

Properties of Water and Aqueous Systems: Metrological Applications

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Water and aqueous systems are widely used in metrology, which is a major focus of the National Institute of Standards and Technology (NIST). In this work, we review several activities at NIST in which research on water and aqueous systems is being applied to improve metrology. The projects include work toward a new formulation for the viscosity of pure water, an examination of the effect of dissolved air on the density and refractive index of water, and utilization of *ab initio* quantum methods for calculation of thermodynamic properties of moist air as required in humidity standards.

1. Introduction

Because of water's importance in science, technology, and life in general, and also because of its easy availability in relatively pure form, it is often used as a standard in measurement science (metrology). IUPAC [1] lists liquid water as a "recommended reference material" for density, surface tension, viscosity, thermal conductivity, heat capacity, relative permittivity and refractive index. In addition, mixtures containing water are often important in metrology; an example is water/air mixtures for humidity standards.

Improving measurement science is a core mission of the U.S. National Institute of Standards and Technology (NIST). In this paper, we will describe three current efforts at NIST that seek to improve knowledge of the thermophysical properties of water and aqueous mixtures for metrological applications.

2. Viscosity of Pure Water

A new reference surface for the viscosity of water [$\eta(T, \rho)$, where T is the temperature and ρ is the density] is being developed by a joint task group of the International Association for the Properties of Water and Steam (IAPWS) and the International Association for Transport Properties (IATP). In this Section, we will describe the reasons for undertaking such an effort at this time, the methods and progress of the effort so far, and future prospects.

The adoption, in 1995, of a new formulation for the thermodynamic properties of water, IAPWS-95

[2], as well as the revision of the temperature scale in 1990 (ITS-90) [3] and an increase in the data available for analysis [4], led to the formation of the abovementioned task group. The improvement of the temperature scale also provided an impetus for the International Organization for Standardization (ISO) to issue an updated technical report on the viscosity of water [5], motivated by the fact that this quantity, near ambient conditions, serves as the basis for the calibration of relative viscometers in many applications. A primary result of this report is a standard value of 1.0016 mPa·s for the viscosity of water at 20 °C and 0.101 325 MPa with a relative uncertainty of 0.17 % (coverage factor approximately 2).

A 1995 analysis of viscosity data near ambient conditions by Bauer *et al.* [6] led to a slightly different recommendation at 20 °C and 0.101 325 MPa [(1.0020 ± 0.0014) mPa·s]. Discussions among IAPWS, IATP and other researchers associated with the ISO analysis have confirmed the difficulty in evaluating experimental measurements from different sources: the two "best" experimental sources leading to the desired metrological standard differ by more than their combined uncertainties [5]. The IAPWS/IATP task group has chosen to use the ISO recommendation as a constraint in its new property surface. The prevalence of discrepant data, using different experimental methods and different samples, is the bane of evaluators attempting to achieve consensus metrological standards; in the development of comprehensive thermophysical property surfaces, the analysis of such data at different state conditions introduces additional complications.

The current standard procedures for expressing uncertainties in measurements [7] should, when strictly and consistently applied, provide a common basis for comparing data for the viscosity of water and could provide a sound statistical basis for developing the input data and uncertainties for a consensus viscosity surface. Unfortunately, these uncertainty protocols were not used for the vast majority of the experimental data needed to establish the viscosity surface, the input data may not be statistically independent, and the mathematical model used to describe the surface is not firmly established. For these reasons, it is difficult to establish an optimal viscosity surface with statistically rigorous uncertainties. Of course, these problems are also found in the development of other property surfaces.

The problem of comparing data from different laboratories is also encountered in establishing key comparison reference values (KCRV) and their uncertainties. These are the metrological quantities used, in part, to compare national implementations of measurement standards, and are thus important to international commerce. The task group decided to attempt to use the recently proposed KCRV evaluation protocols [8] in the development of the viscosity surface. Previous use of these methods has focused on establishing the best single value for an experimentally determined quantity; their implementation in the development of property correlations is not straightforward. The development of this method for the correlation of the dilute-gas contribution to the viscosity surface was described in Ref. [9]. Although the conditions for the use of the KCRV protocols (essentially, (a) measurements performed on identical samples; (b) independent measurements; and (c) a Gaussian distribution of results from each laboratory) were not strictly met, all of these were assumed to hold. Statistical studies leading to the KCRV protocols also considered circumstances in which the individual uncertainty estimates might not be credible; Monte Carlo methods for establishing uncertainties in recommended values or KCRVs were also proposed in some cases [8]. We have not attempted to implement these approaches.

The dilute-gas viscosity at each of 102 nominal isotherms was determined from

$$\eta_0(T) = \frac{\sum_i x_i / u^2(x_i)}{\sum_i 1/u^2(x_i)}, \quad (1)$$

where $\eta_0(T)$ is the consensus value for the dilute-gas viscosity at temperature T determined from several independent determinations (x_i) having an uncertainty of $u(x_i)$. The standard deviation of $\eta_0(T)$ is found from

$$u^2(\eta_0(T)) = \left[\sum_i 1/u^2(x_i) \right]^{-1}. \quad (2)$$

The resulting values of $\eta_0(T)$ and their uncertainties are illustrated in Fig. 1.

The slope of the viscosity isotherms in the limit of zero density has also been examined carefully, with the recent data from Vogel's group [10] of considerable importance. A theoretically based model for this first density correction [11, 12] motivated this aspect of the study, but the empirical isothermal slopes will serve to constrain the viscosity surface within their uncertainties. The theoretical approach to the critical region enhancement of the viscosity [13] will provide an improvement over the earlier viscosity standard, even though the primary data in this region date back to 1975.

The viscosity surface for water can be described as a function of temperature and density:

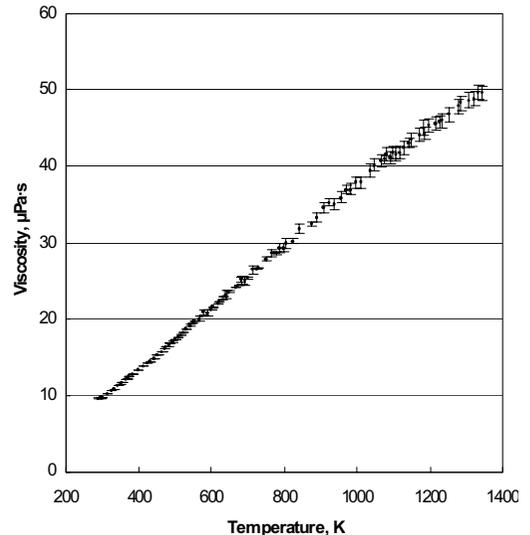


Fig. 1. Dilute-gas viscosity of water determined from data analysis of 102 nominal isotherms [9].

$$\eta(T, \rho) = [\eta_0(T) + \eta_{\text{bk}}(T, \rho)]\eta_{\text{cr}}(T, \rho), \quad (3)$$

where we have indicated the dilute-gas contribution, a background contribution (incorporating the first density correction), and the multiplicative critical enhancement. Several details concerning the new description of the viscosity surface for water are still being finalized, but it will be similar in form to the current IAPWS standard. The general non-linear method of weighted orthogonal distance regression [14], which considers the uncertainties in temperature and density as well as the uncertainty in the experimental viscosity, is being used to determine the coefficients. Much of the structure of the individual terms will be retained in the new description, but availability of new data, the re-evaluation of all of the data, the use of the most accurate standard thermodynamic surface, the incorporation of the current temperature scale, and the use of an improved description of the critical region should all ensure that the new viscosity surface for water will be generally applicable for metrological applications. As a final note, we observe that even the current IAPWS standard [15] is consistent with the 1998 ISO recommendation [5] for the viscosity of water near ambient conditions.

3. Effect of Dissolved Air on the Density and Refractive Index of Liquid Water

While property standards for water are typically for pure, air-free water, the water in real laboratory and industrial situations is often in contact with atmospheric air. Therefore, the effect of dissolved air on the properties of pure water can be important in metrology.

The impetus for this project came from the semiconductor industry, which was studying the feasibility of immersion lithography [16, 17], a new technology in which a layer of fluid (which, at least in the initial application, will be water) between the lens and the chip allows circuit features to be drawn with lines that are narrower by approximately a factor of the refractive index of the immersion liquid. In order to evaluate the technology, it was necessary to know the optical properties of water at atmospheric pressure at a wavelength of 193 nm, deep in the ultraviolet. Since existing high-precision measurements were confined to visible wavelengths, NIST undertook a measurement and modeling effort to describe these properties in the ultraviolet [18-20]. In addition to the refractive

index and its dependence on temperature and wavelength, a quantity of interest was the effect of dissolved air on the index. The effect of dissolved air on the density is a necessary intermediate in the modeling of the effect on the refractive index, and is also of metrological interest in its own right. These calculations will be described in full detail elsewhere [20].

The calculation of the density effect is relatively straightforward. The molar volume V_m of the air-saturated mixture is given by

$$V_m = x_w V_w + \sum_{i=2}^n x_i \bar{V}_i^\infty, \quad (4)$$

where x_w is the mole fraction of water and the x_i are the mole fractions of the solutes, V_w is the molar volume of pure water at the temperature and pressure of interest [21], and \bar{V}_i^∞ is the partial molar volume of solute i in the limit of infinite dilution. The solute mole fractions x_i can be calculated as a function of temperature from the thermodynamic Henry's constants, which are quite accurately known for atmospheric gases. This calculation also requires the partial pressure of each gas; the calculations reported here assume a total pressure (including the partial pressure of water) of 101 325 Pa, but a simple procedure [20] can be used to adjust for different values of the ambient pressure. The partial molar volumes \bar{V}_i^∞ are less accurately known, and are the largest source of uncertainty in these calculations.

The quantity of most interest for metrology is the effect on the mass density, which is

$$\Delta\rho = \frac{M_m}{V_m} - \frac{M_w}{V_w}, \quad (5)$$

where M_m and M_w are the molar masses of the mixture (a mole-fraction weighted average of the pure-component molar masses) and of pure water, respectively. Because of the range in which accurate Henry's constants and partial molar volumes are available, our calculations for $\Delta\rho$ are limited to temperatures from 0 °C to 50 °C, with an uncertainty (primarily due to the \bar{V}_i^∞) near $1 \mu\text{g}\cdot\text{cm}^{-3}$ over most of that range.

Figure 2 shows our calculated values compared with some experimental measurements [22-26] of $\Delta\rho$. These are difficult experiments and the various

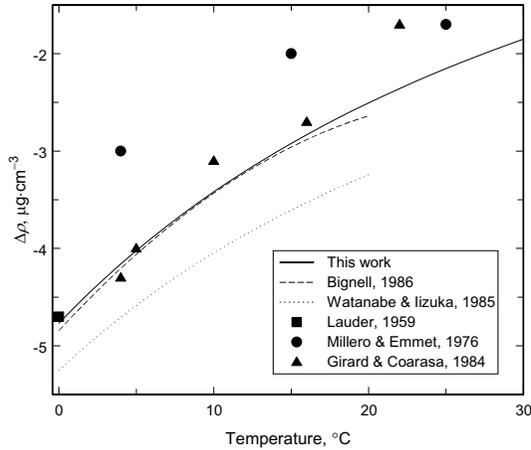


Fig. 2. Calculated (Eqs. 4 and 5) and experimental values for $\Delta\rho$, the change in density of water upon equilibration with air at 101 325 Pa total pressure.

sources of data are not in agreement, but several of them agree with our model. We also note that our model covers a wider range of temperature than the existing experimental data. The calculations shown in Fig. 2 should provide metrologists with a reliable basis for correcting the density of water for dissolved atmospheric air in cases where density changes of a few parts in 10^6 are significant.

Modeling the effect of dissolved air on the refractive index requires a model for mixture refractivity as a function of pure-component contributions. These can be added independently to a good approximation, because the refractive index reflects only the electronic polarization, which is almost unaffected by intermolecular forces. Therefore, we can write the Lorentz-Lorenz equation for a mixture,

$$\frac{n^2 - 1}{n^2 + 2} = \sum_{i=1}^n A_i \rho_i = \rho_m \left(x_w A_w + \sum_{i=2}^n x_i A_i \right), \quad (6)$$

where ρ_m is the molar density of the mixture and the values of the component refractivities A_i are evaluated at the conditions of interest (including wavelength; the dispersion in the UV is large enough that use of visible-wavelength values would introduce significant error) from the IAPWS formulation [27] for water and from available data for the pure solute gases. While the IAPWS refractive-index formulation is not recommended for wavelengths shorter than 200 nm, recent work

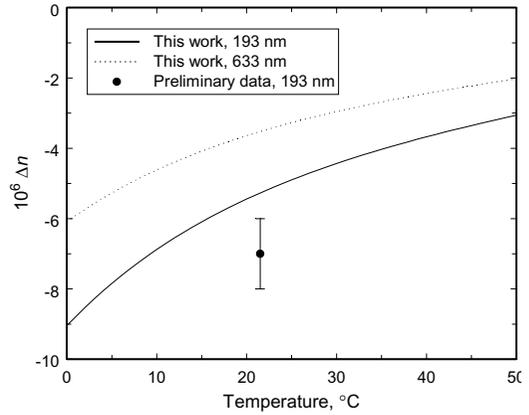


Fig. 3. Calculated (Eq. 6) and experimental values of Δn , the change in the refractive index of water upon equilibration with air at 101 325 Pa total pressure.

[18] has shown that it gives reasonable values near 193 nm. In addition, any error in A_w will cancel out to a first approximation in calculating $\Delta n = n - n_w$, the difference between the mixture refractive index and that of pure water [27] at the same conditions.

Figure 3 shows our calculated values of Δn as a function of temperature at two different wavelengths. Also shown is one preliminary experimental datum for Δn at 193 nm; more refined measurement of this quantity is in progress [20].

The agreement of the calculated values with the experimental datum is only fair; the small disagreement may reflect the preliminary nature of the experiments, or it may reflect inadequacy in the assumption embodied in Eq. (6) that the refractivities of individual components are unaffected by mixing. We note that Δn is about five times as large as had been indirectly estimated in some early NBS work [28] on water's refractive index at visible wavelengths.

4. Second Virial Coefficients from First Principles for Humidity Standards

Standards for humidity require an accurate thermodynamic description of the saturated state (100 % relative humidity), where the vapor is in equilibrium with liquid (or solid) H_2O . The simplest possible calculation would assume that the vapor mixture was an ideal gas, but this is insufficient for precise standards. Instead, humidity standards require calculation of the fugacity coefficient for water in moist air; the degree to

which this quantity differs from unity characterizes the deviation of water's fugacity from that of an ideal gas. The dominant contribution to the fugacity coefficient for conditions relevant to humidity standards comes from the cross second virial coefficient B_{aw} . The second virial coefficient is the first correction to ideal-gas behavior in an expansion about zero density; B_{aw} describes the binary interaction between one water molecule and one "air" molecule. In reality, of course, air is a mixture, but for purposes of humidity standards it can usually be treated as a single component where B_{aw} is a weighted average of the cross second virial coefficients of water with the various components of air.

Unfortunately, the expansion experiments that are typically performed to obtain cross second virial coefficients in mixtures of gases are infeasible for gas-water mixtures, because H_2O tends to adsorb strongly on the walls of experimental apparatus at the temperatures of interest. Some data have been obtained by a gas saturation technique [29, 30], but these are extremely difficult experiments, and the resulting values of B_{aw} have substantial uncertainty and cover a relatively narrow range of temperature (from $-20\text{ }^\circ\text{C}$ to $75\text{ }^\circ\text{C}$).

However, the second virial coefficient for a pair of molecules can be calculated exactly if the intermolecular potential energy U_{12} is known as a function of the distance and mutual orientation of the molecules. The equation is

$$B_{12}(T) = -\frac{1}{2} \int_0^\infty \left\langle e^{-U_{12}/k_B T} - 1 \right\rangle_{\omega_1, \omega_2} d\mathbf{r} \quad (7)$$

$$+ \Delta B_{12}(\text{trans}) + \Delta B_{12}(\text{rot}),$$

where the angle brackets indicate Boltzmann-weighted averaging over all orientations ω_1 and ω_2 of molecules 1 and 2, k_B is Boltzmann's constant, and $d\mathbf{r}$ is the differential volume element of a spherical shell. The first term is the classical result; the next two terms are corrections for translational and rotational quantum effects. These corrections can be significant for light molecules such as H_2O ; the rotational quantum correction is particularly significant due to water's small moment of inertia. Simple first-order expressions for quantum effects [31] are sufficient for water with air components at temperatures of interest here.

The state of the art in computational quantum mechanics has advanced to the point where potential-energy surfaces for pairs of small

molecules can be constructed with an accuracy sufficient for calculating second virial coefficients with low uncertainties. An advantage of such an approach is that, once the potential-energy surface $U_{12}(r, \omega_1, \omega_2)$ is produced, second virial coefficients B_{12} can be calculated at any temperature; in contrast, experimental data typically cover only a small range of temperatures. Also, reasonable upper and lower bounds can be placed on the potential-energy surface, allowing an estimate of the uncertainty of the resulting values of B_{12} .

We have therefore undertaken a program to develop potential-energy surfaces and calculate second virial coefficients for common gases with H_2O . The approach uses scaled perturbation theory (SPT), in which a preliminary potential-energy surface is generated from relatively simple perturbation-theory calculations that give quantitatively correct behavior at large and small intermolecular distances. Scaling factors are employed to obtain quantitative accuracy at intermediate distances; these factors are based on a relatively small number of high-level *ab initio* calculations.

Thus far, we have used SPT to obtain potential-energy surfaces and second virial coefficients for water with helium [32], with neon and argon [33], and with hydrogen [34]. Work on the water-nitrogen system [35] is nearing completion.

In Fig. 4, we illustrate the performance of this approach for the water-argon system, where the SPT results are plotted along with various experimental data [36-40]. The experiments are mutually inconsistent and have relatively large uncertainties; the estimated uncertainty of our calculated values is about $3\text{ cm}^3\cdot\text{mol}^{-1}$ over the range of temperatures shown in Fig. 4. The calculated data are in agreement with three of the five experimental data sources; the other two are inconsistent with the rest.

Our calculations are also in good agreement (again, with much smaller uncertainties) with experimental data [41, 42] for the quantity $\phi_{12} = B_{12} - dB_{12}/dT$ obtained from excess enthalpy measurements. These comparisons are shown in Fig. 5, where the uncertainty of our calculated values of ϕ_{12} is about $4\text{ cm}^3\cdot\text{mol}^{-1}$.

Similarly good results (agreement with the limited data available, significantly smaller uncertainties for the first-principles values than for the experiments) have been obtained for the other water-gas systems examined so far.

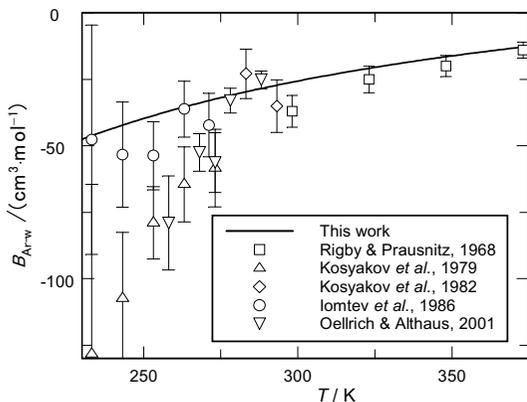


Fig. 4. Calculated (Eq. 7) and experimental values of the cross second virial coefficient of water with argon.

Once work on the water-nitrogen system is completed [35], a similar effort for the water-oxygen system will provide the final data necessary to be able to calculate the water-air virial coefficient B_{aw} ; it is expected that the resulting uncertainty in B_{aw} should be less than for the existing experiments [29, 30]. Unfortunately, quantum calculations for the water-oxygen system are more challenging, because the oxygen molecule does not have a closed electronic shell. Our collaborators are working to extend their methods for developing potential-energy surfaces to open-shell systems, so that we can take this final step toward our goal of improved values of B_{aw} covering a wide range of temperatures.

5. Conclusions

Many thermophysical properties of water are important in metrology. Ongoing work at NIST and elsewhere is producing an improved surface for the viscosity of water, better understanding of the effect of dissolved air on its density and refractive index, and improved water-air second virial coefficients for use in humidity standards.

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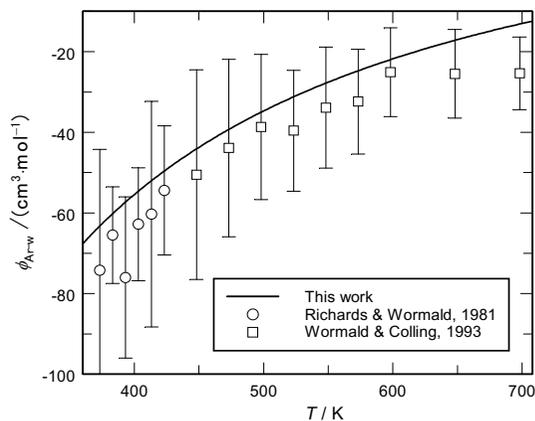


Fig. 5. Calculated (Eq. 7) and experimental values of $\phi_{12} = B_{12} - dB_{12}/dT$ for water with argon.

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