

Transport Properties Calculation for Some Pure Fluids Over Wide Ranges of Temperature and Pressure

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The paper presents the results obtained from computation of transport properties (viscosity and thermal conductivity) for pure fluids, representing a polar associating fluid (H₂O) and two non polar fluids (CO₂ and CH₄). The method of Chung et al. (1988) was applied for the prediction of transport properties using pseudo-experimental densities, and coupled with a cubic general equation of state (GEOS) for the calculation of fluids density. A comparison with available data (NIST data base) over wide ranges of pressure and temperature was made. The study reveals that the transport properties prediction based on GEOS densities is of the same accuracy as that given by using the pseudo-experimental values of density from NIST database for the three studied fluids.

Keywords: equation of state, transport properties, methane, carbon dioxide, water

Transport properties (viscosity, thermal conductivity) of fluids are important for efficient engineering design of processes in chemical and biochemical industries. Knowledge of transport properties is essential also for determination of intermolecular potential energy models and for development of theories for dense fluids. Generally, there are some difficulties in the study of transport properties, related to the accuracy of experimental measurements, as well as the complexity involved in theoretical treatments. It is impossible to measure transport properties for fluids and mixtures in all states of interest, and measurements need to be supplemented by theoretical calculations. An IUPAC volume edited by Millat et al. [1] has discussed the state of theory on transport properties of fluids, with regard to their correlation, prediction and estimation. The chapter 3 of the book [1] provides a definition of the levels of a hierarchy of correlation, prediction and estimation procedures that seek to generate the physical properties of fluids and their mixtures by means other than direct measurements.

Experimental transport properties are measured at different temperatures and pressures, but the density (or specific volume) is the important variable for theory. The conversion of data at given temperature and pressure to temperature and density is made by equations of state. In previous papers [2-4] we proposed the coupling of a density based transport properties model of Chung et al. [5] with a cubic general equation of state (GEOS).

Recently, several studies in the literature have presented similar approaches, coupling empirical density-based viscosity models with a cubic equation of state [6, 7], and with statistical association fluid theory (SAFT) in the so-called SAFT with cubic equation of state [8, 9].

Experimental data on transport properties have been stored in several computerized data banks as MIDAS, PPDS, IUPAC, TRC, CIS presented in IUPAC volume [1]. Accurate thermophysical properties – thermodynamic and transport properties – of a series of pure fluids are available at the National Institute of Standards and Technology (NIST) as Standard Reference Database Number 69 [10].

The available methods for correlation, prediction and estimation of transport properties of pure fluids and mixtures have been reviewed in two excellent books [1, 14], with examples of selected applications.

Using the new available data at NIST, this paper presents the estimation of transport properties of three pure fluids (methane, carbon dioxide and water) based on the method developed by Chung et al. [5] that can be applied to non-polar, polar and associating fluids on a wide range of temperature and pressure. The viscosity and thermal conductivity of dense fluids were empirically correlated as functions of density and temperature [5]. These correlations use Pitzer's acentric factor (ω), the dimensionless dipole moment (μ_r), and an empirically determined association parameter (κ) to characterize the molecular structure effect of polyatomic molecules, the polar effect, and the hydrogen-bonding effect, respectively. For the basic relationships of the method of Chung et al. [5], the reader is referred to original work [5], our paper [2], and Poling et al. [14].

As in the previous papers [2-4], we coupled this method with a cubic general equation of state [11-13], GEOS, used for computation of pure fluids density. A comparison with available transport properties data from NIST database [10], over a wide range of pressure and temperature was made. The computer program allows to extend the present study by using also other cubic EOS. This is possible due the generality of GEOS [12, 13]. The study reveals that the transport properties estimation based on GEOS densities is of the same accuracy as that given by using the pseudo-experimental densities values from NIST database for the three studied fluids.

Experimental part

The geos equation of state

The general cubic equation of state (GEOS) has the form [11-13]:

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V-d)^2 + c} \quad (1)$$

The four parameters a , b , c , d for a pure component are expressed by:

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$$a(T) = \alpha_c \beta(T_r); \quad a_c = \Omega_a \frac{R^2 T_c^2}{P_c}; \quad b = \Omega_b \frac{RT_c}{P_c};$$

$$c = \Omega_c \frac{R^2 T_c^2}{P_c^2}; \quad d = \Omega_d \frac{RT_c}{P_c};$$

The temperature function used is:

$$\beta(T_r) = T_r^{-m} \quad (3)$$

with the reduced temperature $T_r = T/T_c$.

The expressions of the parameters $\Omega_a, \Omega_b, \Omega_c, \Omega_d$ are:

$$\Omega_a = (1-B)^3; \quad \Omega_b = Z_c - B; \quad \Omega_c = (1-B)^2(B-0.25);$$

$$\Omega_d = Z_c - 0.5(1-B)$$

$$B = \frac{1+m}{\alpha_c + m} \quad (5)$$

with α_c - Riedel's criterion.

As observed, the a, b, c, d coefficients of the cubic GEOS equation are finally function of critical data (T_c, P_c and V_c), m and α_c parameters.

As pointed out previously [12, 13], the cubic GEOS equation is a general form for all the cubic equations of state with two, three and four parameters. This is the meaning of the statement *general cubic equation of state* used for GEOS.

Results and discussions

The method of Chung et al. [5] for estimation of transport properties is based on kinetic gas theory. The low pressure gas viscosity and thermal conductivity models are extended to fluids at high densities by introducing empirical correlations as functions of density and temperature. It is very important to predict with accuracy the fluid densities over wide ranges of temperature and pressure. The density errors generate deviations for the calculated values of the transport properties. In addition, the specific deviations of the Chung method should be also considered.

The GEOS equation of state was used to calculate the fluids density. Our previous studies [2-4] indicated that GEOS predicts better fluid densities in comparison with other cubic equations of state.

The fluids used in this study are methane, carbon dioxide and water. The investigated *PVT* range covers single-phase (liquid or gas) and two-phase (liquid-vapor) regions, using recommended NIST data (densities, viscosities and thermal conductivities) as pseudo-experimental values. The calculations were made with the computer program VISCON developed in our laboratory.

The properties of selected fluids (critical data, acentric factor, dipole moment, association parameter) are presented in table 1 together with the m and α_c parameters for GEOS. Ideal heat capacity at constant volume is

computed for methane, carbon dioxide and water with the equation and the coefficient values from literature [14]. Transport properties were studied for each selected fluid over wide ranges of *PVT* states as presented in table 2.

The calculation results using pseudo-experimental densities from NIST data base [10] for the three pure fluids are presented in table 3, as average absolute deviation (AAD%) of viscosity and thermal conductivity on the saturation curve and in single phase region at temperatures up to 1250 K and pressures up to 1000 bar. Higher values of average absolute deviations were obtained for water on the saturation curve and at high temperatures and pressures. In this way, the specific deviations of Chung et al. method can be estimated.

The deviations of viscosity and thermal conductivity calculated from Chung et al. method coupled with GEOS equation for density predictions are presented in table 3 too. There are not significant differences between the errors of Chung et al. method based on experimental densities and those based on densities predicted with GEOS equation for methane and carbon dioxide. For water, the deviations obtained when using densities predicted with cubic GEOS equation are slightly larger, but still comparable with those based on pseudo-experimental densities.

The averages cannot show the details of deviations between the experimental transport data and the calculations. Therefore, we illustrate in the following figures the representative results regarding the deviations between experimental data and calculated viscosities and thermal conductivities in the studied wide ranges of temperature and pressure.

The pressure-viscosity diagrams for methane are displayed in figures 1 and 2. The calculations using pseudo-experimental densities (NIST) and GEOS predicted densities are compared with available viscosity data of NIST. As seen, both sets of densities under consideration can be generally characterized by similar performance, which should be recognized as satisfactorily accurate. However, the deviations are slightly larger on the liquid saturation curve, and on the 100 K isotherm, when densities predicted by GEOS equation are used.

The pressure-thermal conductivity diagrams for methane are depicted in figures 3 and 4. The calculations using pseudo-experimental densities (NIST) and GEOS predicted densities are compared with available thermal conductivity data of NIST. In both diagrams deviations on vapor saturation curve can be observed at pressures higher than 10 bar between the calculated values and available NIST data. Figure 4 shows that deviations at low temperatures are slightly larger when using GEOS predicted densities, but calculated thermal conductivity is still satisfactorily accurate.

The calculated viscosities carbon dioxide versus pseudo-experimental data of NIST are presented in figures 5 and 6. There is a good agreement with NIST data, excepting the saturated liquid curve at pressures lower than 10 bar. The

	H ₂ O	CH ₄	CO ₂
Critical temperature (T_c , K)	647.096	190.564	304.1282
Critical pressure (P_c , bar)	220.640	45.992	73.773
Critical density (ρ_c , kg/m ³)	322.000	162.660	467.600
Critical volume (V_c , cm ³ /mol)	55.948	98.629	94.118
Acentric factor (ω)	0.3443	0.01142	0.22394
Reduced dipole moment (μ_r)	1.855	0	0
Association parameter (κ)	0.075	0	0
m (GEOS parameter)	0.2447	0.1205	0.2854
α_c (GEOS parameter)	7.5027	5.8573	6.9173

Table 1
VALUES OF GENERAL PROPERTIES OF
SELECTED FLUIDS [5, 10] AND m AND α_c
PARAMETERS FOR GEOS [13]

	H ₂ O	CH ₄	CO ₂
Saturation temperature range (<i>T</i> , K)	273.16 – 647.096	90.6941 – 190.564	216.592- 304.1282
Saturation pressure range (<i>P</i> , bar)	0.00611 – 220.52	0.11696 – 43.379	5.1796 – 71.224
Isotherm temperature range (<i>T</i> , K)	273.16-1275	90.6941- 625.0	216.592 - 1100.0
Isotherm pressure range (<i>P</i> , bar)	0.006 – 1000	0- 1000	0 – 1000

Table 2
TEMPERATURE AND PRESSURE RANGES OF EXPERIMENTAL DATA (VISCOSITY AND THERMAL CONDUCTIVITY) FROM NIST DATA BASE [10]

Range	Average absolute deviation (AAD %)			
	Viscosity		Thermal conductivity	
	NIST density	GEOS density	NIST density	GEOS density
CH₄				
Saturation	3.6	7.1	12.8	10.1
100K	3.6	8.9	3.6	6.2
120K	4.8	5.9	4.1	4.2
140K	4.6	5.3	4.8	5.0
180K	2.9	3.6	5.8	4.9
240K	2.1	3.0	4.5	4.4
340K	2.0	2.7	2.9	3.4
500K	2.3	2.7	4.1	4.4
Isotherms average	3.2	4.6	4.3	4.7
CO₂				
Saturation	3.7	5.3	13.2	14.3
250K	2.1	3.3	8.0	7.1
280K	1.1	2.6	7.4	7.6
304K	1.5	2.3	8.7	8.6
350K	1.7	2.6	4.4	5.2
500K	1.9	2.1	5.4	6.3
700K	2.1	2.4	5.4	6.0
900K	2.4	2.6	3.8	4.2
Isotherms average	1.8	2.6	6.2	6.4
H₂O				
Saturation	7.5	10.8	10.3	13.0
280 K	9.6	20.2	17.2	5.1
350 K	5.2	10.4	17.4	15.7
450 K	6.5	6.6	20.9	21.0
550 K	4.8	5.9	22.3	22.8
647.1 K	2.7	3.1	23.6	23.7
900 K	4.3	5.1	25.6	28.2
1100 K	6.2	6.7	25.8	27.9
1275 K	7.8	8.0	38.8	40.5
Isotherms average	5.9	8.3	23.9	23.1

Table 3
AVERAGE ABSOLUTE DEVIATION OF CALCULATED TRANSPORT PROPERTIES IN COMPARISON WITH EXPERIMENTAL DATA (NIST) [10]

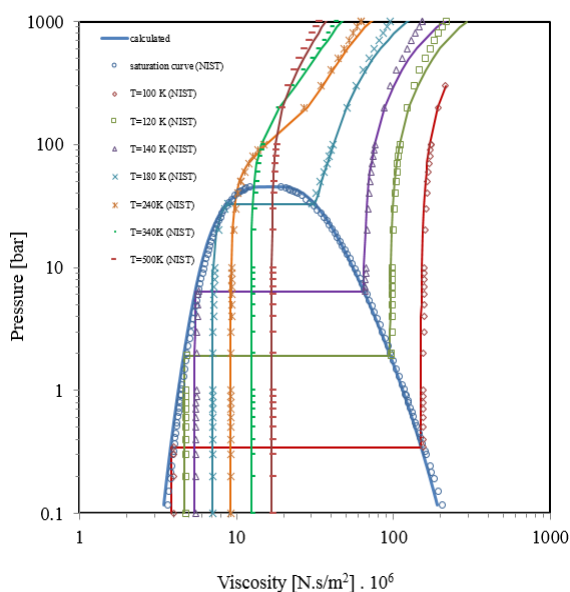


Fig. 1. Pressure-viscosity diagram for methane calculated with Chung et al. method using experimental densities of NIST compared to available viscosity data of NIST

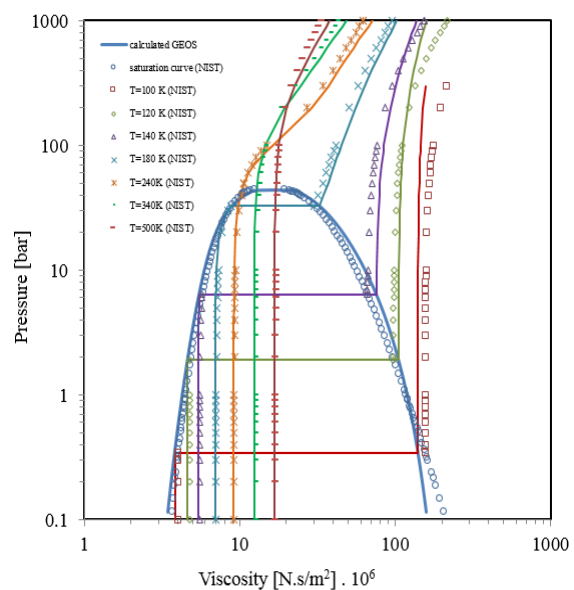


Fig. 2. Pressure-viscosity diagram for methane calculated with Chung et al. method using GEOS predicted densities compared to available viscosity data from NIST

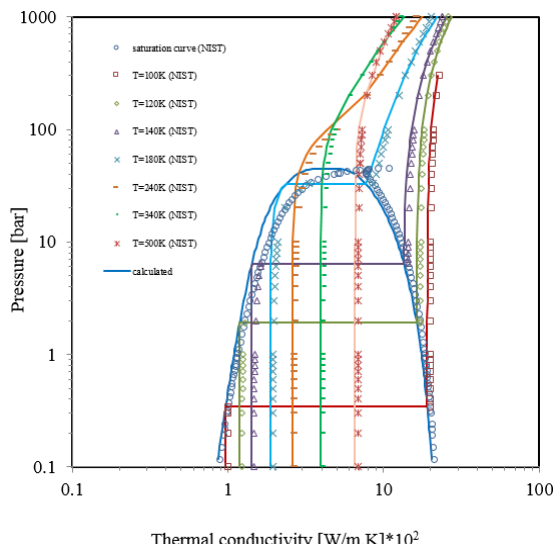


Fig. 3. Pressure-thermal conductivity diagram for methane calculated with Chung et al. method using experimental densities of NIST compared to available thermal conductivity data of NIST

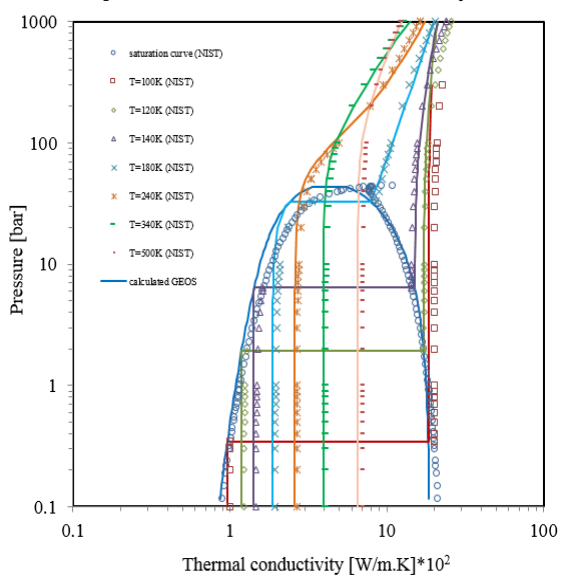


Fig. 4. Pressure-thermal conductivity diagram for methane calculated with Chung et al. method using GEOS predicted densities compared to available experimental data of NIST

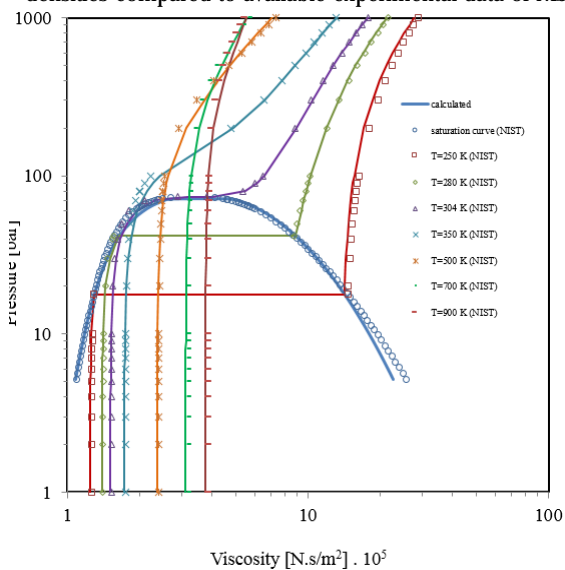


Fig. 5. Pressure-viscosity diagram for carbon dioxide calculated with Chung et al. method using experimental densities of NIST compared to available viscosity data of NIST

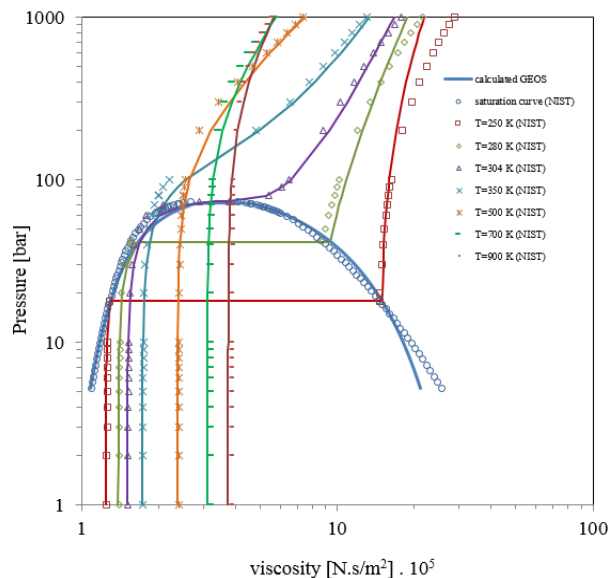


Fig. 6. Pressure-viscosity diagram for carbon dioxide calculated with Chung et al. method using GEOS predicted densities compared to available viscosity data from NIST

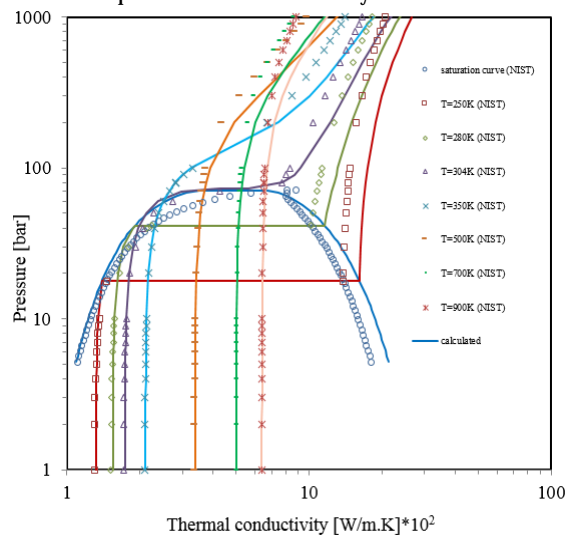


Fig. 7. Pressure-thermal conductivity diagram for carbon dioxide calculated with Chung et al. method using experimental densities of NIST compared to available thermal conductivity data of NIST

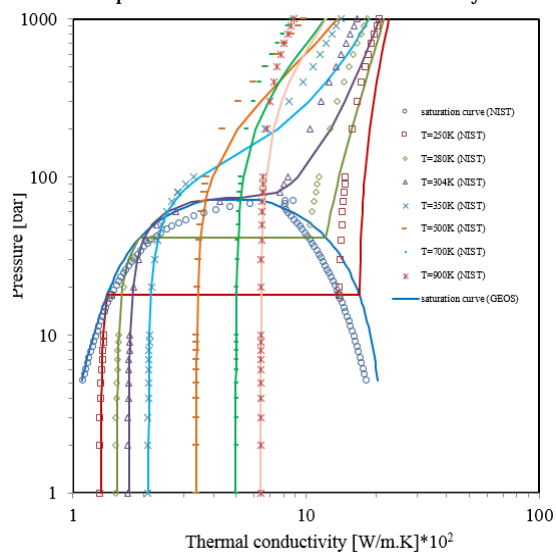


Fig. 8. Pressure-thermal conductivity diagram for carbon dioxide calculated with Chung et al. method using GEOS predicted densities compared to available experimental data of NIST

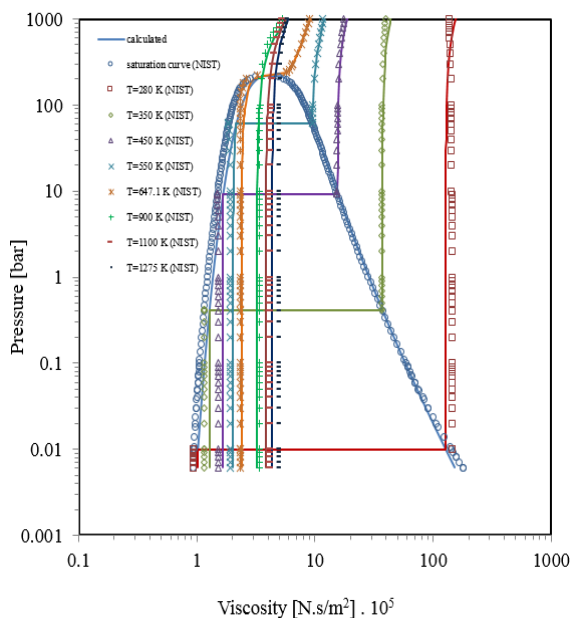


Fig. 9. Pressure-viscosity diagram for water calculated with Chung et al. method using experimental densities of NIST compared to available viscosity data of NIST

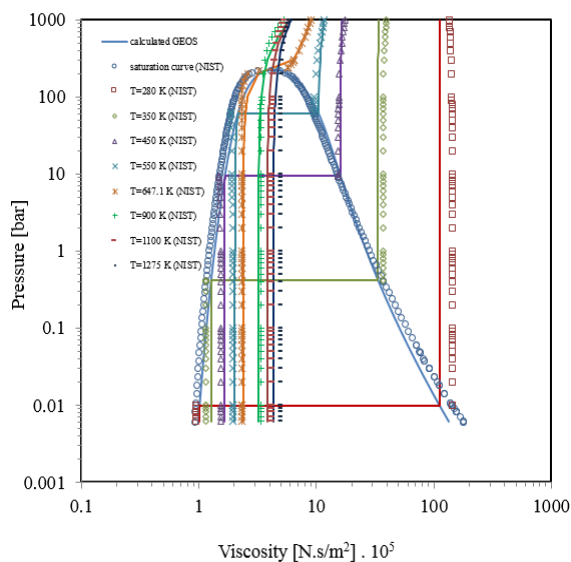


Fig. 10. Pressure-viscosity diagram for water calculated with Chung et al. method using GEOS predicted densities compared to available viscosity data from NIST calculations of the viscosities with densities predicted by GEOS equation are similarly on the saturation curve, some deviations appearing at high pressures on the 250 K isotherm.

The calculated thermal conductivity of carbon dioxide versus pseudo-experimental data of NIST are presented in figures 7 and 8. The deviations from NIST data are larger, notably on the saturated liquid curve and the corresponding liquid range of the isotherms.

Regarding the viscosities of water (figs.9, 10), there is a good agreement with NIST data. Slight larger deviations can be observed on the isotherms when densities predicted by GEOS equation are used, at low temperature (280 K) and at high pressures ($P > 100$ bar).

For thermal conductivity of water (figs.11, 12), the two diagrams present no significant difference on the saturation curve and in the single phase region. The use of densities predicted by GEOS equation does not lead to higher inaccuracy in the calculated thermal conductivity.

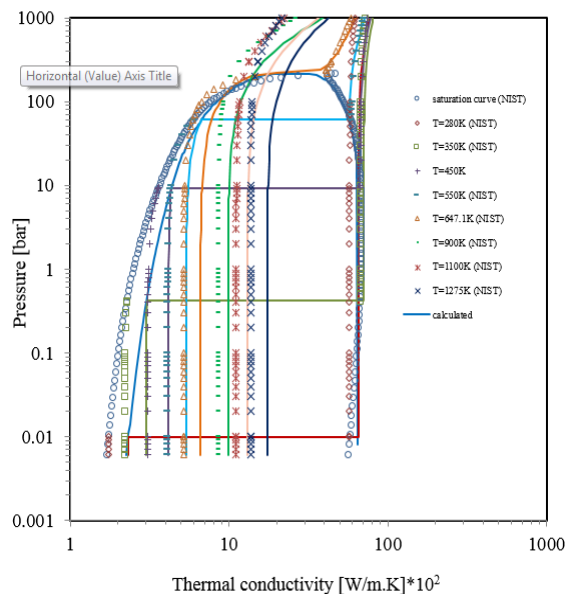


Fig. 11. Pressure-thermal conductivity diagram for water calculated with Chung et al. method using experimental densities of NIST compared to available thermal conductivity data of NIST

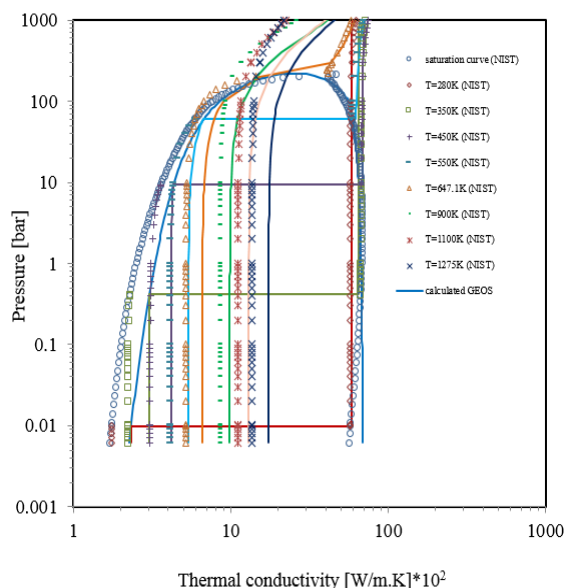


Fig. 12. Pressure-thermal conductivity diagram for water calculated with Chung et al. method using GEOS predicted densities compared to available experimental data of NIST

We can conclude that the calculated curves using the Chung et al. method coupled with GEOS equation show reasonable deviations for viscosity and thermal conductivity in comparison with experimental values (NIST), for all three investigated fluids. An extended study is in progress for the calculation of transport properties of a much larger data base of compounds available at NIST.

Conclusions

The viscosity and thermal conductivity of three fluids, methane, carbon dioxide and water are calculated on the saturation curves and in the single phase region at temperature up to 1250 K and pressure up to 1000 bar, and are compared with available values from NIST data base. The coupling of the Chung et al. method with the cubic general equation of state (GEOS) for the prediction of transport properties (viscosity and thermal conductivity) leads to good results, because the GEOS equation leads to

reliable densities for the fluids in wide ranges of temperature and pressure.

List of symbols

- a, b, c, d - parameters of GEOS equation
- AAD - absolute average deviation
- B - dimensionless parameter in GEOS, defined by eq. (5)
- EOS- equation of state
- m - GEOS parameter
- P, P^s - pressure, saturation pressure
- R - universal gas constant
- T - temperature
- V, V^l, V^v - molar volume, liquid volume, vapor volume

Greeks

- α_c - Riedel's criterium (parameter of GEOS)
- β - reduced temperature function of GEOS
- $\Omega_a, \Omega_b, \Omega_c, \Omega_d$ - parameters of GEOS
- ω - acentric factor
- μ - reduced dipole moment
- κ - association parameter
- ρ - density

Subscripts

- c - critical property
- r - reduced property

References

1. MILLAT J., DYMOND J. H., NIETO de CASTRO C. A., Transport Properties of Fluids. Their correlation, prediction and estimation, Cambridge University Press, 1996.
2. GEANA, D., FEROIU, V., Rev. Chim. (Bucharest), **41**, no.11-12, 1990, p. 872.
3. FEROIU, V., BJOLA, B., GEANA, D., Rev. Chim. (Bucharest), **46**, no. 9, 1995, p. 822.
4. FEROIU, V., BJOLA, B., GEANA, D., Revue Roumaine de Chimie, **43**(5), 1998, p. 461.
5. CHUNG T. H., AJLAN M., LEE L. L., STARLING K.E., Ind. Eng. Chem. Res., **27**, 1988, p.671.
6. MOTAHHARI H., SATYRO M. A., YARRANTON, H. W., Ind. Eng. Chem. Res., **50**, 2011, p. 12831.
7. MOTAHHARI H., SATYRO M. A., YARRANTON, H. W., Fluid Phase Equilibria, **56**, 2012, p. 322. 322"323, 2012, 56.
8. POLISHUK I, Ind. Eng. Chem. Res., **51**, 2012, p. 13527.
9. POLISHUK I, YITZHAK A., Ind. Eng. Chem. Res., **53**, 2014, p. 959.
10. NIST - Thermophysical Properties of Fluid Systems, Database 2010, <http://webbook.nist.gov/chemistry/fluid/>.
11. GEANA, D., Rev. Chim. (Bucharest), **37**, 1986, p. 303, 951; **38**, 1987, p. 975.
12. GEANA, D., FEROIU V., Fluid Phase Equilibria, **174**, 2000, p. 51.
13. GEANA, D., FEROIU V., Equations of State. Applications to Phase Equilibria, Ed. Tehnica, Bucuresti, 2000.
14. POLING B. E., PRAUSNITZ J. M., O'CONNELL J. P., The Properties of Gases and Liquids, McGraw-Hill, fifth edition, 2001

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