A new generalized model to predict speed of sound of refrigerants

Mahboobe Ghaeliniya, Mohammad Akbarzadeh*, Mohammad Hasan Vakili and Ehsan Sanjari

Chemical Engineering Department, Shahreza Branch, Islamic Azad University, Shahreza, Iran.

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Abstract

In consideration of physical and chemical properties of pure substances, speed of sound is one of important quantity which can used to calculate many of other thermo-physical properties such as isothermal compressibility, Joule-Thomson coefficient, isobaric heat capacity and etc. These thermo-physical properties are the main parameters in industrial and chemical processes. Development of accurate models for thermodynamic properties computation such as speed of sound is well expected above all in those fields where very high performance calculations have to be reached. In this present work, a new generalized model as a function of reduced temperature and reduced density is proposed to correlate speed of sound of methane, ethane, propane and butane halogenated refrigerants. Speed of sounds have been calculated and compared with data reported in literatures for 5600 data points of 28 refrigerants, and the overall average absolute percentage deviation of 0.92%. The source of speed of sound data used in this study is the NIST Chemistry WebBook.

Keywords

Speed of sound;
refrigerant;
correlative model;
halogenated refrigerants.

1. Introduction

The thermodynamic properties of refrigerants are a problem of great practical interest, since they are involved in a number of refrigeration processes. Moreover, the equations of state (EOS) are used to estimate the thermodynamic properties of pure substances necessary for many of process designs and other calculations.

The speed of sound is one of the important thermodynamic properties that characterize all substances in their different phases. It is significant property because a diverse number of thermodynamic properties can be derived from it. Also, estimation of the speed of sound is a difficult test for any equation of state because it involves the first and second derivatives of the Hemholtz free energy and of the density with respect to temperature [1-5].

Some methods which predict speed of sounds or correlate experimental data are reported in the literature. Pandey et al., 1999 presented theoretical predictions for speed of sounds from the properties of pure components [6]. Queimada et al., 2006, presented corresponding-states modeling of the speed of sound of long-chain hydrocarbons for C_2-C_{36} alkanes [7].

* Corresponding Author.
Email: akbarzadeh@iaush.ac.ir

Maghari et al., 2007 predicted the sound velocity and heat capacities of n-alkanes from the modified SAFT-BACK equation of state [8]. Also Scalabrin et al., 2007 modeled a speed of sound in a three-parameter corresponding states format for 10 alkane halogenated refrigerants [9].

Pardini et al., in 2016 [10], estimated photoacoustic determination of speed of sound in binary mixtures of water and ethyl and methyl alcohol. Nascimento et al., in 2016 [11], predicted high pressure speed of sound and density of (decalin + n-decane), (decalin + n-hexadecane) and (n-decane + n-hexadecane) systems and thermodynamic modeling with an equation of state. Shin et al., in 2010 [12], estimated speed of sound in dual-layered media using medical ultrasound image deconvolution. Also Shin et al., in 2010 [13], estimated average speed of sound using de-convolution of medical ultrasound data.

Some researchers [14-17] prefer to represent the speed of sound with a ratio of temperature and pressure polynomials. Another possibility is to correlate the square of the speed of sound or the inverse of the square of the speed of sound with polynomials or ratio of polynomials [18, 19].

In this study, a new simple equation based on source data bank that accurately reproduces the speed of sound over a wide range of temperatures and densities region was recommended. Based on this model a correlative corresponding-states correlation is established. The source of speed of sound data used in this study is the NIST Chemistry WebBook [20].

By investigating the modeling approaches applied with successful results in previous works, the proposed method in this study can be regarded as an innovative and original equation to correlate speed of sound for 28 commonly used refrigerants.

2. The proposed model for speed of sound of refrigerants

This work tried to find a rapid simple equation to estimate speed of sound of methane, ethane, propane and butane halogenated refrigerants based on speed of sound data with high accuracy by using reduced temperature and reduced density. There are some available data in sources [20] to allow the proposition of a model for the speed of sound of refrigerants. After multiple regression analysis, a new equation was suggested as follow:

$$\frac{u}{u_0} = A + B T_r^2 + C T_r^4 \tag{1}$$

$$A = 0.59679 \tag{2}$$

$$B(\rho_r) = 1.73565 + 2.6158\rho_r - 5.0303\rho_r^3 \tag{3}$$

$$C(\rho_r) = -1.89277 - 2.23054\rho_r + 4.81053\rho_r^3 \tag{4}$$

Where u is the speed of sound at desired temperature and density, u_0 is the speed of sound in atmospheric pressure (1.0133 bar), $Tr = T/T_c$, is the reduced temperature, and $\rho_r = \rho/\rho_c$ is the reduced density. Seven tuned coefficients are determined by using Marquardt-Levenberg algorithm which minimizes the sum of the squared differences between the values of the observed and correlated values of the dependent variables.

To obtain this equation, first the raw form of equation with non-estimated constant parameters was supposed. Then by regression analysis done by using databank and after that the constant parameters were obtained.

We carried out calculations for more than 75 pure substances. The criteria for comparisons are *AARD%*, *ARD%*, *AAD%* and *RMSD* which calculated as follows:

$$AARD\% = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{u_{r,i,\exp} - u_{r,i,calc}}{u_{r,i,\exp}}\right| \times 100 \tag{5}$$

$$ARD\% = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{u_{r,i,\exp} - u_{r,i,calc}}{u_{r,i,\exp}}\right) \times 100 \tag{6}$$

$$AAD\% = \frac{1}{N}\sum_{i=1}^{N}\left|u_{r,\exp} - u_{r,calc}\right| \times 100 \tag{7}$$

$$RMSD = \frac{1}{N}\sqrt{\sum_{i=1}^{N}\left(\frac{u_{r,i,\exp} - u_{r,i,calc}}{u_{r,i,\exp}}\right)^2} \times 100 \tag{8}$$

Table 1 shows the number of data points, temperature ranges, critical temperatures and critical densities required to set up the correlation.

The presented model in this work is obtained from investigating a large number of speeds of sound data [20] for 28 refrigerants.

3. Result and discussion

The new generalized model to correlate the speed of sound can be calculated from Eqs (1) to (4). Speed of sound for 28 refrigerants from data sources [20] have been calculated from this developed empirical model and have been compared to speed of sound data sources.

Table 1. Number of data points (NDP), temperature ranges (*K*), critical temperature (T_c) and critical density (ρ_c) for considered refrigerants.

Substance	NDP	T_{min} (K)	T_{max} (K)	T_c (K)	ρ_c (mol/lit)
R11	200	162.6	469.5	471.11	4.03
R12	200	116.1	383.8	385.12	4.67
R13	200	92.0	300.9	302.00	5.58
R14	200	98.9	226.8	227.51	7.11
R21	200	200.0	450.2	451.48	5.11
R22	200	115.7	368.0	369.30	6.06
R23	200	118.0	298.4	299.29	7.52
R32	200	136.3	350.2	351.26	8.15
R41	200	175.0	316.6	317.28	9.30
R113	200	236.9	485.9	487.21	2.99
R114	200	273.1	418.1	418.83	3.39
R115	200	173.8	351.3	353.10	3.97
R116	200	173.1	292.4	293.03	4.44
R123	200	166.0	455.4	456.83	3.60
R124	200	120.0	394.1	395.43	4.10
R125	200	172.5	338.3	339.17	4.78
R134a	200	169.8	373.2	374.21	5.02
R141b	200	169.7	475.9	477.50	3.92
R142b	200	142.7	408.9	410.26	4.44
R143a	200	161.3	344.9	345.86	5.13
R152a	200	154.5	385.2	386.41	5.57
R218	200	125.4	343.9	345.02	3.34
R227ea	200	146.3	374.8	375.95	3.41
R236ea	200	242.0	411.6	412.44	3.70
R236fa	200	179.5	396.9	398.07	3.63
R245ca	200	200.0	443.9	447.57	3.91
R245fa	200	200.0	426.1	427.20	3.86
RC318	200	233.3	387.6	388.38	3.10

The values of the speed of sounds, temperatures, critical density and critical temperature were taken from data bank [20].

To compare the accuracy of presented empirical model, calculated vapor pressures for all substances versus corresponded values in data bank has been presented in Figure 1.

In Table 2, the *AARD%*, *ARD%*, *AAD%*, and RMSD of speed of sound calculated from proposed models for each substance with respect to the values given by data bank were presented. It showed that new presented model is an accurate method for all types of refrigerants considered in this study.

In Table 2 indicated that there is good correlation for R11, R218, R124, R123, R116 and R21 with *AARD%* lower that 0.6%. A moderate estimation is done for other refrigerants all lower than 1.45%.

Table 2. *AARD%*, *ARD%*, *AAD%*, and *RMSD* of the values obtained by presented model in comparison with standard source data.

Substances	*AARD%*	*ARD%*	*AAD%*	*RMSD*
R11	0.571	0.404	0.503	0.476
R12	0.950	-0.950	0.879	1.648
R13	1.359	-1.359	1.211	3.181
R14	1.064	-1.064	0.892	2.266
R21	0.550	-0.311	0.499	0.365
R22	0.669	0.631	0.588	0.816
R23	0.752	-0.752	0.612	1.387
R32	0.768	-0.768	0.630	1.033
R41	0.690	0.292	0.602	0.782
R113	0.966	0.966	0.855	1.631
R114	0.740	0.381	0.648	0.905
R115	1.058	1.058	1.027	3.134
R116	0.448	-0.029	0.387	0.361
R123	0.381	0.016	0.338	0.204
R124	0.438	0.380	0.354	0.732
R125	1.033	1.033	0.873	2.887
R134a	1.289	1.289	1.226	2.248
R141b	1.365	-1.365	1.211	2.723
R142b	1.270	1.270	1.191	2.535
R143a	1.218	-1.218	1.092	2.180
R218	0.349	-0.052	0.323	0.217
R227ea	1.206	-1.197	1.085	2.500
R236ea	0.970	-0.970	0.877	2.123
R236fa	0.778	-0.540	0.703	0.953
R245ca	1.405	1.405	1.374	3.591
R245fa	1.270	1.970	1.972	4.755
RC318	0.889	-0.889	0.819	1.423
Average	**0.913**	**-0.002**	**0.856**	**1.756**

Figure 2 shows the cumulative frequency of proposed model versus average absolute relative deviations. Figure 2 also shows the accuracy of the new empirical correlation in calculation of speed of sound for all considered refrigerants.

As indicated in Figure 2, the new method has successfully correlated 70% of all data points with *AARD%* less than 1, and 96% of the data with *AARD%* less than 3. Only 0.6% of the vapor pressure data were correlated with *AARD%* of more than 5 by the new method.

Cumulative frequency analysis is the analysis of the frequency of occurrence of values of a phenomenon less than a reference value. The phenom-

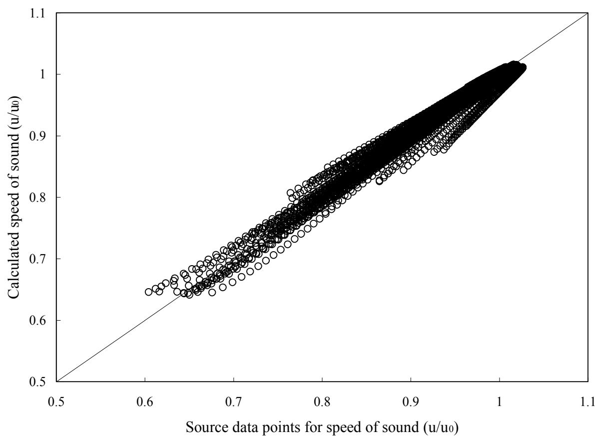

Figure 1. Accuracy of presented model versus sources data.

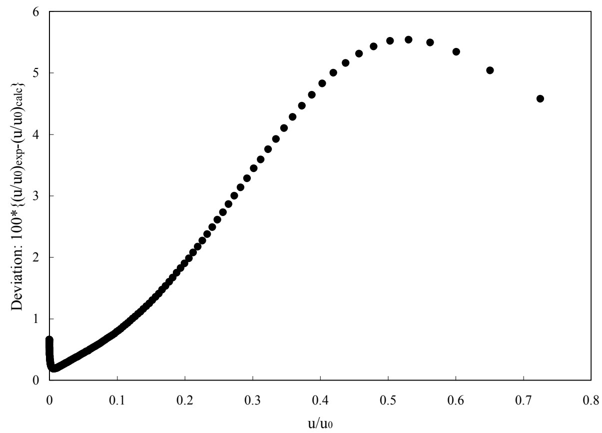

Figure 3. Deviation of 200 data points for R152a refrigerant calculated by new general model.

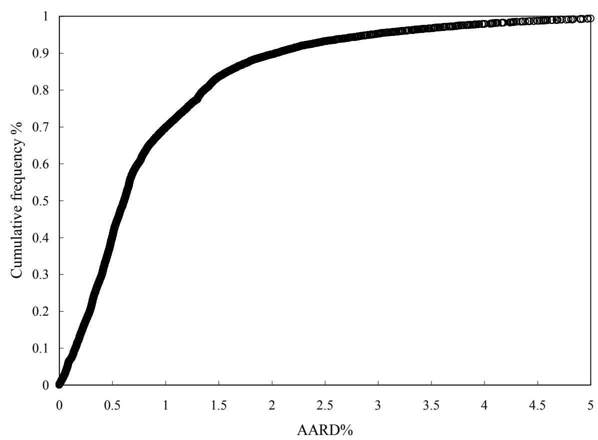

Figure 2. AARD% of various methods in calculating vapor pressure as function of cumulative frequency.

enon may be time-dependent or space-dependent. Cumulative frequency is also called frequency of non-exceedance.

Cumulative frequency analysis is performed to obtain insight into how often a certain phenomenon (feature) is below a certain value. This may help in describing or explaining a situation in which the phenomenon is involved, or in planning interventions, for example in thermodynamic properties.

To estimate the applicability of presented method for calculating speed of sound of refrigerants, deviations ($100\times\{P_{source\ data}-P_{calculated}\}$) of 200 data points of R152 a refrigerant in the range of 154.5K ≤ T ≤ 385.2K are presented in Figure 3. It should be noted that data points of this substance were not employed in regression analysis of new proposed correlation.

It showed that *AARD%* of R152a which is not participated in regression analysis is 1.032%.

4. Conclusion

In the case of the methane, ethane, propane and butane halogenated refrigerants, a new innovative and original equation for the speed of sound of 28 refrigerants as a function of reduced temperature and reduced density was recommended. This seven-non linear model was derived from data sources reported in literatures. To validate the proposed method, the speeds of sound of considered refrigerants with 5600 data points have been examined and an overall average absolute relative deviation of 0.92% was achieved. Also to estimate the applicability of presented method for those data which are not participates in regression analysis; speeds of sound of 200 data points for R152a refrigerant (not employed in fitting) were calculated and the results showed the sufficiency of the new model with *AARD%* of 1.032%.

Nomenclature

NIST	National Institute of Science and Technology
SAFT	Statistical Association of Fluid Theory
AARD	Average Absolute Relative Deviation
ARD	Average Relative Deviation
AAD	Average Absolute Deviation
RMSD	Root Mean Square Deviation
NDP	Number of data points

References

1. Victoria, H.P., Silva, G.A.I., Estrada, M.R., Hall, K.R.A. (2013). "Correlation to predict speed of sound in liquids: 1. n-Alkanes (≥ C5) and their mixtures at high pressures", *Fluid Phase Equilibria.*, Vol. 338, PP. 119-127.

2. Bobik, M. (1978). "Thermodynamic quantities for liquid benzene 1. Sound velocities between 283 and 463 K and up to 62 MPa", *J. Chem. Thermodynamics.*, Vol. 10, PP. 1137-1146.

3. Niepmann, R. (1984). "Thermodynamic properties of propane and n-butane 2. Speeds of sound in the liquid up to 60 MPa", *J. Chem. Thermodynamics.*, Vol. 16, PP. 851-860.

4. Bobik, M., Niepmann, R., Marius, W. (1979). "Thermodynamic quantities for liquid carbon tetrachloride 1. Sound velocities between 265 and 435 K and up to 62 MPa", *J. Chem. Thermodynamics.*, Vol. 11, PP. 351-357.

5. Niepmann, R., Esper, G.J., Riemann, K.A. (1987). "Thermodynamic properties of chlorodifluoromethane and dichloromethane Speeds of sound in the liquid up to 60 MPa", *J. Chem. Thermodynamics.*, Vol. 19, PP. 741-749.

6. Pandey, J. D., Vyas, V.P., Jain, Dubey, G.P., Tripathi, N., Dey, R. (1999). "Speed of sound, viscosity and refractive index of multicomponent systems: Theoretical predictions from the properties of pure components", *J. Mol. Liquids.*, Vol. 81, PP. 123-133.

7. Queimada, A.J., Coutinho, J.A.P., Marrucho, I.M., Daridon, J.L. (2006). "Corresponding-States Modeling of the Speed of Sound of Long-Chain Hydrocarbons", *Int. J. Thermophysics.*, Vol. 27, PP. 1095-1109.

8. Maghari, A., Sadeghi, M.S. (2007). "Prediction of sound velocity and heat capacities of n-alkanes from the modified SAFT-BACK equation of state", *Fluid Phase Equilibria.*, Vol. 252, PP. 152-161.

9. Scalabrin, G., Marchi, P., Grigiante, M. (2007). "Speed of sound predictive modeling in a three-parameter corresponding states format: Application to pure and mixed haloalkanes", *Exp. Therm. Fluid. Sci.*, Vol. 31, PP. 261-278.

10. Pardini, P., Iriarte, D.I., Pomarico, J.A., Ranea-Sandoval, H.F. (2016). "Photoacoustic determination of speed of sound in binary mixtures of water and ethyl and methyl alcohol", *Opt. Int. J. Light. Elect. Opt.*, Vol. 127, PP. 2260–2265.

11. Nascimento, F.P., Paredes, M.L.L., Mehl, A., Lucena, R.S., Costa, A.L.H., Pessoa, F.L.P. (2016). "High pressure speed of sound and density of (decalin + n-decane), (decalin + n-hexadecane) and (n-decane + n-hexadecane) systems and thermodynamic modeling with PHCT equation of state", *J. Chem. Thermodynamics.*, Vol. 95, PP. 124–135.

12. H.C. Shin, R. Prager, H. Gomersall, N. Kingsbury, G. Treece, A. Gee. (2010). "Estimation of speed of sound in dual-layered media using medical ultrasound image deconvolution", *Ultrasonics*, Vol. 50, PP. 716–725.

13. H.C. Shin, R. Prager, H. Gomersall, N. Kingsbury, G. Treece, A. Gee. (2010). "Estimation of Average Speed of Sound Using Deconvolution of Medical Ultrasound Data", *Ultra. Med. Bio.*, Vol. 36, PP. 623–636.

14. Lainez, A., Gopal, P., Zollweg, J. A., Streett, W. B. (1989). "Speed-of-sound measurements for liquid trichlorofluoromethane under pressure", *J. Chem. Thermodynamics.*, Vol. 21, PP. 773-777.

15. Takagi, T., Sakura, T., Guedes, H. J. R. (2002). "Speed of sound in liquid cyclic alkanes at temperatures between (283 and 343) K and pressures up to 20 MPa", *J. Chem. Thermodynamics.*, Vol. 34, PP. 1943-1957.

16. Takagi, T., Sawada, K., Urakawa, H., Ueda, M., Cibulka, I. (2004). "Speed of sound in liquid tetrachloromethane and benzene at temperatures from 283.15 K to 333.15 K and pressures up to 30 MPa", *J. Chem. Thermodynamics.*, Vol. 36, PP. 659-664.

17. Takagi, T., Sawada, K., Urakawa, H., Ueda, M., Cibulka, I. (2004). "Speeds of Sound in Dense Liquid and Vapor Pressures for 1,1-Difluoroethane", *J. Chem. Eng. Data.*, Vol. 49, PP. 1652-1656.

18. Daridon, J.L., Lagrabette, A., Lagourette, B. (1998). "Speed of sound, density, and com-

pressibilities of heavy synthetic cuts from ultrasonic measurements under pressure", *J. Chem. Thermodynamics.*, Vol. 30, PP. 607-623.

19. Khasanshin, T.S., Poddubskij, O.G., Shchamialiou, A.P., Samuilov, V.S. (2006). "The thermodynamic properties of 1-alkenes in the liquid state: 1-Hexadecene", *Fluid Phase Equilibria.*, Vol. 245, PP.26-31.

20. NIST Chemistry WebBook, NIST Standard Reference Database, National Institute of Standards and Technology, Gaithersburg MD, 2005, http://webbook.nist.gov.