International Journal of Thermophysics, Vol. 27, No. 6, November 2006 (© 2006)
DOI: 10.1007/s10765-006-0119-1

Viscosity of Molten Sodium Nitrate[1]

V. M. B. Nunes,[2,3] M. J. V. Lourenço,[3,4] F. J. V. Santos,[3,4] and C. A. Nieto de Castro[3–5]

New experimental data for the viscosity of molten sodium nitrate from its melting point up to 752 K, at atmospheric pressure, with an estimated uncertainty of 2.1%, were measured with an oscillating cup viscometer. A preliminary reference correlation and reference data are proposed, based on the best available data for the viscosity of molten sodium nitrate, for temperatures between 590 and 750 K, with an estimated absolute uncertainty of 0.066 mPa · s ($k = 2$).

KEY WORDS: high temperature; molten sodium nitrate; oscillating cup viscometer; reference correlation; viscosity.

1. INTRODUCTION

Molten alkali nitrates have emerged as high-temperature fluids for several technological processes, such as high-temperature energy storage in batteries and solar plants, waste treatment, among other novel applications. Knowledge of accurate data for the transport coefficients of these fluids is very important, as has been recently demonstrated [1]. We have recently reported on the viscosity of molten potassium nitrate [2], proposed as a

[1] Paper presented at the Seventeenth European Conference on Thermophysical Properties, September 5-8, 2005, Bratislava, Slovak Republic.

[2] Escola Superior de Tecnologia, Instituto Politécnico de Tomar, Campus da Quinta do Contador, 2300-313 Tomar, Portugal.
[3] Centro de Ciências Moleculares e Materiais, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal.
[4] Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal.
[5] To whom correspondence should be addressed. E-mail: cacastro@fc.ul.pt

standard for high temperature measurements [3,4], and our results have shown good agreement with previous authors.

Contrary to KNO_3, the viscosity of molten $NaNO_3$ has been less studied. The recommended values of the Molten Salts Data Centre (MSDC) [5] were based mostly on the work of Zuca and co-workers [6,7]. As far as we know, the last work published about the viscosity of molten $NaNO_3$is due to Brovkina et al. [8] in 1974. The MSDC's recommended equation in the temperature interval from 589 to 731 K, with an estimated uncertainty of 3% [5][6] is

$$\eta = 0.1041 \times \exp\left(\frac{16259.3}{RT}\right) \tag{1}$$

where η is the absolute viscosity in mPa · s, R is the universal gas constant in $J \cdot mol^{-1} \cdot K^{-1}$, and T is the absolute temperature in K.

This paper reports new experimental data for the viscosity of molten sodium nitrate from its melting point up to about 752 K, at atmospheric pressure.

In order to contribute to the existence of reference data for viscosity measurements at high temperatures, we propose a preliminary reference correlation for molten sodium nitrate, and a set of reference data. The importance of reference data for the viscosity of liquids has been recognized recently with the publication of standard reference data for the viscosity of toluene [9]. The quality of the existing data for this liquid is such that recommended values could be proposed with uncertainties of 0.5% ($k = 2$ or 95% confidence level) for $260K \leqslant T \leqslant 370K$ and 2% for $210K \leqslant T < 260K$ and $370K < T \leqslant 400K$. However, for molten salts we are far from achieving such an uncertainty and data are needed for higher temperatures.

2. EXPERIMENTAL

The experimental apparatus (oscillating cup viscometer) used in the present work was described in detail elsewhere [10]. Briefly, the method is based on the damped oscillations of a torsion wire connected to a rod and a cup containing the fluid. The viscosity is computed from the measured period and logarithmic decrement (in units of 2π) of oscillations, with the empty and filled cup, (T_0, Δ_0) and (T, Δ), respectively. The only needed measurements are mass, temperature, and time, which can be achieved

[6] At those times the reported values refer to one standard deviation of the fit.

with great accuracy. The working equations were explained in previous publications [2,10], and will not be reproduced here.

An improved data acquisition system was introduced, allowing better accuracy in temperature and time interval measurements. A time interval counter (Stanford Research Systems, Model SR620) and a digital multimeter (Hewlett Packard, 3478A) were connected to a personal computer through an IEEE-488 interface, permitting the manipulation of all the instrument parameters from the computer. In each run at a given temperature, the computer stores the *emf* of a calibrated Type K thermocouple (used to measure temperature) and the time intervals that a laser beam reflected from the oscillation system takes to cross two optical detectors, conveniently placed. A simple *QuickBasic* program calculates the mean period of oscillation and its standard deviation, the logarithmic decrement and standard deviation, as well as other important parameters, like the height of fluid in the cup, obtained from the cup radius, r, the density of the melt, and the moment of inertia, I. Finally the fluid's viscosity at the mean temperature of the experiment is calculated.

One of the most common experimental error sources for this type of measurements includes failed period measurements, sometimes due to deficient response of one of the laser detectors. New validation routines were developed and introduced in the data acquisition program to remove these values from the final calculation of the melt viscosity. This improved system allows better accuracy for the measurement of Δ and therefore better uncertainty for the viscosity, which is now estimated to be within 2.1%.

The sample ($NaNO_3$ from Merck, Germany), with a minimum stated purity of 99.5%, was dried overnight, and the cup was successively filled in a separate furnace, to ensure the compactness of the solid sample and to minimize the amount of air inside the sample. The amount of salt loaded into the cup was chosen in order to comply with the fact that the meniscus effects in the viscosity measurements have to be rendered negligible, as explained in a previous publication [11]. The cup was then finally closed in a dry box under nitrogen atmosphere. Measurements were restricted to temperatures below 773 K, as it was previously reported that for higher temperatures the melt decomposes into $NaNO_2$ and O_2 [12,13]. The $NaNO_3$ sample was tested for alkalinity due to the possible presence of the nitrite ion, due to the decomposition of nitrate as follows:

$$NO_3^- \rightarrow NO_2^- + \tfrac{1}{2}O_2$$

although the residual presence of the nitrite ion does not seriously affect the measured viscosity as previously reported by Nissen et al. [14], at least at lower temperatures.

Table I. Physical Parameters of the Oscillating System for the Present Measurements on Molten Sodium Nitrate

r (mm)	8.590 ± 0.005
$10^7 I(\text{kg} \cdot \text{m}^2)$	555.77 ± 4
T_0 (s)	1.6007 ± 0.0003
$10^4 \Delta_0$	2.106 ± 0.03

3. RESULTS AND DISCUSSION

The physical parameters of the oscillating system were re-determined and are listed in Table I. The viscosity was measured from the melting point of $NaNO_3$ up to about 752 K, using density data taken from the literature [5]. Table II shows the obtained data. The reproducibility of the measurements can be demonstrated around 600 K, obtained on different days, as we have three independent measurements. Using Eq. (1) to correct the three data points to a nominal temperature of 600 K, we obtain an average value of $2.677 \pm 0.047\,\text{mPa} \cdot \text{s}$, with a relative standard deviation of 1.8%. The total uncertainty, calculated from the root-mean-square deviations of the different contributions, taking already into account the uncertainty of 0.5% in density, was estimated to be 2.1%, at a 95% confidence level ($k = 2$) as shown in Table III. Data points were obtained for both increasing and decreasing temperatures (see note in Table II), and no appreciable hysteresis was observed.

As explained in a previous publication, the assignment of the real temperature of the melt is very important [2]. Since this previous publication, a better furnace was introduced in the system (Carbolite, Type CTF 12/65/550, with Eurotherm controller 902P). This furnace has better temperature stability, management, and control. In order to have an estimate of the temperature difference between the molten salt and the thermocouple probe used to monitor the temperature near the bottom of the cell, a blank measurement was made with the cell open to the atmosphere, suspended in the same position in the tubular furnace, by immersing a second calibrated Type K thermocouple in the melt. The temperature of the furnace was then scanned in the temperature interval used for the viscosity measurements, in steps of 100 K, and the temperatures measured by both thermocouples were recorded as a function of the temperature of the outside probe. For this furnace, a systematic positive temperature difference was found, increasing with temperature. This is in agreement with the expected axial temperature profile. An average correction as a function of

Table II. Experimental Results

T(K)	T(s)	$10^4\Delta$	η(mPa · s)
590.3[a]	1.6028	19.15	2.854
599.3	1.6025	18.93	2.740
600.0	1.6032	18.91	2.658
600.3	1.6032	18.87	2.638
613.2	1.6054	18.14	2.437
640.9[a]	1.6040	17.39	2.155
653.6	1.6041	17.10	2.050
673.2	1.6040	16.26	1.811
676.8[a]	1.6044	16.24	1.768
691.9	1.6035	15.73	1.719
709.7	1.6040	15.81	1.627
714.6[a]	1.6046	15.49	1.537
732.4	1.6045	15.61	1.564
752.1[a]	1.6056	15.15	1.430

[a]Data points obtained with decreasing temperature.

Table III. Uncertainty Analysis

Parameter	s_i(%)	Contribution to s_η(%)[a]
Logarithmic decrement, δ	0.5	1.5
Period of oscillation, T	0.01	≈ 0
Moment of inertia, I	0.7	1.3
Cup radius, r	0.06	0.17
Sample mass, m	0.03	0.03
Density, ρ	0.5	0.5
Total uncertainty (%)[b]		2.1

[a]All numbers are expressed at the 95% confidence level.

[b]Calculated using the standard formula $s_\eta^2 = \sum_i \left(\frac{\partial \eta}{\partial s_i}\right)^2 s_i^2$, with $s_i = 2u_i$, the relative uncertainty at the 95% confidence level.

temperature was then applied to all measured temperatures, to obtain the cell temperature, as displayed in Table II.

Figure 1 shows the measured viscosity as a function of absolute temperature. The present data can be fitted to the Arrhenius equation, which is also represented in Fig. 2. The least-squares fit to the Arrhenius law gives the following equation:

$$\eta = 0.1087 \times \exp\left[\frac{15936}{RT}\right] \tag{2}$$

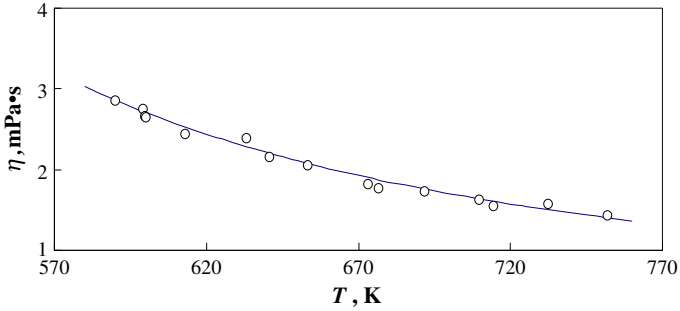

Fig. 1. Viscosity of molten $NaNO_3$: ○ present work; line—MSDC recommendations [5].

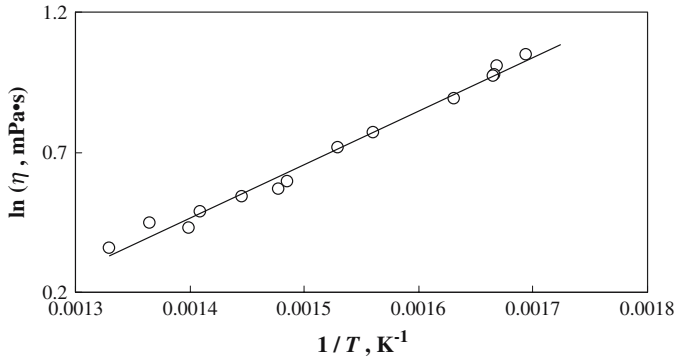

Fig. 2. Arrhenius representation of present data.

with all the quantities expressed in the same units as in Eq. (1) and a regression coefficient of 0.9940. The activation energy for viscosity, $E_\eta = 15.936\,\mathrm{kJ \cdot mol^{-1}}$, was found to be 2% lower than the value given by the MSDC recommendation [5].

Figure 3 shows comparisons with other previous authors. As mentioned before, the available data are scarce. The data of Brovkina et al. [8], Smotrakov et al. [15], and Rhodes et al. [16] are smoothed data, not experimental data points.

The present data show an average deviation between −1 and −5% for temperatures less than 720 K, increasing to +4% at the highest temperatures, relative to the recommendations of the MSDC. As explained before, this correlation was based on previous work of Zuca and collaborators [6, 7] and the differences are possibly related to the equations used by previous authors, temperature measurement, inadequate wetting of cell

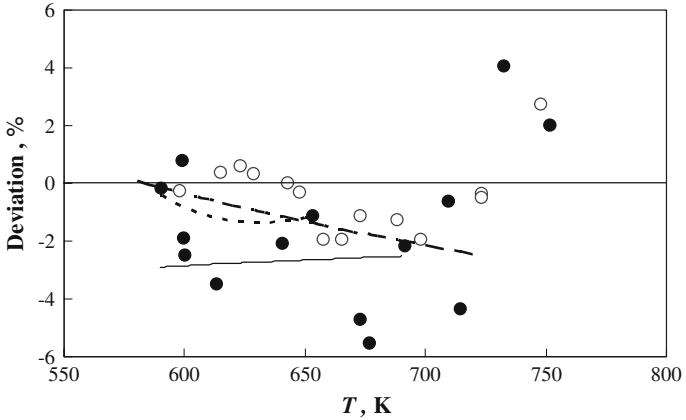

Fig. 3. Deviations of the available data from the recommendations of the MSDC correlation [5], in %. • present work; ○ Zuca et al. [19]; – – Brovkina et al. [8]; —— Smotrakov et al. [15]; ..... Rhodes et al. [16].

by the molten material, or end effects not accounted for in the working equations. Ferriss et al. [17] have recently shown that the equations derived by Brockner et al. [18], from the theory of Beckwitt and Newell, are more accurate and should be adopted for viscosity measurements, as we used in our laboratory [2]. Zuca [19] published different data for sodium nitrate, using the oscillating sphere method, with a claimed uncertainty of 2–3%, agreeing with the present data within the mutual uncertainty. It is clear from Fig. 3 that the data from this study, from Zuca [19], and from Brovkina et al. [8] show a different slope for the temperature variation of viscosity than that proposed by MSDC.

4. PROVISIONAL REFERENCE DATA CORRELATION

In view of the previous discussion, we suggest that previous recommendations should be revised as the data show a sigmoid shape in the deviations, current data are below the recommended values at low temperatures and above the recommended values at temperatures greater than 720 K.

On developing a reference correlation, two types of equations have been proposed: the classical Arrhenius law, used in Eqs. (1) and (2), and the IUPAC reference equation, used by Santos et al. [9]. We adopt the methodology developed in the paper by Santos et al. [9] and select as primary data the present results and those reported by Zuca [19], as they both show similar deviations to the previously proposed correlation by the

Molten Salt Data Centre, in 1972, and were obtained with two different methods of measurement. The material used in both sets of data was obtained from a commercial source with high purity (greater than 99.5%) or recrystallized and dried, melted under nitrogen atmosphere. Table IV shows the data chosen and their characterization.

The Arrhenius law can be applied to these two sets of data, and Eq. (3) is obtained. The absolute uncertainty of the data calculated directly from this fit, using the ISO definition ($k = 2$), is 0.080 mPa·s. The extrapolated value for the viscosity at the melting point (Janz [20], $T_m = 580$ K) is 2.98 mPa · s. The predicted activation energy for viscosity is $E_\eta = 16.012\ \text{kJ} \cdot \text{mol}^{-1}$, a value which agrees very well with that obtained in the present work;

$$\eta = 0.1078 \times \exp\left[\frac{16012}{RT}\right] \tag{3}$$

The IAPS formulation for the transport properties of water as developed by Sengers et al. [21] and Kestin et al. [22] was used in the following form:

$$\ln\left(\eta^*\right) = A + \frac{B}{T^*} + \frac{C}{(T^*)^2} + \frac{D}{(T^*)^3} \tag{4}$$

where $\eta^*$and T^* are dimensionless variables defined as

$$T^* = T / T_m \tag{5}$$

$$\eta^* = \frac{\eta\,(T)}{\eta_m} \tag{6}$$

and T_m is the value of the melting temperature, chosen from Janz [20], as $T_m = 580$ K. Using the data of the MSDC, we have made an estimate of the viscosity for the molten salt at the melting point, by extrapolating the

Table IV. Primary Sources of Experimental Data for the Viscosity of Sodium Nitrate

Literature source	Technique	Temperature Range (K)	No. of data points	Assigned uncertainty (%)	Purity class
Zuca (1970) [19]	OS[a]	598–748	14	2–3	MPFP[c]
This work	OC[b]	590–752	14	2	MPFP[c]

[a]Oscillating sphere.
[b]Oscillating cup.
[c]MPFP—manufacturer's stated purity, further purification.

viscosity data to the melting point temperature, $\eta_m = \lim_{T \to T_m} \eta(T)$, following the philosophy previously employed by Nunes et al. [23]. The result thus found was 3.033 mPa · s. The equation obtained for the correlation was

$$\ln(\eta^*) = 26.689 - \frac{97.54}{T^*} + \frac{112.5}{(T^*)^2} - \frac{41.70}{(T^*)^3} \tag{7}$$

This equation, capable of describing most of the experimental data sets within their own stated accuracy, for temperatures from 590 to 750 K, was established with two data sets composed of 28 data points and two different measurement techniques, as summarized in Table IV and represented in Fig. 4. The maximum deviation of the primary experimental data from the proposed correlation is −3.5%, as shown on the deviation plots of the primary data from the correlation expressed by Eq. (7) given in Fig. 5. The absolute uncertainty of the data calculated directly from this fit, using the ISO definition ($k = 2$), is 0.066 mPa · s, a value smaller than from Eq. (3). Also shown as lines are the smoothed data of the MSDC correlation given by Eq. (1) [5], Brovkina et al. [8], Smotrakov et al. [15], and Rhodes et al. [16].

Using Eq. (7), recommended values for the viscosity of molten sodium nitrate are presented in Table V, for nominal temperatures, between 590 and 750 K, with an uncertainty of 0.066 mPa · s ($k = 2$).

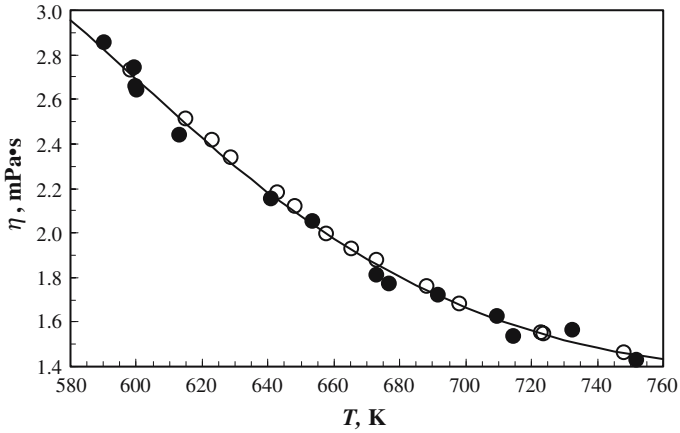

Fig. 4. Proposed reference correlation, Eq. (6), including the primary data, for $590 \leqslant T \leqslant 750$ K. • present work; ○ Zuca et al. [19]; —— correlation.

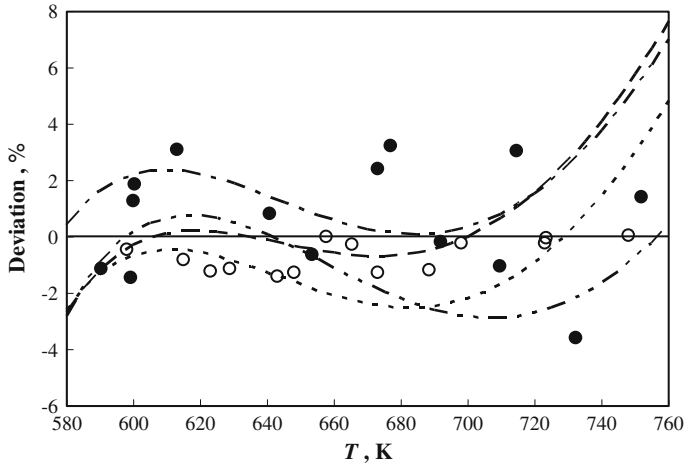

Fig. 5. Deviations of primary data (• present work, ○ Zuca et al. [19]) from the proposed correlation. Also shown are: ..... the MSDC correlation given by Eq. (1), [5] and the smoothed data from: — – Brovkina et al. [8]; –·–· Smotrakov et al. [15]; –··– Rhodes et al. [16].

Table V. Recommended Viscosities for Molten $NaNO_3$

T(K)	η(mPa · s)	T(K)	η(mPa · s)
590	2.83	675	1.84
595	2.76	680	1.80
600	2.69	685	1.76
605	2.62	690	1.73
610	2.56	695	1.70
615	2.49	700	1.66
620	2.43	705	1.64
625	2.36	710	1.61
630	2.30	715	1.58
635	2.24	720	1.56
640	2.18	725	1.54
645	2.13	730	1.52
650	2.07	735	1.50
655	2.02	740	1.48
660	1.97	745	1.47
665	1.93	750	1.46
670	1.88		

5. CONCLUSIONS

New data for the viscosity of molten sodium nitrate between 590 and 752 K are reported. These data were obtained with a modified oscillating cup viscometer, by improving the temperature control in the cell and developing a new data acquisition system. The estimated uncertainty of the present data is 2.1% ($k=2$).

The obtained data along with data from other authors were used to establish a preliminary recommendation for the viscosity of molten alkali nitrates, in the temperature range of 590–750 K, with an estimated absolute uncertainty of 0.066 mPa · s ($k=2$).

REFERENCES

1. V. M. B. Nunes, M. J. V. Lourenço, F. J. V. Santos, and C. A. Nieto de Castro, *J. Chem. Eng. Data* **48**:446 (2003).
2. M. J. C. Lança, M. J. V. Lourenço, F. J. V. Santos, V. M. B. Nunes, and C. A. Nieto de Castro, *High Temps. High Press*. **33**:427 (2001).
3. G. J. Janz , *High Temp. Sci.* **19**:173 (1985).
4. Y. Sato, A. Potapov, and T. Yamamura, "Viscosity of Molten KNO_3 as Standard Data of Molten Salts," 2nd *IATP Meeting*, London (21–22 August, 2002).
5. G. J. Janz, U. Krebs, H. Siegenthaler, and R. Tomkins, *J. Phys. Chem. Ref. Data* **1**:588 (1972).
6. R. Borcan and S. Zuca, *Electrochim. Acta* **15**:1817 (1970).
7. I. G. Murgulescu and S. Zuca, *Electrochim. Acta* **14**:519 (1969).
8. I. Brovkina, A. Farmakovskaya, and V. Khokhlov, *Electrochem. Molten Solid Electrolytes* **21**:14 (1974).
9. F. J. V. Santos, C. A. Nieto de Castro, J. H. Dymond, N. K. Dalaouti, M. J. Assael, and A. Nagashima, *J. Phys. Chem. Ref. Data* **35**:1 (2006).
10. V. M. B. Nunes, M. J. V. Lourenço, F. J. V. Santos, and C. A. Nieto de Castro, *Int. J. Thermophys.* **19**:427 (1998).
11. V. M. B. Nunes, M. J. V. Lourenço, F. J. V. Santos, and C. A. Nieto de Castro, *High Temps.-High Press.* **35–36**:75 (2003/2004).
12. K. H. Stern, *J. Phys. Chem. Ref. Data* **1**:747 (1972).
13. J. G. Janz, C. B. Allen, N. P. Bansai, R. M. Murphy, and R. P. T. Tomkins, *Natl. Stand. Ref. Data Ser.* **61**, Part II (NBS) (1979).
14. D. A. Nissen, *J. Chem. Eng. Data* **27**:269 (1982).
15. V. G. Smotrakov, N. P. Popovskaya, and V. A. Tereshchenko, *Zhur. Priklad. Khim*. **45**:2627 (1972).
16. E. Rhodes, W. E. Smith, and A. R. Ubbelhode, *Trans. Farad. Soc.* **63**:1943 (1967).
17. D. H. Ferriss and P. Quested, *NPL Report CMMT(A)* 306 (2000).
18. W. Brockner, K. Torklep, and H. A. Oye, *Ber. Bunsenges. Phys. Chem.* **83**:1 (1979).
19. S. Zuca, *Rev. Roumaine Chim*. **15**:1277 (1970).
20. G. J. Janz, *J. Phys. Chem. Ref. Data* **9**:791 (1980).

21. J. V. Sengers, J. T. R. Watson, R. S. Basu, B. Kamgar-Parsi, and R. C. Hendricks, *J. Phys. Chem. Ref. Data* **13**:893 (1984).
22. J. Kestin, J. V. Sengers, B. Kamgar-Parsi, and J. M. H. Levelt Sengers, *J. Phys. Chem. Ref. Data* **13**:175 (1984).
23. V. M. B. Nunes, F. J. V. Santos, M. J. V. Lourenço, and C. A. Nieto de Castro, *Proc. 6th Asian Conf. on Thermophy. Props.* Vol. 2, M. N. Bora ed., Guwahati, India (2001), p. 290.