June 20th, 2009, Boulder Meeting

Minutes of the 9th IATP Meeting

1. INTRODUCTION

The meeting was opened by the Chairman, Prof. W.A. Wakeham, who welcomed all present and thanked Dr R. Perkins for the excellent arrangements as the local organiser of the meeting. Prof. M.J. Assael, IATP's Secretary, announced that Prof. W.A. Wakeham has been knighted for his services to Chemical Engineering and Higher Education. All present congratulated Prof. W.A. Wakeham.

The meeting was divided into the usual scientific session and a business session. The proceedings are recorded here in that order.

2. SCIENTIFIC SESSION

2.1 Zero-Density Thermal Conductivity of Water Vapor. Comparison of the IAPWS Formulation with Theoretically Calculated Values Including Original Experimental Data
E. Bich, E. Vogel (Germany)

2.2 Progress Report on the Background Thermal Conductivity of Water
D.G. Friend, M.L. Huber, R.A. Perkins, J.V. Sengers (USA), M.J. Assael, I.N. Metaxa (Greece)

2.3 Thermal Diffusivity of H_2O near the Critical Point.
J.V. Sengers, M.L. Huber, R.A. Perkins (USA), B. Le Neindre (France)

2.4 On the Prediction of the Viscosity and Thermal Conductivity of Liquid Hydrocarbon Mixtures on Considerations Based Upon the Hard Sphere Theory
M.J. Assael, A. Kalyva, K. Antoniadis, K. Kakosimos (Greece)

2.5 Current Status of Viscosity and Thermal Conductivity of Ionic Liquids
C.A. Nieto de Castro (Portugal)

2.6 Binary Diffusion in Ionic Liquid Co-Solvent Mixtures by Dynamic Light Scattering (DLS)
A. Froeba, J. Lehmann, A. Leipertz (Germany)

2.7 Thermophysical Properties of DIDP
F. Peleties, J.P.M. Trusler (UK)

2.8 The Necessity for Reference Fluids for Viscosity Measurements of Viscous Fluids at High Pressures
M.J.P. Comunas, A.S. Pensado, X. Paredes, J. Fernandez (Spain), K.R. Harris (Australia)

2.9 Development of High Temperature/High Pressure High Viscosity Standard for Industry.
Kurt Schmidt (Canada)

Each presentation engendered discussion and a few points of special interest are noted here:

a) Prof. Vogel argued that in the temperature range 600-1200 K his theoretical correlation for the zero density thermal conductivity of water differs up to 6% from the IAPWS 1985 correlation - revised in 1998. Both IAPWS correlations and previous ones, were based on the work of Vargaftik and co-workers which could be wrong, owing to taking inadequate account of convective effects present in his steady-state transient hot-wire. In order to improve the IAPWS correlation in that region more measurements would be necessary. It was argued on the other hand, that IAPWS takes into consideration the existing measurements and thus the only thing possible for now would be to increase the level of uncertainty in that region.

Dr Perkins presented the progress on the background correlation of the new IAPWS correlation for the thermal conductivity of water. A large improvement on the high-pressure region is here expected. Prof. Sengers presented the new advancements in the critical enhancement of the thermal conductivity and demonstrated that the new IAPWS correlation for the thermal conductivity of water in the critical region will be completely consistent with the Formulation adopted by IAPWS for the viscosity of water. It was noted that the behaviour in the critical region may be better known than elsewhere, a great change from the past.

b) Ms Kalyva presented an easier formulation for the application of the hard-spheres originated V_o scheme to pure fluids and discussed different mixing rules for its application to mixtures.

c) Prof Castro showed viscosity data on $[C_4mim]\{BF_4]$, which is a common ionic fluid whose density has been measured by many investigators. The discrepancies in the viscosity values between various investigators were up to ±20% at 298 K. He further discussed the progress in existing correlations, and pointed out problems related to the water content. He also showed the large discrepancies between the various thermal and electrical conductivity values reported by various investigators.

d) Ms Lehmann discussed Dynamic Light Scattering measurements of the mutual diffusion coefficient of different ionic co-solvents mixtures and showed that with this method the mutual diffusion coefficient can be determined over the entire composition range.

e) Prof. Trusler discussed new advances on the thermophysical properties of DIDP, and presented measurements over an extended temperature range and up to 140 MPa. He further described the derivation of a new EoS for the liquid range and a new correlation for viscosity, based on new measurements on high pressures.

f) Prof. Fernandez, investigating the possibility of a new high viscosity standard, presented a critical review of the viscosity data of DIDP, Squalane, Bis(2-ethylhexyl) Phthalate, 2-Ethylhexyl Benzoate, Di(2-ethylhexyl) Sebacate. For the low viscosity range possible candidates could be DIDP and Squalane, but for the higher viscosity standard, the only possible candidate seems to be Dipentaerythritol hexaisononanoate. The group was reminded that the industry requires a fluid of 30 mPas viscosity for work on lubricants, and up to 240 mPas for work on the gear boxes and the four-stroke engine.

g) Dr Schmidt discussed the need of accurate viscosity data for the simulation of the fluids that enter the production/injection rates in the reservoirs. In these simulations the largest uncertainty (>15%) is from the viscosity. Today, in their laboratory, they use oscillating-piston or falling body viscometers and they need viscosity standards to calibrate them.
In addition to normal requirements for a viscosity standard, they further need a viscosity standard in the range of 200 cP at 300'C and 35,000 psi, with an uncertainty of ±1%, or more realistic a viscosity standard in the range of 200 cP at 25,000 psi, with an uncertainty of ±2%.

3. BUSINESS SESSION

3.1. PROJECTS CONCLUDED

1. Evaluation of the Viscosity Effect upon the Vibrating U-tube Densimeter
   J.P.M. Trusler (UK), J. Fernandez, M.J.P. Comunas, L. Lugo (Spain), F.J.P. ***Caetano,*** *J.M.N.A. Fareleira (Portugal), A. Goodwin (USA), K. Harris (Australia), B. Rathke (Germany)*
   Work completed. A review paper will be prepared by Prof. Trusler and published under the auspices of IATP.

3.2. CONTINUING PROJECTS

The following projects were discussed and it was agreed to continue them:

1. Viscosity and Thermal Conductivity of Water & Steam
   M.J. Assael (Greece), E. Vogel, J. Millat (Germany), A. Nagashima (Japan), D. Friend, J.V. Sengers (USA)
   The proposal of Prof. Vogel (see 2a above) will be examined especially in relation to the measurements of Vargaftik, Prof. Vogel and Prof. Sengers will submit a proposal for an ICRN (IAWPS Certified Research Need) at the annual meeting of IAPWS in September 2009 on the thermal conductivity of the dilute gas, but the development of the new IAWPS correlation will not wait for new measurements to be carried out before it is commenced. The next discussion will take place in September at the IAPWS Meeting.

2. Density and Viscosity of Molten Metals Cu and Sn
   M.J. Assael (Greece), W.A. Wakeham (UK), I. Egry (Germany), P. Quested (UK), J.T. Wu (R.P. China), E. Kaschnitz (Austria), M. Banish (USA)
   A proposal for funding for this work was submitted to IUPAC by the Secretary Prof. Assael and had been approved. The first meeting of this group was planned for Sunday. At that meeting after a preliminary first evaluation of all data for the density and viscosity of Cu and Sn, the data to be considered as primary data were selected. The next and final meeting will take place in Santiago, Spain, in June 2010, where the project will be concluded.

3. High Viscosity Standards
   J.M.N.A. Fareleira (Portugal), W.A. Wakeham, J.P.M. Trusler (UK), A.P. Froba, A. Leipertz, B. Rathke (Germany), K. Harris (Australia), A.R.H. Goodwin, A. Laesecke (USA), J. Fernandez (Spain), F. Caetano (Portugal), K. Schmidt (Canada), Chr. Boned (France).
   There was no progress report. However the group was planning to meet that afternoon to discuss the proposal from Mr. Schmidt. **Details of the afternoon working group meeting are given at the end of these minutes**. The next meeting will be in 2010.

4 Reviews of Modern Viscosity Measurement Techniques
   A.H.R. Goodwin(USA), W.A. Wakeham(UK), M.J. Assael (Greece), K. Harris (Australia) and colleagues to be appointed
   No progress so far, still continues.

5. Short Review Paper on Evaluation of Existing Thermal Conductivity Measurements
   M.J. Assael (Greece), W.A. Wakeham (UK), J. Wu (R.P. China), C.A. Nieto de Castro (Portugal), M. Banish (USA)
   Prof Assael reported the compilation of all literature data over the last 10 years. Work continues.

6. Ionic Liquids Viscosity, Thermal Conductivity Measurements for a new IUPAC standard.
   C.A. Nieto de Castro (Portugal), A. Froeba, A. Leipertz, U. Hammerschmidt (Germany), J. Fernandez (Spain), R. Perkins (USA), and K. Harris (Australia)..
   Work continues aiming to propose new Ionic liquids standards.

4. MEMBERSHIP

No alteration to the membership list was carried out.

5. FUTURE MEETINGS

The following dates and places of the IATP meetings were decided

5.1. 10th IATP Meeting, 2010

The 10th IATP Meeting will take place in Santiago, Spain in the middle of June. Prof Fernandez will be the local host.

5.2. 11th IATP Meeting, 2011

The 11th IATP Meeting will take place in Thessaloniki on Friday September 2nd, just after the 19th ECTP (August 26th - September 1st, 2011), which will also occur in the same place. Prof Assael will be the local organiser.

6. LIST OF ATTENDEES

List of People that attended the meeting:
1) Prof. William A. Wakeham (UK), Chairman
2) Prof. Marc J. Assael (Greece), Secretary
3) Prof. Carlos Nieto de Castro (Portugal)
4) Prof. Akira Nagashima (Japan)
5) Prof. Jan V. Sengers (USA

6) Dr Anneke L. Sengers (USA)
7) Dr Richard Perkins (USA)
8) Dr Marcia Huber (USA)
9) Dr DAn Friend (USA)
10) Prof. Eckhard Vogel (Germany)
11) Prof. Antoine Baylaucq (France)
12) Dr Ulf Hammerschmidt (Germany)
13) Dr Arno Laesecke (USA)
14) Prof. J.P. Martin Trusler (UK)
15) Dr Antony Goodwin (USA)
16) Dr Robert F. Berg (USA)
17) Prof. Sergio Quinones-Cisneros (Mexico)
18) Dr Kurt Schmidt (Canada)
19) Prof. Stefan Will (Germany)
20) Prof. Andreas Froeba (Germany)
21) Dr Bernd Rathke (Germany)
22) Prof. Christian Boned (France)
23) Dr Guillaume Galliero (France)
24) Dr Robert Hellmann (Germany)
25) Prof. Josefa Fernandez (Spain)
26) Dr Michael Banish (USA)
27) Dr Ken Marsh (New Zealand)
28) Mr Daniel Buttig (Germany)
29) Ms Agni Kalyva (Greece)
30) Mr Sebastian Herrmann (Germany)
31) Mr Benjamin Jaeger (Germany)
32) Ms Julia Lehmann (Germany)
33) Ms Tanja Kugler (Germany

International Association for Transport Properties
http://transp.cheng.auth.gr/iatp.html

IATP Working Group on High-Temperature, High-Pressure Viscosity Standards

Minutes of the Inaugural Meeting June 20th, 2009, 16:45 - 17:30 MDT in the Engineering Center of the University of Colorado Boulder, Colorado, USA

Recorders: A. Laesecke, K. Schmidt

1. INTRODUCTION

The meeting was convened following the 9th annual IATP meeting to continue the discussions that had ensued after the presentation of Kurt Schmidt on the need for high-temperature, high-pressure viscosity standards. Sir William Wakeham chaired the meeting and facilitated the discussion.

2. LIST OF ATTENDEES

Attending the meeting were:

Prof. Sir William A. Wakeham (University of Southhampton, UK), Chairman

In alphabetical order:
Prof. Antoine Baylaucq (University of Pau, France)
Prof. Christian Boned (University of Pau, France)
Prof. Josefa Fernández (University of Santiago de Compostela, Spain)
Dr. Anthony R. H. Goodwin (Schlumberger, USA)
Dr. Arno Laesecke (NIST Boulder, Colorado, USA)
Prof. Sergio Quiñones-Cisneros (UNAM, Mexico City, Mexico and University Cologne, Germany)
Dr. Bernd Rathke (University Bremen, Germany)
Dr. Kurt A. G. Schmidt (DBR Technology Center, Schlumberger, Canada)
Prof. J.P. Martin Trusler (Imperial College, London, UK)

Excused:
Prof. Ken Marsh (University of Canterbury, Christchurch, New Zealand)

The working group is open for additional participants.

3. DISCUSSION

Industrial viscometry in the oil and gas industry continues to advance to more and more challenging conditions. Unconventional reservoirs at greater depths, elevated temperatures, and elevated pressures are increasingly being exploited. Consequently, an expansion of viscosity standards to elevated conditions is a critical need of this industry. Desired target specifications of high-temperature, high-pressure (HTHP) viscosity standard reference materials were given by K. Schmidt as follows:

In the short term:
Dynamic viscosity of 200 mPa·s at 200 °C (473.15 K) and 173 MPa (25,000 psi) with an uncertainty of ±2 %.

In the long term:
Dynamic viscosity of 200 mPa·s at 300 °C (573.15 K) and 241 MPa (35,000 psi) with an uncertainty of ±1 %.

Certified viscosity reference liquids for calibrations and adjustments of viscometers are currently available in the temperature range from 20 °C to 100 °C and at atmospheric pressure with viscosities ranging from 0.4 mPa·s to 63.5 Pa·s. The expanded uncertainties in the viscosities of these standards range from 0.16 % to 0.53 %. A few certified viscosity standards are available at 150 °C and atmospheric pressure.

The required viscosity standard specifications exceed those of the available viscosity standards considerably. The discussion in the working group centered predominantly on the possible materials that possess the required properties of the HTHP viscosity standard. The required high viscosity at elevated temperature and pressure may require the group to consider materials that are solid at room temperature. Compounds that can be subcooled considerably below their melting temperature may also be a possibility (aromatic hydrocarbons, glass-formers). The thermal stability of the HTHP standard material is a critical issue. High viscosity at elevated conditions requires complex molecules that may decompose below 300 °C. A. Laesecke mentioned perfluorinated hydrocarbons which are rather stable but have lower viscosities than the conjugated hydrocarbons because of the higher repulsive part of the intermolecular potential due to the lower polarizability of the fluorine atoms. B. Rathke mentioned micellar phases as possible materials. Other materials mentioned were biodiesel compounds, lubricants, and suspensions. S. Quiñones-Cisneros suggested the group investigate compounds which are studied in tribology.

It was decided to form a **materials selection group** chaired by A. Laesecke and joined by A. Baylaucq, J. Fernández, A. Goodwin, K. Marsh, B. Rathke, and S. Quiñones-Cisneros.

The discussions touched also the available viscometric methods to determine the viscosity of the HTHP standard at 300 °C and high pressures. Several laboratories have vibrating-wire viscometers that can be operated at the required conditions. Falling-body viscometers are available to cover the short and long term pressures but their temperature capabilities need to be developed to reach 300 °C. NIST Boulder has a torsionally vibrating crystal viscometer for absolute measurements to at least 600 K but the pressure range of the instrument reaches currently to 68 MPa. In addition, J. P. M. Trusler, suggested that it may be of importance for the oil and gas industry to evaluate alternative viscometric techniques (e.g. vibrating wire). A. Baylaucq and K. Schmidt mentioned that presently the falling body method was the most common form of measurement in the oil and gas industry.

It was decided to form a **viscometric techniques group** chaired by J. P. M. Trusler and joined by J. Fernández, A. Goodwin, and A. Laesecke.

Steering the overall development of the project was assigned to Sir Wakeham, A. Goodwin, and K. Schmidt. These members will look further into the HTHP viscosity standard requirements and recommend a staged approach to fulfilling the needs of industry. Initially, the global requirements described by K. Schmidt will be taken back to industry to determine if the requirement of 200 mPa·s at both 200 °C (473.15 K) and at 173 MPa (25,000 psi) is truly needed. This group will also determine the business case (e.g. funding and timing) for the development of such a standard.

4. FUTURE MEETINGS

It is expected that the next meeting of the working group will be held in conjunction with the 10th IATP Meeting in Santiago de Compostela, Spain, in the middle of June 2010. Local host will be Prof. J. Fernández. Additional meetings may be held as needed.

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