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A new correlation for the prediction of refractive index and liquid densities of 1-alcohols

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ABSTRACT

This paper presents a new correlation for the refractive index of 1-alcohols. The correlation relies upon a linear behavior with temperature from (293 to 353) K. This correlation uses the carbon number as a variable, and the universal constants result from curve fits of 117 experimental refractive index measurements for 1-alcohols from methanol to 1-decanol. The new equation correlates the refractive index within an average absolute percentage deviation of 0.05%. The correlation for the density also uses the temperature, the carbon number and the refractive index as variables. The new density equation correlates the density of 1-alcohols from (159 to 373) K within an average absolute percentage deviation of 0.08%. The extrapolative ability of both equations agrees with the data within the experimental error.

1. Introduction

Refractive index is a parameter related to the behavior of light as it crosses a medium. From a microscopic point of view, the refractive index depends upon the electric and magnetic characteristics of the medium, and the temperature and the wave length of the emitted light [1]. The refractive index can indicate the purity of a substance or quantify the amount of a component in a binary mixture. Ortega [2] measured the refractive index of pure 1-alcohols from methanol to 1-decanol at temperatures from (293 to 353) K. He used a straight line to represent the temperature functionality of the refractive index. Several authors [3,4] have tried to calculate the refractive index of mixtures using different mixing rules. To the best of our knowledge, no correlation exists for the pure 1-alcohols refractive indices. This work presents a generalized correlation for the refractive index of 1-alcohols as a function of the carbon number and the temperature.

Development of generalized correlations for the prediction of densities is important for design of unit operations equipment, and to determine flow through pipes, heat exchangers or mass transfer equipment [5].

Many researchers have developed different correlations for the densities of homologous series [6,7]. Generalized correlations for the density of 1-alcohols at atmospheric pressure do not exist, but some attempts exist to provide generalized correlations for the density of 1-alcohols at high pressure. Assael et al. [8] correlated the liquid densities for methanol through 1-dodecanol using individual polynomials of temperature. Later, Saleh et al. [9] proposed an isothermal equation for the molar volume of pure 1-alcohols as a linear function of the number of CH_2 groups. Their equation predicts the density from ethanol to higher carbon number alcohols. Nasrifar and Moshfeghian [10] developed an equation to calculate the liquid densities of pure components and their mixtures using as variables the critical properties and the dipole moments of the pure components. In the literature, relationships exist between the refractive index and the liquid density such as the Lorentz–Lorenz [11,12], Dale–Gladstone [13], Eykman [14], Oster [15], Arago–Biot [16] and Newton [17] equations. This work uses this concept to develop a generalized correlation for the calculation of the liquid densities of 1-alchols. No generalized correlations for the liquid densities of 1-alcohols appear in the literature. The new correlation uses the number of carbon atoms and the temperature as independent variables.

In this work, it became obvious that the Eykman [14] relationship successfully correlates refractive indices with the liquid densities for 1-alcohols to form a generalized correlation.

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Also, the new equation can predict the density of binary mixtures of 1-alcohols within the experimental error.

2. Methodology

Generally, correlations for the density of a homologous series that contain carbon atoms are functions of the number of carbon atoms and use the Bronsted–Koefoed principle [18]. For the 1-alcohol densities, the problem is that in the series methanol has a higher density than ethanol at the same conditions, as shown in Fig. 1. This behavior makes it difficult to develop a generalized correlation using the Congruence Principle. This work presents an alternative approach to this problem by noting that the refractive index of liquids is related to their densities. The relationships that exist between the refractive index and density are

Eykman [14]:

$$\rho = \frac{n_D^2 - 1}{n_D + 0.4} \times \frac{1}{K} \tag{1}$$

Lorentz–Lorenz [11,12]:

$$\rho = \frac{n_D^2 - 1}{n_D^2 + 2} \times \frac{1}{K} \tag{2}$$

Dale–Gladstone [13]:

$$\rho = (n_D - 1) \times \frac{1}{K} \tag{3}$$

Arago–Biot [16]:

$$\rho = n_D \times \frac{1}{K} \tag{4}$$

Oster [15]:

$$\rho = \frac{(n_D^2 - 1)(2n_D^2 + 1)}{n_D^2} \times \frac{1}{K} \tag{5}$$

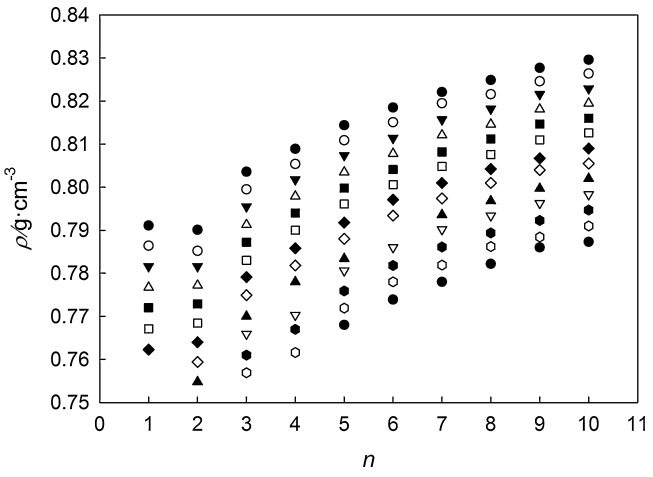

Fig. 1. Density behavior of 1-alcohols with respect to the number of carbon atoms: ●: 293.15 K; ○: 298.15–K; ▼: 303.15 K; △: 308.15 K; ■: 313.15 K; □: 318.15 K; ◆: 323.15 K; ◇: 328.15 K; ▲: 333.15 K; ▽: 338.15 K; ⬢: 343.15 K; ⬡: 348.15 K, ●: 353.15 K.

and Newton [17]:

$$\rho = (n_D^2 - 1) \times \frac{1}{K} \tag{6}$$

where n_D, ρ, and K are the refractive index, the liquid density and a characteristic constant, respectively.

Ortega [2] postulated that refractive index has a linear behavior with temperature as apparent in Fig. 2. Therefore,

$$n_D = k_1 + k_2 t \tag{7}$$

where the k_1's are characteristic parameters, and t is the temperature in degrees Celsius. He also showed that the value of k_2 is almost constant for the refractive indices of 1-alcohols from methanol to 1-decanol at temperatures from (293 to 353) K.

2.1. Experimental

This work uses Eq. (7) to correlate the refractive indices of 1-alcohols from methanol to 1-decanol at temperatures from (293 to 353) K using a single function for the number of carbon atoms,

$$n_D = 1.8792 - 0.5491n^{-0.1165} - 0.0014n + \frac{0.0132}{n^{13.5442}} - 4 \times 10^{-4} t \tag{8}$$

The average absolute percentage deviation of Eq. (8) from the experimental refractive index is 0.27%.

Having a generalized correlation for the refractive indices, it is possible to obtain a correlation for the densities of 1-alcohols by selecting an expression from Eqs. (1)–(6) and an expression for the constant K as shown in Fig. 3.

3. Results

The performance of Eq. (8) improves if the temperature term is also a function of the number of carbon atoms

$$n_D = a_0 + a_1 n^{a_2} + a_3 n + \frac{a_4}{n^{a_5}} + (a_6 + a_7 n^{0.5} + a_8 n^{0.75})t \tag{9}$$

in which t is the temperature in degrees Celsius and the a_i are universal parameters. Eq. (9) correlates the refractive indices of 1-alcohols from methanol to 1-decanol at temperatures from (293 to 353) K within 0.049%. Fig. 4 shows the residuals of the refractive indices from Eq. (9) and Table 1 shows the numerical values of the parameters. Having a generalized correlation for the refractive indices, it is possible to select experimental density data [2,18,19] for 1-alcohols from methanol to 1-decanol and at temperatures

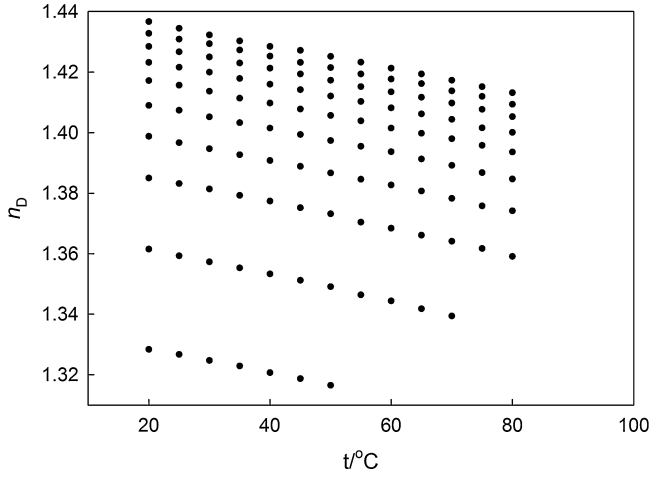

Fig. 2. Behavior of the refractive index with temperature.