# Density−Pressure Relationship in Hydrogen-Bonded Mixtures: 1,4-Butanediol + 1-Dodecanol

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The pressure dependence of the molar volume of the 1,4-butanediol + 1-dodecanol system has been measured at 298.15 K for $0.1 \le P/\text{MPa} \le 40.0$ and for the whole concentration range. All the results can be described by an equation with a single fitting parameter which takes a value similar to those obtained for non-hydrogen-bonded mixtures. The volumetric results at ambient pressure can be described by a lattice-fluid theory which incorporates the effect of the hydrogen bonds. The same theory is able to reproduce the compressibility of the pure components over the whole pressure range. However, it is not able to predict the compressibility of the mixtures nor the excess Gibbs energy.

## Introduction

Hydrogen-bonded fluids are of the utmost importance in biology and in chemical technology.[1] In the last 10 years, there have been significant advances in the statistical mechanical description of fluid mixtures. They have allowed one to include the contribution of internal degrees of freedom, arising from the flexibility of the molecules, to the thermophysical properties. Also, the contributions of specific interactions with strong directional character have been dealt with.[2] Good results are frequently obtained when the theoretical predictions are compared with computer simulations; however, the situation is less satisfactory when the theory and simulation are compared with results for complex fluids.[3] Mixtures of flexible molecules that can form intra- and intermolecular hydrogen bonds are in the limit of what current theories for fluids are able to model and therefore are good candidates for testing the ability of any theory to predict the thermophysical properties of fluid mixtures.

We have chosen the system $(1 - x)$ 1,4-butanediol + $x$ 1-dodecanol because, in addition to forming intra- and intermolecular hydrogen bonds, this system shows a noticeable change in the dielectric permittivity ($\epsilon$) with mole fraction ($x$).[4] The change in $\epsilon$ is expected to modify the intermolecular interactions between the molecules. Furthermore, both components have rather different surface tension ($\gamma$) values, and even for very small values of $x$, the surface tension is much smaller than the value corresponding to 1,4-butanediol, which suggests a strong surface excess adsorption of 1-dodecanol.[5]

The equation of state surface is a key property for any fluid system, directly related to the interaction potential between the molecules and from which most of the thermophysical properties can be derived. Therefore, in this paper, we report the pressure ($P$)−molar volume ($V$)−composition surface for the $(1 - x)$ 1,4-butanediol + $x$ 1-dodecanol system in the pressure interval $0.1 < P/\text{MPa} < 40.0$, over the whole composition range and at 298.15 K. The results are compared with the values calculated with a lattice-fluid model that takes into account the existence of hydrogen bonds in the mixtures.

## Experimental Section

1,4-Butanediol, and 1-dodecanol, of the maximum purity available, were purchased from Fluka (U.S.A.) and were dried over 0.4 nm molecular sieves. All the mixtures were prepared by mass using an analytical balance precise to ±0.01 mg. The uncertainty in the mole fraction is $\pm 3 \times 10^{-5}$. The densities ($\rho$) were obtained with a high-pressure vibrating tube (Anton Paar, model 512). The experimental setup and the calibration procedure have been described in detail in a previous work.[6] To account for the effect of viscosity on the period of vibration, we have followed the method of Ashcroft et al.[7] The precision in the measurements was ±0.01 MPa in $P$, ±0.5 mK in $T$, and $\pm 5 \times 10^{-7}$ s in $\tau$, the period of vibration. Considering the above values of precision, together with typical values of the isothermal compressibility and isobaric expansivity of these fluid systems, would lead to an uncertainty in the density of the order of 0.02 $\text{kg·m}^{-3}$. However, the calibration curve [i.e., the curve $\rho = \rho(\tau, P)$] is the main source of error (see ref 7), thus leading to a final uncertainty in $\rho$ of ±0.1 $\text{kg·m}^{-3}$ for the whole pressure range $0.1 \le P/\text{MPa} \le 40.0$. The densities of the pure components were obtained at 0.1 MPa using a vibrating tube (Anton Paar, model DMA 620). The value obtained at 298.15 K for 1-dodecanol, 829.77 $\text{kg·m}^{-3}$, compares well with the values reported in the literature: 829.95 $\text{kg·m}^{-3}$ [8] and 830.4 $\text{kg·m}^{-3}$.[9] For 1,4-butanediol, we have obtained a value of 1012.6 $\text{kg·m}^{-3}$, while $\rho = 1015.0$ $\text{kg·m}^{-3}$ has been reported in ref 9 and $\rho = 1012.89$ $\text{kg·m}^{-3}$ is given by ref 10 at 293.15 K.

## Results

The data were measured at 298.15 K and between $0.1 \le P/\text{MPa} \le 40.0$. The $P-\rho$ data are given in Table 1. 1-Dodecanol could not be measured above 6.87 MPa because it is not fluid at room temperature. Figure 1 shows the effect of pressure on the volume as a function of composition. Very dilute mixtures have been included in this study because strong surface tension reductions are observed in that composition range, and correlations between $\gamma$ and $P-V-T$ data have been reported.[12] As it can be observed, the effect of pressure on the molar volume is lower for the mixtures richer in the component that can form a denser hydrogen-bond network (1,4-butanediol).

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**Table 1. Experimental Data of (1 − $x$) 1,4-Butanediol + $x$ 1-Dodecanol at 298.15 K**

| $x$ | $10^{-3}\rho$/kg·m$^{-3}$ | $P$/MPa | $10^{-3}\rho$/kg·m$^{-3}$ | $P$/MPa | $10^{-3}\rho$/kg·m$^{-3}$ | P/MPa | $10^{-3}\rho$/kg·m$^{-3}$ | P/MPa |
|---|---|---|---|---|---|---|---|---|
| 0.0 | 1.01278 | 0.21 | 1.01634 | 9.07 | 1.02214 | 23.84 | 1.02621 | 34.33 |
| | 1.01284 | 0.54 | 1.01709 | 10.88 | 1.02300 | 26.07 | 1.02687 | 36.04 |
| | 1.01307 | 1.26 | 1.01802 | 13.05 | 1.02399 | 28.42 | 1.02759 | 37.93 |
| | 1.01364 | 2.61 | 1.01890 | 15.22 | 1.02441 | 29.56 | 1.02800 | 39.14 |
| | 1.01463 | 4.95 | 1.01958 | 17.04 | 1.02480 | 30.43 | | |
| | 1.01546 | 6.94 | 1.02118 | 21.30 | 1.02547 | 32.27 | | |
| 0.00166 | 1.01271 | 0.33 | 1.01722 | 11.94 | 1.02252 | 24.52 | 1.02485 | 30.87 |
| | 1.01302 | 0.66 | 1.01797 | 13.91 | 1.02313 | 25.65 | 1.02512 | 31.58 |
| | 1.01343 | 1.74 | 1.01920 | 16.93 | 1.02345 | 26.52 | 1.02567 | 32.48 |
| | 1.01412 | 3.48 | 1.02102 | 20.42 | 1.02364 | 27.06 | 1.02655 | 34.79 |
| | 1.01491 | 5.43 | 1.02133 | 21.37 | 1.02396 | 27.94 | 1.02710 | 36.35 |
| | 1.01560 | 7.53 | 1.02179 | 22.52 | 1.02422 | 28.85 | 1.02796 | 38.32 |
| | 1.01631 | 9.50 | 1.02220 | 23.78 | 1.02443 | 29.77 | | |
| 0.00551 | 1.01268 | 0.48 | 1.01634 | 9.62 | 1.02151 | 21.97 | 1.02626 | 34.24 |
| | 1.01324 | 1.36 | 1.01719 | 11.68 | 1.02242 | 24.30 | 1.02701 | 36.31 |
| | 1.01331 | 2.83 | 1.01797 | 13.59 | 1.02343 | 27.05 | 1.02747 | 37.68 |
| | 1.01453 | 4.68 | 1.01887 | 15.85 | 1.02413 | 28.94 | 1.02797 | 38.94 |
| | 1.01509 | 6.50 | 1.01990 | 17.70 | 1.02464 | 30.59 | | |
| | 1.01552 | 7.60 | 1.02055 | 19.46 | 1.02539 | 32.46 | | |
| | 1.01597 | 8.78 | 1.02147 | 21.84 | 1.02592 | 33.35 | | |
| 0.04995 | 0.99925 | 0.16 | 1.00344 | 9.42 | 1.00935 | 22.54 | 1.01372 | 33.59 |
| | 0.99937 | 0.43 | 1.00465 | 11.42 | 1.01013 | 24.63 | 1.01458 | 35.94 |
| | 0.99978 | 1.34 | 1.00567 | 13.92 | 1.01080 | 26.63 | 1.01519 | 37.70 |
| | 1.00059 | 2.98 | 1.00651 | 15.89 | 1.01146 | 28.41 | 1.01590 | 39.40 |
| | 1.00154 | 5.05 | 1.00742 | 18.16 | 1.01218 | 30.22 | | |
| | 1.00258 | 7.52 | 1.00850 | 20.49 | 1.01272 | 31.45 | | |
| 0.18292 | 0.96259 | 0.14 | 0.96527 | 6.04 | 0.97123 | 18.39 | 0.97581 | 29.24 |
| | 0.96273 | 0.44 | 0.96621 | 7.96 | 0.97214 | 20.23 | 0.97667 | 30.92 |
| | 0.96262 | 0.96 | 0.96729 | 10.31 | 0.97284 | 22.11 | 0.97718 | 32.41 |
| | 0.96308 | 1.64 | 0.96837 | 12.11 | 0.97407 | 24.78 | 0.97798 | 34.43 |
| | 0.96338 | 2.34 | 0.96938 | 14.27 | 0.97449 | 26.64 | 0.97897 | 36.73 |
| | 0.96426 | 4.30 | 0.96991 | 15.81 | 0.97498 | 27.21 | 0.97963 | 38.41 |
| 0.25292 | 0.94479 | 0.65 | 0.95021 | 11.69 | 0.95608 | 24.31 | 0.96062 | 34.60 |
| | 0.94547 | 1.86 | 0.95137 | 13.83 | 0.95700 | 26.41 | 0.96153 | 36.88 |
| | 0.94647 | 3.87 | 0.95229 | 16.26 | 0.95772 | 28.02 | 0.96222 | 38.58 |
| | 0.94729 | 5.64 | 0.95323 | 18.09 | 0.95886 | 30.37 | 0.96242 | 39.07 |
| | 0.94818 | 7.53 | 0.95427 | 20.15 | 0.95876 | 30.41 | | |
| | 0.94917 | 9.36 | 0.95522 | 22.33 | 0.95948 | 32.07 | | |
| 0.35391 | 0.92119 | 0.22 | 0.92816 | 13.79 | 0.93457 | 27.49 | 0.93825 | 35.50 |
| | 0.92150 | 0.75 | 0.92919 | 16.14 | 0.93575 | 30.35 | 0.93882 | 36.72 |
| | 0.92216 | 2.21 | 0.93049 | 18.82 | 0.93613 | 31.08 | 0.93970 | 39.24 |
| | 0.92454 | 6.86 | 0.93143 | 20.77 | 0.93683 | 32.72 | 0.93982 | 39.40 |
| | 0.92599 | 9.31 | 0.93251 | 22.93 | 0.93710 | 33.25 | | |
| | 0.92706 | 11.76 | 0.93358 | 25.43 | 0.93792 | 34.93 | | |
| 0.55674 | 0.88190 | 0.68 | 0.88773 | 11.59 | 0.89359 | 23.92 | 0.89846 | 34.24 |
| | 0.88240 | 1.78 | 0.88881 | 13.66 | 0.89495 | 26.54 | 0.89920 | 35.77 |
| | 0.88375 | 4.05 | 0.88957 | 15.41 | 0.89614 | 29.26 | 0.89993 | 37.75 |
| | 0.88469 | 5.97 | 0.89057 | 17.45 | 0.89625 | 29.52 | 0.90034 | 38.82 |
| | 0.88549 | 7.52 | 0.89181 | 20.06 | 0.89681 | 30.61 | 0.90043 | 39.06 |
| | 0.88639 | 9.27 | 0.89265 | 21.86 | 0.89762 | 32.35 | | |
| 0.73024 | 0.85577 | 0.58 | 0.86083 | 9.43 | 0.86603 | 19.41 | 0.86826 | 23.95 |
| | 0.85629 | 1.63 | 0.86196 | 11.48 | 0.86607 | 19.72 | 0.86898 | 25.53 |
| | 0.85675 | 2.36 | 0.86212 | 11.77 | 0.86611 | 19.83 | 0.86949 | 26.46 |
| | 0.85753 | 3.28 | 0.86328 | 14.18 | 0.86653 | 20.49 | 0.87004 | 27.55 |
| | 0.85842 | 4.91 | 0.86402 | 15.64 | 0.86684 | 21.22 | 0.87062 | 28.35 |
| | 0.85945 | 6.73 | 0.86501 | 17.49 | 0.86779 | 22.51 | | |
| | 0.86004 | 7.88 | 0.86509 | 17.65 | 0.86769 | 22.97 | | |
| | 0.86019 | 8.16 | 0.86588 | 19.02 | 0.86808 | 23.81 | | |
| 1.0 | 0.83019 | 0.68 | 0.83294 | 4.87 | 0.83345 | 5.76 | 0.83377 | 6.52 |
| | 0.83065 | 1.61 | 0.83285 | 5.02 | 0.83371 | 6.41 | 0.83404 | 6.87 |
| | 0.83166 | 3.18 | 0.83306 | 5.18 | 0.83381 | 6.45 | | |

However, this cannot be taken as a general result, since $V/V_0$ shows a smaller pressure dependence for water than for 1,4-butanediol.

The data have been fitted to the Tait equation

$$\rho = \frac{\rho_0}{1 - B_2 \ln\left(\dfrac{B + P}{B + P_0}\right)} \qquad (1)$$

where $\rho_0$ is the density at the reference pressure ($P_0$, 0.1 MPa in this work) and $B$ and $B_2$ are constants independent of $P$ and characteristic of each sample. Table 2 gives the parameters of eq 1 obtained for the pure substances and for the mixtures, as well as the mean standard deviations of the fits.

The effect of $P$ on the excess properties can be calculated through

$$\Delta G^{\mathrm{E}}(P) - \Delta G^{\mathrm{E}}(P{=}0) = \int_{P_0}^{P} V^{\mathrm{E}}(P, T)\, \mathrm{d}P \qquad (2)$$

where $V^{\mathrm{E}}$ and $G^{\mathrm{E}}$ are the excess volume and excess Gibbs energy, respectively. As can be observed in Figure 2, increasing the pressure stabilizes the (1 − $x$) 1,4-butanediol

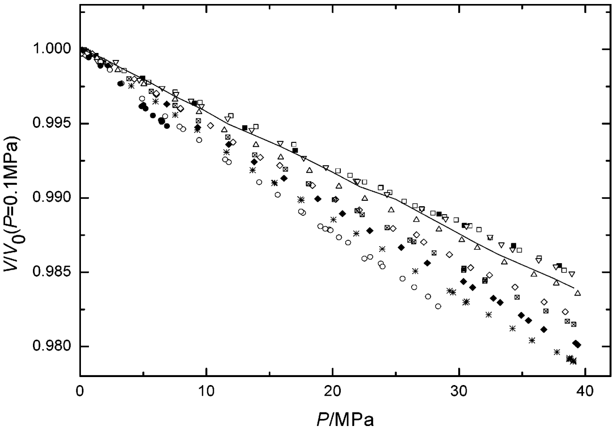

**Figure 1.** Effect of the pressure on the molar volume of the (1 − $x$) 1,4-butanediol (1) + $x$ 1-dodecanol (2) mixture at 298.15 K. The line shows the corresponding data for water. The symbols correspond to experimental data for different values of the mole fraction of 1-dodecanol: ■, $x$ = 0.0; □, $x$ = 0.001 66; ▽, $x$ = 0.005 51; △, 0.049 95; ◇, $x$ = 0.182 92; □ with an "×" in the middle, $x$ = 0.252 92; ◆, $x$ = 0.353 91; ○, $x$ = 0.556 74; ∗, $x$ = 0.730 24; ●, $x$ = 1.0. The continuous line represents the data for pure water.

**Table 2. Characteristics of the Fittings of the Experimental Data to the Tait Equation (eq 1)[a]**

| $x$ | $10^{-3}\rho_0$/kg·m$^{-3}$ | $10B_2$ | $10^{-3}B$/MPa | $\sigma(\rho)$/kg·m$^{-3}$ |
|---|---|---|---|---|
| 0.0 | 1.0126 | 0.9893 | 0.2392 | 0.05 |
| 0.00166 | 1.0125 | 0.9857 | 0.2335 | 0.1 |
| 0.005 51 | 1.0125 | 0.9982 | 0.2375 | 0.1 |
| 0.049 95 | 0.9992 | 0.5203 | 0.1062 | 0.09 |
| 0.182 92 | 0.9623 | 0.6121 | 0.1144 | 0.1 |
| 0.252 92 | 0.9446 | 0.8598 | 0.1615 | 0.06 |
| 0.353 91 | 0.9211 | 0.8235 | 0.1436 | 0.07 |
| 0.556 74 | 0.8815 | 0.7335 | 0.1173 | 0.07 |
| 0.730 24 | 0.8556 | 0.7183 | 0.1054 | 0.1 |
| 1.0 | 0.8297 | 0.5184 | 0.0644 | 0.07 |

[a] $x$ is the mole fraction of 1-dodecanol, the $B_i$ values are the constants of the Tait equation, and $\sigma(\rho)$ is the variance of the fit of the density data ($\rho$).

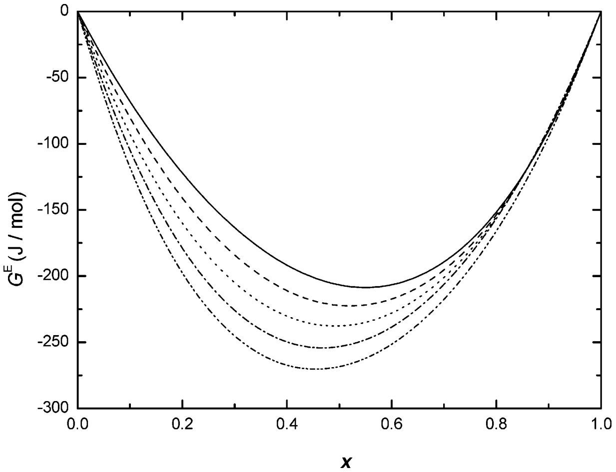

**Figure 2.** Effect of the pressure on the excess Gibbs energy of the mixture. The values corresponding to 0.1 MPa have been measured by laser light scattering.[4] The lines correspond to different values of $P$ in megapascals: ——, 0.1; − − −, 10; · · · · ·, 20; · − · − ·, 30; − · · − · · −, 40.

+ $x$ 1-dodecanol system and shifts the minimum of the $G^E$ curves toward lower 1-dodecanol concentrations. In Figure 2, the values of $G^E$ at $P$ = 0.1 MPa were obtained from laser light scattering experiments.[5]

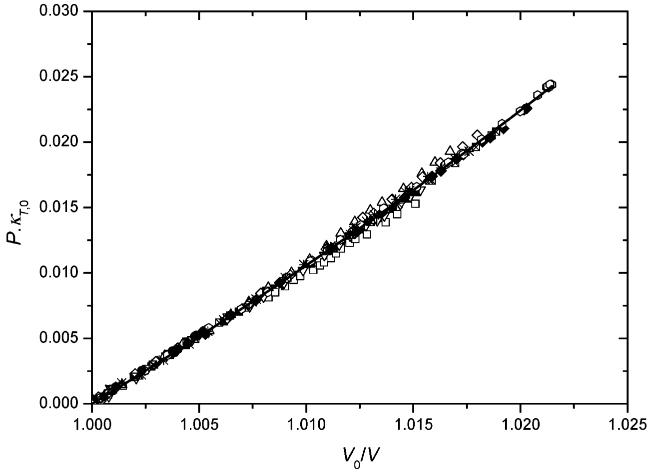

**Figure 3.** Test of the corresponding states equation proposed by Sanchez et al.[9] for the mixture at different compositions. The symbols correspond to different values of the mole fraction of 1-dodecanol: ■, $x$ = 0.0; □, $x$ = 0.001 66; ▽, $x$ = 0.005 51; △, 0.049 95; ◇, $x$ = 0.182 92; □ with an "×" in the middle, $x$ = 0.252 92; ◆, $x$ = 0.353 91; ○, $x$ = 0.556 74; ∗, $x$ = 0.730 24; ●, $x$ = 1.0.

## Discussion

Sanchez et al.[13] have proposed the following universal equation to represent the $P-\rho-T$ data of fluids:

$$P\kappa_{T,0} = (\rho^{\delta} - 1)/\rho \tag{3}$$

where $\kappa_{T,0}$ is the isothermal compressibility at $P$ = 0.1 MPa and $\delta$ is a parameter characteristic of each system. Equation 3 has been found to describe the experimental data for different mixtures,[12] within the experimental uncertainty, with values of $\delta$ ranging from 10.93 to 12.26. Figure 3 shows that the experimental results of the (1 − $x$) 1,4-butanediol + $x$ 1-dodecanol system agree well with the values calculated with eq 3 using the value $\delta = 12.3 \pm 0.2$ obtained from the fit of the 1,4-butanediol data.

## Comparison with the Predictions of a Lattice-Fluid Model

In this work, we will test the lattice-fluid model developed by Panayiotou and Sanchez for hydrogen-bonded mixtures[14] which has been found to give a reasonable description of the bulk properties of nonaqueous mixtures. In the present work, we will only give the equation of state (EoS) and the equations that account for the hydrogen bonds.

The EoS is

$$\tilde{P} + \tilde{\rho}^2 + \tilde{T}[\ln(1 - \tilde{\rho}) + \tilde{\rho}(1 - 1/\tilde{r})] = 0 \tag{4}$$

where the reduced variables are defined by $\tilde{P} = P/P^*$, $\tilde{T} = T/T^*$, $\tilde{\rho} = \rho/\rho^*$, with $P^* = \epsilon^*/V^*$, $T^* = \epsilon^*/R$, and $\rho^* = 1/V^*$ being substance-dependent parameters that define the van der Waals type interactions between the molecules ($\epsilon^*$) and their size ($V^*$). The average number of segments per molecule is defined by

$$1/\tilde{r} = 1/r - \nu_{\mathrm{H}} \tag{5}$$

where $\nu_{\mathrm{H}}$ is the fraction of hydrogen bonds in the system and $r$ is the average number of segments per molecule.

For pure 1,4-butanediol, we have assumed that the molecules have $d$ = 2 donor groups and $a$ = 2 acceptor

**Table 3. Pure Component Parameters of the Lattice-Fluid Theory for the Pure Components[a]**

| | $P^*$/MPa | $T^*$/K | $\rho^*$/kg·mol$^{-1}$ | $r$ |
|---|---|---|---|---|
| 1,4-butanediol | 475.2 | 561.4 | 1090.4 | 8.41 |
| 1-dodecanol | 419.5 | 536.9 | 913.6 | 19.17 |

[a] Hydrogen-bond parameters: $E° = -25.1$ kJ·mol$^{-1}$; $S° = -26.5$ J·mol$^{-1}$·K$^{-1}$; $V° = -5.6 \times 10^{-6}$ m$^3$·mol$^{-1}$.

groups, while, for the 1-dodecanol molecules, $d = 1$ and $a = 1$. The model leads to the following equation

$$r\nu_{\mathrm{H}} = [d + a - \{A_{ij}(A_{ij} + 2(d + a)) + (d - a)^2\}^{1/2} - A_{ij}]/2 \quad (6)$$

with $A_{ij} = (r/\tilde{\rho}) \exp[(G_{ij}^0/RT)]$ and $G_{ij}^0 = E_{ij}^0 - TS_{ij}^0 + PV_{ij}^0$, where the energy, entropy, and volume are characteristics of the hydrogen bond. We have used for these parameters the same values as those in ref 14. The pure component parameters $P^*$, $T^*$, and $\rho^*$ have been obtained from the fit of the $P-V-T$ surface of each pure component to eqs 4−6, and they are given in Table 3.

For the mixture, it is necessary to make use of mixing rules to relate the interaction of unlike segments with those of the like ones. We have assumed one fluid mixing rule

$$\epsilon^* = \sum_i \sum_j \phi_i \phi_j \epsilon_{ij}^*; \quad \epsilon_{ij,i\neq j} = \xi_{ij}\sqrt{\epsilon_{ii}^*\, \epsilon_{jj}^*}$$

$$V^* = \sum_i \sum_j \phi_i \phi_j V_{ij}^*; \quad V_{ij,i\neq j} = \zeta_{ij}\sqrt{V_{ii}^*\, V_{jj}^*} \quad (7)$$

Also, we have taken into account self- and cross-association, which leads to a system of coupled equations

$$\nu_{ij}A_{ij} = r\left(\frac{N_d^i}{rN} - \sum_{k=i}^{n}\nu_{ik}\right)\left(\frac{N_a^j}{rN}\sum_{k=j}^{m}\nu_{kj}\right) \quad (8)$$

The two binary parameters $\xi$ and $\zeta$ have been fitted to the excess volume data of the mixture at $P = 0.1$ MPa. $\xi$ takes into account the weakness or strength of the binary interactions with respect to those between like molecules, and $\zeta$ takes into account the change in the core volume ($V^*$) in the mixture with respect to a linear combination of the pure component values. Figure 4 shows the best fits of the excess molar volume of the mixture ($V^{\mathrm{E}}$) for the model. As can be observed, the use of $\zeta \neq 0$ ($\xi = 1.040 \pm 0.004$; $\zeta = 0.989 \pm 0.005$) highly improves the prediction of the volumetric properties, although the mean standard deviation of the fit ($3 \times 10^{-6}$ m$^3$/kg) is higher than that of the experimental values ($1 \times 10^{-6}$ m$^3$/kg). In fact, when $\zeta = 0$ ($\xi = 1.11 \pm 0.01$), the results of the model are very similar to those of the model when no hydrogen bonds are included. Moreover, the $\xi$ parameter becomes closer to unity than when $\zeta = 0$. The prediction of the pressure dependence of $V/V_0$ is shown in Figure 5 for the two pure components and for one intermediate composition (similar predictions were obtained for other compositions). The theory is able to describe correctly the compressibility of the pure components over the whole pressure range when the effect of the hydrogen bonds is taken into account, without any significant difference between the model with one or two fitting parameters. However, for binary mixtures, the theory is not able to describe the experimental results, with the effect of including the effect of hydrogen bonds being minor, leading to values of the molar volume larger than the experimental ones. The predictions of the model when $\zeta \neq 0$ are not significantly better than those when $\zeta = 0$ for the mixtures and are only marginally better than the predictions of the model when no hydrogen bonds are taken into account. The model is not able to reproduce the experimental values of $G^{\mathrm{E}}$, leading to more negative values (up to 100% error for the minimum of the $G^{\mathrm{E}}$ curve) and a minimum which is skewed toward low 1-dodecanol concentrations.

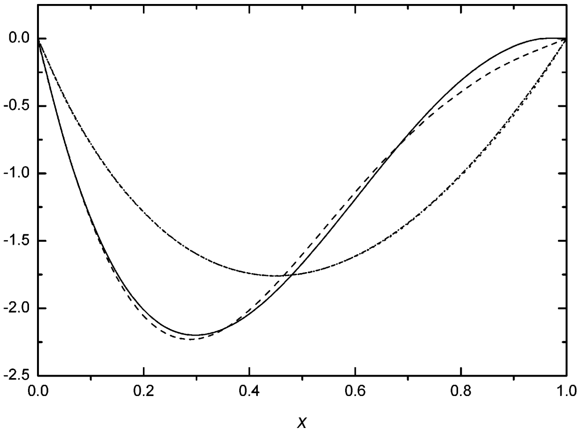

**Figure 4.** Comparison of the experimental and calculated excess volume results at 0.1 MPa and 298.15 K. The thick line corresponds to the experimental values, the dotted lines represent the calculations without considering hydrogen bonds and also those considering hydrogen bonds but with $\zeta = 0$, and the dashed line corresponds to the theory considering hydrogen bonds. The values of $\xi$ and $\zeta$ are given in the text.

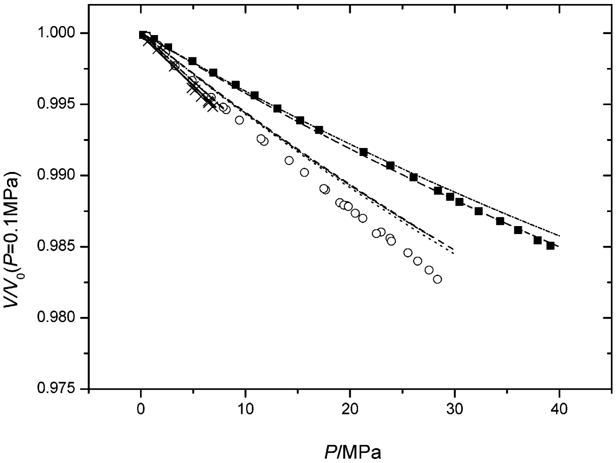

**Figure 5.** Comparison of the pressure effect on the reduced molar volume with the predictions of the lattice-fluid theory. The symbols correspond to experimental data: ■, $x = 0.0$; ●, $x = 0.730\ 24$; ×, $x = 1.0$. The continuous lines are the predictions of the theory without considering hydrogen bonds; the dotted line includes hydrogen bonds and one energetic fitting parameter; and the dashed line includes two fitting parameters, one energetic and one volume related one. Note that the dashed and dotted lines are almost indistinguishable.

## Conclusions

The pressure dependence of the molar volume of the $(1 - x)$ 1,4-butanediol + $x$ 1-dodecanol system has been measured at 298.15 K using a vibrating tube densimeter. The results for all the compositions and pressures can be cast on a master curve according to the suggestion of Sanchez et al.,[13] with a value of the fitting parameter that is close to that of other mixtures without hydrogen bonds.

The experimental results have been compared with the predictions of the lattice-fluid model of Panayiotou and Sanchez.[14] It has been found that including the effect of hydrogen bonds has an important effect on the ability of the model to fit the excess molar volume at ambient pressure, especially if two fitting parameters are considered. However, the model does not reproduce adequately the compressibility of the mixtures and including the effect of hydrogen bonds does not have a noticeable effect on the predictions of the model.

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