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Evaluation of the Physicochemical Authenticity of Aviation Kerosene Surrogate Mixtures. Part 2: Analysis and Prediction of Thermophysical Properties

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Received April 20, 2010. Revised Manuscript Received June 24, 2010

In part 1 (10.1021/ef100496j) of this series of two papers, we presented an evaluation strategy that can be applied to surrogate mixtures for finished fuels. This strategy uses the advanced distillation curve approach to evaluate the surrogate in terms of physicochemical authenticity or how well the surrogate represents the chemical and physical properties of the finished fuel. While this protocol can be applied to any surrogate family, of particular interest here are surrogates for Jet-A/JP-8. The volatility was studied in detail as described in part 1 (10.1021/ef100496j), whereas here, we focus on density, speed of sound, and viscosity. We calculated these properties for the common Jet-A/JP-8 surrogates and Jet-A, with the National Institute of Standards and Technology (NIST) REFPROP program (which incorporates equations of state and a transport property model). We then used REFPROP as a surrogate mixture design tool and developed a simple, three-component surrogate mixture (*n*-dodecane, *n*-tetradecane, and 1,2,4-trimethylbenzene with mass fractions of 0.31, 0.38, and 0.31, respectively). This mixture was subsequently formulated in the laboratory and measured with the advanced distillation curve approach. We found the agreement with the theory to be excellent (within 1.5 °C), and we also found that the ability of such a simple mixture to represent Jet-A/JP-8 was also excellent. Comparisons made to the calculated density, speed of sound, and viscosity were also excellent.

Introduction

Because of the complexities inherent with the study of finished liquid fuels, researchers must often resort to the measurement of surrogate fluids in the determination of many fundamental and engineering parameters.[1] Despite the need to simplify, there is a clear desire to employ surrogate mixtures that are physicochemically authentic to the finished fuel that it is intended to represent. In part 1 (10.1021/ef100496j) of this series of papers, we argued that, although there are many ways to evaluate the physicochemical authenticity, metrics based on the measurement of volatility [with the advanced distillation curve (ADC) of the surrogate mixture, as compared to that of the finished fuel] are the most practical avenue.[2] We then compared a representative series of simple (two- or three-component) and complex (more than three-component) surrogates on that basis. Those surrogates were developed over several years by fuel engineering researchers worldwide. In this paper, we expound on that evaluation strategy by adding examinations of the simple and complex surrogates based on predictions from equations of state and transport property models. Subsequent to this, we used the modeling approach that we have developed for fuels from another perspective: to design a potential surrogate mixture that would fulfill our criteria for physicochemical authenticity. That surrogate was then tested in two ways. First, we applied the ADC method to the predicted mixture and evaluated the agreement with the theory. Second, we applied to this mixture the same thermophysical property examinations that were applied to the simple and complex surrogate mixtures discussed in part 1 (10.1021/ef100496j).

Theory

In our approach to modeling, an equation of state and a viscosity and thermal conductivity surface for each pure fluid of a surrogate mixture are required. We use mixtures of real components, similar to the method suggested by Eckert and Vanek, instead of pseudo-components, as is common in the petroleum industry.[3,4] For nonpolar hydrocarbons, simple cubic equations of state, such as the Peng–Robinson or a variant of the statistical associating fluid theory (SAFT) equation (although the association term is unnecessary for the fluids in this work) are often applicable.[5]

In this work, we typically use the "short" Span–Wagner equation of state, in which the Helmholtz energy is expressed as the sum of an ideal and residual Helmholtz energy term.[6] This energy is written as an expansion in terms of reduced density and temperature, with the critical temperature and critical density of the fluid as the primary reducing properties. This form was developed with data from several simple

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(1) Edwards, T.; Maurice, L. Q. Surrogate mixtures to represent complex aviation and rocket fuels. *J. Propul. Power* **2001**, *17* (2), 461–466.

(2) Bruno, T. J.; Smith, B. L. Evaluation of the physicochemical authenticity of aviation kerosene surrogate mixtures. Part 1: Analysis of volatility with the advanced distillation curve. *Energy Fuels* **2010**, *24*, DOI: 10.1021/ef100496j.

(3) Eckert, E.; Vanek, T. New approach to the characterization of petroleum mixtures used in the modeling of separation processes. *Comput. Chem. Eng.* **2005**, *30* (2), 343–356.

(4) Eckert, E. V. New approach to the characterization of petroleum mixtures used in the modeling of separation processes. *Proceedings of the 31st International Conference of the Slovak Society of Chemical Engineering*; Tatranské Matliare, Vysoké Tatry, Slovakia, 2004; Paper 113.

(5) Gross, J.; Sadowski, G. Perturbed-chain SAFT: An equation of state based on a perturbation theory for chain molecules. *Ind. Eng. Chem. Res.* **2001**, *40* (4), 1244–1260.

(6) Span, R.; Wagner, W. Equations of state for technical applications. I. Simultaneously optimized functional forms for nonpolar and polar fluids. *Int. J. Thermophys.* **2003**, *24* (1), 1–39.

hydrocarbons, such as the normal alkanes, methane through *n*-octane, isobutene, cyclohexane, and several other nonpolar fluids, and is expected to apply well to fluids that comprise the surrogates studied here. In addition, the National Institute of Standards and Technology (NIST) ThermoData Engine (TDE) database[7] can generate the coefficients automatically in a format that is easily incorporated into the NIST REFPROP[8] computer program that we use for our mixture modeling, discussed in the next section. For fluids with limited data, predicted property data can be easily incorporated into the equation development. Viscosity and thermal conductivity surfaces for each of the pure constituent fluids were developed by use of experimental data, predictive methods, and an extended corresponding states model,[9] in most cases with *n*-dodecane as the reference fluid.[10,11] The resultant estimated uncertainty for the pure-fluid models is dependent upon the experimental data used in the development of the equations; in general, the expanded uncertainty ($k = 2$) for liquid density for typical fuel constituent fluids is on the order of 3%, vapor pressures from 1 to 5%, and for the viscosity and thermal conductivity, the uncertainty is approximately 5−10%.

For calculations of the thermodynamic properties of mixtures, we use a mixture model explicit in Helmholtz energy that can use any equation of state, provided that it can be expressed in terms of the Helmholtz energy.[12] This form of model has been used successfully for refrigerant mixtures[12] and natural gas mixtures.[13] The basic idea is to represent the molar Helmholtz energy, a, of a mixture as a sum of an ideal solution contribution, a^{id}, and a departure contribution, a^{dep}, according to

$$a = a^{id} + a^{dep} \quad (1)$$

$$a^{id} = \sum_{j=1}^{m} x_i [a_i^0(\rho, T) + a_i^r(\delta, \tau) + RT \ln x_i] \quad (2)$$

$$a^{dep} = RT \sum_{i=1}^{m-1} \sum_{j=i+1}^{m} x_i x_j F_{ij} \sum_k N_k \delta^{d_k} \tau^{t_k} \exp(-\delta^{l_k}) \quad (3)$$

where ρ and T are the mixture molar density and temperature, respectively, δ and τ are the reduced mixture density and reciprocal temperature, respectively, m is the number of components, a_i^0 is the ideal gas Helmholtz energy of component i, a_i^r is the residual (or real fluid) Helmholtz energy of component i, x_i values are the mole fractions of the constituents of the mixture, $d_k, t_k, l_k,$ and N_k are coefficients found from fitting experimental data, and F_{ij} is an interaction parameter. Mixing rules are used

to determine the reducing parameters ρ_{red} and T_{red} for the mixture that are defined as

$$\delta = \rho/\rho_{red} \quad (4)$$

$$\tau = T_{red}/T \quad (5)$$

$$\rho_{red} = \left[\sum_{i=1}^{m} \frac{x_i}{\rho_{c_i}} + \sum_{i=1}^{m-1} \sum_{j=i+1}^{m} x_i x_j \xi_{ij} \right]^{-1} \quad (6)$$

$$T_{red} = \sum_{i=1}^{m} x_i T_{c_i} + \sum_{i=1}^{m-1} \sum_{j=i+1}^{m} x_i x_j \varsigma_{ij} \quad (7)$$

where ξ_{ij} and ς_{ij} are binary interaction parameters that define the shapes of the reducing temperature and density curves, respectively.

The model has a total of three binary interaction parameters, ξ_{ij}, ς_{ij}, and F_{ij}, that can be determined by fitting experimental data when available. Because the constituent fluids in this work are chemically similar (that is, they are linear, branched, and aromatic hydrocarbons), we set the excess contribution to zero (i.e., $F_{ij} = 0$) and the ξ_{ij} interaction parameter to zero, resulting in a simpler model with only one binary interaction parameter, ς_{ij}. Previous studies on refrigerant mixtures have shown that ς_{ij} is the most important binary parameter. This parameter can be found by fitting binary mixture data, or when data are unavailable, as is the case in this work, the following predictive scheme is used:[14]

$$\varsigma_{ij} = \frac{T_{c_2}}{T_{c_1}} (40.4 - 25.03 \times 2^s) \quad (8)$$

$$s = \left(\frac{T_{c_1}}{T_{c_2}} \frac{p_{c_2}}{p_{c_1}} \frac{\omega_2}{\omega_1} \right) \quad (9)$$

where the fluid with the smaller dipole moment is designated as fluid "1" and ω is the acentric factor. This scheme was developed with a database of mixture data primarily for refrigerant mixtures and resulted in average absolute deviations of 4.5% in bubble point pressure and 1.7% in density; we anticipate similar results for the fluid mixtures in this study.

The model for calculating the transport properties of a mixture is an extended corresponding states method.[15−20]

(7) Muzny, C. D.; Lemmon, E. W.; Chirico, R. D.; Diky, V.; Dong, Q.; Frenkel, M. Dynamic equation of state evaluation with ThermoData Engine. *Abstr. Pap. Am. Chem. Soc.* **2005**, *230*, U1008–U1008.

(8) National Institute of Standards and Technology (NIST). *NIST Standard Reference Database 23, NIST Reference Fluid Thermodynamic and Transport Properties Database* (*REFPROP*): *Version 8.0, Standard Reference Data*; NIST: Gaithersburg, MD, 2007.

(9) Huber, M. L.; Laesecke, A.; Perkins, R. A. Model for the viscosity and thermal conductivity of refrigerants, including a new correlation for the viscosity of R134a. *Ind. Eng. Chem. Res.* **2003**, *42*, 3163–3178.

(10) Huber, M. L.; Laesecke, A.; Perkins, R. A. Transport properties of *n*-dodecane. *Energy Fuels* **2004**, *18*, 968–975.

(11) Lemmon, E. L.; Huber, M. L. Thermodynamic properties of *n*-dodecane. *Energy Fuels* **2004**, *18*, 960–967.

(12) Lemmon, E. W.; Jacobsen, R. T. Equations of state for mixtures of R-32, R-125, R-134a, R-143a, and R-152a. *J. Phys. Chem. Ref. Data* **2004**, *33* (2), 593–620.

(13) Kunz, O.; Klimeck, R.; Wagner, W.; Jaeschke, M. *The GERG-2004 Wide-Range Reference Equation of State for Natural Gases and Other Mixtures, GERG Technical Monograph*; Fortschr.-Ber. VDI, VDI-Verlag: Dusseldorf, Germany, 2007.

(14) Lemmon, E. W.; McLinden, M. O. Method for estimating mixture equation of state parameters. *Thermophysical Properties and Transfer Processes of New Refrigerants Conference*; International Institute of Refrigeration, Commission B1: Paderborn, Germany, 2001; pp 23−30.

(15) Huber, M. L.; Laesecke, A.; Perkins, R. A. Model for the viscosity and thermal conductivity of refrigerants, including a new correlation for the viscosity of R134a. *Ind. Eng. Chem. Res.* **2003**, *42* (13), 3163–3178.

(16) Chichester, J.; Huber, M. L. *Extended Corresponding States Model for Viscosity and Thermal Conductivity of Pure Fluids and Their Mixtures as Implemented in REFPROP, Version 8, NIST IR 6650*; National Institute of Standards and Technology (NIST): Boulder, CO, 2008.

(17) Huber, M. L.; Ely, J. F. Prediction of the thermal conductivity of refrigerants and refrigerant mixtures. *Fluid Phase Equilib.* **1992**, *80*, 249–261.

(18) Huber, M. L.; Ely, J. F. Prediction of the viscosity of refrigerants and refrigerant mixtures. *Fluid Phase Equilib.* **1992**, *80*, 239–248.

(19) Klein, S. A.; McLinden, M. O.; Laesecke, A. An improved extended corresponding states method for estimation of viscosity of pure refrigerants and mixtures. *Int. J. Refrig.* **1997**, *20* (3), 208–217.

(20) McLinden, M. O.; Klein, S. A.; Perkins, R. A. An extended corresponding states model for the thermal conductivity of pure refrigerants and refrigerant mixtures. *Int. J. Refrig.* **2000**, *23* (1), 43–63.

The basic procedure is based on the earlier work of Ely and Hanley.[21,22] In this approach, the viscosity or thermal conductivity of a mixture is calculated in a two-step procedure. First, mixing and combining rules are used to represent the mixture in terms of a hypothetical pure fluid, and then the properties of the hypothetical pure fluid are determined by mapping onto a reference fluid through the use of "shape factors"; details are given elsewhere.[9,16−20] For both refrigerant mixtures and mixtures of natural gas components, the viscosity and thermal conductivity are typically represented to within 5−10%, and we expect similar results with the fluid mixtures in this work.

The two models discussed briefly above, the Helmholtz energy mixing model for thermodynamic properties and the extended corresponding states model for viscosity and thermal conductivity, are implemented in the REFPROP computer program. This program contains highly accurate equations of state for many pure fluids, including some that have been adopted as international standards. Moreover, REFPROP has been adopted as a *de facto* standard in the refrigeration industry.[23−25] The most recent version contains a model under consideration as an international standard for the calculation of the thermodynamic properties of natural gas mixtures that is a form of the Helmholtz energy mixing model described above.[26] In this work, we added the ability to compute the thermodynamic and transport properties of the candidate fluids to the REFPROP program and use it in all calculations because it already contains all of the algorithms necessary to compute phase equilibrium (bubble points) and thermophysical properties.

In this paper, we use the REFPROP program, with the formalism described above, to provide comparisons of the density, speed of sound, and viscosity for the surrogate mixtures presented in part 1 (10.1021/ef100496j)[2] and also for the two Jet-A fluids.[27] We chose to focus on these properties rather than the entire suite of properties available in REFPROP. The volatility is important because it is the primary property that we used to evaluate the physicochemical authenticity in part 1 (10.1021/ef100496j). We also calculate the viscosity because this property shows appreciable change, with both composition and temperature, in pure fluid measurements as well as our measurements of Jet-A. To clarify, we note that the change in viscosity with composition is far more pronounced at lower temperatures, as we mentioned in part 1 (10.1021/ef100496j) of this series of two papers. The density and speed of sound, while not showing

great variability with compositional changes, are important in the specification and use of aviation fuels. The density is a property that is subject to the JP-8 specification,[28] and the speed of sound is used in the measurement of fuel levels in aircraft fuel tanks.[29] After a comparison of the simple and complex surrogates on the basis of these properties, we then use REFPROP as a tool to predict the composition of a potential (simple) surrogate mixture that fulfills the criteria of physicochemical authenticity. This serves as a demonstration of how a surrogate mixture can be constructed on the basis of prediction, in keeping with the philosophy that "math is cheaper than chemistry".

Once this surrogate was optimized with REFPROP, we prepared it in the laboratory and compared the measured volatility (with the ADC method) to the prediction and then to the behavior of Jet-A. We then used REFPROP to compare the predicted density, viscosity, and speed of sound to those of Jet-A. These were then compared to the predictions for the best performing surrogates resulting from the evaluation of part 1 (10.1021/ef100496j): the modified Aachen and Shultz surrogates.

Experimental Section

This experimental description pertains to the test of the surrogate mixture that was designed according to the modeling protocol that was described above. *n*-Dodecane, *n*-tetradecane, and 1,2,4-trimethylbenzene used in this work were obtained from commercial sources at the highest available purity, 99.9% (mass/mass). The fluids were analyzed by gas chromatography with mass spectrometric detection.[30,31] All fluids were found to meet or exceed the purity specification of the manufacturer, and all were used as received. The mixture that was designed by the modeling approach discussed above was prepared volumetrically at ambient temperature and consisted of mass fractions of *n*-dodecane, *n*-tetradecane, and 1,2,4-trimethylbenzene of 0.31, 0.38, and 0.31, respectively. The details of the distillation of the surrogate mixture described above are identical to those presented in part 1 (10.1021/ef100496j) and, thus, will not be repeated here. The required fluid for the distillation curve measurement (in each case, 200 mL) was placed into the boiling flask with a 200 mL volumetric pipet. The thermocouples were then inserted into the proper locations to monitor T_k (the temperature measured directly in the fluid) and T_h (the temperature measured at the bottom of the takeoff position in the distillation head). A schematic diagram is provided in Figure 1 of part 1 (10.1021/ef100496j). As with the fluids of part 1 (10.1021/ef100496j), measurements of the onset conditions and distillation curves were performed for this mixture.

Results and Discussion

This section will be divided into four sub-sections. First, we will discuss the calculation results applied to the surrogate mixtures of part 1 (10.1021/ef100496j) with the REFPROP program, specifically for density, viscosity, and speed of sound. Among the thermophysical properties, the density

(21) Ely, J. F.; Hanley, H. J. M. Prediction of transport properties. 1. Viscosity of fluids and mixtures. *Ind. Eng. Chem. Fundam.* **1981**, *20* (4), 323–332.

(22) Ely, J. F.; Hanley, H. J. M. Prediction of transport properties. 2. Thermal conductivity of pure fluids and mixtures. *Ind. Eng. Chem. Fundam.* **1983**, *22* (1), 90–97.

(23) Tillner-Roth, R.; Baehr, H. D. An international standard formulation for the thermodynamic properties of 1,1,1,2-tetrafluoroethane (HFC-134a) for temperatures from 170 to 455 K and pressures up to 70 MPa. *J. Phys. Chem. Ref. Data* **1994**, *23* (5), 657–730.

(24) Tillner-Roth, R.; Yokozeki, A. An international standard equation of state for difluoromethane (R-32) for temperatures from the triple point at 136.34 to 435 K and pressures up to 70 MPa. *J. Phys. Chem. Ref. Data* **1997**, *26* (6), 1273–1328.

(25) Wagner, W.; Pruss, A. The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. *J. Phys. Chem. Ref. Data* **2002**, *31* (2), 387–535.

(26) Kunz, O.; Klimeck, R.; Wagner, W.; Jaeschke, M. The GERG-2004 wide range equation of state for natural gases and other mixtures, GERG TM15. *Fortschr.-Ber. VDI* **2007**, *6* (557).

(27) Huber, M. L.; Lemmon, E. W.; Bruno, T. J. Surrogate mixture models for the thermophysical properties of aviation fuel Jet-A. *Energy Fuels* **2010**, *24*, 3565–3571.

(28) Detail Specification Turbine Fuel, Aviation, Kerosene Type JP-8 (NATO F-34), NATO F-35, and JP-8 + 100 (NATO F-37); MIL-DTL-83133F, April 11, 2008, and references therein.

(29) Senibi, S. D.; Anderson, D. M.; Banks, D. L.; Childress, J. J.; Rassanian, M. Ultrasonic fuel gauging system. U.S. Patent 6,925,869, 2005.

(30) Bruno, T. J.; Svoronos, P. D. N. *CRC Handbook of Basic Tables for Chemical Analysis*, 2nd. ed.; Taylor and Francis, CRC Press: Boca Raton, FL, 2004.

(31) Bruno, T. J.; Svoronos, P. D. N. *CRC Handbook of Fundamental Spectroscopic Correlation Charts*; Taylor and Francis, CRC Press: Boca Raton, FL, 2006.
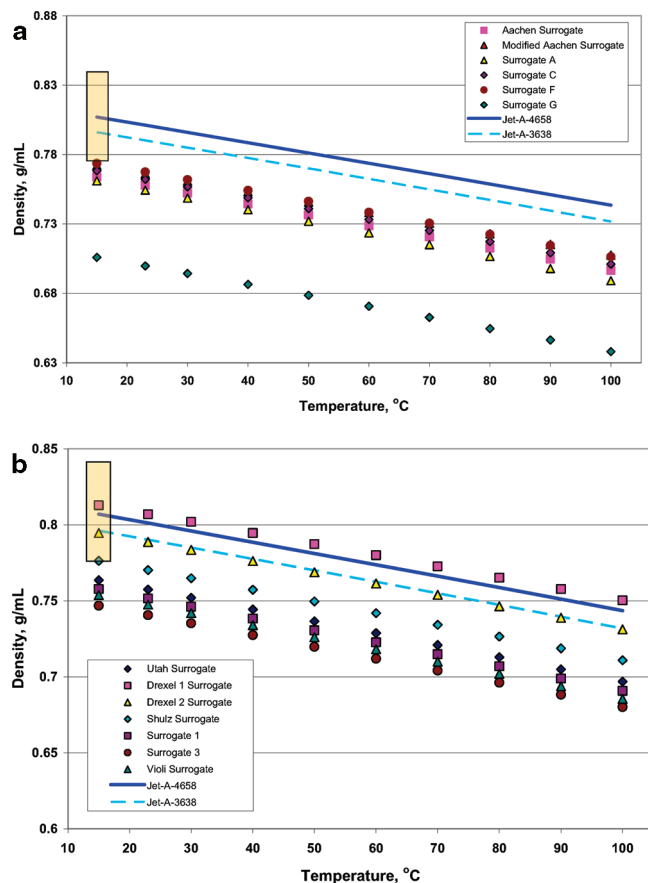
Figure 1. Comparison of the density, as calculated by REFPROP, for the (a) simple and (b) complex surrogate fluids [as classified in part 1 (10.1021/ef100496j)] and the two Jet-A fuels. The inset shows the allowable density range specified for JP-8.

and speed of sound are of value for fuel design and viscosity is of value because it shows significant variability with composition and temperature. Second, we will discuss the use of the REFPROP program for the design of a physicochemically authentic surrogate. Third, we will compare the predicted behavior of that surrogate to the experiment by use of the ADC. Only this aspect of the Results and Discussion derives from the experimental procedure outlined above. Finally, we will examine the behavior of the designed surrogate mixture in terms of the calculated density, speed of sound, and viscosity.

Thermophysical Properties of Aviation Fuel Surrogates. As mentioned in the Introduction, we used the REFPROP program as a tool to compare the calculated values of selected thermophysical properties (density, speed of sound, and viscosity) for the simple and complex surrogate mixtures presented in part 1 (10.1021/ef100496j). The calculated densities (as a function of the temperature from 15 to 100 °C, at a pressure of 101.3 kPa) for the simple and complex surrogates are presented in panels a and b of Figure 1, respectively. We include values at 15 °C because the density of JP-8 is specified at that temperature (0.775–0.84 g/mL)[28] and at 23 °C because this is the approximate ambient temperature at which all surrogate mixtures have been prepared in our work and in that of other researchers. We also include the density of the two Jet-A samples that were measured and modeled in our previous work, and at 15 °C, we show by the shaded inset the allowable density range provided in the specification of JP-8. On the basis of the comparison of the experimental and

modeled densities of a large number of pure fluids and mixtures (over several years), we estimate the uncertainty of our predictions in density presented here to be approximately 0.3%.[32−37] We note that, for the simple surrogates, all of the calculated densities are well below the values for the real Jet-A samples that we have measured and all are below the specification range for JP-8.

Among the complex surrogates, we note that the density of the Drexel 1 surrogate is slightly higher for all temperatures than the density of Jet-A-4658 and that the Drexel 2 surrogate is slightly lower than that of Jet-A-3638.[38] We also note that, along with the Drexel 1 and 2 surrogates, the Shultz surrogate is within the range of the JP-8 density specification at 15 °C.[39] Among these three fluids, we concluded in part 1 (10.1021/ef100496j) that the Shultz surrogate was the most physicochemically authentic on the basis of the match to the distillation curves of real Jet-A. The Drexel surrogates were also relatively close to the Jet-A curves on the basis of our evaluation criteria, but we noted a mismatch in the shape of their curves, which led to them being considered combined bimodal instead of sigmoidal. We therefore could not further evaluate their slopes.

In panels a and b of Figure 2, we present the calculated speed of sound for the simple and complex surrogates, respectively. Also, in each figure are the modeled speeds of sound for the two Jet-A samples that we measured. We note *inter alia* that our ability to model the speed of sound of Jet-A with REFPROP is systematically in error; the model predicts values that are approximately 1.5% too high. This discrepancy is very minor for most practical applications and is due in part to our decision to emphasize the match with other properties that we consider more critical. The first point to note is that there is very little variation between the measured and modeled speeds of sound for the two real Jet-A samples. This was discussed in part 1 (10.1021/ef100496j) and was one of the reasons that we rejected this parameter as an evaluation criterion for physicochemical authenticity. Indeed, we calculate it here only because a measure of the speed of sound is often used onboard aircraft to determine the fuel level in tanks.[29] We also note that there is considerably more variability in the speed of sound of the surrogate mixtures than in the real fuels and that the magnitude of this variability varies

(32) Huber, M. L.; Smith, B. L.; Ott, L. S.; Bruno, T. J. Surrogate mixture model for the thermophysical properties of synthetic aviation fuel S-8: Explicit application of the advanced distillation curve. *Energy Fuels* **2008**, *22*, 1104–1114.

(33) Huber, M. L.; Lemmon, E. W.; Diky, V.; Smith, B. L.; Bruno, T. J. Chemically authentic surrogate mixture model for the thermophysical properties of a coal-derived-liquid fuel. *Energy Fuels* **2008**, *22*, 3249–3257.

(34) Huber, M. L.; Lemmon, E.; Kazakov, A.; Ott, L. S.; Bruno, T. J. Model for the thermodynamic properties of a biodiesel fuel. *Energy Fuels* **2009**, *23*, 3790–3797.

(35) Huber, M. L.; Lemmon, E.; Ott, L. S.; Bruno, T. J. Preliminary surrogate mixture models for rocket propellants RP-1 and RP-2. *Energy Fuels* **2009**, *23*, 3083–3088.

(36) Huber, M. L.; Lemmon, E.; Bruno, T. J. Effect of RP-1 compositional variability on thermophysical properties. *Energy Fuels* **2009**, *23*, 5550–5555.

(37) Huber, M. L.; Laesecke, A.; Perkins, R. A. Model for the viscosity and thermal conductivity of refrigerants, including a new correlation for the viscosity of R-134a. *Ind. Eng. Chem. Res.* **2003**, *42*, 3163–3178.

(38) Natelson, R. H.; Kurman, M. S.; Cernansky, N. P.; Miller, D. L. Experimental investigation of surrogates for jet and diesel fuels. *Fuel* **2008**, *87* (10−11), 2339–2342.
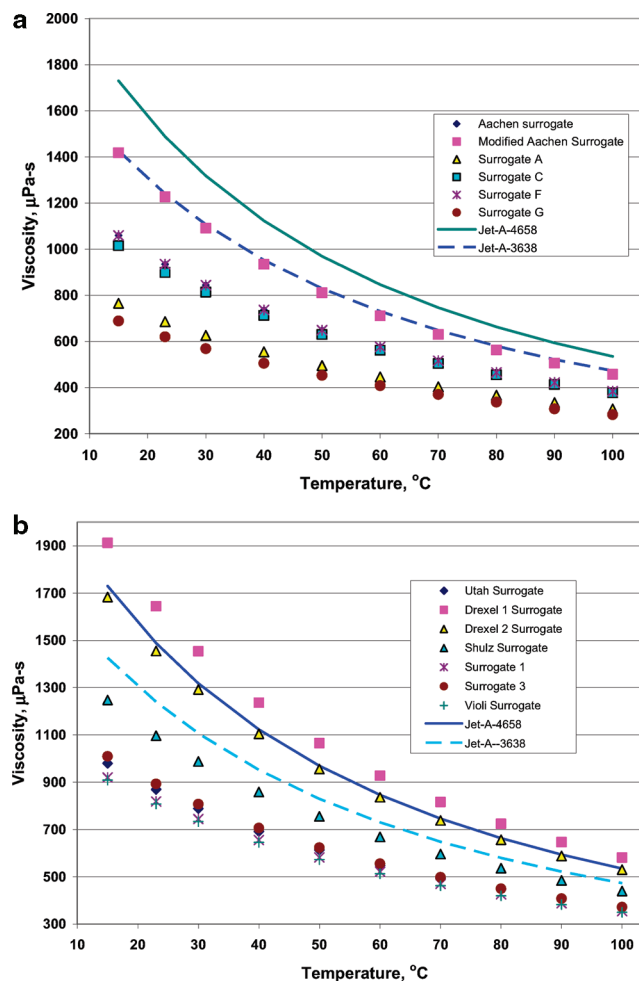
(39) Shulz, W. D. Oxidation products of surrogate JP-8 fuel. *Symposium on the Structure of Jet Fuels III*; Division of Petroleum Chemistry, American Chemical Society, San Francisco, CA, 1991.
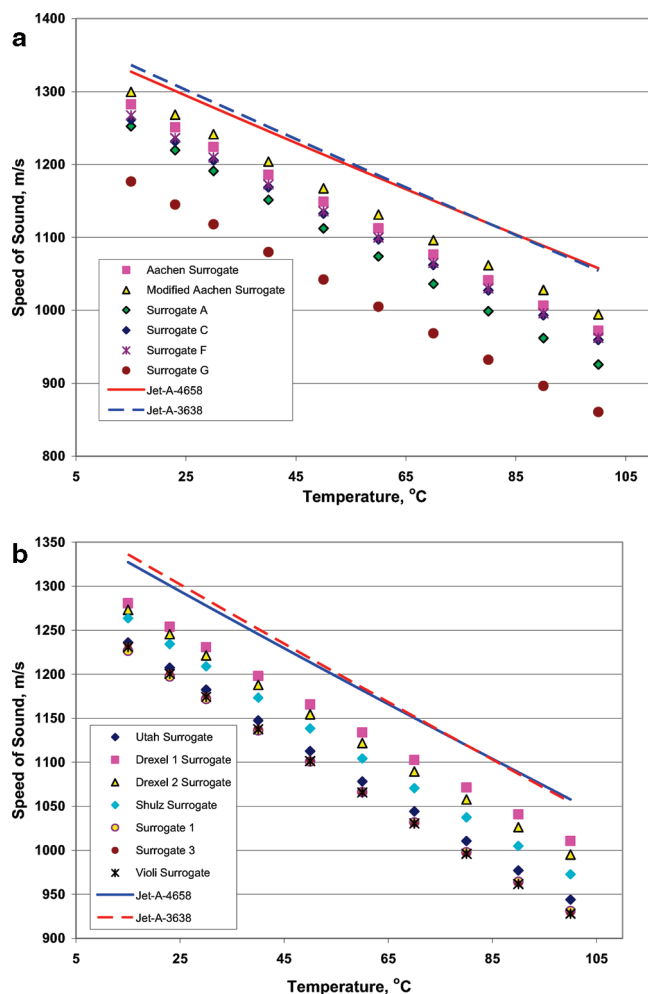
Figure 2. Comparison of the speed of sound, as calculated by REFPROP, for the (a) simple and (b) complex surrogate fluids [as classified in part 1 (10.1021/ef100496j)] and the two Jet-A fuels.

Figure 3. Comparison of the viscosity, as calculated by REFPROP, for the (a) simple and (b) complex surrogate fluids [as classified in part 1 (10.1021/ef100496j)] and the two Jet-A fuels.

little as a function of the temperature. Among the simple surrogates, the modified Aachen surrogate comes closest to the speed of sound of the Jet-A fluids. We concluded in part 1 (10.1021/ef100496j) that this surrogate was the most physicochemically authentic of the simple fluids. Among the complex surrogates, the Drexel 1 fluid comes closest but not as close as the modified Aachen surrogate.

In panels a and b of Figure 3, we present the calculated viscosity of the simple and complex surrogate mixtures, respectively. Also, in each figure are the viscosities of the two Jet-A fluids that we measured and modeled. On the basis of the comparison of the experimental and modeled viscosities of a large number of pure fluids and mixtures, we estimate the uncertainty of our predictions in viscosity presented here to be approximately 1%.[32−37] We have noted that the viscosity is relatively sensitive to changes in composition in finished fuels, and after volatility, it can be used to demonstrate compositional variability. Although we did not choose viscosity as the evaluation criteria in part 1 (10.1021/ef100496j), it is nonetheless valuable to examine this property. We note that, for all of the surrogate fluids, there is a large variability at the lower temperatures but that this decreases with an increasing temperature. This is typical of the viscosity behavior of fluids. Among the simple fluids, the viscosity of the modified Aachen surrogate is remarkably close to that of Jet-A-3638. Among the complex surrogates,

the viscosities of the Drexel 1, Drexel 2, and Shultz surrogates are relatively close to those of the Jet-A fluids. The viscosity of the Drexel 2 surrogate is remarkably close to that of Jet-A-4658, and the viscosity of Drexel 1 is somewhat above that of Jet-A-3638, while the Shultz surrogate is somewhat below that of Jet-A-3638.

Surrogate Mixture Design by Thermophysical Property Modeling. In part 1 (10.1021/ef100496j) of this series, we examined the physicochemical authenticity of surrogate fluids on the basis of volatility, as determined by the ADC method. In the discussion above, we have expounded upon these evaluations to also examine some other thermophysical properties (calculated with the REFPROP program) that are of relevance. While not specifically addressed above, we can also calculate the volatility in terms of the distillation curve with the REFPROP program. Indeed, by choosing the properties of most relevance, we can use REFPROP not only as an evaluation tool but also as a surrogate fluid design tool. We used this approach previously to design surrogate mixtures for Jet-A, which reproduced most of the thermophysical properties within experimental uncertainty.[27] The properties included in the model development were the volatility, density, speed of sound, viscosity, thermal conductivity, and cetane number. Because we can focus very precisely on the individual properties, this process resulted in two separate surrogate mixtures for Jet-A-4658 and Jet-A-3638.

Each of these surrogates contained seven components; these components were chosen more for their precise representation of the measurements and the availability of data on the surrogate constituents. They were not chosen for ease of formulation in the laboratory (including the commercial availability of the components), or for use in measurements and engineering tests.

In this aspect of the work, we sought to develop a simple (three-component) surrogate mixture to represent Jet-A. Because of our precise and targeted approach, we were able to focus on the representation of the composite Jet-A mixture, Jet-A-4658. The purpose of this was two-fold. First, we seek to demonstrate that we can indeed use the modeling approach described above as a tool to develop targeted, physicochemically authentic surrogates that are specific enough to represent even a particular Jet-A fluid (among the many possible fluids) that might be of interest. Second, the design of a relatively simple surrogate affords the opportunity to experimentally verify our modeling and fluid design strategy. This experimental test has not been performed hitherto.

We began this process with a few initial conditions. First, as stated above, our desire was to produce a simple rather than complex surrogate in the context of the categories set out in part 1 (10.1021/ef100496j). Thus, the total number of constituents was limited to three. Our component palette was limited as well. We focused on the pure fluids composing the surrogates listed in part 1 (10.1021/ef100496j), plus fluids that we could easily obtain commercially. We note that this is not a serious constraint, because a large number of applicable fluids are readily available. Finally, among the components of this palette, we favored fluids for which at least some data were available, to avoid application of pure fluid equations of state solely based on predictions.

We use a multi-property regression algorithm, similar to that used in developing equations of state and define the objective function as a weighted sum of squared deviations. Because of the availability of reliable data on the volatility, density, and speed of sound of Jet-A-4658 and the pure fluids that might form the surrogate fluid palette, these properties were chosen for regression. Following this reasoning, the objective function becomes

$$F = \sum_{i=1}^{N_{dis}} W_{i,\,dis} F_{i,\,dis}{}^2 + \sum_{i=1}^{N_{PVT}} W_{i,\,PVT} F_{i,\,PVT}{}^2 + \sum_{i=1}^{N_{SS}} W_{i,\,SS} F_{i,\,SS}{}^2 \tag{10}$$

In eq 10, the weights for each data point are denoted by W_i, the objective function is F, and the subscripts dis, PVT, and SS refer to the data type (distillation, density, and speed of sound, respectively). The objective functions are defined as the percent deviations between the calculated value and the experimental value for each type

$$F_{dis} = 100(T_{calc} - T_{exp})/T_{exp} \tag{11}$$

$$F_{PVT} = 100(\rho_{calc} - \rho_{exp})/\rho_{exp} \tag{12}$$

$$F_{SS} = 100(SS_{calc} - SS_{exp})/SS_{exp} \tag{13}$$

where T is a temperature on the distillation curve (in K), ρ is a density, and SS is a speed of sound. The distillation curve contains the initial boiling point as its first point. One may assign equal weights to each data type or weight more heavily the more important properties. One may also weight within a

Table 1. Simple Surrogate Mixture That Was Designed To Represent the Behavior of Jet-A-4658

component	mass fraction
n-dodecane	0.31
n-tetradecane	0.38
1,2,4-trimethylbenzene	0.31

Table 2. Initial Boiling Behavior of the H−B Surrogate Mixture, the Composition of Which Is Listed in Table 1[a]

observed temperature	H−B surrogate (°C, at 81.57 kPa)
onset	193.8
vapor rise	197.1

[a] The vapor rise temperature is that at which vapor is observed to rise in the distillation head, considered to be the initial boiling temperature of the fluid. These temperatures have been adjusted to 1 atm with the Sydney Young equation; the experimental atmospheric pressures are provided to allow for recovery of the actual measured temperatures. The uncertainties are discussed in the text.

particular data type. For example, all distillation points can be assigned the same weight, or one can weight a particular point within the same data type more than another. For the development of a simple Jet-A-4658 surrogate, we weighted the distillation curve heavily and the density and speed of sound less heavily, because that reflected the desired outcome for physicochemical authenticity, as discussed in part 1 (10.1021/ef100496j). We note that other properties, such as viscosity and thermal conductivity, were not included in this regression because of gaps in pure fluid property data. The regression converged after 30 iterations, resulting in the composition of the Huber−Bruno (H−B) surrogate mixture listed in Table 1.

Before we compare the performance of this model-designed surrogate mixture to those discussed in part 1 (10.1021/ef100496j), we must first compare how the predicted properties compare to what can actually be measured. Fortunately, the mixture is simple, and the components are readily obtainable at very high purity. Note that this is not always the case with predicted surrogate mixtures for fuels, especially highly complex mixtures containing components that might not even be found in the finished fuel. The mixture proposed in Table 1 was prepared volumetrically at ambient temperature (23 °C) and pressure (approximately 83 kPa), and the volatility was measured with the ADC approach. We performed three measurements of the distillation curve of this mixture. The average onset and vapor rise temperatures are listed in Table 2, and the corresponding distillation curve temperatures are presented in Table 3. The uncertainty in temperature (with a coverage factor $k = 2$) was 0.3 °C.

In Figure 4, we present a comparison of the measured distillation curve (plotted as individual points) and the predicted curve (plotted as the solid line). The measurement was performed at a local ambient pressure of 81.57 kPa, but the data plotted have been adjusted to standard atmospheric pressure with the modified Sydney Young equation, as described in part 1 (10.1021/ef100496j). This was performed to facilitate comparisons to the other surrogates and the aviation kerosene samples, which were measured at slightly different atmospheric pressures. One can see from Figure 4 that the agreement between experiment and theory is excellent; the absolute deviation average is 1.5 °C over the entire distillation curve. We note that the agreement with Jet-A-4658, plotted as the dotted line, is also excellent. Here, the average deviation is only 2.0 °C. We can apply the three point

by point metrics that were described in part 1 (10.1021/ef100496j). The results of these comparisons are provided in Table 4, along with those of the other simple surrogate mixtures that we discussed in part 1 (10.1021/ef100496j). We note that for all of the comparison metrics, the H−B surrogate is much closer to the behavior of the Jet-A samples.

Table 3. Representative Distillation Curve Data of the H−B Surrogate Mixture[a]

distillate volume fraction (%)	H−B surrogate (81.57 kPa)	
	T_k (°C)	T_h (°C)
5	198.7	189.4
10	200.6	191.5
15	202.9	193.1
20	205.5	196.9
25	208.7	200.2
30	212.3	204.0
35	216.0	207.8
40	220.0	212.9
45	224.1	216.8
50	228.6	221.9
55	232.6	226.7
60	235.8	231.1
65	239.2	234.9
70	242.1	237.8
75	244.0	240.8
80	246.7	243.5
85	249.3	246.5

[a] These temperatures have been adjusted to 1 atm with the Sydney Young equation; the experimental atmospheric pressures are provided to allow for recovery of the actual measured temperatures. The uncertainties are discussed in the text.
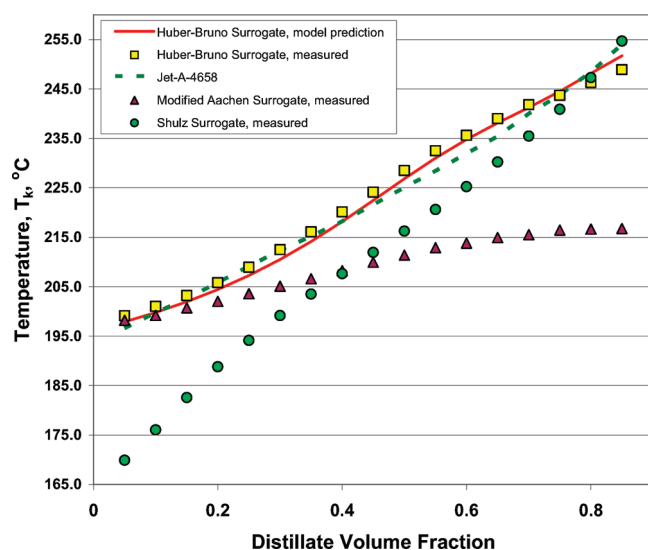
Figure 4. Comparison of the measured distillation curves of the H−B surrogate mixture to the predictions made with the REFPROP program and also to the measured curve for Jet-A-4658. For comparison, we also show the measured distillation curves for the modified Aachen and Schultz surrogate mixtures.

The slope evaluation is also superior to the other mixtures. The shape of the curve is excellent (on the basis of the residual plot and normal probability plot), and the slope is only 3% lower than that of Jet-A-4658. On the basis of the volatility behavior, the H−B mixture is the most authentic of all of the fluids that we have considered [in part 1 (10.1021/ef100496j) and part 2 (10.1021/ef1004978)] from a physicochemical viewpoint. We note that the same conclusion is reached upon comparison of the H−B surrogate to the complex surrogate mixtures that were discussed in part 1 (10.1021/ef100496j). As a further comparison, the measured distillation curves for the modified Aachen and Shultz surrogate mixtures [presented in part 1 (10.1021/ef100496j)] are also shown in Figure 4.[2] These two mixtures were the most physicochemically authentic among the simple and complex surrogate mixtures, respectively.

We can also compare the performance of the H−B surrogate on the basis of the other thermophysical properties that we examined earlier in Figures 1−3. In Figure 5a, we show the calculated density of the H−B surrogate mixture, as compared to the two Jet-A fuels. While the density of the H−B surrogate is below that of Jet-A-3638 for the entire temperature range, it is within the specification range for JP-8 (shown by the inset at 15 °C). The only other surrogate fluids that fall within the density specification were the Drexel 1, Drexel 2, and Shultz surrogates. None of the simple surrogates from part 1 (10.1021/ef100496j) fall within the specification. Of the four surrogate mixtures that in fact meet the density specification for JP-8, only the H−B and Shultz surrogates meet the criteria presented in part 1 (10.1021/ef100496j) for physicochemical authenticity. For comparison, the calculated density for the modified Aachen and Shultz surrogate mixtures is also shown in Figure 5a.

In Figure 5b, we show the calculated speed of sound for the H−B surrogate mixture, as compared to the two Jet-A fuels. As noted earlier, our models typically overpredict the speed of sound for the Jet-A fluids (by 1.5%) and do likewise for the H−B surrogate. When we compare the speed of sound agreement of the other surrogate mixtures, simple and complex, we see that no other mixture comes closer to the Jet-A fluids than the H−B surrogate. Only the modified Aachen surrogate is comparable; this was the most physicochemically authentic surrogate mixture identified in part 1 (10.1021/ef100496j). For comparison, the calculated speed of sound for the modified Aachen and Shultz surrogate mixtures is also shown.

In Figure 5c, we show the calculated viscosity for the H−B surrogate mixture, as compared to the two Jet-A fuels. We note that the viscosity of the H−B surrogate closely matches that of Jet-A-3638 and lies below that of Jet-A-4658. In this respect, the performance of the H−B surrogate is (again) very similar to that of the modified Aachen surrogate. Other mixtures that provide relatively close representations of the Jet-A viscosities are the Drexel 1 and 2 and Schultz surrogates (see Figure 3). Of these, the H−B, modified Aachen,

Table 4. Listing of the Comparison Measures Applied to the Suite of Simple Surrogate Mixtures Studied in Part 1 (10.1021/ef100496j),[2] Including the H−B Surrogate Mixture

criterion	surrogate A	surrogate B	surrogate C	surrogate F	surrogate G	Aachen	modified Aachen	H−B
metric 1	69.20	64.00	32.40	44.90	66.50	49.30	13.50	2.70
metric 2	4.25	3.77	2.20	2.36	4.06	2.63	0.60	0.16
metric 3	50.26	45.11	14.85	26.01	47.58	30.34	4.51	2.69
slope validity	poor	good	poor	invalid	poor	invalid	good	excellent
slope	0.70	0.42	0.99	NA	0.66	NA	0.25	0.68
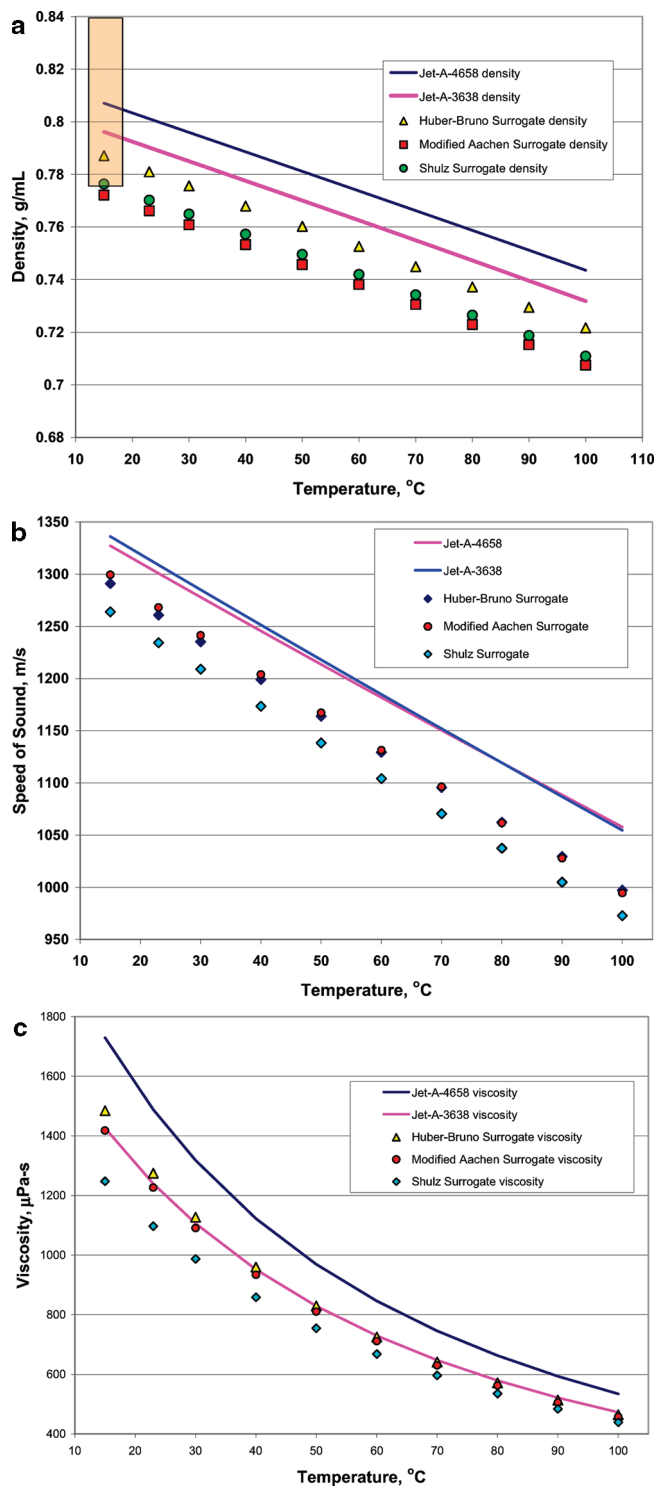
Figure 5. Calculated (a) density, (b) speed of sound, and (c) viscosity of the H–B surrogate mixture and those of the two Jet-A fluids. The inset shows the allowable density range specified for JP-8. For comparison, the calculated density, speed of sound, and viscosity for the modified Aachen and Shultz surrogate mixtures are also shown.

and Schultz surrogates meet our criteria for physicochemical authenticity. For comparison, the calculated viscosity for the modified Aachen and Shultz surrogate mixtures is also shown.

We emphasize that, except for the data from the ADC measurement, the property comparisons discussed above are not to experimental data but rather to calculations performed with the equations of state and transport models in REFPROP. While comparisons to measurements might be more satisfactory, it is not clear that this would be necessary for a preliminary evaluation, nor is it clear that the ultimate conclusions would be altered. Moreover, such a comparison would be costly and time-consuming. We argue that the results presented herein demonstrate that such a preliminary evaluation of physicochemical authenticity is indeed possible. We also argue that the formalism can be used effectively to design a surrogate, even a very simple surrogate, the physicochemical authenticity of which can be experimentally verified in terms of the volatility.

Conclusions

In this, the second part in a series of two papers, we expand upon our evaluation of the physicochemical authenticity of the surrogate mixtures that have been proposed and prepared during the course of work by a large research community on aviation kerosene. Herein, we compared the surrogate mixtures on the basis of several selected thermophysical properties (calculated with a state-of-the-art model): density, speed of sound, and viscosity. In terms of density, none of the simple surrogate mixtures listed in part 1 (10.1021/ef100496j) meets the specification for JP-8, and for the complex surrogate mixtures, only the Drexel 1, Drexel 2, and Schultz surrogates meet the specification. Of these, the Schultz surrogate also met the volatility-based criteria for physicochemical authenticity. The modified Aachen surrogate (among the simple mixtures) and the Drexel 1, Drexel 2, and Schultz surrogates (among the complex mixtures) were closest to the calculated speed of sound of Jet-A. In terms of calculated viscosity, the modified Aachen surrogate (among the simple mixtures) and the Drexel 1, Drexel 2, and Schultz surrogates (among the complex mixtures) were closest to the viscosity of Jet-A. Among these, the modified Aachen and Schultz met the volatility-based criteria for physicochemical authenticity.

We subsequently used our modeling formalism to design a new surrogate mixture. This mixture was prepared in the laboratory and tested by both measurement (with the ADC method) and the calculated thermophysical properties discussed above. We found that the measured distillation curve for this mixture, which we called the H–B surrogate, placed it far closer to the composite Jet-A sample than any other mixture studied in this work [see part 1 (10.1021/ef100496j)]. We also noted that this mixture met the density specification for JP-8, the speed of sound was closest to Jet-A (with there being little variation in the two Jet-A comparison fluids), and the calculated viscosity was very close to that of Jet-A-3638. We argue that the protocol described in these two papers can be used in the future to further develop surrogate fuels in an efficient and cost-effective manner. This statement is applicable for not only aviation kerosenes but also alternative, sustainable fuels containing novel components and additives. The design of future surrogates can be refined to include specific components of choice, for example, components for which detailed kinetic mechanisms are available. Moreover, added weight can be given to other properties, such as the threshold sooting index, cetane number, etc.