

Viscosity of Molten Sodium Nitrate

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Abstract

Molten alkali nitrates emerged as high temperature fluids for several technological processes, like high temperature energy storage in batteries and solar plants, waste treatment, among other novel applications; nonetheless, the implementation of these fluids requires the knowledge of accurate data for their transport coefficients. New experimental data for the viscosity of molten sodium nitrate from melting point up to 752 K, at atmospheric pressure, with an estimated accuracy 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; viscosity; reference correlation

1. Introduction

Molten alkali nitrates have emerged as high temperature fluids for several technological processes, like high temperature energy storage in batteries and solar plants, waste treatment, among other novel applications. The knowledge of accurate data for the transport coefficients of these fluids is very important, as it has been recently demonstrated [1]. We have recently reported on the viscosity of molten potassium nitrate [2], proposed as a standard for high temperature measurements [3,4], and our results have shown a good agreement with previous authors.

Contrarily 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 obtained mostly in the basis of 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] is:

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

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

This paper reports new experimental data for the viscosity of molten sodium nitrate from 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 $260 \text{ K} \leq T \leq 370 \text{ K}$ and 2% for $210 \text{ K} \leq T < 260 \text{ K}$ and

370 K < $T \leq$ 400 K. However for molten salts we are far from achieving such an uncertainty and data is 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. 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 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 *e.m.f* of a calibrated type K thermocouple (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 , and the density of 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 are the failed period measurements, due sometimes to deficient response of one of the laser detectors. New validation routines were created 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 % (see table 3 in the next section).

The sample (NaNO₃ 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 kept 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 NaNO₂ and O₂ [12,13]. The NaNO₃ sample was tested for alkalinity due to the possible presence of the nitrite ion, due to the decomposition of nitrate as follows:



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 the lower temperatures.

3. Results and Discussion

The physical parameters of the oscillating system were re-determined and are listed in Table 1.

The viscosity was measured from melting point up to about 752 K, using density data taken from literature [5]. Table 2 resumes the obtained data. The reproducibility of the measurements can be demonstrated around 600 K, obtained in different days, as we have three independent measurements. Using Eq.(1) to correct the three data points to nominal temperature of 600K, we obtain an average value of 2.677 ± 0.047 mPa.s, a value of 1.8 %. The total uncertainty, calculated from the root mean square deviations of the different contributions, taken already in account the uncertainty of 0.5% in density, was estimated to be 2.1 %, as shown in Table 3. Data points were obtained both

on increasing and decreasing temperature (see note in Table 2) 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 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 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 real 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 temperature was then applied to all measured temperatures, to obtain the cell temperature, as displayed in Table 2.

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

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

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

Figure 3 shows the comparison with other previous authors. As mentioned before, the available data is 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 shows an average deviation between -1 and -5% for temperatures smaller than 720 K, increasing to + 4 % at the highest temperatures, relative to the recommendations of the MSDC. As explained before, this correlation was based in previous works of Zuca and collaborators [6,7] and it is possibly related to the used equations by previous authors, temperature measurement, inadequate wetting of cell by the molten material or end effects not accounted 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 use in our laboratory [2]. Zuca [19] published different data for sodium nitrate, using the oscillating sphere method, with a claimed accuracy of 2-3%, agreeing with the present data within their mutual uncertainty. It is clear from Fig.(3) that our data, Zuca [19] and Brovkina *et al.* [8] show a different slope for the temperature variation of viscosity than the MSDC proposal.

4. Provisional Reference Data Correlation

In view of the previous discussion, we may suggest that previous recommendations should be revised as the data show a sigmoid shape in the deviations, below the recommended values at low temperatures and above for 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 some 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 4 shows the data chosen and their characterization.

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 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 $E_\eta = 16.012$ kJ.mol⁻¹, a value which agrees very well with that obtained in the present work.

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

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 form:

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

where η^* and T^* are the dimensionless variables defined as:

$$T^* = T / T_m \quad (5)$$

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

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

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

This equation, capable of describing most of the experimental data sets within their own stated accuracy, for temperatures from 590 K to 750 K, was established with 2 data sets composed of 28 data points and 2 different measurement techniques, as summarised in Table 4 and represented in Figure 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 Figure 5. The absolute uncertainty of the data calculated directly from this fit, using ISO definition ($k = 2$), is $0.066\text{ mPa}\cdot\text{s}$, a value smaller than the one produced by 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 5, for nominal temperatures, between 590 and 750 K, with uncertainty of $0.066\text{ mPa}\cdot\text{s}$ ($k = 2$).

5. Conclusions

New data for the viscosity of molten sodium nitrate between 590 and 752 K is 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 expected uncertainty of the present data is 2.1% .

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 590 K to 750 K, with an estimated absolute uncertainty of $0.066\text{ mPa}\cdot\text{s}$ ($k = 2$).

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Table 1. Physical parameters of the oscillating system for the present measurements with molten sodium nitrate

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

Table 2. Experimental results

T / K	T / s	$10^4 \Delta$	$\eta / \text{mPa.s}$
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 3. Uncertainty analysis

Parameter	$s_i / \%$	Contribution to $s_\eta / \%$
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 / %		2.1

Table 4. Primary sources of experimental data for the viscosity of sodium nitrate

Literature source	Technique	Temperature Range / K	No. of data points	Assigned uncertainty / $\pm \%$	Purity class
Zuca (1970) [19]	OS ^a	598 - 748	14	2-3	MPFP ^c
Nunes <i>et al.</i> (2005) [this work]	OC ^b	590 - 752	14	2	MPFP

^a Oscillating sphere; ^b Oscillating cup; ^c MPFP - manufacturers stated purity, further purification

Table 5. Recommended viscosities for molten NaNO₃

<i>T / K</i>	<i>η / mPa.s</i>	<i>T / K</i>	<i>η / mPa.s</i>
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		

Figure Captions

Figure 1. The viscosity of molten NaNO_3 : \circ - present work; line - MSDC recommendations [5].

Figure 2. Arrhenius representation of present data

Figure 3. Deviations of the available data from the recommendations of the MSDC correlation [5], in percentage. \bullet - present work; \diamond Zuca *et al.* [19]; - - - Brovkina *et al.* [8]; — Smotrakov *et al.* [15]; Rhodes *et al.* [16].

Figure 4. – Proposed reference correlation, Eq.(6), including the primary data, for $590 \leq T \leq 750$ K. \circ - present work; \diamond Zuca *et al.* [19].

Figure 5. – Deviations of primary data from the proposed correlation. Also shown are the MSDC correlation given by Eq.(1) [5] and the smoothed data of Brovkina *et al.* [8], Smotrakov *et al.* [15] and Rhodes *et al.* [16].

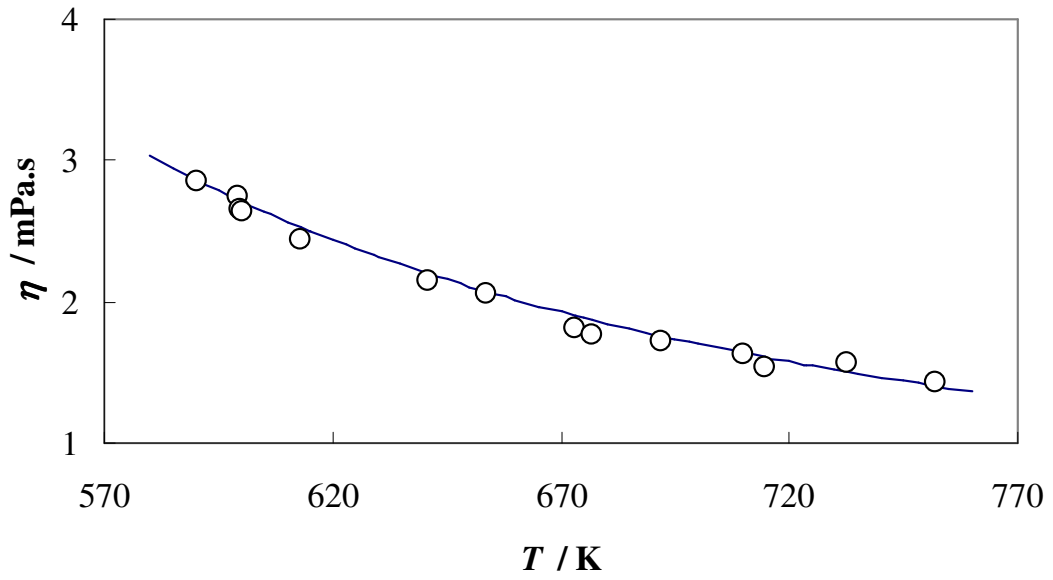


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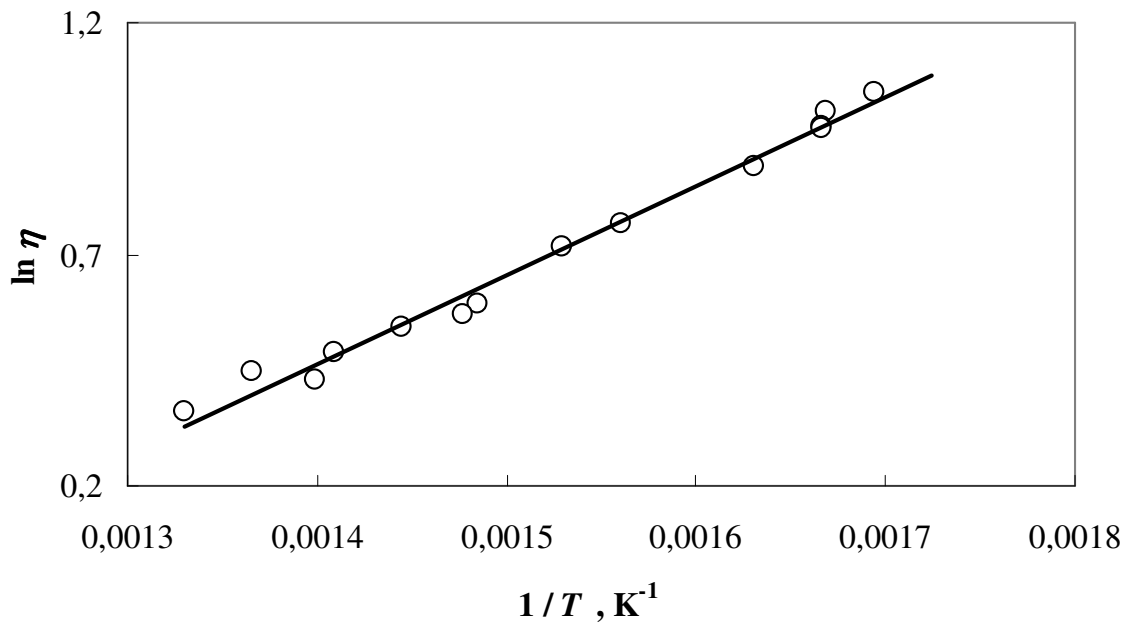


Figure 2. Arrhenius representation of present data

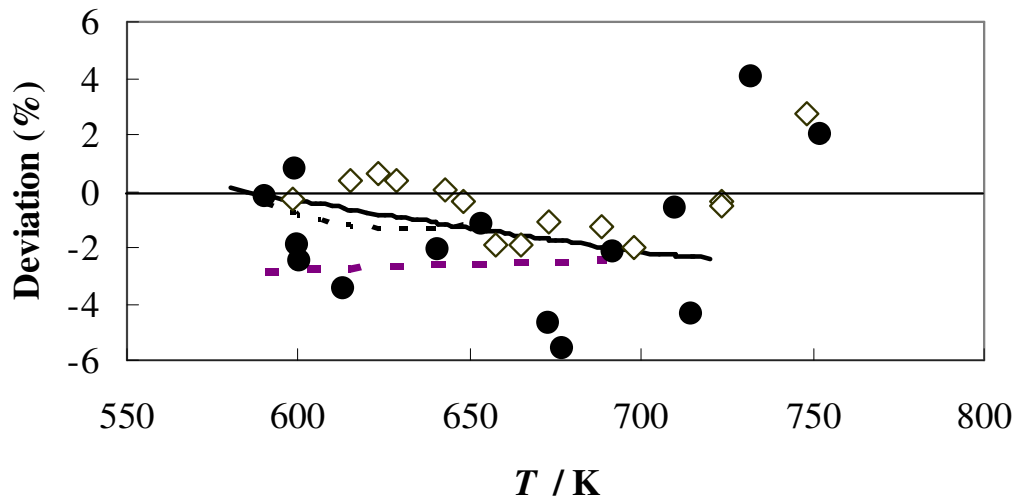


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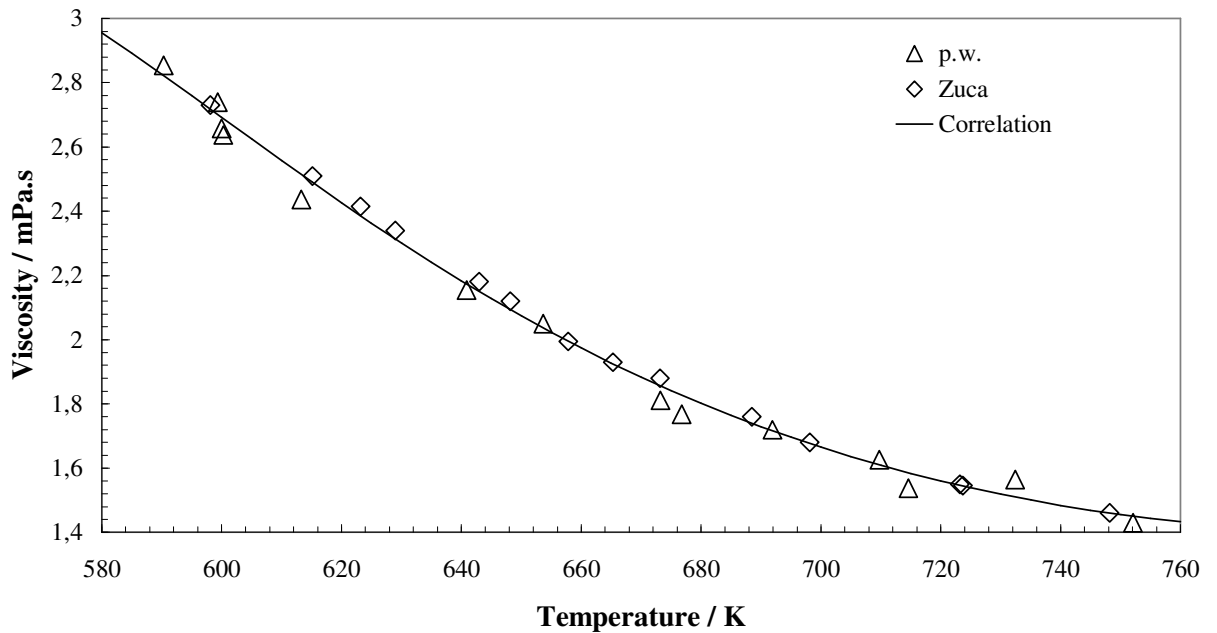


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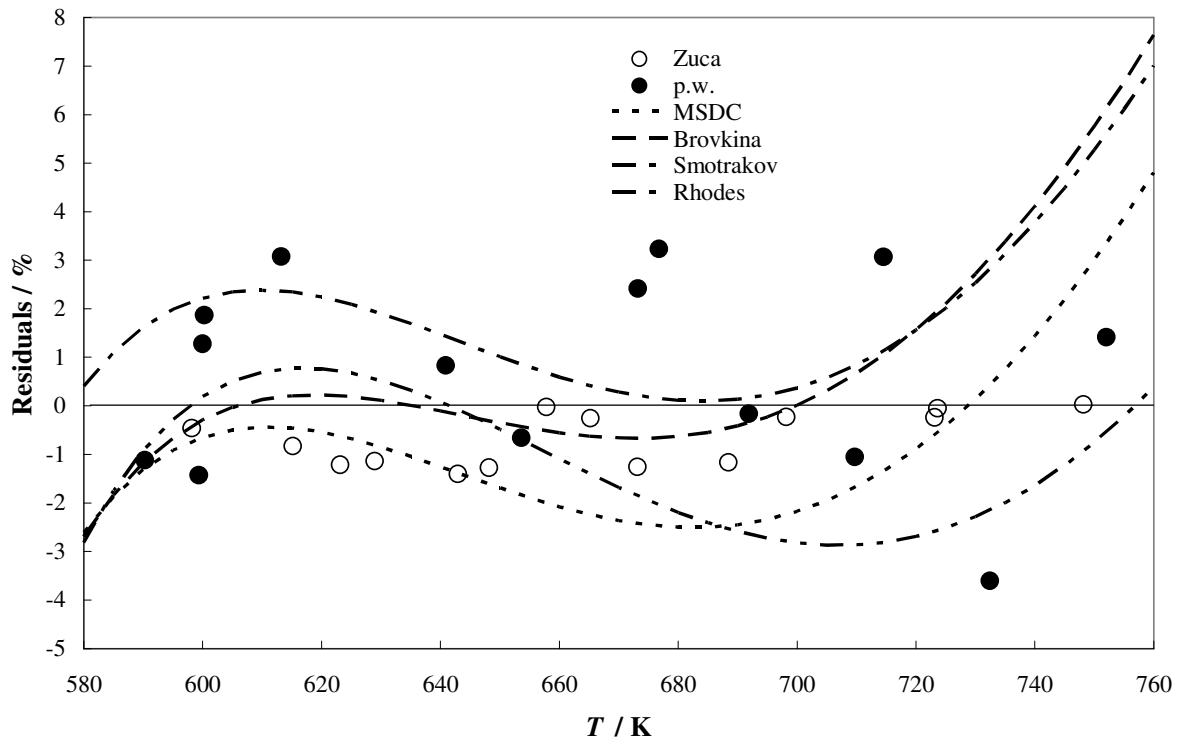


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