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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

On Application of PC–SAFT Model for Estimating the Speed of Sound in Synthetic and Natural Oil-and-Gas Mixtures

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Abstract—Opportunities given by applying the PC–SAFT (Perturbed Chain–Statistical Association Fluid Theory) for estimating and calculating the speed of sound in natural gas were considered. Examples are presented of prognosticating the density and the speed of sound for five multicomponent gas mixtures containing alkanes, isoalkanes, nitrogen, and carbon dioxide in a wide range of temperatures and pressures (250–450 K and 0.5–60 MPa). The results of calculations are compared with published experimental data. It is shown that the model reproduces with high precision the experimental values of the density and the speed of sound.

Keywords: thermodynamic properties, speed of sound, modeling, equation of state, PC–SAFT, oil-and-gas mixtures, natural gas

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The speed of sound is an important thermophysical quantity widely used in practical purposes for characterizing homogeneous and heterogeneous mixtures, estimating the density of reservoir fluids in oil wells in a wide range of external conditions [1, 2]. Together with temperature and pressure, speed of sound is one of easily experimentally determined parameters, which can be used to find the molecular mass and the density of a gas mixture and estimate the consumption of natural gas at gas-distributing plants [3, 4]. The thermodynamic speed of sound is of particular interest for researchers verifying the opportunities of equations of state for its precise description (this quantity is related to the adiabatic compressibility of a substance and is expressed via the second-order derivative of the Helmholtz energy with respect to volume). The calculation of the speed of sound u is based on the knowledge of thermodynamic quantities, such as the total volume V (or density), isobaric C_P and isochoric C_V heat capacities, and derivative of pressure over the total volume at fixed temperature and total number of moles in the system $(\partial P/\partial V)T,n$ in accordance with the known formula

$$u = \sqrt{-\frac{V^2}{M_w}\frac{C_P}{C_V}\left(\frac{\partial P}{\partial V}\right)_{T,n}},$$

where $M_w = \sum_i n_i M_{Wi}$ is the molecular mass of the system with consideration for the number of moles and molecular masses of ith components.

Equations of the SAFT (Statistical Association Fluid Theory) family stand out among modern equations of state, tested in the last 5–7 years by various researchers in order to improve the quantitative description of the speed of sound in pure and mixed fluids of varied nature [5–7]. One of such equations of states is the equation of state based on the statistical theory of associating fluid with a perturbed chain (Perturbed Chain–SAFT) was suggested by Gross and Sadowski [8]. This equation is a modified variant of the known and recently popular in engineering calculations molecular-statistical model SAFT. It is based on the results of perturbation theory and a molecular simulation for a fluid formed by chains of hard spheres. The molecular model underlying the PC–SAFT equation takes into account the effects of formation of chains of

hard spheres, dispersion interaction described in terms of Barker and Henderson's perturbation theory [9], and the association. It is assumed that there are contact sites on the surface of a molecule, which are capable of specific interactions with contact sites of other molecules.

It is noteworthy that the PC–SAFT model has been successfully tested by Iranian colleagues in calculations of thermodynamic characteristics of natural gas mixtures [10], which are the object of consideration in the present study. The PC–SAFT model is being intensively developed, and new variants of equations of state are already developed on its basis, which are aimed, in particular, to more precisely describe the speed of sound [11–19], with the description of the *P–V–T* properties, including the density of a fluid and the saturated vapor pressure, remaining reliable. In [12], an approach was suggested, improving the accuracy in describing the speed of sound with the PC–SAFT equation of state for the example of n-alkanes with various carbon chain lengths. Two approximations were tested: (i) using the speed of sound as the input thermodynamic property for determining the model parameters of pure components and (ii) using the speed of sound to obtain universal constants in evaluating the dispersion component of the Helmholtz energy and estimating the model parameters. The authors of [13] compared in detail the performance capabilities of the SAFT and PC–SAFT models for prognosticating the thermodynamic properties of nonpolar and associating substances. However, despite the reasonable description of the speed of sound, significant differences with experimental data were observed in prognostication of the heat capacity at a constant volume. In [14], a variant of the PC–SAFT equation of state was considered on the basis of group-contribution method for describing the thermodynamic properties of pure hydrocarbons of different classes in a wide range of temperatures and pressures. A modification of the PC–SAFT equation of state that provided a more precise estimate of the speed of sound in various systems was tested by Polishuk et al. [11, 15–19]. The authors surpassed some shortcomings of the original version of PC–SAFT (inaccurate prognostication of the speed of sound in the liquid phase, overestimated values of the critical constants of pure components, incorrect description of heat capacities at very high pressures) and introduced insignificant refinements into the expressions of contributions to the "residual" Helmholtz energy for an improved description of the thermodynamic properties of pure substances and binary mixtures under widely varying conditions, including the single- and two-phase states and the near-critical region.

In the present study we used this variant of the PC–SAFT model to estimate and prognosticate the speed of sound for a number of multicomponent systems containing oil-and-gas fluids. The model calculations we performed yielded good results sufficient for practical estimates and monitoring the speed of sound (and densities) in the fluid mixtures under consideration. A detailed description of the CP–PC–SAFT (Critical Point-based Perturbed Chain–Statistical Association Fluid Theory) model and the procedure for calculation with this equation of state were presented in [15, 16], and, therefore, we restrict ourselves to a brief consideration.

MODELING

According to the CP–PC–SAFT model, the expression for the "residual" (due to the intermolecular interaction) contribution to the Helmholtz energy in the absence of associating and polar components in the system can be written as follows (by analogy with the PC–SAFT model):

$$A_{\text{res}} = A^{\text{hc}} + A^{\text{disp}}, \tag{1}$$

where the first term is connected with the contribution from the formation of chains from hard spheres, and the second, with the dispersion part of the Helmholtz energy responsible for the attraction-related interactions.

The formulas for calculating the constituents of the sum (1) were reported in [8, 15, 16]. Useful expression for calculating thermodynamic quantities related with first- and second-order derivatives of the Helmholtz energy with respect to volume (density) can also be found in [10]. An expression for the equation of state, written in terms of the compressibility factor or pressure, can be easily derived from (1) with the use of the known formulas of thermodynamics. When the model is applied to mixtures, the combination Lorentz–Berthelot rules are used, with only a single fitting binary-interaction parameter k_{ij} introduced, which corrects the dispersion term of the interactions in the CP–PC–SAFT equation

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j), \tag{2}$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}(1 - k_{ij}), \tag{3}$$

where the subscripts i and j belong to different segments of the system; σ_i, the diameter of ith segment; ε_i, the

Table 1. Compositions of oil-and-gas mixtures, used to calculate the density and the speed of sound

Component	Concentration, mol fractions				
	synthetic gas mixture	natural oil-and-gas mixture (Gulf Coast) [21]	natural oil-and-gas mixture (Amarillo) [21]	natural oil-and-gas mixture (Statoil Dry Gas) [21]	natural oil-and-gas mixture (Statoil Statvordgass) [21]
CH_4	0.879427	0.96561	0.90708	0.83980	0.74348
C_2H_6	0.060000	0.01829	0.04491	0.13475	0.12005
C_3H_8	0.020430	0.00410	0.00815	0.00943	0.08251
n-C_4H_{10}	0.002998	0.00098	0.00141	0.00067	0.03026
i-C_4H_{10}	0.001995	0.00098	0.00106	0.00040	
n-C_5H_{12}		0.00032	0.00065	0.00008	0.00575
i-C_5H_{12}		0.00046	0.00027	0.00013	
n-C_6H_{14}		0.00067	0.00034		0.002 30
N_2	0.015020	0.00262	0.03113	0.00718	0.00537
CO_2	0.020130	0.00597	0.00500	0.00756	0.01028

Table 2. Results obtained in calculations of the density and the speed of sound in the systems under consideration

Gas mixture or field	Number of experimental points	Temperature, K	Pressure range, MPa	MAPE for density, %	MAPE for speed of sound	Reference
Synthetic gas mixture	22	323.31	4.86–56.69	1.30	1.14	[20]
	22	346.48	5.11–56.69	1.25	1.11	
	24	369.41	4.79–56.90	1.16	1.12	
	18	392.34	6.12–56.86	1.08	1.27	
	18	415.45	6.90–58.37	0.85	1.36	
Gulf coast	12	250.00	0.59–10.41		0.95	[21]
	13	275.00	0.50–10.33		0.38	
	14	300.00	0.47–10.31		0.38	
	17	325.00	0.54–10.38		0.36	
	14	350.00	0.63–10.40		0.32	
Amarillo	11	250.00	0.67–10.88		1.20	[21]
	10	275.00	0.65–10.47		0.43	
	6	298.00	6.89–23.39		1.71	
	11	300.00	0.56–10.43		0.38	
	19	325.00	0.69–10.43		0.37	
	15	350.00	0.86–10.64		0.30	
Statoil dry gas	18	250.00	0.80–10.34		2.51	[21]
	11	275.00	0.52–10.42		0.65	
	18	300.00	0.53–10.30		0.41	
	17	325.00	0.47–10.40		0.42	
Statoil statvord-gass	12	300.00	1.86–10.38		1.37	[21]
	14	325.00	0.42–9.89		0.79	
	16	350.00	0.64–10.44		0.86	

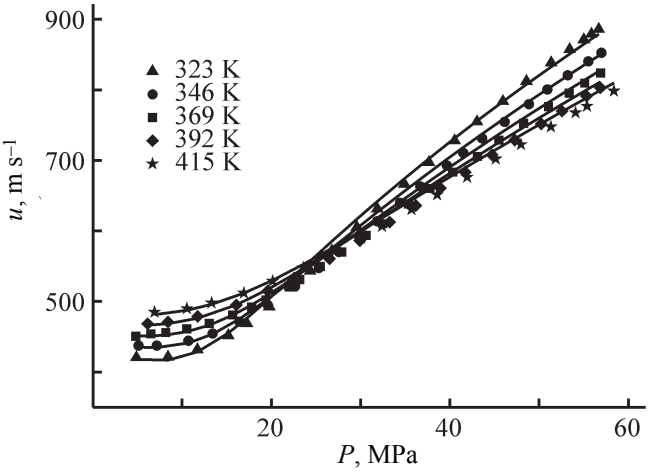
interaction energy of segments of *i*th type; k_{ij}, parameter of a binary interaction of the dissimilar segments *i* and *j* of molecules–component chains.

Four parameters are required for describing a pure nonpolar substance *i* in terms of the CP–PC–SAFT model: number m_i of segments forming a chain-molecule, segment diameter σ_i, energy of segment interaction ε_i/k (*k* is the Boltzmann factor). Additionally, it is necessary to know the parameter δv_c responsible for the shift of the critical volume (ratio between the critical volume calculated in terms of the model to its experimental value). The parameters of the CP–PC–SAFT equation of state for many oil-and-gas components have been reported in the literature [15]; the list of parameters becomes wider and includes polar and associating components [16–19]. Additionally, the universal parameters (constants) of the original PC–SAFT model are re-estimated, these parameters being required for evaluating the dispersion component of the "residual" Helmholtz energy. A calculation procedure based on a numerical solution and aimed to find the equation-of-state parameters [15] differs from the method for estimating (fitting) parameters of the PC–SAFT model. The approach being used consists in that the parameters of the CP–PC–SAFT equation are determined at experimental critical points of pure components (for the given values of the critical constants) and from data on the fluid density at the triple point (from thermodynamic databases). The binary interaction parameters k_{ij} for describing binary and multicomponent systems were taken to be zero, and, therefore, the results obtained in calculating the speed of sound and the density in the present study can be only considered a prognosis.

RESULTS AND DISCUSSION

We tested the CP–PC–SAFT equation of state and verified the working capacity of the procedure suggested by Polishuk and co-workers in estimating the speed of sound for multicomponent systems containing components of natural gas with various methane contents (74–97 mol %). The synthetic gas mixture and natural-gas mixtures from different fields and the compositions of these are presented in Table 1 (for the same compositions, experimental values of the speed of sound are known in a wide range of pressures for a number of temperatures) [20, 21].

A comparison of the results given by the CP–PC–SAFT model and experimental data (see the figure) was



Dependence of the speed of sound in natural gas on pressure at various temperatures. Symbols, experimental data; lines, calculation by the CP–PC–SAFT equation of state.

based on the mean absolute percentage error (MAPE) (Table 2):

$$\mathrm{MAPE} = \frac{100\%}{N}\sum_{i=1}^{N}\left|\frac{W^{\mathrm{calc}}}{W^{\mathrm{exp}}} - 1\right|,$$

where *W* is a thermodynamic property; W_{calc}, the gas-phase density or the speed of sound, calculated from the equation of state; W_{exp}, experimental values of the density or speed of sound; and *N*, number of experimental points. It can be seen in Table 2 that the average absolute error for the values obtained for the speed of sound does not exceed 2.0% for all the systems under consideration, which points to the high precision of the results for the properties of the gas mixtures under study. According to published data [20], the results of prognostication of the speed of sound and density for the synthetic gas mixture with the use of the CP–PC–SAFT model are somewhat inferior in precision to the multiparametric correlation equation of state GERG-2008 [22] (0.1%) which is recommended and popular in engineering calculations for oil and gas industries. It is noteworthy that the GERG-2008 equation has a predominantly empirical substantiation, in contrast to the PC-SAFT equation of states and its analogs (modified variants).

CONCLUSIONS

It was found that the results obtained in calculating the speed of sound and the density in systems formed by oil and gas components are indicative that further use of the PC–SAFT model for evaluating the thermodynamic

and thermophysical properties of natural gas is promising for practical purposes.

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