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Modeling of density and calculations of derived volumetric properties for *n*-hexane, toluene and dichloromethane at pressures 0.1–60 MPa and temperatures 288.15–413.15 K

GORICA R. IVANIŠ#, ALEKSANDAR Ž. TASIĆ, IVONA R. RADOVIĆ#, BOJAN D. DJORDJEVIĆ#, SLOBODAN P. ŠERBANOVIĆ# and MIRJANA LJ. KIJEVČANIN*#

Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia

Abstract: Densities data of *n*-hexane, toluene and dichloromethane at temperatures 288.15–413.15 K and at pressures 0.1–60 MPa, determined in a previous article, were fitted to the modified Tait equation of state. The fitted temperature–pressure dependent density data were used to calculate the following derived properties: the isothermal compressibility, the isobaric thermal expansivity, the difference between specific heat capacity at constant pressure and at constant volume and the internal pressure, over the entire temperature and pressure intervals specified above. In order to assess the proposed modeling procedure, the obtained values for the isothermal compressibility and the isobaric thermal expansivity were compared with the corresponding literature data. The average absolute percentage deviations for the isothermal compressibility were for *n*-hexane 2.01–3.64 %, for toluene 0.64–2.48 % and for dichloromethane 1.81–3.20 %, and for the isobaric thermal expansivity, they were for *n*-hexane 1.31–4.17 %, for toluene 0.71–2.45 % and for dichloromethane 1.16–1.61 %. By comparing the obtained deviations values with those found in the literature, it could be concluded that the presented results agree well with the literature data.

Keywords: high pressure; isobaric thermal expansivity; isothermal compressibility; *n*-hexane; toluene; dichloromethane.

INTRODUCTION

In a previous article,[1] the experimental densities of compressed liquid *n*-hexane, toluene and dichloromethane, determined using a set-up based on a density measuring cell AP DMA HP coupled with a DMA 5000 vibrating tube densimeter, were reported. The measurements were performed over the temperature

and pressure ranges: 288.15–413.15 K and 0.1–60 MPa, respectively. It was shown that the obtained data are in good and acceptable agreement with the corresponding literature values.

This paper, as well as the previous one related to the density measurements for the same pure compounds-solvents, is a part of the systematic investigation of crucial thermodynamic properties of important solvents, used in both industry and the laboratory.

Correlation of the volumetric information mentioned above allows the evaluation of temperature and pressure effects on various thermomechanical properties,[2] such as isothermal compressibility, κ_T, and isobaric thermal expansivity, α_p; based on these properties, the internal pressure p_{int} and the difference of the isobaric and isochoric heat capacities, C_p–C_V, can also be determined. By coupling the mentioned isothermal and isobaric properties κ_T and α_p, and using the isentropic compressibility, κ_S, which is related to the thermodynamic speed of sound, some additional properties can be calculated; in this respect, the isobaric heat capacity, C_p, and isochoric heat capacity, C_V, could be mentioned.

Various methods, dealing with the correlation of measured densities as a function of temperature and pressure, have been established in the literature. In the present work, a Tait-like equation was applied. The obtained correlation was used to compute the aforementioned parameters.

CALCULATIONS

The experimental density data presented in a previous paper[1] were fitted to the Tait-like equation:

$$\rho(T,p) = \frac{\rho^{\text{ref}}(T)}{1 - C(T)\ln\left(\dfrac{B(T) + p}{B(T) + p^{\text{ref}}}\right)} \tag{1}$$

where, T and p refer to temperature and pressure, respectively, and $C(T)$ and $B(T)$ are parameters that were assumed to be temperature dependent and can be calculated from the second order polynomials:

$$B(T) = \sum_{i=0}^{2} b_i T^i \tag{2}$$

$$C(T) = \sum_{i=0}^{2} c_i T^i \tag{3}$$

ρ^{ref} is the density at the reference pressure, p^{ref}, and it can be calculated from the second order polynomial:

$$\rho^{\text{ref}}(T) = \sum_{i=0}^{2} a_i T^i \tag{4}$$

In Eqs. (2)–(4), a_i, b_i and c_i are adjustable parameters.

As stated previously, a number of derived properties exist that can be calculated from density data.

The isothermal compressibility, κ_T, represents a measure of the sensitivity of density to a pressure change at constant temperature and it depends on the fluid structure. It can be expressed as:

$$\kappa_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T \tag{5}$$

Coupling Eqs. (1) and (5) leads to the expression for the calculation of κ_T:

$$\kappa_T = \frac{C(T)}{\left(B(T)+p\right)\left(1-C(T)\ln\dfrac{B(T)+p}{B(T)+p^{\mathrm{ref}}}\right)} \tag{6}$$

The isobaric thermal expansivity, α_p, is a measure of the relative fluid density change in response to a temperature change at constant pressure:

$$\alpha_p = \frac{1}{\rho}\left(\frac{\partial p}{\partial T}\right)_\rho\left(\frac{\partial p}{\partial \rho}\right)_T^{-1} = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \tag{7}$$

When Eq. (1) is included into Eq. (7), an expression for the calculation of the isobaric thermal expansivity is obtained:

$$\alpha_p = \frac{-\rho^{\mathrm{ref}\prime}(T)}{\rho^{\mathrm{ref}}(T)} - \frac{C(T)\dfrac{B'(T)(p^{\mathrm{ref}}-p)}{(B(T)+p)(B(T)+p^{\mathrm{ref}})}+C'(T)\ln\dfrac{B(T)+p}{B(T)+p^{\mathrm{ref}}}}{\left(1-C(T)\ln\dfrac{B(T)+p}{B(T)+p^{\mathrm{ref}}}\right)} \tag{8}$$

where $\rho^{\mathrm{ref}\prime}(T)$, $B'(T)$ and $C'(T)$ stay for the derivatives of the parameters ρ^{ref}, $B(T)$ and $C(T)$ of Eq. (1), respectively:

$$\rho^{\mathrm{ref}\prime} = \sum_{i=0}^{2} i a_i T^{i-1} \tag{9}$$

$$B' = \sum_{i=0}^{2} i b_i T^{i-1} \tag{10}$$

$$C' = \sum_{i=0}^{2} i c_i T^{i-1} \tag{11}$$

Another thermodynamic property that can be calculated from the aforementioned equations is the ratio of the isobaric thermal expansivity to the isothermal compressibility, $i.e.$, the thermal pressure coefficient, γ:

$$\gamma = \frac{\alpha_p}{\kappa_T} \tag{12}$$

The thermal pressure coefficient is associated with the internal pressure, p_{int}, which represents the change of the internal energy of a sample when it isothermally expands or

contracts, thus describing intermolecular interactions. It is easy to calculate the internal pressure when the isobaric thermal expansivity and the isothermal compressibility are known:

$$p_{\text{int}} = \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_\rho - p = T\gamma - p = \frac{T\alpha_p}{\kappa_T}p \tag{13}$$

where, U denotes the internal energy of a sample and V is its volume.

An important thermodynamic property that can be calculated from the quantities defined above is the difference between specific heat capacity at constant pressure, c_p, and specific heat capacity at constant volume, C_V:

$$C_p = C_V + T\frac{\left(\frac{\partial p}{\partial T}\right)_\rho^2}{\rho^2\left(\frac{\partial p}{\partial \rho}\right)_T} \tag{14}$$

Linking Eqs. (5) and (7) with Eq. (14) gives the expression:

$$C_p - C_V = \frac{\alpha_p^2 T}{\rho\kappa_T} \tag{15}$$

The relation given by Eq. (15) is significant because it can be used to calculate the heat capacity at constant volume instead of its experimental determination. Heat capacity at constant pressure can be measured or calculated from speed of sound data and the above-defined coefficients by combining Eqs. (16)–(18).

Isentropic compressibility, κ_S, is defined as:

$$\kappa_S = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_S \tag{16}$$

and can be calculated as follows:

$$\kappa_S = \frac{1}{\rho u^2} \tag{17}$$

where, u is the speed of sound waves spreading through the sample.

Further, the specific heat capacity at constant pressure can be obtained from the equation:

$$C_p = \frac{\alpha_p^2 T}{\rho(\kappa_T - \kappa_S)} \tag{18}$$

RESULTS AND DISCUSSION

The criteria used to assess the quality of fitting were the absolute average percentage deviation, *AAD*, the percentage maximum deviation, *MD*, the average percentage deviation, *Bias*, and standard deviation, σ:

$$AAD = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{\rho_i^{\text{exp}} - \rho_i^{\text{cal}}}{\rho_i^{\text{exp}}}\right| \tag{19}$$

$$MD = \max\left(100 \left| \frac{\rho_i^{\mathrm{exp}} - \rho_i^{\mathrm{cal}}}{\rho_i^{\mathrm{exp}}} \right| \right), \; i=1,N \tag{20}$$

$$Bias = \frac{100}{N} \sum_{i=1}^{N} \frac{\rho_i^{\mathrm{exp}} - \rho_i^{\mathrm{cal}}}{\rho_i^{\mathrm{exp}}} \tag{21}$$

$$\sigma = \sqrt{\frac{\sum_{i=1}^{N} \left(\rho_i^{\mathrm{exp}} - \rho_i^{\mathrm{cal}} \right)^2}{N - m}} \tag{22}$$

where, ρ^{exp} is the experimentally determined density, ρ^{cal} denotes the density value obtained from Eq. (1), N is the number of experimental data and m represents the number of parameters included in the correlation of the Tait-like equation.

The reference pressure in Eq. (1) was chosen to be 1 MPa. Hence, the density data of a sample at 1 MPa were first used for the optimization of the a_i parameters. Then, all the density data, presented for the studied compounds in a previous work[1] were employed for the determination of the b_i and c_i parameters. All the parameters were obtained applying the Marquardt algorithm for the minimization of the objective function, *i.e.*, the standard deviation.

The obtained parameters of Eqs. (2)–(4) and the corresponding deviations are given in Table I.

TABLE I. Fitting parameters of Eqs. (2)–(4)

Parameter	*n*-Hexane	Toluene	Dichloromethane
a_0 / kg m^{-3}	791.280	1082.499	1599.209
a_1 / kg m^{-3} K^{-1}	−0.035271	−0.55689	−0.10023
a_2 / kg m^{-3} K^{-2}	−0.14039×10^{-2}	−0.60343×10^{-3}	−0.28367×10^{-2}
b_0 / MPa	349.513	504.019	654.433
b_1 / MPa K^{-1}	−1.46894	−1.96093	−2.80478
b_2 / MPa K^{-2}	0.15855×10^{-2}	0.20102×10^{-2}	0.30968×10^{-2}
c_0	0.18450	0.15696	0.29779
c_1 / K^{-1}	−0.58799×10^{-3}	−0.39307×10^{-3}	−0.11415×10^{-2}
c_2 / K^{-2}	0.87278×10^{-6}	0.54981×10^{-6}	0.15929×10^{-5}
AAD / %	0.023	0.008	0.019
MD / %	0.191	0.028	0.128
Bias / %	0.002	0.003	0.001
σ / kg m^{-3}	0.209	0.090	0.332

From the presented deviation values, it could be concluded that the proposed Eqs.(1)–(4) fit well the densities of the selected substances.

The isothermal compressibility, the isobaric thermal expansivity, the difference between the specific heat capacities at constant pressure and constant volume and the internal pressure for all three examined compounds, at temperatures 288.15–413.15 K and pressures 0.1–60 MPa, are presented in Tables S-I–S-III of the Supplementary material to this paper.

In order to verify the accuracy of the density data modeling and the procedure of calculating the derived properties listed in the previous section, the obtained values of the isothermal compressibility and isobaric thermal expansivity were compared to those found in the literature. The criteria for the evaluation of the agreement were the same as in a previous paper:[1] the absolute average percentage deviation (*AAD*), the percentage maximum deviation (*MD*) and the average percentage deviation (*Bias*), but here, instead of density, the corresponding values of the isothermal compressibility and the isobaric thermal were used.

n-*Hexane*

Data on *n*-hexane density were modeled and the calculated values of the isothermal compressibility, given in Table S-I, were compared to those published by Daridon *et al.*[3] The comparison was performed at temperatures 293.15––373.15 K and at pressures 0.1–60 MPa; the obtained deviations were: *AAD* = = 3.64 %, *MD* = 5.67 % and Bias = –3.64 % (Fig. 1a).

Aiming at assessing the accuracy of the presented density modeling, the isentropic compressibility was compared. Values of the speed of sound were retrieved from the literature[3] and the isentropic compressibility was calculated using Eq. (17); the obtained values were compared to the literature data[3] at temperatures 293.15–373.15 K and pressures 5–60 MPa. The corresponding deviations were *AAD* = 0.10 %, *MD* = 0.29 % and *Bias* = 0.01 %; these deviations represent one more proof that the modeling procedure was properly selected.

The calculated isothermal compressibility data were compared to those given by Rendzio *et al.*[4] at several temperatures in the range 313.15–363.15 K and at pressures 0.1–60 MPa. Values of the criteria were *AAD* = 2.63 %, *MD* = 4.73 % and *Bias* = –2.56 %.

Rendzio *et al.*[4] also reported equations for the calculation of isobaric thermal expansivity. Hence, their data with those reported in Table S-I were compared at temperatures 288.15–393.15 K and at pressures 0.1–60 MPa. The obtained deviations were *AAD* = 0.99 %, *MD* = 3.73 % and *Bias* = –0.68 %, indicating very good agreement (shown in Fig. 1b).

Tronkoso *et al.*[5] gave the isothermal compressibility of *n*-hexane in the somewhat narrower ranges of pressure and temperature than did the aforementioned authors, and hence the comparison is realized at temperatures 293.15–

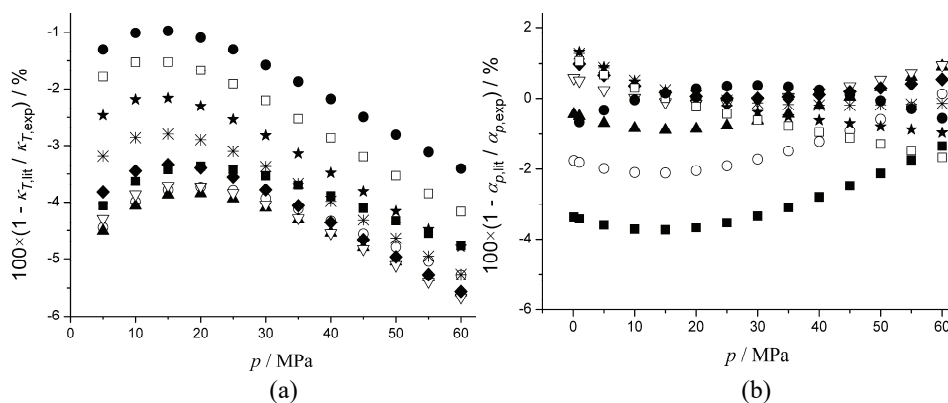–413.15 K and at pressures 0.1–40 MPa. The deviations were *AAD* = 2.01 %, *MD* = 3.31 % and *Bias* = –2.01 %.

Fig. 1. Comparisons of the calculated derived properties with literature data for *n*-hexane: a) the isothermal compressibility with Daridon *et al.*[3] at (■) 293.15, (○) 303.15, (▲) 313.15, (▽) 323.15, (◆) 323.15, (✳) 343.15, (★) 353.15, (□) 363.15 and (●) 373.15 K; b) the isobaric thermal expansivity with Rendzio *et al.*[4] at (■) 288.15, (○) 303.15, (▲) 318.15, (▽) 333.15, (◆) 343.15, (✳) 353.15, (★) 363.15, (□) 373.15 and (●) 393.15 K.

The values of the isobaric thermal expansivity presented in this work were compared to those reported by Zhou *et al.*[6] at temperatures 293.15–413.15 K and at pressures 0.1–40 MPa and the obtained deviation criteria were: *AAD* = 4.17 %, *MD* = 6.08 % and *Bias* = –3.86 %.

Cardeirine *et al.*[7] gave the isobaric thermal expansivities at atmospheric pressure and at temperatures 293.15–333.5 K. The results of the comparison of those data and the present ones were *AAD* = 2.06 %, M*D* = 3.71 % and *Bias* = = –1.69 %.

Considering the values of the deviations that the cited authors reported in their papers, it could be concluded that the agreement of the present results with those found in the literature was acceptable.

Toluene

The isothermal compressibility data of toluene, given in Table S-II, were compared to those reported by Chorazewski *et al.*[8] The comparison was performed at temperatures 303.15–373.15 K and pressures 0.1–60 MPa and the obtained results were: *AAD* = 1.19 %, *MD* = 1.97 % and *Bias* = –1.18 % (Fig. 2a).

Chorazewski *et al.*[8] gave equations for the determination of the isobaric thermal expansivities of toluene and hence, the data presented in Table S-II were compared to these values over wide ranges of temperature and pressure, 288.15–
–413.15 K and 0.1–60 MPa, respectively. The obtained deviations were *AAD* =
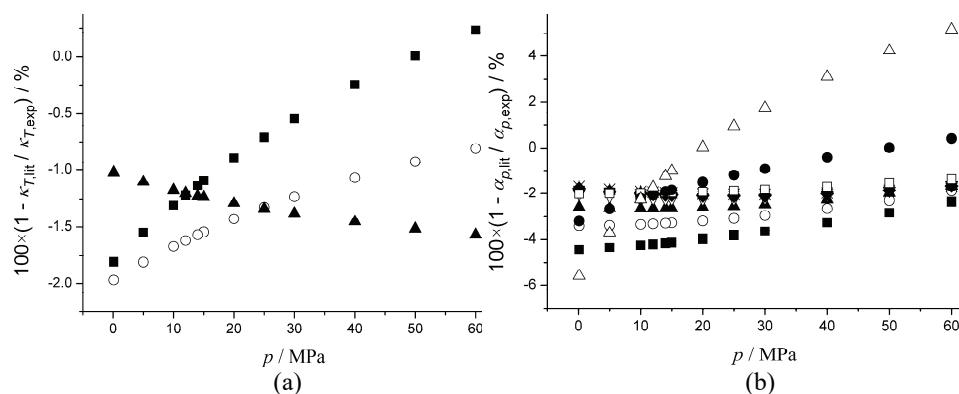= 2.45 %, *MD* = 5.18 % and *Bias* = –2.29 % (Fig. 2a).

Fig. 2. Comparisons of the calculated derived properties with literature data for toluene: a) the isothermal compressibility with Chorazewski *et al.*[8] at (■) 303.15, (○) 323.15 and (▲) 373.15 K, and b) the isobaric thermal expansivity with Chorazewski *et al.*[8] at (■) 288.15, (○) 303.15, (▲) 318.15, (▽) 333.15, (◆) 343.15, (✳) 353.15, (★) 363.15, (□) 373.15, (●) 393.15 and (△) 413.15 K.

The values of the isothermal compressibility obtained in this paper were also compared to those given by Zéberg-Mikkelsen *et al.*[9] at temperatures 303.15––333.15 K and at pressures 0.1–30 MPa. The deviations were rather low: $AAD =$ $= 0.64$ %, $MD = 1.48$ % and $Bias = -0.20$ %.

In addition, Zéberg-Mikkelsen *et al.*[9] reported the isobaric thermal expansivities of toluene at the same temperatures and pressures as they did for the isothermal compressibility. For this property, the values of the appropriate criteria were $AAD = 0.71$ %, $MD = 2.39$ % and $Bias = -0.17$ %.

Easteal *et al.*[10] presented the values for the isothermal compressibility and the isobaric thermal expansivity of toluene under the same conditions. The comparison was performed at temperatures 288.15–323.15 K and pressures 0.1–50 MPa and the attained results were: for the isothermal compressibility $AAD = 2.48$ %, $MD = 4.01$ % and $Bias = -2.38$ % and for the isobaric thermal expansivity $AAD = 1.29$ %, $MD = 2.63$ % and $Bias = -0.21$ %.

The values of the deviation criteria obtained for the isothermal compressibility and the isobaric thermal expansivity of toluene were sufficiently low for it to be concluded that the results calculated in this work agree well with the literature data.

Dichloromethane

Gonçalves *et al.*[11] recently presented results for the isothermal compressibility and the isobaric thermal expansivity for dichloromethane at temperatures 300–400 K and pressures 0.1–100 MPa. The application of Eqs. (1)–(11) enabled the calculation of the values for the mentioned properties at the same temperatures and at pressures up to 60 MPa. A comparison of the calculated data with

literature results[11] resulted in the following: for the isothermal compressibility *AAD* was 1.81 %, *MD* was 5.04 % and *Bias* was 0.38 % (Fig. 3a) and for the isobaric thermal expansivity *AAD* = 1.16 %, *MD* = 3.53 % and *Bias* = 0.19 % (Fig. 3b).
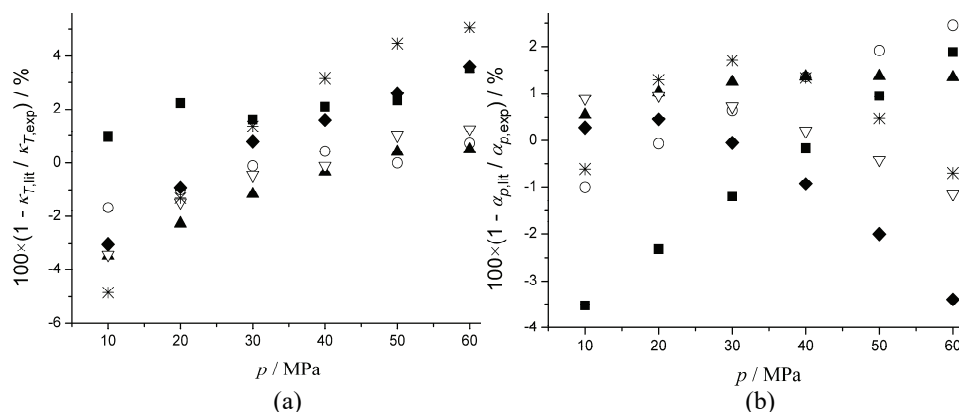

Fig. 3. Comparisons of the calculated derived properties with literature data for dichloromethane: a) the isothermal compressibility with Ferreira *et al.*[11] at (■) 300, (○) 320, (▲) 340, (▽) 360, (◆) 380 and (✳) 400 K, and b) the isobaric thermal expansivity with Ferreira *et al.*[11] at (■) 300, (○) 320, (▲) 340, (▽) 360, (◆) 380 and (✳) 400 K.

Easteal *et al.*[10] gave the values of the isothermal compressibility and the isobaric thermal expansivity of dichloromethane at two temperatures, 288.15 and 298.15 K, and at pressures 0.1–50 MPa. The isothermal values presented in Table S-III agree with those taken from literature[10] with: *AAD* of 3.20 %, *MD* of 3.56 % and Bias of 3.20 %. When comparing the isobaric thermal expansivities from Table S-III, the following deviations were obtained: *AAD* = 1.61 %, *MD* = 3.33% and *Bias* = –1.43 %.

Although the mentioned values of the criteria for the comparison of both properties for dichloromethane were slightly higher than those for toluene, they could still be considered as good.

CONCLUSIONS

The density data of *n*-hexane, toluene and dichloromethane, reported in a previous paper,[1] were fitted to a Tait-like equation; the obtained parameters, and the results of assessment of the modeling, by the comparison with literature information, are given in this work. The calculated values of the isothermal compressibility, the isobaric thermal expansivity, the difference between specific heat capacity at constant pressure and at constant volume as well as the internal pressure for each of three investigated compounds, at temperatures 288.15–413.15 K and at pressures 0.1–60 MPa, are also presented herein. In order to assess the proposed modeling procedure, the obtained values of the isothermal compres-

sibility and the isobaric thermal expansivity were compared to corresponding literature data, and the good agreement was achieved.

SUPPLEMENTARY MATERIAL

The calculated values of the isothermal compressibility, κ_T, the isobaric thermal expansivity, α_p, the difference between the specific heat capacities at constant pressure and constant volume, C_p–C_V, and the internal pressure, p_{int}, for *n*-hexane, toluene and dichloromethane, at temperatures 288.15–413.15 K and pressures 0.1–60 MPa, are available electronically from http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

ИЗВОД

МОДЕЛОВАЊЕ ГУСТИНЕ И ПРОРАЧУН ИЗВЕДЕНИХ ВОЛУМЕТРИЈСКИХ СВОЈСТАВА НА ПРИТИСЦИМА ОД 0,1 ДО 60 МПа И НА ТЕМПЕРАТУРАМА ОД 288,15 ДО 413,15 К

ГОРИЦА Р. ИВАНИШ, АЛЕКСАНДАР Ж. ТАСИЋ, ИВОНА Р. РАДОВИЋ, БОЈАН Д. ЂОРЂЕВИЋ, СЛОБОДАН П. ШЕРБАНОВИЋ и МИРЈАНА Љ. КИЈЕВЧАНИН

Технолошко-металурушки факултет, Универзитет у Београду, Карнегијева 4, 11120 Београд

Густине *n*-хексана, толуена и дихлорметана на температурама 288,15–413,15 К и притисцима 0,1–60 МПа су моделоване прилагођеном Тејтовом једначином. У овом раду су наведене одговарајуће једначине за рачунање изотермске стишљивости, изобарске топлотне експанзивности, разлике између специфичног топлотног капацитета при сталном притиску и оног при сталној запремини и унутрашњег притиска у читавом поменутом опсегу притисака и температура, као и вредности наведених изведених величина. У циљу процене предложене методе моделовања поређене су добијене вредности коефицијента изотермске стишљивости и коефицијента изобарског топлотног ширења са онима из литературе. Просечно апсолутно процентуално одступање за изотермску стишљивост је било: за *n*-хексан 2,01–3,64 %, за толуен 0,64–2,48 % и за дихлорметан 1,81––3,20 %; а за изобарско топлотну експанзивност: за *n*-хексан 1,31–4,17 %, за толуен 0,71–2,45 % и за дихлорметан 1,16–1,61 %. Поређењем добијених одступања са оним која се могу наћи у литератури долази се до закључка да се представљени резултати добро слажу са литературним.

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