PREDICTION OF DENSITY AND ULTRASONIC VELOCITY OF HYDROXYLIC COMPOUNDS (C_1-C_6) AS A FUNCTION OF TEMPERATURE

Rebecca da Silva Andrade[a], Cristina González[b], Miguel Angel Iglesias Duro[c]

[a] Universidade Federal do Recôncavo da Bahia, Av. Centenário, 697, Sim, CEP 44042-280 Feira de Santana, BA, Brazil.
[b]Dpto. de Ingeniería Química. Facultad de Farmacia. Universidad del País Vasco, UPV/EHU. Apto. 450. Vitoria, Spain.
[c] Universidade Federal da Bahia, Rua Aristides Novis, 2, Federação, CEP 40210-630 Salvador, BA, Brazil.

Abstract: The present work deals with the modelling and experimental measurement (density and ultrasonic velocity) of thermophysical properties of short chain hydroxylic compounds (C_1-C_6). Fitting equations were applied to the experimental data in order to correlate for later computer based design. Different derived magnitudes were computed from the experimentally measured density and ultrasonic velocity, due to their importance for theoretical calculations and development of new models. The estimation of the studied properties was made by the application of different theoretical procedures. A wide comparison was made with available open literature, being evident the lack of reliable information in the ranges studied until now.

Keywords: Alcohol; thermodynamic properties; temperature; theoretical model; prediction.

PREDIÇÃO DE DENSIDADE E VELOCIDADE DO SOM DE COMPOSTOS HIDROXÍLICOS (C_1-C_6) COMO FUNÇÃO DA TEMPERATURA

Resumo: O presente trabalho trata da modelagem e medição experimental (densidade e velocidade do som) de propriedades termofísicas de compostos hidroxílicos de cadeia curta (C_1-C_6). Equações de ajuste foram aplicadas aos dados experimentais visando propor correlações a serem usadas em ferramentas computacionais de projeto. Diferentes magnitudes derivadas foram calculadas devido à sua importância para cálculos teóricos e desenvolvimento de novos modelos. A estimativa das propriedades estudadas foi feita pela aplicação de diferentes procedimentos teóricos. Foi feita uma ampla comparação com a literatura aberta disponível, ficando evidente a falta de informações confiáveis nas faixas estudadas até o momento.

Palavras-chave: Álcool; propriedades termodinâmicas; temperatura; modelo teórico; predição.

1. INTRODUCTION

Modern development in chemical industry requires the minimization of environmental impact using clean processes and new production strategies. An important part of the environmental impact is related to the nature of the solvents used, as well as, their potential hazards profile [1-3]. In recent years it has boosted the use of water and alcohols in industrial processes due to its high polar character, low cost, environmental low impact, wide availability and high capacity solvent [4-5]. Alcohols can be used as a beverage, as combustion engine fuel and for different scientific, medical, and industrial applications. Methanol is made primarily from natural gas, and is an intermediate material to produce thousands of derivative products evolving key chemicals (acetic acid, formaldehyde, ethanoic acid and different methyl esters), acrylic plastics, synthetic fibers, adhesives, ink, paints, construction materials, agrichemicals and pharmaceutical compounds. The versatility of this alcohol is making it a promising fuel resource as core energy carrier for factories and electricity generation, as well as, for portable power sources (direct methanol fuel cells) [6]. Ethanol in the form of alcoholic beverages has been consumed by humans since pre-historic times. It is possible to trace alcoholic beverages made by humans to about nine millennia ago but probably, alcoholic products based on fruit juice fermentation may be consumed many centuries earlier [7], and today it is widely associated with socializing for adult population into occidental countries. Different studies in the last few years have shown some potential health benefits under moderate consumption conditions [8]. Ethanol can be used as promising alternative to fossil fuel or fuel additive for internal combustion motors, due to it can be obtained from renewable biomass sources. Fuel performance can be increased in forced induction internal combustion engines by injecting alcohols into the air intake after the turbocharger has pressurized the air. Brazil is the world´s second largest producer of ethanol fuel (30094 millions of litres in 2018-2019), rising 23.3% in the last period, representing 27.7% of the total produced ethanol fuel. Brazil´s fuel program is based on the most efficient agricultural technology for sugarcane cultivation; however any authors consider that this model is only sustainable under advanced agro industrial processes, cheap feedstock and giant amount of available land. Since 1979, Brazil is the only country in the world that uses hydrated ethanol as fuel for combustion engines adapted specifically for mixed use (gasoline, ethanol or any degree of mixture (commonly called gasohol)), currently 85% of the vehicles in circulation in the country use this kind of adapted engine. Today, there are already different successfully experiences of application of hydrated ethanol for motorcycles in Brasil (since 2009, biofuel engine of Honda and Yamaha) or as an additive for diesel engines or as a single fuel (since 1997, MAD7 (diesel-blended alcohol), since 2006, Bioethanol for Sustainable Transport, BEST-Program, E95 for buses (95% ethanol and 5% additives)) or for air transport (since 2005, different EMBRAER projects, Ipanema EMB202A or E195, for example). Besides ethanol, different studies are available evolving different mixtures of alcohols as promising alternative fuel [9-12]. Propanol is used as solvent (as entrainer for azeotropic distillation, for printing inks, electrodeposition paints), personal care products (soaps, antifreezer, lacquer formulation, etc) and cleaning products (window cleaners, adhesives, etc) and as intermediate product for halides, propyl amine, propyl acetate, esters and ethers production. Also is used for medical applications (as antiseptic, hand-sanitizer, nebulizer, pain relief medication and

supraventricular arrhythmias/ventricular tachycardias treatment) and as constituent of many kinds cosmetics. Alcohol beverages nearly always gather propanol as fermentation component, as well as in many foodstuff and non-alcoholic drinks, being an important element of the flavor profile. Despite uses and applications of propanol are rising significantly, the cost of production is too expensive for a massive consumption as a combustion fuel but promising alternatives are being proposed for direct fuel cells. Butanol is an important commodity in manufacturing industry (used in polymers, lubricants, brake fluids, synthetic rubber, as polishing and cleaning products, and as artificial food flavoring), cosmetic laboratories (used for soaps, shampoo, and personal-care products) and chemical industry (as intermediate to produce other compounds, as amino resins, different acetates and amines, glycol ether and acrylate esters). As potential fuel for combustion engines, butanol is an alternative fuel that offers high energy content, fewer emissions and lower corrosion . Fermentative production of butanol for application as feedstock or biofuel is regarded as a promising renewable technology, but for the moment remains a barrier for a cost-effective production.

Chemistry and Chemical Engineering need high quality thermodynamic information for accurate modelling/simulation processes and develop new production strategies, cheap and effective procedures and then, implement adequate decisions in terms of global optimization. From a more fundamental point of view, thermodynamics data is key information for understanding the molecular mechanisms of interactions and dispersion. The test of models and development of new methods for prediction of these thermodynamic magnitudes, gather a particular significance because they are the only way to ensure accurate results by theoretical studies and simulations.

In response to this concern, our research group is evolved on determining multicomponent thermodynamics (phase equilibria, reology, acoustical, optical, volumetric and calorimetric magnitudes in order to optimize simulation studies and understand the mixing mechanisms into complex mixtures. Besides its own practical importance, density and ultrasonic velocity are two key magnitudes closely linked with the determination of Henry's law constants and air-water partition coefficients, mass transfer coefficient measurement and calorimetric studies by means of Maxwell's coefficients. A considerable amount of data is available for organic hydrocarbons in open databases, which are of major environmental and health concern. Less attention has been paid to hydroxylic compounds, for which only a few number of wide experimental collections of data are available in the literature, as well as, accurate studies related to the dependence of their properties with temperature, pressure or composition. Moreover, it can be observed a considerable lack of accuracy or thermodynamic consistency in some open data literature, which is due to experimental errors, impurities of chemicals or differences on technical devices used for measuring. A worse perspective is obtained for mixture references owed to the recent development of accurate techniques, the relatively important non-ideality of such compounds into mixture, as well as, the time-consuming nature of the experimental measuring procedures.

Thermochemical properties of liquid compounds that may have hydroxyl molecular groups and strongly polarizable electron pairs like alkanols, aromatic alcohols, poliols or amines depend to a large extent on the intermolecular interactions by hydrogen bonding. The length of the molecular chain and the branched structures of the molecules influence the intensity of the interactions, there

being high non-ideality for those compounds with relatively small and non-branching molecules. Highly polar substances such as water, and short hydroxyl compounds as methanol, produce strong interactions due to its relatively low molecular volume and large polarity.

Different previous published works report data compilations of physical and thermal properties of hydroxylic compounds but this information is not systematic, it can be found disperse and many properties have not been studied in a wide extension, mainly those of acoustic nature. This kind of information is of high interest for the understanding of the evolution of flexibility, package trend, hydrophobicity and polar-hydrogen bond potential as a function of molecular structure, as well as, for the development of group contribution methods for prediction of thermophysical properties. All chemicals selected for this study contain an unique hydroxylic group and aliphatic or aromatic residual structures of low molar mass.

With these facts in mind, as a continuation of our scientific work investigating physical properties related to characterization of compounds of industrial interest, we present the temperature dependence of density and ultrasonic velocity at the range of temperature 278.15-323.15 K and atmospheric pressure of a wide collection of alcohols (methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol, butan-2-ol, 2-methyl-propan-1-ol, 2-methyl-propan-2-ol, pentan-1-ol, 2-methyl-butan-1-ol, 3-methyl-butan-1-ol, and phenylmethanol). For density estimation, a simplification of the Nasrifar–Moshfeghian liquid density correlation (MNM method) was applied, replacing the Mathias and Copeman temperature-dependent term with the original Soave–Redlich–Kwong equation of state (SRK EOS) temperature-dependent term. This replacement has overcome the limitations in use for the original model, which were due to the Mathias and Copeman vapor pressure dependent parameters. The Rackett equation of state and its modification was also tested, as well as other different methods (Bradford-Thodos, Riedel, Narsimham, Yen-Woods, Bhirud and Campbell-Thodos models), in order to analyze how accurate densities are predicted.

The Collision Factor Theory (CFT) was applied to estimate the isentropic compressibility of these compounds using the estimated collision factor for pure compounds. Satisfactory predictions were obtained for both properties, a good accuracy being obtained for a wide range of temperatures. Finally, a wide comparison was made with disposable open literature for the studied compounds, an analysis being made of the obtained results.

2. METHODOLOGY

All chemical solvents used in the experimental studies were of Merck quality with richness better than 99.0 mol%. The pure components were stored in sun light protected form and constant humidity and temperature. Usual manipulation and purification in our experimental works was applied, as earlier explained. The molar mass, open literature data and experimental results at standard condition are shown in Table 1. The densities and ultrasonic velocities of pure components were measured with an Anton Paar DSA-5000M vibrational tube densimeter and sound analyzer, with a resolution of 10^{-5} gcm^{-3} and 1 ms^{-1}.

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3. RESULTS AND DISCUSSION

Modern process design involves the use of computer aided process design procedures. The physical property packages used in chemical simulators typically rely on generalized equations for predicting properties as a function of temperature, pressure, etc. Despite the success developing several procedures of density estimation for pure compounds or mixtures, only a few of them may be of real application for chemicals of non-ideal trend or high molar mass. An important criteria for estimating the density of these substances, is to understand the complex mechanisms of mixing process, commonly linked to the number and kind of selected "active" molecular groups, and the molecular configuration in terms of 3D structure. Second, the estimation strategy must be account for the strong temperature dependency of density. Both criteria are important for the design of processing facilities and policies that are frequently missing or not taken into account carefully. Perhaps the second criteria is more difficult to develop due to a set of factors are related as branching, molecular flexibility and disperse forces for this kind of compounds which obstruct to translate these facts into an efficient mathematical model.

In this work, different models for density prediction were tested. In this case, a simplification for the Nasrifar–Moshfeghian liquid density correlation (NM correlation) was applied, replacing the Mathias and Copeman temperature-dependent term with the original Soave–Redlich–Kwong equation of state (SRK EOS) temperature-dependent term. This replacement has overcome the limitations in use for the original model which were due to the Mathias and Copeman vapor pressure dependent parameters. In order to test the accuracy of different corresponding states methods for the prediction of saturated liquid density of this kind of compounds, we applied the methods proposed by Bradford-Thodos, Riedel, Narsimham, Yen-Woods, Bhirud and Campbell-Thodos. The root mean square deviations between experimental and estimated data are shown in the Table 1.

Table 1 Root mean square deviations for predictive density values by Bradford-Thodos, Riedel, Narsimham, Yen-Woods, Rackett, modified Rackett by Spencer and Danner, Bhirud, Campbell-Thodos and the simplified Nasrifar and Moshfeghian models with respect to corresponding experimental data at 278.15 – 323.15 K.

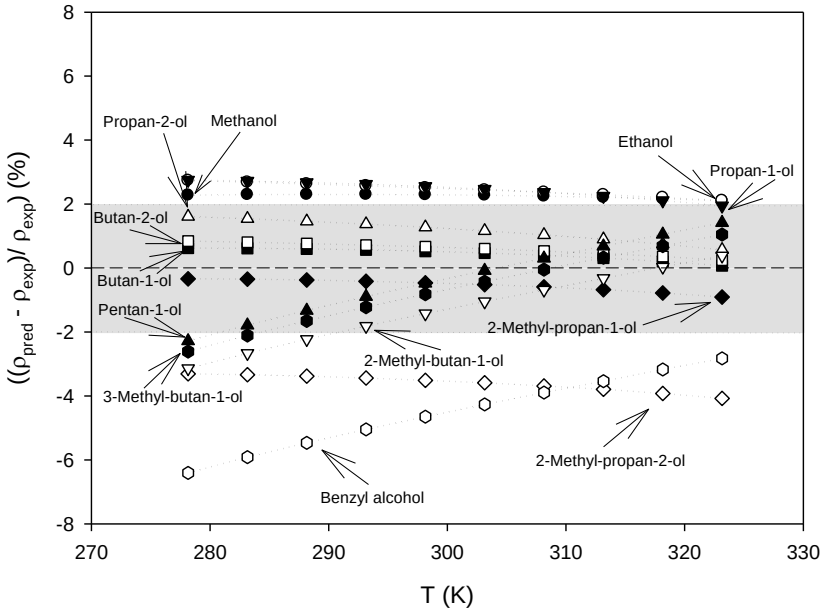
Alcohol	Bradford -Thodos	Riedel	Narsimham	Yen-Woods	Rackett	Rackett-Spencer-Danner (* and **)		Bhirud	Campbell-Thodos	MNM
Methanol	0.04557	0.04432	0.01798	0.01742	0.09740	0.05813	0.02208	0.03981	0.02921	0.04447
Ethanol	0.01621	0.06129	0.01941	0.01590	0.04431	0.02837	0.08833	0.02532	0.01879	0.06139
Propan-1-ol	0.00589	0.06535	0.01973	0.01060	0.02406	0.06782	0.12544	0.09670	0.02375	0.06334
Propan-2-ol	0.00611	0.05828	0.00950	0.00317	0.01443	0.05753	0.12595	0.09361	0.04137	0.05895
Butan-1-ol	0.01334	0.05116	0.00386	0.00980	0.00318	0.07103	0.12126	0.09552	0.04619	0.04782
Butan-2-ol	0.00541	0.04962	0.00504	0.00236	0.01254	0.05388	0.09937	0.07616	0.03547	0.05006
2-Methyl-propan-1-ol	0.01996	0.04271	0.00444	0.01627	0.00702	0.06161	0.11004	0.08522	0.04590	0.04104
2-Methyl-propan-2-ol	0.05070	0.01774	0.02885	0.04787	0.04023	0.04464	0.09896	0.07289	0.02221	0.01996
Pentan-1-ol	0.01930	0.04807	0.00918	0.01747	0.00853	0.07310	0.12001	0.09601	0.05274	0.04533
2-Methyl-butan-1-ol	0.04189	0.03871	0.01365	0.05068	0.03646	0.09371	0.14186	0.11700	0.07176	0.03518
3-Methyl-butan-1-ol	0.03663	0.04559	0.01033	0.04369	0.03051	0.09944	0.15179	0.12508	0.05704	0.04371
Phenylmethanol	0.03176	0.01345	0.04868	0.02813	0.01036	0.04146	0.03092	0.03311	0.40696	0.02472

*Considering $\beta = 0.2908-0.099\omega+0.04\omega^2$ **Considering $\beta = 0.29056-0.08775\omega$.

A good agreement (percentage error ≤ 2%) is observed, appearing the lower deviations for Narsimham, Yen-Woods, Bradford-Thodos and Rackett equations at higher temperatures for all studied alcohols. In general terms, Butan-1-ol, Butan-2-ol, 2-Methyl-propan-1-ol, Propan-2-ol and Pentan-1-ol gather the best results (Figure 1).

In the last few years an increasingly interest for the application of low/high frequency ultrasound techniques for thermodynamic applications has occurred. Without doubt it is caused by the versatile uses that these measurements may have as heat capacity, compressibility studies or simple and accurate concentration measurements. Ultrasonic velocity has been systematically measured in the last years but this data are scarce yet for simple compounds or any kind of complex mixtures. Predictive procedures are then of primary interest, the same problems that were observed for density prediction being found.

Figure 1. Density deviation between experimental and predicted data (Nasrihham model) at the temperatures 278.15-323.15 K.The shaded area indicates deviations smaller than 2%.

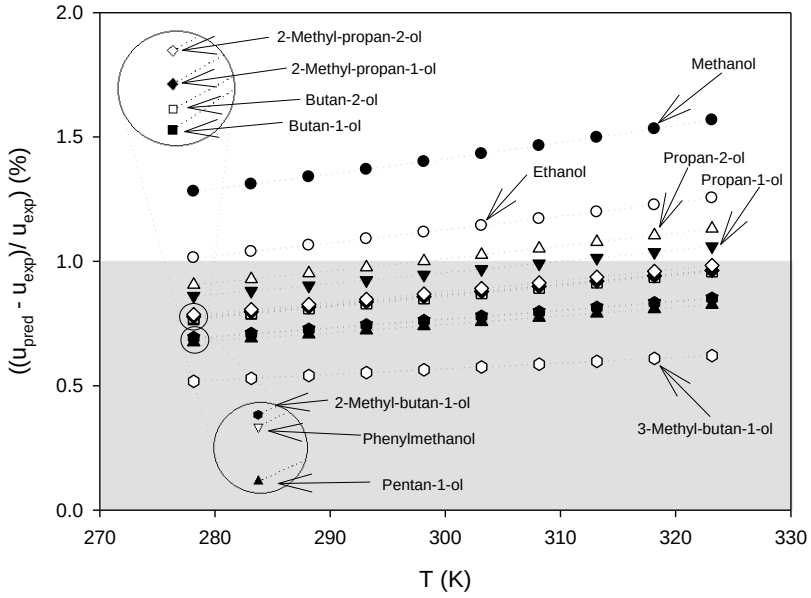


The Collision Factor Theory (CFT) computes the isentropic compressibility by means of collision factors parameters which are a function of temperature into pure solvent or mixture. The pertinent relations for this calculation and it theoretical basis were detailed described in the literature indicated above. The collision factors (S) of the pure solvents used in the CFT calculations were estimated by using the experimental ultrasonic velocities, and the molar volumes enclosed in this paper. The characteristic molar volumes were calculated by the group contribution method of Bondi. The experimental data for the ultrasonic velocities of the chemicals studied here were compared with values determined by this theoretical procedure. The deviations of this procedure for the studied alcohols are gathered in Table 2 and Figure 2. As observed, the lowest deviations are obtained for the heavier alcohols (lower than 1%), an overestimation being obtained at any case. As observed, temperature is a secondary factor and slightly affects the final prediction.

Table 2 Root mean square deviations for predictive ultrasonic velocities values by means of Collision Factor Theory with respect to corresponding experimental data for the used chemicals at the range 278.15 – 323.15 K.

Component	CFT
Methanol	15.54
Ethanol	13.04
Propan-1-ol	11.46
Propan-2-ol	11.45
Butan-1-ol	10.34
Butan-2-ol	10.34
2-Methyl-propan-1-ol	10.34
2-Methyl-propan-2-ol	10.34
Pentan-1-ol	9.51
2-Methyl-butan-1-ol	9.50
3-Methyl-butan-1-ol	9.50
Phenylmethanol	8.62

Figure 2. Ultrasonic velocity deviation between experimental and predicted data (CFT model) at the temperatures 278.15- 323.15 K. The shaded area indicates deviations smaller than 1%.



4. CONCLUSION

Density and ultrasonic velocity has been a subject of core interest during the recent past years due to measurements of these magnitudes in solutions formed by liquid components show the degree of deviation from ideality behaviour. These deviations have been used to gain insight into nature and degree of molecule interactions among the enclosed components into the studied systems. Accurate data of density and ultrasonic velocity as a function of composition and temperature/pressure help to understand the nature of the individual chemicals and molecular interactions in complex systems and extreme operational conditions.

Thermodynamically important parameters giving useful information has also been derived from the experimental physical properties. Isobaric expansibility (α), intermolecular free length (Lf), van der Waals constant (b), molecular radious (r), geometrical volume (B), molar surface area (Y), available volume (Va), volume at

absolute zero (V0), molar sound velocity (Ra), collision factor (S) and specific acoustic impedance (Z) were analyzed as a function of temperature.

In what is referred to theoretical estimation, as it could be observed in Figs. 1-2, the better results are showed for the applied models at high temperatures for density, the Nasrimham model offering the best results, and low temperatures for ultrasonic velocity prediction using CFT model. As a whole, the studied models are, at least, of qualitative accuracy in terms of estimation. Deviations yielded for these magnitudes should be considered as a satisfactory result, supporting their validity as predictive tools for the studied alcohols.

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