 8.1
D_3PO_4(aq)	3841.6 ± 3.8	3133.7 ± 3.2	313.7 ± 2.3	100.1 ± 0.7	1022.0 ± 7.4	1022.2 ± 7.4

Table 3 Experimental sodium chloride molar conductivities, Λ(NaCl) in H_2O, used to verify our calibration from $T = 298$ K to $T = 573$ K at $p = 20$ MPa*

T /K	p /MPa	$m \times 10^6$ /mol·kg^{-1}	$c \times 10^6$ /mol·L^{-1}	Λ(NaCl) #1 / S·cm^2·mol^{-1}	Λ(NaCl) #2 / S·cm^2·mol^{-1}
298.16	20.48	1027.11	1033.25	119.95	N/A
373.15	20.89	957.86	927.00	342.83	346.32
423.31	20.20	1027.11	952.79	501.54	507.63
473.07	20.17	998.01	876.41	653.31	660.91
522.88	20.19	1101.58	899.62	787.54	787.65
548.10	20.93	1124.57	877.19	821.89	821.42
572.80	20.77	964.37	710.49	885.53	885.04

*Measurements were made alongside those reported by Plumridge et al. [62]

where T is the temperature in Kelvin and ρ_{D2O} the solvent density in g·cm^{-3}. Values for ρ_{D2O} were taken from [40].

Finally, molar conductivities for each solution, Λ^{exp}, were calculated from the corrected conductivities, κ, using the relationship:

Table 4 Experimental sodium chloride molar conductivities, Λ(NaCl) in D_2O, used to verify our calibration from $T = 298$ K to $T = 573$ K at $p = 20$ MPa*

T /K	p /MPa	$m \times 10^6$ /mol·kg^{-1}	$c \times 10^6$ /mol·L^{-1}	Λ(NaCl) #1 /S·cm^2·mol^{-1}	Λ(NaCl) #2 /S·cm^2·mol^{-1}
298.16	20.48	919.32	1024.84	100.06	N/A
373.15	20.89	870.66	934.99	301.34	301.40
423.31	20.20	919.32	946.15	443.43	445.52
473.07	20.17	1147.37	1116.89	586.63	590.88
522.88	20.19	933.53	843.85	708.86	712.26
548.10	20.93	1124.57	877.19	745.50	744.47
572.80	20.77	943.20	766.98	805.79	806.05

*Measurements were made alongside those reported by Plumridge et al. [62]

Table 5 Experimental limiting sodium chloride molar conductivities, $\Lambda°$(NaCl) in H_2O, used to verify our calibration from $T = 298$ K to $T = 573$ K at $p = 11.5$ MPa

T /K	p MPa	$\Lambda°$(NaCl) #1 /S·cm^2·mol^{-1}	$\Lambda°$(NaCl) #2 /S·cm^2·mol^{-1}	$\Lambda°$(NaCl) [24] /S·cm^2·mol^{-1}
298.15	11.55	129.73	126.74	126.78
423.35	11.49	536.33	536.83	527.16
473.21	11.54	700.14	700.37	687.48
498.22	11.55	778.00	779.19	764.10
523.19	11.53	854.70	855.08	839.57
548.21	11.53	921.01	920.19	916.73
573.43	11.52	1001.66	1002.72	1001.44

*Measurements were made alongside those reported by Plumridge et al. [62]

$$\Lambda^{\text{exp}} = \frac{1000\kappa}{c} \tag{5}$$

where κ is in SI units of S·m^{-1} and concentration, c, is in mol·dm^{-3}. In this study, these were converted to units of S·cm^{-1} and mol·cm.$^{-3}$, respectively. Solution molarities were converted into molarity values following the methodology previously reported by Erickson et al. [18, 19]

Molalities, molarities, conductivities κ, $\kappa_{\text{w}}^{\text{exp}}$ and $\kappa_{\text{w}}^{\text{pure}}$, and the corresponding experimental molar conductivities, Λ^{exp}, for each aqueous solute are tabulated in Tables 1 and 2, along with the average temperature (IPTS-90) and pressure. The uncertainties in these tables were estimated using procedures identical to those reported in Refs [18, 19, 29].

3 Conductivity Data Treatment and Methodology to Calculate Δp*K*

3.1 Conductivity Data

3.1.1 Limiting Molar Conductivities

The limiting conductivity data for each aqueous electrolyte, $\Lambda°$, in both light and heavy water were calculated using both the FHFP [25] and QV [26–28] models for fully dissociated electrolytes. Bianchi et al. [41] have evaluated the different theoretical equations [25, 42–45] for the concentration dependence of molar conductivity, Λ, in H_2O and have recommended the FHFP treatment for 1:1 electrolytes which yields values to within an accuracy of ~ 1% over the range 0–0.1 $\text{mol}\cdot\text{cm}^{-3}$. Although the QV model does not reduce to the FHFP model for 1:1 electrolytes [29], the results presented below indicate that the QV model gives the same level of accuracy for dilute electrolytes between 298 and 573 K, with the added advantage that it can be used for non-symmetrical electrolytes in H_2O and D_2O.

As in our previous work [18, 19], experimental molar conductivity values in light and heavy water were calculated from Eq. 5 and values for the molarities, c, in H_2O and D_2O were calculated from the molalities, m, and solution density. Solution densities were calculated from the density of pure solvents, ρ_{H2O} and ρ_{D2O}, and the HKF standard partial molar volumes, $V°$, [46] in light water (the uncertainties associated with approximating the apparent molar volume with $V°$ calculated from the HKF model are less than the experimental uncertainties). For the phosphoric acid aqueous solutions, at each temperature, values of $V°$ [$V° = \alpha\cdot V°(H^+) + \alpha\cdot V°(H_2PO_4^-)$—$(1-\alpha)\cdot V°(H_3PO_4)$] were calculated through an iterative process where initial estimates for the degree of dissociation, α, in Eq. 15 were taken from Mesmer and Baes' results [47] for H_3PO_4 (aq) assuming a temperature independent value of $\Delta pK_{a1} = 0.21$ [12] for D_3PO_4(aq). For CH_3COOH (aq) and CH_3COOD (aq), the initial estimates for the degree of dissociation were calculated using Mesmer et al. [48] for pK_a and Erickson et al. [18, 19] for ΔpK_a.

Numerical values for the limiting molar conductivities, $\Lambda°$, for each electrolyte measured in this work are reported in Tables 1 and 2.

3.1.2 Single-Ion Limiting Molar Conductivities

Values for the limiting molar conductivities of the chloride single ion, $\lambda°(Cl^-)$, in both light and heavy water were determined from the molar conductivity data listed in Tables 1 and 2, using KCl and NaCl transference numbers calculated following the methods described by Plumridge et al. [34]:

$$\log_{10}\frac{t^{o}_{Cl^-}}{t^{o}_{K^+}}\left(H_2O\right) = -\frac{25.68}{T} + 0.1027 \tag{6}$$

$$\log_{10}\frac{t^{o}_{Cl^-}}{t^{o}_{K^+}}\left(D_2O\right) = -\frac{25.68}{T} + 0.09394 \tag{7}$$

$$\log_{10}\frac{t^{\mathrm{o}}_{\mathrm{Cl}^-}}{t^{\mathrm{o}}_{\mathrm{Na}^+}}\left(\mathrm{H_2O}\right) = -\frac{55.57}{T} + 0.01049 \tag{8}$$

$$\log_{10}\frac{t^{\mathrm{o}}_{\mathrm{Cl}^-}}{t^{\mathrm{o}}_{\mathrm{Na}^+}}\left(\mathrm{D_2O}\right) = -\frac{55.57}{T} + 0.01416 \tag{9}$$

where T is the temperature in K.

The limiting conductivity for the chloride anion was then determined from:

$$\lambda^{\mathrm{o}}_{\mathrm{Cl}^-} = t^{\mathrm{o}}_{\mathrm{Cl}^-}\cdot\Lambda^{\mathrm{o}}_{\mathrm{KCl}} \text{ or } \lambda^{\mathrm{o}}_{\mathrm{Cl}^-} = t^{\mathrm{o}}_{\mathrm{Cl}^-}\cdot\Lambda^{\mathrm{o}}_{\mathrm{NaCl}} \tag{10}$$

using the Eqs. 6–9 and the experimental conductivities of aqueous KCl or NaCl to yield single ion limiting conductivities for K^+ and Na^+ at each experimental condition. The other single ion limiting conductivity values were deduced from the KCl or NaCl molar conductivities using Kohlrausch's law. Single ion limiting conductivity data for K^+, Na^+, Cl^-, CH_3COO^-, $H_2PO_4^-/D_2PO_4^-$, H_3O^+/D_3O^+ and OH^-/OD^- in light and heavy water are tabulated in Tables 6 and 7 together with the values of $t°(Cl^-)$ used to split the molar conductivity results.

3.2 Equations Used to Calculate ΔpK

3.2.1 Equations Used to Calculate Phosphoric Acid and Acetic Acid First Ionization Constants in H_2O and D_2O

Phosphoric acid can undergo three successive dissociation reactions in water according to the following equilibria:

$$\begin{array}{llll} \mathrm{H_3PO_4} \rightleftharpoons & \mathrm{H_2PO_4^-} & + \mathrm{H^+}; & K_{\mathrm{a1,c}} \\ (1-\alpha)c & \alpha_1 c & \left(\alpha_1 + 2\alpha_2 + 3\alpha_3\right)c & \end{array} \tag{11}$$

$$\begin{array}{llll} \mathrm{H_2PO_4^-} \rightleftharpoons & \mathrm{HPO_4^{2-}} & + \mathrm{H^+}; & K_{\mathrm{a_2,c}} \\ \alpha_1 c & \alpha_2 c & \left(\alpha_1 + 2\alpha_2 + 3\alpha_3\right)c & \end{array} \tag{12}$$

$$\begin{array}{llll} \mathrm{HPO_4^{2-}} \rightleftharpoons & \mathrm{PO_4^{3-}} & + \mathrm{H^+}; & K_{\mathrm{a_{3,c}}} \\ \alpha_2 c & \alpha_3 c & \left(\alpha_1 + 2\alpha_2 + 3\alpha_3\right)c & \end{array} \tag{13}$$

where $\alpha = \alpha_1 + \alpha_2 + \alpha_3$ is the total degree of dissociation, and α_1, α_2, α_3 are the fractions of dissociation for Eqs. 11–13.

The equilibrium constant for the first ionization of phosphoric acid (expressed in the molarity basis), $K_{a_1,c}$, which is the equilibrium constant we seek to measure, can be calculated from the fractions of dissociation, the stoichiometric concentration of phosphoric acid, c, and the activity coefficients:

Table 6 Experimental single ion limiting molar conductivities, λ°, for Cl^-, Na^+, K^+, H_3O^+, OH^-, CH_3COO^-, and $H_2PO_4^-$ in H_2O from $T = 298$ K to $T = 573$ K at $p = 20$ MPa and $p = 11.5$ MPa using the FHFP data treatment

T	p	$t°(Cl^-)$	$t°(Cl^-)$	$λ°(Cl^-)$	$λ°(Cl^-)$	$λ°(Na^+)$	$λ°(K^+)$	$λ°(H_3O^+)$	$λ°(OH^-)$	$λ°(OH^-)$	$λ°(CH_3COO^-)$	$λ°(H_2PO_4^-)$
		NaCl	KCl	NaCl	KCl				NaOH	KOH		
K	MPa			$S·cm^2·mol^{-1}$								
298.15	11.55	0.5999	0.5095	78 ± 1	-	52 ± 1	–	342 ± 3	42 ± 1	–	38 ± 1	–
298.17	20.30	0.5999	0.5095	–	77 ± 1	–	74 ± 1	348 ± 3	–	198 ± 2	–	–
374.22	21.28	0.5788	0.5196	–	206 ± 1	–	191 ± 1	659 ± 6	–	440 ± 5	–	–
423.35	11.49	0.5691	0.5242	305 ± 2	311 ± 2	231 ± 2	282 ± 2	745 ± 8	567 ± 6	563 ± 6	189 ± 3	166 ± 4
423.30	21.31	0.5691	0.5242	–	300 ± 2		273 ± 2	785 ± 8	–	523 ± 6	–	–
473.21	11.54	0.5613	0.5279	393 ± 3	401 ± 3	307 ± 2	359 ± 3	769 ± 9	679 ± 7	646 ± 8	250 ± 4	229 ± 5
471.88	21.30	0.5614	0.5278	–	390 ± 3		349 ± 3	812 ± 9	–	653 ± 8	–	–
498.22	11.55	0.5579	0.5294	434 ± 3	–	344 ± 2	-	818 ± 9	682 ± 8	–	279 ± 5	–
498.02	21.07	0.5579	0.5294	–	447 ± 3	–	397 ± 3	830 ± 10	–	735 ± 9	–	–
523.19	11.53	0.5549	0.5308	474 ± 3	482 ± 3	380 ± 3	426 ± 3	848 ± 10	700 ± 8	661 ± 8	309 ± 5	291 ± 6
523.56	21.14	0.5548	0.5308	–	486 ± 4	–	430 ± 3	855 ± 10	–	781 ± 9	–	-
548.21	11.53	0.5521	0.5321	509 ± 4	520 ± 4	413 ± 3	457 ± 3	852 ± 11	729 ± 9	907 ± 10	346 ± 6	322 ± 7
548.63	20.14	0.5521	0.5321	–	526 ± 4	–	463 ± 3	846 ± 11	–	786 ± 10	–	–
573.43	11.52	0.5496	0.5333	550 ± 4	564 ± 4	451 ± 3	494 ± 4	850 ± 11	788 ± 9	791 ± 10	394 ± 6	346 ± 7
571.91	21.15	0.5497	0.5332	–	558 ± 4	–	488 ± 4	881 ± 11	–	847 ± 10	–	–

Table 7 Experimental single ion limiting molar conductivities, λ°, for Cl^-, K^+, D_3O^+, OD^-, CH_3COO^-, and $D_2PO_4^-$ in D_2O from $T = 298$ K to $T = 573$ K at $p = 20$ MPa and $p = 11.5$ MPa using the FHFP data treatment

T	p	$t°(Cl^-)$	$t°(Cl^-)$	$λ°(Cl^-)$	$λ°(Cl^-)$	$λ°(Na^+)$	$λ°(K^+)$	$λ°(D_3O^+)$	$λ°(OD^-)$	$λ°(OD^-)$	$λ°(CH_3COO^-)$	$λ°(D_2PO_4^-)$
		NaCl	KCl	NaCl	KCl				NaOD	KOD		
K	MPa			$S·cm^2·mol^{-1}$								
298.15	11.55	0.5979	0.5045	62 ± 1	-	42 ± 1	-	241 ± 2	101 ± 1	–	32 ± 1	–
298.17	20.30	0.5979	0.5045	–	62 ± 1	–	61 ± 1	247 ± 2	–	113 ± 1	–	–
374.22	21.28	0.5767	0.5146	–	177 ± 1	–	167 ± 1	465 ± 5	–	232 ± 3	–	–
423.35	11.49	0.5670	0.5191	268 ± 2	273 ± 2	205 ± 1	253 ± 2	561 ± 7	406 ± 5	403 ± 5	165 ± 3	144 ± 3
423.30	21.31	0.5670	0.5191	–	258 ± 2	–	239 ± 2	569 ± 6	–	212 ± 4	–	–
473.21	11.54	0.5592	0.5228	348 ± 2	354 ± 3	275 ± 2	323 ± 2	618 ± 8	431 ± 5	435 ± 6	222 ± 4	202 ± 4
471.88	21.30	0.5594	0.5227	–	337 ± 2	–	307 ± 2	630 ± 7	–	461 ± 6	–	–
498.22	11.55	0.5558	0.5244	386 ± 3	–	309 ± 2	-	649 ± 8	446 ± 6	–	249 ± 4	–
498.02	21.07	0.5558	0.5244	–	381 ± 3	–	345 ± 2	669 ± 8	–	570 ± 7	–	–
523.19	11.53	0.5528	0.5258	423 ± 3	430 ± 3	342 ± 2	387 ± 3	667 ± 9	494 ± 6	499 ± 7	273 ± 5	257 ± 5
523.56	21.14	0.5528	0.5258	-	420 ± 3	–	379 ± 3	688 ± 9	–	611 ± 8	–	–
548.21	11.53	0.5500	0.5271	460 ± 3	467 ± 3	376 ± 3	419 ± 3	680 ± 9	559 ± 7	569 ± 8	296 ± 5	282 ± 6
548.63	20.14	0.5500	0.5271	–	463 ± 3	–	415 ± 3	674 ± 9	–	556 ± 8	–	–
573.43	11.52	0.5475	0.5283	500 ± 4	507 ± 4	413 ± 3	453 ± 3	684 ± 10	620 ± 8	621 ± 8	359 ± 6	304 ± 6
571.91	21.15	0.5476	0.5282	–	503 ± 4	–	449 ± 3	682 ± 9	–	675 ± 9	–	–

$$K_{a_1,H_2O} = \frac{\alpha_1\left(\alpha_1 + 2\alpha_2 + 3\alpha_3\right)c}{(1-\alpha)} \frac{\gamma_{H_2PO_4^-}\gamma_{H^+}}{\gamma_{H_3PO_4}} \tag{14}$$

where $\gamma_{H_2PO_4^-}$, γ_{H^+} and $\gamma_{H_3PO_4}$ are the activity coefficients of the $H_2PO_4^-$, H^+ and H_3PO_4. Optimal experimental conditions where the contributions from reactions 12 and 13 are negligible compared to reaction 11 (i.e. $\alpha \approx \alpha_1$, and $\alpha_2 \approx \alpha_3 \approx 0$) were determined by estimating the chemical speciation between 373 and 573 K using equilibrium constants for Eqs. 11–13 taken from the computer program SUPCRT [46] and neglecting activity coefficient effects (i.e. $\gamma_i = 1$).

Under these optimized experimental conditions, the equilibrium constant for the first ionization reaction of phosphoric acid, K_{a_1,H_2O}, can be calculated assuming:

$$K_{a_1,c} = \frac{\alpha^2 c}{(1-\alpha)}\gamma_{\pm}^2 \tag{15}$$

where the degree of dissociation can be derived from the conductivity results:

$$\alpha = \frac{\Lambda^{exp}}{\lambda(H^+) + \lambda\left(HPO_4^{2-}\right)} \tag{16}$$

In Eq. 15, $\gamma_{\pm}$ is the mean activity coefficient of the electrolyte solution based on the hypothetical 1 mol·L^{-1} standard state extrapolated to infinite dilution; values of $\gamma_{\pm}$ were calculated using the extended Debye–Hückel equation [25, 34]. In Eq. 16, Λ^{exp} is the experimental molar conductivity of phosphoric acid and $[\lambda(H^+)+\lambda(H_2PO_4^-)]$ corresponds to the molar conductivity of the fully dissociated acid (at the same ionic strength $I=\alpha\cdot c$).

Values of $[\lambda(H^+)+\lambda(H_2PO_4^-)]$ were calculated from the experimental molar conductivity values of hydrochloric acid, potassium dihydrogenphosphate and potassium chloride, according to Eq. 17,

$$\lambda\left(H^+\right) + \lambda\left(H_2PO_4^-\right) = \Lambda^{exp}(HCl) - \Lambda^{exp}(KCl) + \Lambda^{exp}\left(KH_2PO_4\right) \tag{17}$$

where the experimental molar conductivities were corrected for small differences in ionic strength using the Fuoss-Hsia-Fernández-Prini ("FHFP") [34] and the Quint-Viallard ("QV") conductivity equations [26–28] for fully dissociated electrolytes assuming Bjerrum's definition for the distance of closest approach.

The exact same methodology was adopted to determine the equilibrium constant for the first ionization of phosphoric acid in D_2O. In the analysis, the properties of water (density, ρ_w, viscosity, η_w and static dielectric constant, ε_w) were calculated from the equations of state recommended by the International Association for The Properties of Water and Steam (IAPWS) using software distributed by the National Institute of Standards and Technology (NIST) [40]. The software does not include an equation of state for the dielectric constant of D_2O, and corresponding values were calculated following the approach developed by Trevani et al. [16]. Briefly, the method is based on the assumption that values of ε_w in H_2O and D_2O at each temperature should be equal at the same number density of water molecules, as suggested from the high temperature study by Okada et al. [49]; values for ε_w in H_2O were calculated from the Uematsu-Franck equation [50].

A similar approach was taken to examine the acetic acid data to yield temperature-dependent ionization constants for:

$$\begin{array}{llll} CH_3COOH \rightleftharpoons & CH_3COO^- & + H^+; & K_{a,c} \\ (1-\alpha)c & \alpha c & \alpha c & \end{array} \tag{18}$$

with:

$$\lambda\left(H^+\right) + \lambda\left(CH_3COO^-\right) = \Lambda^{exp}(HCl) - \Lambda^{exp}(NaCl) + \Lambda^{exp}\left(CH_3COONa\right) \tag{19}$$

3.2.2 Hydrolysis Corrections to KH_2PO_4 and $NaCH_3COO$ Conductivity Data

The present method is based on measurements made at a single ionic strength for each electrolyte and can only be applied at conditions where ion association is negligible. In this study, experimental molar conductivities were measured at an ionic strength of ~ 10^{-3} mol·kg^{-1}. The determination of $\lambda(K^+)+\lambda(H_2PO_4^-)$ from $\Lambda^{exp}(KH_2PO_4)$ and of $\lambda(Na^+)+\lambda(CH_3COO^-)$ from $\Lambda^{exp}(NaCH_3COO)$ was complicated by the hydrolysis of $H_2PO_4^-/CH_3COO^-$, according to the reactions:

$$H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^-;\ K_w/K_{a_1,H_2O} \tag{20}$$

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+;\ K_{a_2,H_2O} \tag{21}$$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-;\ K_w/K_{a,H_2O} \tag{22}$$

To address this complication, KH_2PO_4 experimental molar conductivities were corrected at each temperature following the method described by Tsurko et al. [51], using the following equation:

Table 8 Fitted parameters (Eq. 25) for single ion limiting conductivities for Cl^-, K^+, H^+/H^+, OH^-/OD^-, CH_3COO^- and $H_2PO_4^-/D_2PO_4^-$ ions in H_2O and D_2O

Ion	Fit (Eq. 25)			Source
	a	*b·R*	*c·R*	
Cl^-/H_2O	14.49 ± 1.63	−2054 ± 97	280.8 ± 14.8	Ref. [29]
Cl^-/D_2O	14.23 ± 1.77	−2215 ± 105	300.1 ± 15.8	
K^+/H_2O	19.57 ± 1.34	−2396 ± 78	326.6 ± 12.0	
K^+/D_2O	15.42 ± 3.05	−2670 ± 174	363.9 ± 26.1	
H^+/H_2O	19.78 ± 2.18	−3627 ± 130	533.6 ± 19.8	
H^+/D_2O	22.59 ± 1.62	−3796 ± 96	545.5 ± 14.5	
OH^-/H_2O	16.61 ± 3.69	−2641 ± 169	382.4 ± 25.9	
OH^-/D_2O	9.60 ± 6.90	−2812 ± 342	397.3 ± 51.6	
CH_3COO^-/H_2O	21.04 ± 3.53	−2344 ± 271	308.2 ± 41.0	This work
CH_3COO^-/D_2O	17.24 ± 9.04	−3676 ± 702	498.8 ± 104.6	
$H_2PO_4^-$	8.91 ± 1.21	−2756 ± 269	370.0 ± 39.43	
$D_2PO_4^-$	9.37 ± 1.02	−2899 ± 214	384.8 ± 30.95	

$$\Lambda\left(\mathrm{K}^{+}+\mathrm{HPO}_4^{2-}\right)=\frac{\Lambda^{\exp}\left(\mathrm{KH_2PO_4}\right)-2\left(1-\alpha'-\beta\right)\lambda\left(\mathrm{HPO}_4^{2-}\right)-\left(1-\alpha'-2\beta\right)\lambda\left(\mathrm{H}^{+}\right)-\left(1-\alpha'\right)\lambda\left(\mathrm{K}^{+}\right)}{\alpha'} \tag{23}$$

where α' is the primary degree of dissociation and β is the fraction of undissociated molecules of phosphoric acid as defined by Tsurko et al. [51]. The molality of each species at chemical equilibrium was calculated using the pK_{a1} and ΔpK_{a1} values determined in this work together with the equilibrium constants reported by Mesmer et al. [47] for the second ionization of phosphoric acid, and ΔpK_{a2} = 0.468, assumed to be temperature independent [12]. In these calculations, the molar conductivity for HPO_4^{2-}, DPO_4^{2-}, H^+, D^+, $\mathrm{K}^+/\mathrm{H_2O}$ and $\mathrm{K}^+/\mathrm{D_2O}$ were calculated using the Debye–Onsager limiting law [24, 52], using limiting conductivities λ° from Conrad et al. [29] for $\mathrm{K}^+/\mathrm{H_2O}$ and $\mathrm{K}^+/\mathrm{D_2O}$ and estimates derived from the data of Muccitelli and DiAngelo [53] for HPO_4^{2-}. The values for λ°(DPO_4^{2-}) were estimated from those of λ°(HPO_4^{2-}) by correcting the viscosity effect difference between both solvents based on insights from Ref. [34]. The hydrolysis corrections for sodium acetate were done following the same methodology. In all cases, corrections were < 2.5% for acetate and < 0.5% for hydrogen phosphate. (Table 8)

3.2.3 Ionization Constants in H_2O and D_2O

Tables 8 and 9 report temperature-dependent ionization constants for phosphoric acid and acetic acid in $\mathrm{H_2O}$ and $\mathrm{D_2O}$ calculated from the conductivity results following the methodology described above. The equilibrium constants are expressed in terms of the hypothetical 1 molar (mol·L^{-1} of solution) standard state (p$K_{a,c}$ = $-\log_{10} K_{a,c}$), and in terms of the hypothetical 1 molal (mol·kg^{-1} of water) standard states (p$K_{a,m}$ = $-\log_{10} K_{a,m}$), where:

$$K_{a,m}=K_{a,c}\left(\frac{1}{\rho_w}\right)^{\Delta\nu_i} \tag{24}$$

here $\Delta\nu_i$ is the difference in stoichiometry between the aqueous product and reactant species. For example, for Eq. 11 $\Delta\nu_i$ = +1, and $K_{a,m} = K_{a,c}/\rho_w$.

Experimental values for the difference in pK, ΔpK = p$K_{a1,\mathrm{D_2O}}$ − p$K_{a1,\mathrm{H_2O}}$, are also listed in Tables 9 and 10. Standard uncertainties were estimated using procedures identical to those reported in Ref. [29]. Hydrolysis corrections were calculated by estimating the fractions of dissociation using the methodology described in Sect. 3.1, where the temperature-dependent values for limiting conductivities of OH^- and OD^- were taken from Refs [29] and [54] (see discussion below in Sect. 4.1).

4 Results and Discussion

4.1 Limiting Conductivity Results

4.1.1 Molar Limiting Conductivity

To illustrate the accuracy of the present results, experimental molar conductivities for hydrochloric acid, potassium chloride and potassium hydroxide in $\mathrm{H_2O}$ and $\mathrm{D_2O}$ are

Table 9 Experimental equilibrium constants for the first ionization of phosphoric acid in H_2O and D_2O, pK_{a1}, and deuterium isotope shift, ΔpK, from $T = 298$ K to $T = 573$ K at $p = 20$ MPa, expressed in molality and molarity standard-state scales using the FHFP data treatment

T K	p MPa	$pK_{a1,m}D_2O$	$pK_{a1,m}H_2O$	$\Delta pK_{a1,m}$	$pK_{a1,c}D_2O$	$pK_{a1,c}H_2O$	$\Delta pK_{a1,c}$
298.17	20.30	2.4612 ± 0.0086	2.0657 ± 0.0211	0.3955 ± 0.0227	2.4140 ± 0.0086	2.0631 ± 0.0211	0.3509 ± 0.0227
374.22	21.28	2.9519 ± 0.0115	2.5839 ± 0.0167	0.3679 ± 0.0203	2.9211 ± 0.0115	2.5984 ± 0.0167	0.3227 ± 0.0203
423.30	21.31	3.2508 ± 0.0085	2.8803 ± 0.0109	0.3705 ± 0.0139	3.2380 ± 0.0085	2.9126 ± 0.0109	0.3254 ± 0.0139
471.88	21.30	3.5117 ± 0.0065	3.1306 ± 0.0069	0.3812 ± 0.0095	3.5224 ± 0.0065	3.1860 ± 0.0069	0.3364 ± 0.0095
498.02	21.07	3.7269 ± 0.0064	3.3078 ± 0.0066	0.4192 ± 0.0092	3.7531 ± 0.0064	3.3784 ± 0.0066	0.3747 ± 0.0092
523.56	21.14	3.9371 ± 0.0066	3.5344 ± 0.0066	0.4027 ± 0.0093	3.9809 ± 0.0066	3.6224 ± 0.0066	0.3586 ± 0.0093
548.63	20.14	4.1467 ± 0.0064	3.7710 ± 0.0065	0.3757 ± 0.0091	4.2121 ± 0.0064	3.8799 ± 0.0065	0.3321 ± 0.0091
571.91	21.15	4.3628 ± 0.0063	4.0238 ± 0.0064	0.3390 ± 0.0090	4.4511 ± 0.0063	4.1551 ± 0.0064	0.2961 ± 0.0090

Table 10 Experimental equilibrium constants for the ionization of acetic acid in H_2O and D_2O, pK_a, and deuterium isotope shift, ΔpK, from $T = 298$ K to $T = 573$ K at $p = 11.5$ MPa, expressed in molality and molarity standard-state scales using the FHFP data treatment

T K	p MPa	$pK_{a,D,m}$	$pK_{a,H,m}$	$\Delta pK_{a,m}$	$pK_{a,D,c}$	$pK_{a,H,c}$	$\Delta pK_{a,c}$
298.15	11.549	5.3971 ± 0.0071	4.7604 ± 0.0081	0.637 ± 0.011	5.3517 ± 0.0071	4.7594 ± 0.0081	0.592 ± 0.011
423.35	11.488	5.7191 ± 0.0077	5.1951 ± 0.0078	0.524 ± 0.011	5.7088 ± 0.0077	5.2299 ± 0.0078	0.479 ± 0.011
473.21	11.544	6.0166 ± 0.0079	5.4261 ± 0.0079	0.590 ± 0.011	6.0314 ± 0.0079	5.4856 ± 0.0079	0.546 ± 0.011
498.22	11.546	6.2302 ± 0.0080	5.6188 ± 0.0079	0.611 ± 0.011	6.2607 ± 0.0080	5.6936 ± 0.0079	0.567 ± 0.011
523.19	11.531	6.4637 ± 0.0081	5.8557 ± 0.0079	0.608 ± 0.011	6.5127 ± 0.0081	5.9486 ± 0.0079	0.564 ± 0.011
548.21	11.531	6.7542 ± 0.0082	6.2207 ± 0.0079	0.534 ± 0.011	6.8260 ± 0.0082	6.3358 ± 0.0079	0.490 ± 0.011
573.43	11.517	7.1209 ± 0.0082	6.3699 ± 0.0080	0.751 ± 0.012	7.2225 ± 0.0082	6.5138 ± 0.0080	0.709 ± 0.012

compared in Fig. 2 to other literature studies [18, 19, 54–56] which used the same experimental technique. The limiting molar conductivities of HCl, DCl, KCl/H_2O, KCl/D_2O and KOH agree with other literature studies [18, 19, 54–56] to within the combined experimental uncertainties between 373 and 573 K. The KOD results measured at $p = 20$ MPa differ from those reported by Arcis et al. [54]; the viscosity effect on the $\Lambda°$(KOD) data measured in this work is not smooth, suggesting an experimental problem with the solution preparation, as illustrated by the discrepancy for the two data points measured at 373 K and 423 K. These data were originally measured for the hydrolysis correction and were discarded. The viscosity effect on the limiting molar conductivity of KH_2PO_4 and KD_2PO_4 at 20 MPa was also found to be irregular and supplementary measurements were conducted at 11.5 MPa to replace these data (the 20 MPa KH_2PO_4/KD_2PO_4 data were not considered in the final analysis because of problems with the solution preparation, confirmed by the subsequent set of experiments at 11.5 MPa). No literature comparisons were done as no experimental limiting conductivity data have been reported for KH_2PO_4 in H_2O or D_2O above 323 K. Except for a few outliers, the $NaCH_3COO$, NaCl (in H_2O and D_2O), NaOH and NaOD results were found to be consistent with Refs, [34, 54] and [57] to within the experimental uncertainties.

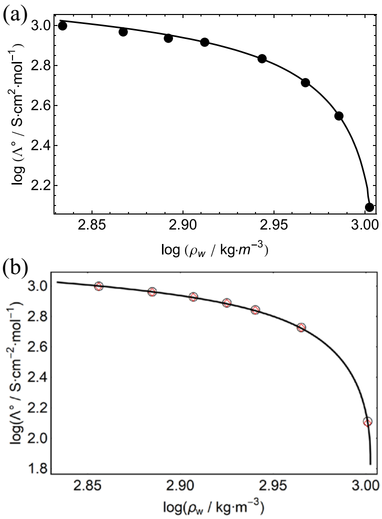

Fig. 1 **a** Experimental limiting conductivity of NaCl from $T=298$ K to $T=598$ K at $p=20$ MPa: filled circle, this work; solid line, best fit from Zimmerman et al. [84]; **b** Experimental limiting conductivity of NaCl from $T=298$ K to $T=573$ K at $p=11.5$ MPa: open circle, this work (run 1); open diamond, this work (run 2); solid line, best fit from Zimmerman et al. [84]

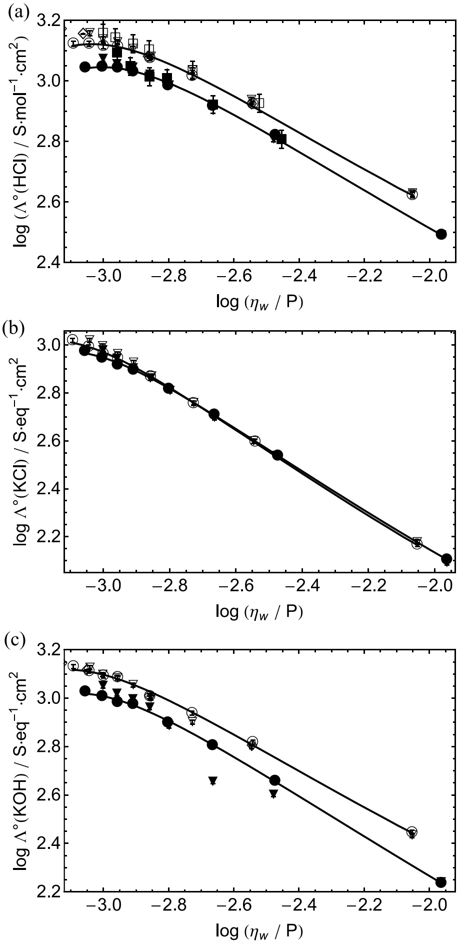

Fig. 2 Limiting molar conductivity of **a** hydrochloric acid, **b** potassium chloride, **c** potassium hydroxide in H_2O and D_2O from 298 to 573 K:open inverted triangle, this work; filled inverted triangle, this work; open circle, Ref. [5]; filled circle, Ref. [5]; open diamond, Refs [31, 32] ; open square, Refs. [21, 22]; filled square, Refs [21, 22] solid line, fit [5] (open and filled symbols refer to H_2O and D_2O data, respectively)

4.1.2 Single Ion Limiting Conductivity

Single ion limiting conductivities are compared with other literature results for dihydrogenphosphate [51] and acetate [18, 19, 57–60] in Fig. 3.

The new acetate results compare much better with previous literature studies [57–60] in H_2O and D_2O (Fig. 3) over the whole temperature range, and confirmed the previous measurements by Erickson et al. [18, 19] were not accurate.

The 11.5 MPa $H_2PO_4^-$ conductivity data in light water are consistent with the low temperature data from Tsurko et al. [51], however it became evident that there was an issue with the $H_2PO_4^-$ and $D_2PO_4^-$ conductivity data measured at 20 MPa. No other data could be identified for comparison; because of the limited concentration range investigated and the lower accuracy of the static method the KH_2PO_4 and NaH_2PO_4 conductivity measurements from Ref. [53] could not be used to derive accurate limiting conductivity data for $H_2PO_4^-$. The $H_2PO_4^-$ and $D_2PO_4^-$ conductivity measurements at 20 MPa were therefore discarded. The discrepancy at 20 MPa is believed to be due to errors in the solution preparation combined with non-optimal experimental concentrations. Recognising that it was not practical to duplicate the full set of phosphoric acid measurements, the analysis that follows used the $H_2PO_4{}^-$ and $D_2PO_4^-$ limiting conductivities measured at 11.5 MPa and corrected to 20 MPa using fitted values (Eq. 25). Because no measurements were made at 298 K and 11.5 MPa it was decided to use Tsurko's 298 K data in the fit that is presented below; Tsurko's 298 K data was also used for $D_2PO_4^-$ once corrected for viscosity effects [34]. This approach is supported by our recent results [29, 34, 54].

The semi-empirical model proposed by Plumridge et al. [34] (Eq. 25) was fitted to the experimental limiting conductivities for $H_2PO_4^-$, $D_2PO_4^-$ and CH_3COO^- (in H_2O and D_2O) reported in Tables 6 and 7.

$$\log_{10}\left(\lambda_i^{\circ}\eta_w\right) = a + \frac{b}{T} + \frac{c}{T-228} + \frac{d}{T}\log_{10}\rho_w \tag{25}$$

where ρ_w is the solvent density in kg·m^{-3} and η_w is the solvent viscosity in Poise (P). Fitting parameters listed in Table 10, some of which had been reported in our earlier studies [29, 34, 54], were found to represent the temperature dependence of the limiting conductivity in Tables 6 and 7 to within the experimental uncertainties, and no attempts were made to further fine-tune the parameters.

4.2 Equations of State for the First Ionization Constant of Phosphoric Acid and the Ionization Constant of Acetic Acid in H_2O

Following [20, 21, 29] the equilibrium constants in light water for the ionization of H_3PO_4 and CH_3COOH were fitted as a function of temperature and molar volume by using a modified form of the 'density' model reported by Mesmer et al. [61]:

$$\mathrm{p}K_{\mathrm{a,m}} = p_1 + \frac{p_2}{T} - \frac{p_3}{T}\log_{10}V^*_{\mathrm{H_2O}} \tag{26}$$

where p_1, p_2, and p_3 are adjustable fit parameters, T is the temperature in Kelvin, and the solvent density ρ_{H2O} has been replaced by its molar volume, $V^*_{H_2O} = M_{H_2O}/\rho_{H_2O}$, in cm^3·mol^{-1}. The thermodynamic justification for using molar volumes of the two solvents rather than densities in this model is discussed in more detail in Ref. [20].

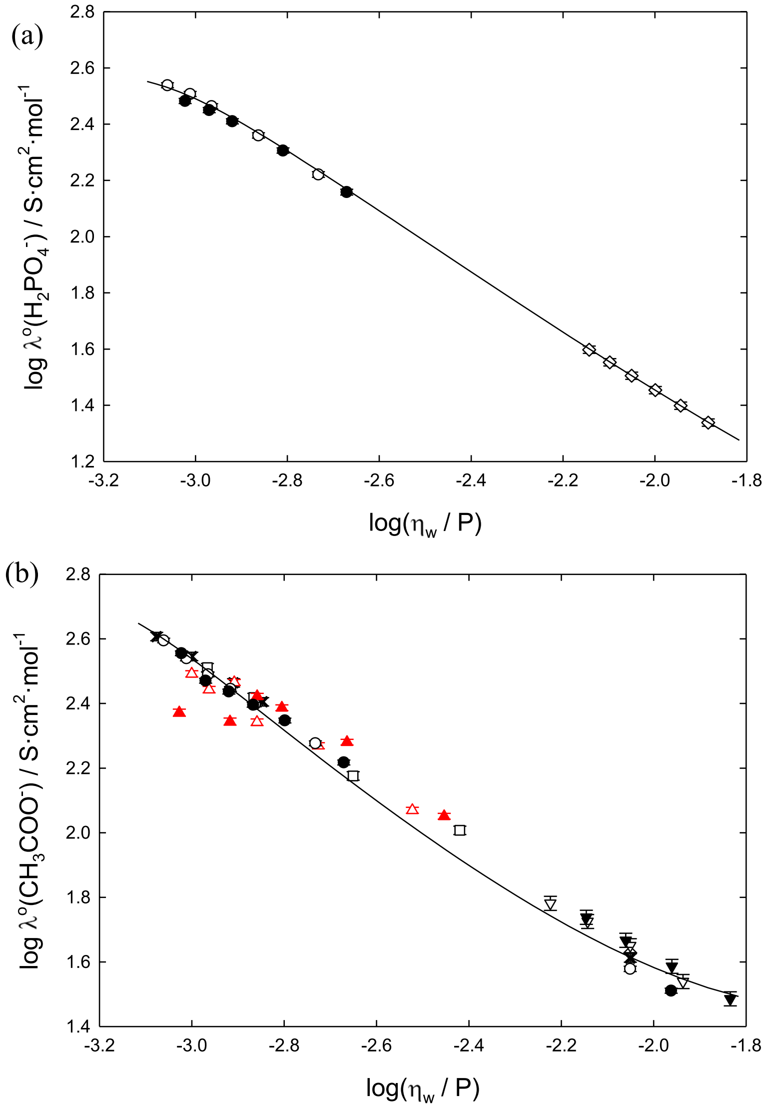

Fig. 3 Limiting conductivity of **a** dihydrogenphosphate and **b** acetate in H_2O and D_2O versus solvent viscosity from 288 to 573 K: **a** open circle, this work (H_2O); open diamond, [75]; filled circle, this work (D_2O); solid line, Eq. 25 (p_{sat}); **b** open diamond, [36], open inverted triangle, (H_2O) [11]; filled inverted triangle, (D_2O) [11]; multiplication sign , [81]; open square, [48]; red open triangle, (H_2O) [21, 22] (not included in the fit); red filled triangle (D_2O) [21, 22], (not included in the fit); open circle, this work (H_2O); filled circle, this work (D_2O); solid line, Eq. 25 (p_{sat})

Equation 26 was fitted to the experimental values of $pK_{a,m}$ tabulated in Tables 9 and 10 for H_3PO_4 and CH_3COOH along with literature sources listed in Tables 11 and 12. Parameters are tabulated in Tables 11 and 12. Our experimental $pK_{a,m}$ values are compared with other literature studies in Figs. 4 and 5 for H_3PO_4 [62–68] and for CH_3COOH [18, 19, 48, 57, 58, 69–78].

Table 11 Fitted parameters for Eqs. 26, 27, 28 to yield the first ionization constants of phosphoric acid in H_2O and D_2O and their deuterium isotope effect as a function of temperature and solvent molar volume based on the FHFP data treatment

Parameter	Value	Uncertainty	Sources
$\mathrm{p}K_{\mathrm{a,m}}\ (\mathrm{H_3PO_4}) = p_1 + \frac{p_2}{T} - \frac{p_3}{T}\log_{10}V^*_{\mathrm{H_2O}}$			
p_1	2.724	0.060	[47, 62–68]
$p_2 \times 10^{-3}$	− 8.709	0.218	
$p_3 \times 10^{-3}$	− 6.791	0.187	
$\Delta \mathrm{p}K_{\mathrm{a,m}} = \Delta p_1 + \frac{\Delta p_2}{T} - \frac{\Delta p_3}{T}\log_{10}V^*_{\mathrm{D_2O}} - p_3\log_{10}\frac{V^*_{\mathrm{D_2O}}}{V^*_{\mathrm{H_2O}}}$			
Δp_1	1.031	0.133	[65], this work
$\Delta p_2 \times 10^{-3}$	1.412	0.318	
$\Delta p_3 \times 10^{-3}$	1.309	0.285	
$\mathrm{p}K_{\mathrm{a,m}}\ (\mathrm{D_3PO_4}) = p_1 + \frac{p_2}{T} - \frac{p_3}{T}\log_{10}V^*_{\mathrm{D_2O}}$			
p_1	3.755	0.146	
$p_2 \times 10^{-3}$	− 7.297	0.386	
$p_3 \times 10^{-3}$	− 5.482	0.341	

4.2.1 Phosphoric Acid p$K_{\mathrm{a,m}}$ in H_2O

There have been several studies of the first ionization constant of phosphoric acid in H_2O [47, 62–68, 74]. Briefly, Nims [62], Schwarzenbach et al. [74], Glasoe and Long [75], McDougall and Long [63], Salomaa et al. [64], Paabo and Bates [65] and Mesmer and Baes [47] used potentiometry, Read [66] conductivity, Izatt et al. [67] calorimetry and Rudolph [68] Raman spectroscopy techniques. At 373 K and above, the p$K_{\mathrm{a,m}}$ values reported by Rudolph [68], Read [66] and Izatt et al. [67] are consistent with our results to within the combined experimental uncertainties. The results are also consistent with the potentiometric measurements from Mesmer and Baes [47] up to 450 K; but above this temperature the temperature dependence differs. The residuals in the fit, or differences between the experimental data and the fit under the same conditions (pK_{exp}−pK_{fit}), are shown in Fig. 4.b and

Table 12 Fitted parameters for Eqs. 26, 27, 28 to yield the ionization constants of acetic acid in H_2O and D_2O and their deuterium isotope effect as a function of temperature and solvent molar volume based on the FHFP data treatment

Parameter	Value	Uncertainty	Sources
$pK_{\mathrm{a,m}}(\mathrm{CH_3COOH}) = p_1 + \frac{p_2}{T} - \frac{p_3}{T}\log V^*_{\mathrm{H_2O}}$			
p_1	3.903	0.049	[19, 48, 57, 69, 71–73, 75–78, 82]
$p_2 \times 10^{-3}$	− 10.47	0.197	
$p_3 \times 10^{-3}$	− 8.534	0.167	
$\Delta \mathrm{p}K_{\mathrm{a,m}} = \Delta p_1 + \frac{\Delta p_2}{T} - \frac{\Delta p_3}{T}\log_{10}V^*_{\mathrm{D_2O}} - p_3\log_{10}\frac{V^*_{\mathrm{D_2O}}}{V^*_{\mathrm{H_2O}}}$			
Δp_1	0.388	0.026	[19, 58, 64, 75, 76], this work
$\Delta p_2 \times 10^{-3}$	− 0.750	0.565	
$\Delta p_3 \times 10^{-3}$	− 0.625	0.518	
$\mathrm{p}K_{\mathrm{a,m}}\ (\mathrm{CH_3COOD}) = p_1 + \frac{p_2}{T} - \frac{p_3}{T}\log_{10}V^*_{\mathrm{D_2O}}$			
p_1	4.291	0.026	
$p_2 \times 10^{-3}$	− 11.22	0.598	
$p_3 \times 10^{-3}$	− 9.159	0.544	

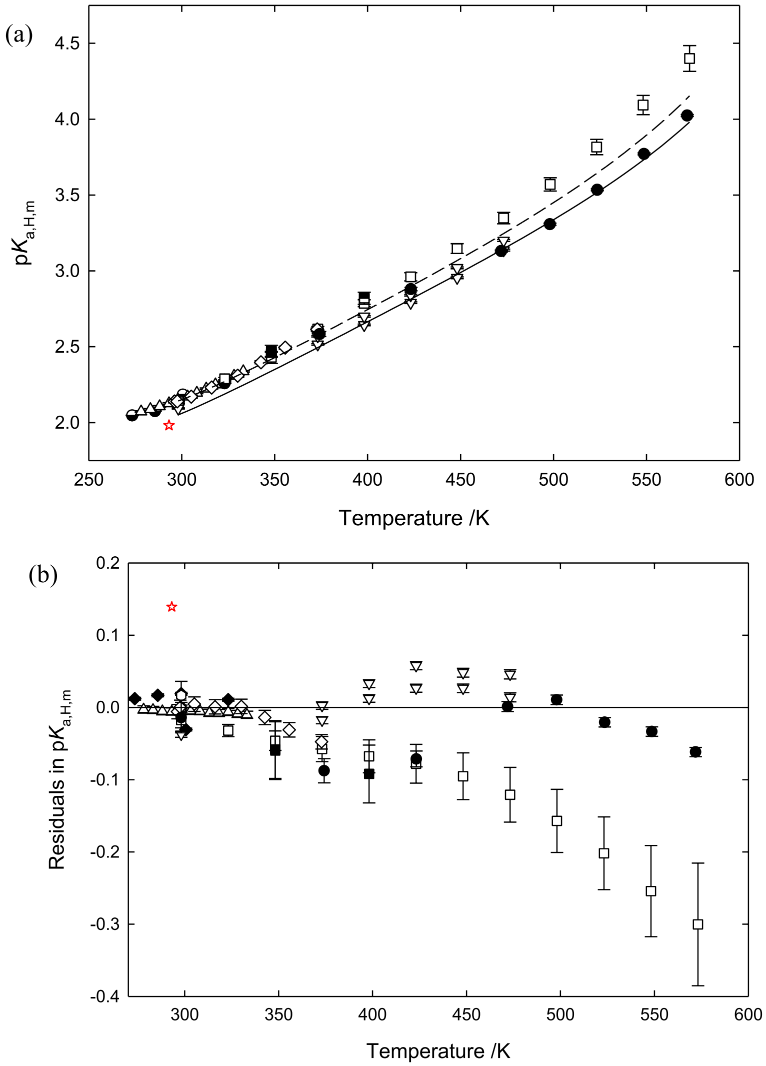

Fig. 4 **a** Phosphoric acid first ionization constant in H_2O, p$K_{a1,m}$ vs T from 288 to 573 K, **b** deviation plot between experimental and fitted values (pK_{exp}–pK_{fi}): Literature data ($p = p_{sat}$) open square, [49]; filled diamond, [56]; open hexagon, [47]; open circle, [70]; open triangle, [60]; open inverted triangle, [67]; filled square, [33]; red open diamond, [69]; open star, [71] (not included in the fit); filled circle, This Work ($p = 20$ MPa); solid line, Eq. 26 ($p = 20$ MPa); doted solid line, Eq. 26 ($p = p_{sat}$)

reach up to ~ 0.3 pK units at 573 K. The cause of the discrepancy with the other studies observed at high temperature is not clear; Read [66] postulated the presence of polyphosphate species in Mesmer and Baes' experimental solutions. The data from Mesmer and Baes were included in our fit (Eq. 26) which is able to represent their data up to 450 K to within their reported experimental uncertainties.

The fitted value given by Eq. 26 at 298 K and 0.1 MPa (p$K_{a,m} = 2.143 \pm 0.016$) is consistent with the Nuclear Energy Agency's (NEA) recommended value for the first

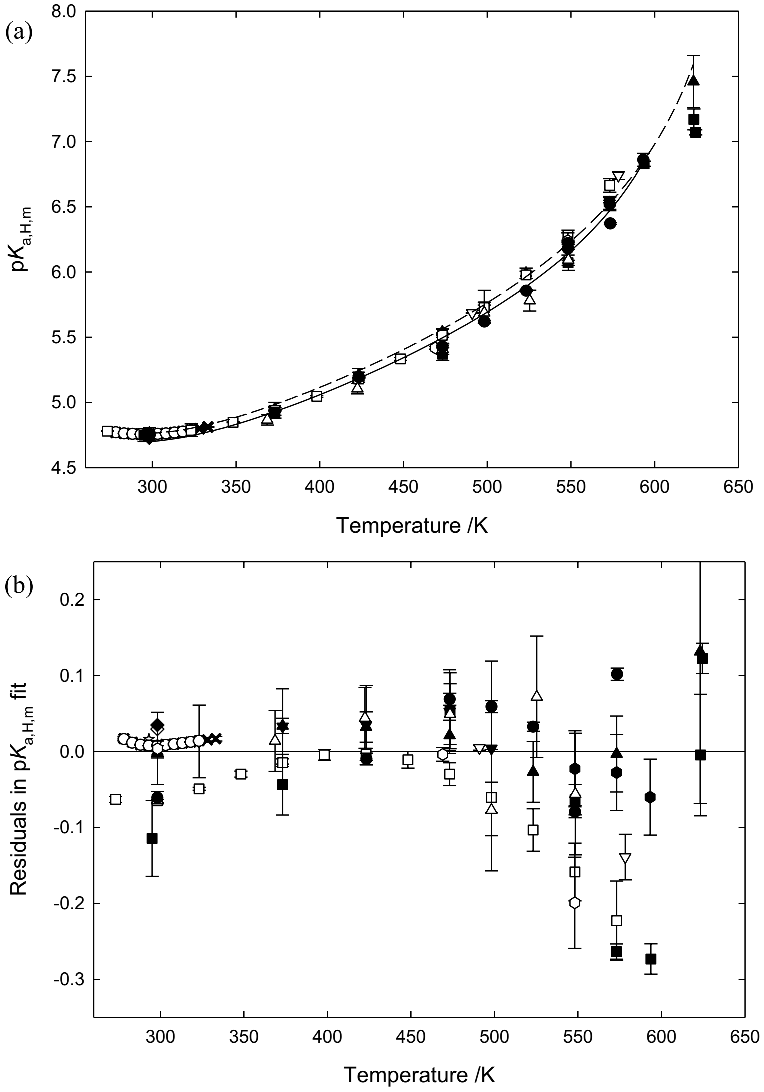

Fig. 5 **a** Acetic acid ionization constant in H_2O, $pK_{a,m}$ vs T from 288 to 623 K, **b** deviation plot between experimental and fitted values: plus, [43]; open inverted triangle, [57] recalculated by [81]; multiplication sign , [29]; open star, [71]; open diamond, [35]; filled diamond, [26]; filled inverted triangle, [20]; open circle, [25]; filled triangle, [24]; filled hexagon, [59]; open square, [52]; open hexagon, [81]; filled square, [73]; open triangle, [21, 22]; filled circle, This Work; solid line, Eq. 26 ($p = 20$ MPa); doted solid line, Eq. 26 ($p = p_{sat}$)

ionization constant of phosphoric acid in light water ($pK_{a,m} = 2.140 \pm 0.030$) [79, 80] and the more recent critical evaluation by Rard and Wolery [81]. These recommended values compare well with Read's result [$pK_{a,m}$(298.15, 0.1 MPa) = 2.15 ± 0.01], which was carefully estimated from his 20 MPa measurements [$pK_{a,m}$(298.15, 20 MPa) = 2.09 ± 0.01] by considering the change in the partial molar volume of reaction ($\Delta_r V^\circ$) for Eq. 11. Our result

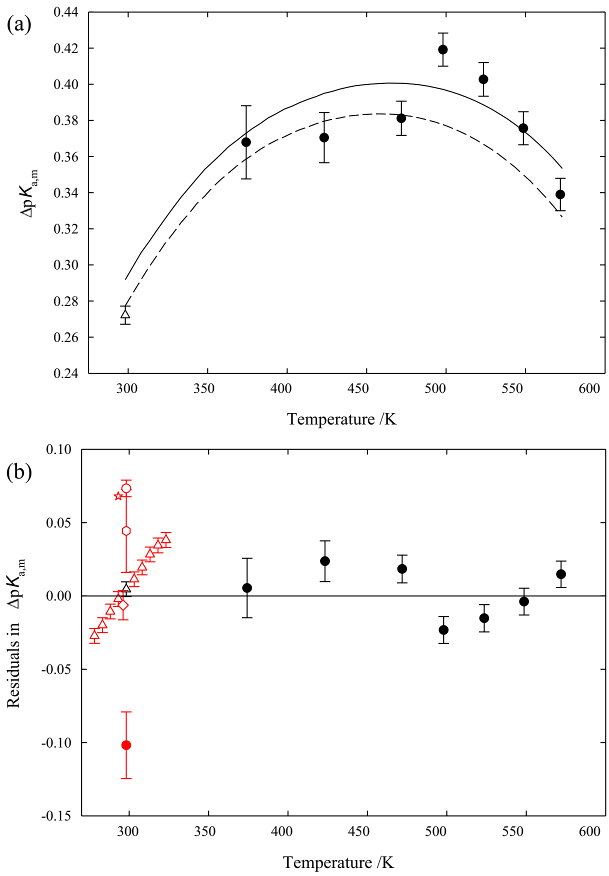

Fig. 6 **a** Deuterium isotope effect on the ionization constant, $\Delta pK_{a,m}$, of phosphoric acid vs *T*. **b** Residuals: open star, [71]; open hexagon, [47]; open circle, [70]; open triangle, [60]; open diamond, [69]; filled circle, this work; solid line, Eq. 26 ($p = 20$ MPa); doted solid line, Eq. 26 ($p = p_{sat}$). Symbols in red were not included in the fit

at 298 K and 20 MPa ($pK_{a,m} = 2.07 \pm 0.02$) is consistent with Read to within the combined experimental uncertainties and the pressure effect is similar to that for the ionization constant of light water at 298.15 K [$pK_{w,m}$(0.1 MPa)−$pK_{w,m}$(20 MPa) = 0.074] [39].

4.2.2 Acetic Acid $pK_{a,m}$ in H_2O

The ionization constant of acetic acid has also been well-studied in H_2O [18, 19, 48, 57, 58, 69–78, 82]. Briefly, Noyes et al. [69], MacInnes and Shedlovsky [70], La Mer et al. [58, 82], Ellis [71], Fisher and Barnes [72], Zimmerman and Wood [57], and Erickson et al. [18, 19] used conductivity, Harned and Ehlers [73], Schwarzenbach et al. [74], Glasoe and Long [75], Gary et al. [76], Mesmer et al. [48], Sue et al. [77] used potentiometry, and Oscarson et al. [78] used calorimetry techniques. Between 373 and 450 K, our results agree with the literature to within the combined experimental uncertainties. Above 450 K larger discrepancies appear, consistent with the difficulties with making hydrothermal measurements using different techniques. Except for Mesmer et al. [48] these remain to within ± 0.1 p*K* units, as shown by the residual plot in Fig. 5b. Similar to what was observed for H_3PO_4, the acetic acid potentiometric p*K* data from Mesmer et al. start to deviate from the other results around 450 K, showing up to 0.3 p*K* units difference at 573 K. It might be that there is a systematic error in the Oak Ridge National Laboratory (ORNL) results that becomes gradually more significant above 450 K due to assumptions in their data treatment. This matter was not addressed in their study and deserves closer attention. The data from Mesmer et al. were included in the fit (Eq. 26) weighted by the inverse square of their standard uncertainties.

The fitted value given by Eq. 26 at 298 K and 0.1 MPa ($pK_{a,m} = 4.764 \pm 0.014$) is consistent with MacInness and Shedlovsky's value for the first ionization constant of acetic acid in light water ($pK_{a,m} = 4.756 \pm 0.010$) [70] and the other low temperature literature studies (e.g., [57, 73]). The pressure effect on our conductivity result [$pK_{a,m}$(298.15 K,11.5 MPa) = 4.701 ± 0.014] is similar to that observed for the ionization constant of phosphoric acid.

4.3 D_2O Isotope Effect Δp*K* on the First Ionization Constant of Phosphoric Acid and the Ionization Constant of Acetic Acid

Experimental values of $\Delta pK_{a,m} = [pK_{a,m}(D_2O)$—$pK_{a,m}(H_2O)]$ for phosphoric and acetic acid are listed in Tables 9 and 10 and plotted in Fig. 6 alongside literature results for phosphoric acid and acetic acid. To maintain consistency with our experimental approach to yield the most accurate *difference* in the ionization constant between light and heavy water, we chose to model the experimental values for $\Delta pK_{a,m}$ directly [20, 21, 29] according to the expression:

$$\Delta pK_{a,m} = pK_{a,m}(D_2O) - pK_{a,m}(H_2O) = \Delta p_1 + \frac{\Delta p_2}{T} - \frac{\Delta p_3}{T}\log_{10}V^*_{D_2O} - p_3\log_{10}\frac{V^*_{D_2O}}{V^*_{H_2O}} \quad (27)$$

where Δp_1, Δp_2, and Δp_3 are adjustable fit parameters, T is the temperature in Kelvin, and $V^*_{D_2O} = M_{D_2O}/\rho_{D_2O}$ is D_2O molar volume in $cm^3 \cdot mol^{-1}$. The fitted parameters are given with their uncertainties in Tables 11 and 12. Combining these parameters with those for Eq. 26 from the light water data will yield the corresponding equation for heavy water, as given in Tables 11 and 12.

No other groups have reported experimental data on Δp*K* for any of these ionization reactions above 323 K. A few studies on the deuterium isotope effect on the first ionization constant of phosphoric acid have been reported [63–65, 68, 74], and except for Ref. [65], which reported $pK_{a1,m}D_3PO_4$ from $T = 278$ K to $T = 323$ K, all the studies focused on ambient conditions. Similar for observations can be made about the acetic acid system [18, 19, 58, 64, 75, 76], with the measurements reported from other groups also stopping at 323 K [76].

4.3.1 Selected Values for $D_3PO_4$and CH_3COOD ΔpK_a at 298.15 K

A few studies have reported ΔpK_a values for D_3PO_4 and CH_3COOD at 298 K. For D_3PO_4 Glasoe and Long reported $\Delta pK_{a,c} = 0.20$ ($\Delta pK_{a,m} = 0.24$) [75], McDougall and Long $\Delta pK_{a,c} = 0.234$ ($\Delta pK_{a,m} = 0.278$) [63], Paabo and Bates $\Delta pK_{a,m} = 0.272$ [65], Salomaa et al. $\Delta pK_{a,c} = 0.205$ ($\Delta pK_{a,m} = 0.249$) [64] and Rudolph $\Delta pK_{a,m} = 0.280$ [68]; for CH_3COOD La Mer et al. reported $\Delta pK_{a,c} = 0.514$, ($\Delta pK_{a,m} = 0.559$) [58, 82],

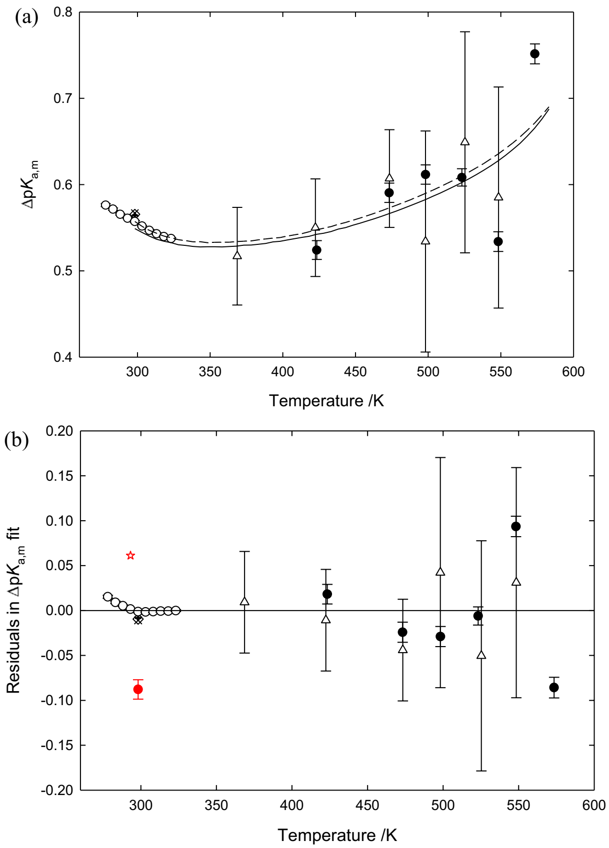

Fig. 7 **a** Deuterium isotope effect on the ionization constant, $\Delta pK_{a,m}$, of acetic acid vs T. **b** Residuals: open star, [71]; open diamond, [35, 36]; addition sign, [26]; multiplication sign , [70]; open circle, [25]; open triangle, [21, 22]; filled circle, This Work; solid line, Eq. 26 ($p = 20$ MPa); doted solid line, Eq. 26 ($p = p_{sat}$). Symbols in red were not included in the fit

Glasoe and Long $\Delta pK_{a,m} = 0.56$ [75] and Gary et al. $\Delta pK_{a,m} = 0.557$ [76]. All these data were measured at 0.1 MPa. While the acetic acid $\Delta pK_{a,m}$ data are in fair agreement, the phosphoric acid literature show some discrepancies. At 293 K the results from Schwarzenbach et al. [$\Delta pK_{a,m}(D_3PO_4) = 0.249$, $\Delta pK_{a,m}(CH_3COOD) = 0.499$] [74] compare less well with Paabo and Bates [$\Delta pK_{a,m}(D_3PO_4) = 0.181$] [65] and Gary et al. [$\Delta pK_{a,m}(CH_3COOD) = 0.561$] [76].

Our 298 K result at 20 MPa for D_3PO_4 ($\Delta pK_{a,c} = 0.351$, $\Delta pK_{a,m} = 0.396$) and CH_3COOD ($\Delta pK_{a,c} = 0.592$, $\Delta pK_{a,m} = 0.637$) does not compare well with the other literature data at 0.1 MPa, with differences of about ~0.12 and ~0.08 pK units, respectively. The cause of the discrepancies between our conductivity results and the other literature data at 298 K is not clear and the effect seems too large to attribute to a pressure effect in going from 0.1 to 20 MPa. The change in the partial molar volume of reaction ($\Delta_r V°$) for the ionization of D_3PO_4 and CH_3COOD were not investigated as part of this work and further studies are underway in our laboratory to quantify these effects. Paabo and Bates [65] did not study the deuterium isotope effect on $\Delta pK_{a,m}(D_3PO_4)$ directly and instead made use of data from Bates [83] measured 19 years previously. They noted that some of the assumptions in their pK_a calculations could have introduced “major uncertainty”. Salomaa et al. [64] also observed discrepancies up to 0.07 pK units between the results from their potentiometric and conductivity techniques.

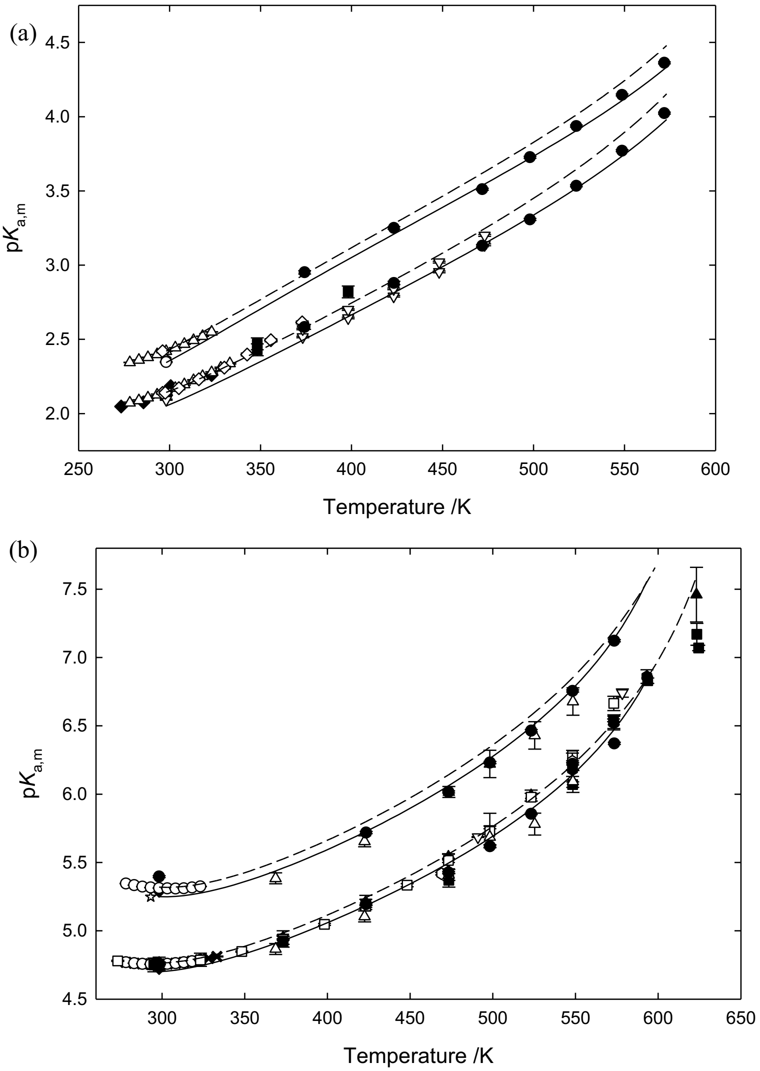

Fig. 8 Acid ionization constants for **a** phosphoric and **b** acetic acid in H_2O and D_2O, p*K* vs *T*, from this work and literature. **a** open square, [50]; filled diamond, [56]; open hexagon, [47]; open circle, [70]; open triangle, [60]; open inverted triangle, [67]; filled square, [33]; open diamond, [69]; open star, [71] (not included in the fit); filled circle, This Work; solid line, Eq. 26 ($p = 20$ MPa); ---, Eq. 26 ($p = p_{sat}$); **b** open triangle, [21, 22]; open square, [52]; open hexagon, [81]; open diamond, [35, 36]; open inverted triangle, [57] recalculated by [81]; addition sign , [43]; filled inverted triangle, [20]; filled triangle, [24]; multiplication sign , [29]; open star, [71]; filled diamond, [26]; open circle, [25]; filled square, [73]; filled hexagon, [59]; filled circle, This Work; solid line, Eq. 26 ($p = 20$ MPa); doted solid line, Eq. 26 ($p = p_{sat}$)

$\Delta pK_{a,m}$ experiments are difficult and because our flow conductivity instrument is designed for high temperature measurements it was decided not to anchor the fit discussed below to the 298 K data reported in this study. For phosphoric acid the 298 K value from Paabo and Bates ($\Delta pK_{a,m} = 0.272$) [65] was included, whereas for acetic acid all the literature sources at low temperature were included in the fit.

4.3.2 Equations of State for the First Ionization Constant of Phosphoric Acid and the Ionization Constant of Acetic Acid in D_2O

The temperature and pressure dependence of the ionization of phosphoric and acetic acids in heavy water are given by:

$$\mathrm{p}K_{\mathrm{a,m}} = p_1 + \frac{p_2}{T} - \frac{p_3}{T}\log_{10} V^*_{\mathrm{D_2O}} \tag{28}$$

where p_1, p_2, and p_3 were calculated by adding the adjustable fit parameters for Eqs. 26 and 27. Parameters are tabulated in Tables 11 and 12 and the difference in ionization are shown in Figs. 7 and 8.

5 Conclusions

This work reports accurate $\Delta \mathrm{p}K_{\mathrm{a,m}}$ measurements of the first ionization of phosphoric acid between 373 and 573 K. These are the first experimental D_3PO_4 ionization constants reported above 323 K. The results are consistent with other literature studies to within the combined experimental uncertainties and confirm that the supercritical flow AC conductivity cell is a powerful tool to measure ionization constants and the D_2O isotope effect under hydrothermal conditions. Observed differences up to 0.3 pK units in $\mathrm{p}K_{\mathrm{a,m}}$ for both phosphoric and acetic acid in H_2O from Mesmer et al. [47, 48] suggest that there might be a systematic error in the ORNL treatment resulting in an increasing systematic error above 450 K. Discrepancies with other studies observed at 298 K were not resolved as part of this work and will be addressed in a future publication. The $\Delta \mathrm{p}K_{\mathrm{a,m}}$ results reported here complete a series of experimental projects on acid ionization started in our research group [16–22] and together the results of these studies provide the basis for developing a predictive model for transition metal hydrolysis and oxide solubility in D_2O under CANDU-PHW primary coolant conditions, from H_2O-based measurements. We are exploring the use of DFT methods [7] to seek a better understanding of the differences in ionic hydration between light and heavy water systems, and these results together with the new-built high temperature D_2O database will be used to derive algorithms for computer codes used by the nuclear industry to calculate and monitor chemical speciation and pH in heavy water coolant and moderator conditions such as the EPRI code MULTEQ [84].

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Declarations

Competing interests The authors declare no competing interests.

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